Baran Reagents · Bargellini reaction
Baran Reagents · Bargellini reaction
Cattallani reaction · Danheiser annulation
Cattallani reaction · Danheiser annulation
Elbs oxidation · Hofmann elimination
Elbs oxidation · Hofmann elimination
McMillan catalyst · Anti-Markovnikov
McMillan catalyst · Anti-Markovnikov
Sanford reaction · Yu C–H activation
Sanford reaction · Yu C–H activation
Zaitsev elimination
Zaitsev elimination

Jie Jack Li

Name Reactions

A Collection of Detailed Mechanisms and Synthetic Applications, Fifth Edition

Springer

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A Collection of Detailed Mechanisms and Synthetic Applications

Fifth Edition

Springer

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ISBN 978-3-319-03978-7 ISBN 978-3-319-03979-4 (eBook)
DOI 10.1007/978-3-319-03979-4
Springer Cham Heidelberg New York Dordrecht London

Library of Congress Control Number: 2014930574

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

To Prof. Claire Castro

Kurt Alder
1902–1958
Nobel Prize, 1950

Adolf von Baeyer
1835–1917
Nobel Prize, 1905

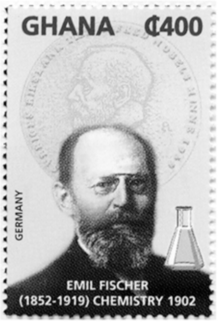
Derek H. R. Barton
1918–1999
Nobel Prize, 1969

Eduard Buchner
1860–1917
Nobel Prize, 1907

Elias James Corey
1928–
Nobel Prize, 1990

Otto Paul Hermann Diels
1876–1954
Nobel Prize, 1950

Emil Fischer
1852–1919
Nobel Prize, 1902



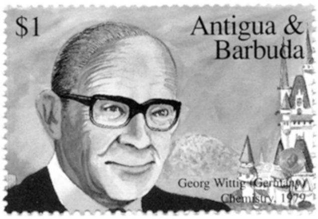
Robert Robinson
1886–1975
Nobel Prize, 1947

Otto Wallach
1847–1931
Nobel Prize, 1910

Victor Grignard
1871–1935
Nobel Prize, 1912

Hermann Staudinger
1881–1965
Nobel Prize, 1953

Georg Wittig
1897–1987
Nobel Prize, 1979



Karl Ziegler
1898–1973
Nobel Prize, 1963

Preface

Four years have gone by since the fourth edition was published and much has happened since then. Professionally, I have moved from industry to academia to teach organic and medicinal chemistry. This change is reflected in my choice to include most of the basic name reactions so that this book will be useful for my undergraduate students. I have also had the opportunity to make corrections to several quinoline- and isoquinoline-related mechanisms. In addition, new name reactions have emerged, and new references appeared for old name reactions. I have added 27 new name reactions to reflect the latest developments in organic chemistry and updated synthetic applications for each old name reaction. By popular demand, a brief biographical description of the inventor of nearly *every* name reaction has been added to this edition.

As in previous editions each reaction is delineated by its detailed step-by-step, electron-pushing mechanism, supplemented with the original and the latest references, especially review articles. Now, with the addition of many synthetic applications, this book is not only an indispensable resource for senior undergraduate and graduate students for learning mechanisms and the synthetic utility of name reactions and preparing for their exams, but it is also a good reference book for all organic chemists in both industry and academia.

I wish to thank Dr. Jonathan W. Lockner at Scripps Research Institute and Dr. Jun Cindy Shi of Bristol-Myers Squibb for their help in preparing and proofreading the manuscript. I also wish to thank Prof. Neil K. Garg at UCLA and his students, Grace Chiou, Adam Goetz, Liana Hie, Dr. Travis McMahon, Tejas Shah, Noah Fine Nathel, Joel M. Smith, Amanda Silberstein, and Evan D. Styduhar for proofreading the final version of the manuscript. Their knowledge and input have tremendously enhanced the quality of this book. Any remaining errors are, of course, solely my own responsibility.

As always, I welcome your critique! Please send your comments to this email address: lijiejackli@gmail.com.

October 2013 Jie Jack Li
San Francisco, CA

Table of Contents

Abbreviations and Acronyms

	Polymer support
Δ	Solvent heated under reflux
$(DHQ)_2$-PHAL	1,4-*bis*(9-*O*-Dihydroquinine)-phthalazine
$(DHQD)_2$-PHAL	1,4-*bis*(9-*O*-Dihydroquinidine)-phthalazine
[bimim]Cl•$2AlCl_3$	1-Butyl-3-methylimidazolium chloroaluminuminate
3CC	Three-component condensation
4CC	Four-component condensation
9-BBN	9-Borabicyclo[3.3.1]nonane
A	Adenosine
Ac	Acetyl
ADDP	1,1′-(azodicarbonyl)dipiperidine
AIBN	2,2′-azobisisobutyronitrile
Alpine-borane®	*B*-isopinocampheyl-9-borabicyclo[3.3.1]-nonane
AOM	*p*-Anisyloxymethyl = *p*-$MeOC_6H_4OCH_2$-
Ar	Aryl
B:	Generic base
BINAP	2,2′-*bis*(Diphenylphosphino)-1,1′-binaphthyl
Bn	Benzyl
Boc	*tert*-Butyloxycarbonyl
BQ	Benzoquinone
BT	Benzothiazole
Bz	Benzoyl
Cbz	Benzyloxycarbonyl
CuTC	Copper thiophene-2-carboxylate
DABCO	1,4-Diazabicyclo[2.2.2]octane
dba	Dibenzylideneacetone
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCC	1,3-Dicyclohexylcarbodiimide
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

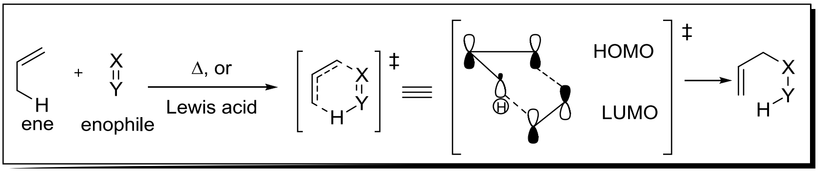
de	Diastereoselctive excess
DEAD	Diethyl azodicarboxylate
DIAD	Diisopropyl azodidicarboxylate
DIBAL	Diisobutylaluminum hydride
DIPEA	Diisopropylethylamine
DMA	*N*,*N*-dimethylacetamide
DMAP	4-*N*,*N*-dimethylaminopyridine
DME	1,2-Dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMFDMA	*N*,*N*-dimethylformamide dimethyl acetal
DMS	Dimethylsulfide
DMSO	Dimethylsulfoxide
DMSY	Dimethylsulfoxonium methylide
DMT	Dimethoxytrityl
DPPA	Diphenylphosphoryl azide
dppb	1,4-*bis*(Diphenylphosphino)butane
dppe	1,2-*bis*(Diphenylphosphino)ethane
dppf	1,1′-*bis*(Diphenylphosphino)ferrocene
dppp	1,3-*bis*(Diphenylphosphino)propane
dr	Diastereoselctive ratio
DTBAD	Di-*tert*-butylazodicarbonate
DTBMP	2,6-Di-*tert*-butyl-4-methylpyridine
E1	Unimolecular elimination
E1cB	2-Step, base-induced β-elimination *via* carbanion
E2	Bimolecular elimination
EAN	Ethylammonium nitrate
EDCI	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
EDDA	Ethylenediamine diacetate
ee	Enantiomeric excess
Ei	Two groups leave at about the same time and bond to each other as they are doing so
Eq	Equivalent
Et	Ethyl
EtOAc	Ethyl acetate
HMDS	Hexamethyldisilazane
HMPA	Hexamethylphosphoramide
HMTA	Examethylenetetramine
HMTTA	1,1,4,7,10,10-Hexamethyltriethylenetetramine
IBX	*o*-iodoxybenzoic acid
Imd	Imidazole
KHMDS	Potassium hexamethyldisilazide
LAH	Lithium aluminum hydride
LDA	Lithium diisopropylamide
LHMDS	Lithium hexamethyldisilazide

LTMP	Lithium 2,2,6,6-tetramethylpiperidide
M	Metal
m-CPBA	*m*-chloroperoxybenzoic acid
MCRs	Multicomponent reactions
Mes	Mesityl
MPM	Methyl phenylmethyl
MPS	Morpholine-polysulfide
Ms	Methanesulfonyl
MTBE	Methyl tertiary butyl ether
MVK	Methyl vinyl ketone
MWI	Microwave irradiation
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide
NMP	1-Methyl-2-pyrrolidinone
Nos	Nosylate (4-nitrobenzenesulfonyl)
N-PSP	*N*-phenylselenophthalimide
N-PSS	*N*-phenylselenosuccinimide
Nu	Nucleophile
PCC	Pyridinium chlorochromate
PDC	Pyridinium dichromate
PE	Premature ejaculation
Piv	Pivaloyl
PMB	*para*-Methoxybenzyl
PPA	Polyphosphoric acid
PPTS	Pyridinium *p*-toluenesulfonate
PT	Phenyltetrazolyl
$PyPh_2P$	Diphenyl 2-pyridylphosphine
Pyr	Pyridine
Red-Al	Sodium *bis*(methoxy-ethoxy)aluminum hydride
Red-Al	Sodium *bis*(methoxy-ethoxy)aluminum hydride (SMEAH)
Salen	*N,N′*-disalicylidene-ethylenediamine
SET	Single electron transfer
SIBX	Stabilized IBX
SM	Starting material
SMEAH	Sodium *bis*(methoxy-ethoxy)aluminum hydride
S_N1	Unimolecular nucleophilic substitution
S_N2	Bimolecular nucleophilic substitution
S_NAr	Nucleophilic substitution on an aromatic ring
SSRI	Selective serotonin reuptake inhibitor
TBABB	tetra-*n*-butylammonium bibenzoate
TBAF	tetra-*n*-butylammonium fluoride
TBAO	1,3,3-Trimethyl-6-azabicyclo[3.2.1]octane
TBDMS	*tert*-Butyldimethylsilyl

TBDPS	*tert*-Butyldiphenylsilyl
TBS	*tert*-Butyldimethylsilyl
t-Bu	*tert*-Butyl
TDS	Thexyldimethylsilyl
TEA	Triethylamine
TEMPO	2,2,6,6-Tetramethylpiperidinyloxy
TEOC	Trimethysilylethoxycarbonyl
Tf	Trifluoromethanesulfonyl (triflyl)
TFA	Trifluoroacetic acid
TFAA	Trifluoroacetic anhydride
TFP	Tri-2-furylphosphine
THF	Tetrahydrofuran
TIPS	Triisopropylsilyl
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
TMG	1,1,3,3-Tetramethylguanidine
TMP	Tetramethylpiperidine
TMS	Trimethylsilyl
TMSCl	Trimethylsilyl chloride
TMSCN	Trimethylsilyl cyanide
TMSI	Trimethylsilyl iodide
TMSOTf	Trimethylsilyl triflate
Tol	Toluene or tolyl
Tol-BINAP	2,2′-*bis*(di-*p*-tolylphosphino)-1,1′-binaphthyl
TosMIC	(*p*-tolylsulfonyl)methyl isocyanide
Ts	Tosyl
TsO	Tosylate
UHP	Urea-hydrogen peroxide

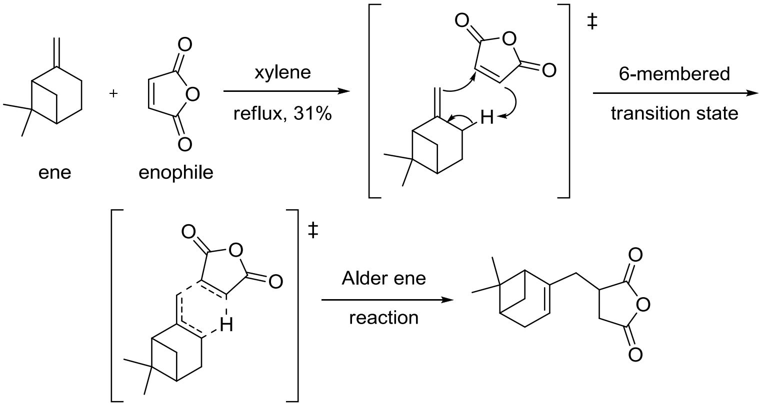
Alder ene reaction

The Alder ene reaction, also known as the hydro-allyl addition, is addition of an enophile to an alkene (ene) *via* allylic transposition. The four-electron system including an alkene π-bond and an allylic C–H σ-bond can participate in a pericyclic reaction in which the double bond shifts and new C–H and C–C σ-bonds are formed.



X=Y: C=C, C≡C, C=O, C=N, N=N, N=O, S=O, *etc.*

Example 1[5]



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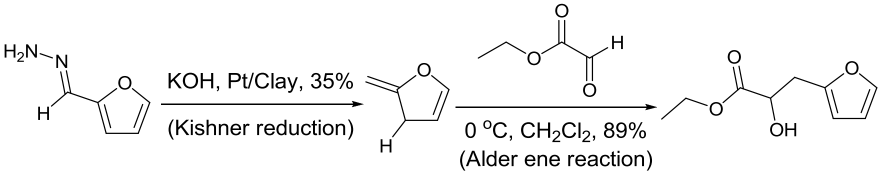
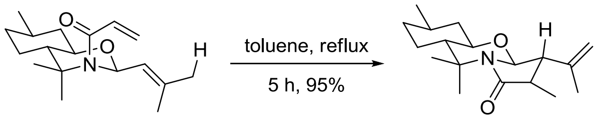
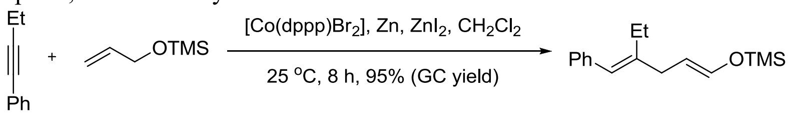


Example 3, Intramolecular Alder ene reaction[8]



Example 4, Cobalt-catalyzed Alder ene reaction[9]



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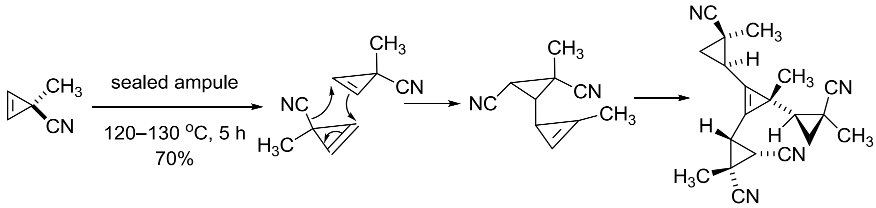
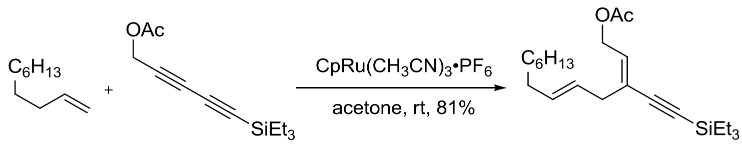
DOI 10.1007/978-3-319-03979-4_1, © Springer International Publishing Switzerland 2014

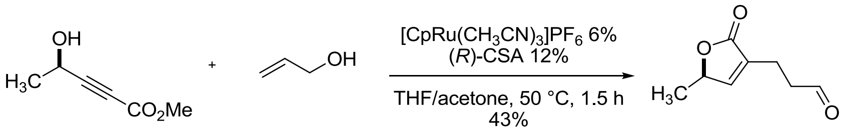
Example 5, Nitrile Alder ene reaction[10]



Example 6[11]



Example 7[13]

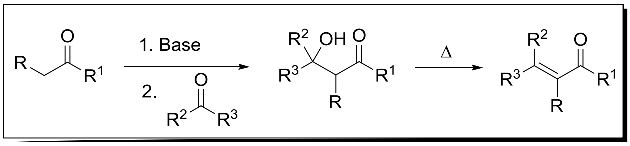


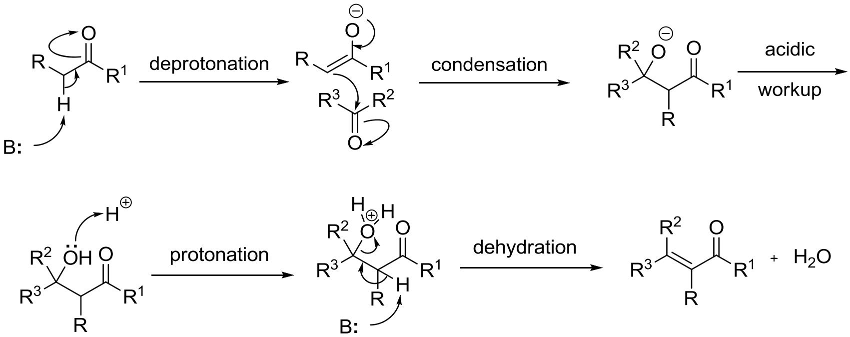
References

1. Alder, K.; Pascher, F.; Schmitz, A. *Ber.* **1943,** *76*, 27–53. Kurt Alder (Germany, 1902–1958) shared the Nobel Prize in Chemistry in 1950 with his teacher Otto Diels (Germany, 1876–1954) for the development of the diene synthesis.
2. Oppolzer, W. *Pure Appl. Chem.* **1981,** *53*, 1181–1201. (Review).
3. Johnson, J. S.; Evans, D. A. *Acc. Chem. Res.* **2000,** *33*, 325–335. (Review).
4. Mikami, K.; Nakai, T. In *Catalytic Asymmetric Synthesis;* 2nd edn.; Ojima, I., ed.; Wiley–VCH: New York, **2000,** 543–568. (Review).
5. Sulikowski, G. A.; Sulikowski, M. M. *e-EROS Encyclopedia of Reagents for Organic Synthesis* **2001,** Wiley: Chichester, UK.
6. Brummond, K. M.; McCabe, J. M. *The Rhodium(I)-Catalyzed Alder ene Reaction*. In *Modern Rhodium-Catalyzed Organic Reactions* **2005,** 151–172. (Review).
7. Miles, W. H.; Dethoff, E. A.; Tuson, H. H.; Ulas, G. *J. Org. Chem.* **2005,** *70*, 2862–2865.
8. Pedrosa, R.; Andres, C.; Martin, L.; Nieto, J.; Roson, C. *J. Org. Chem.* **2005,** *70*, 4332–4337.
9. Hilt, G.; Treutwein, J. *Angew. Chem. Int. Ed.* **2007,** *46*, 8500–8502.
10. Ashirov, R. V.; Shamov, G. A.; Lodochnikova, O. A.; Litvynov, I. A.; Appolonova, S. A.; Plemenkov, V. V. *J. Org. Chem.* **2008,** *73*, 5985–5988.
11. Cho, E. J.; Lee, D. *Org. Lett.* **2008,** *10*, 257–259.
12. Curran, T. T. *Alder Ene Reaction*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 2–32. (Review).
13. Trost, B. M.; Quintard, A. *Org. Lett.* **2012,** *14*, 4698–4670.
14. Karmakar, R.; Mamidipalli, P.; Yun, S. Y.; Lee, D. *Org. Lett.* **2013,** *15*, 1938–1941.

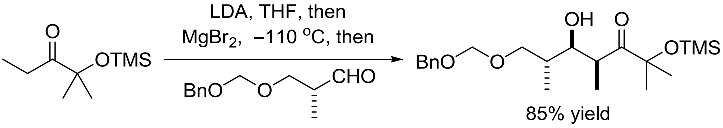
Aldol condensation

The aldol condensation is the coupling of an enolate ion with a carbonyl compound to form a β-hydroxycarbonyl, and sometimes, followed by dehydration to give a conjugated enone. A simple case is addition of an enolate to an **ald**ehyde to afford an alcoh**ol**, thus the name **aldol**.

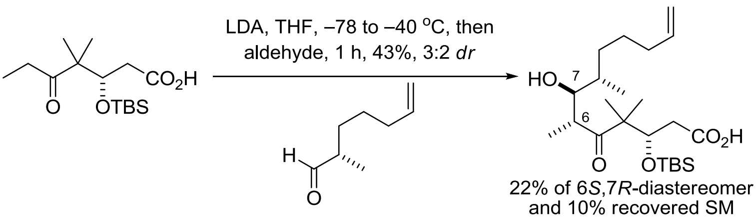




Example 1[3]



Example 2[8]



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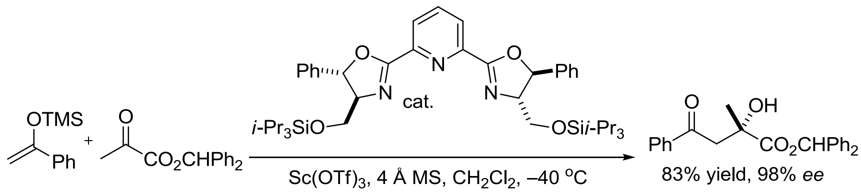
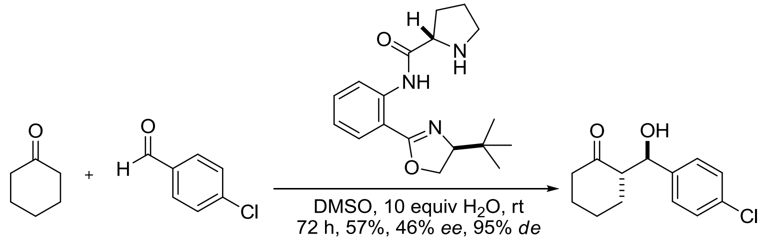
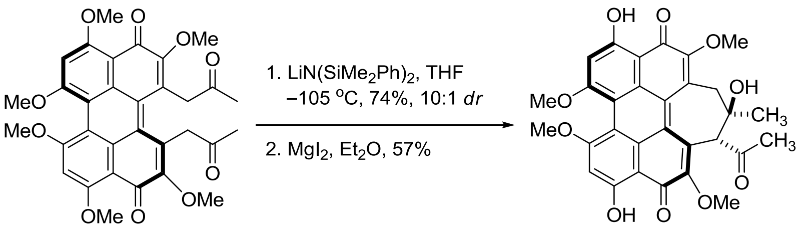
Example 3, Enantioselective Mukaiyama aldol reaction[10]



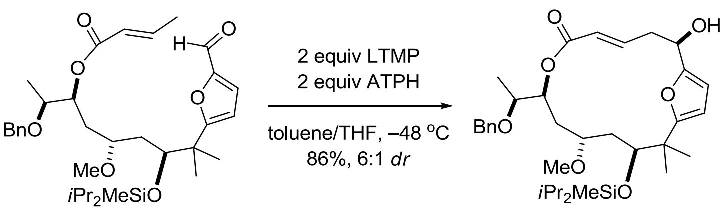
Example 4, Intermolecular aldol reaction using organocatalyst[12]



Example 5, Intramolecular aldol reaction[13]



Example 6, Intramolecular vinylogous aldol reaction[15]



References

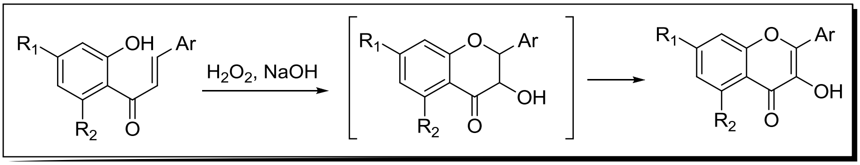
1. Wurtz, C. A. *Bull. Soc. Chim. Fr.* **1872,** *17,* 436–442. Charles Adolphe Wurtz (1817–1884) was born in Strasbourg, France. After his doctoral training, he spent a year under Liebig in 1843. In 1874, Wurtz became the Chair of Organic Chemistry at the Sorbonne, where he educated many illustrous chemists such as Crafts, Fittig, Friedel, and van't Hoff. The Wurtz reaction, where two alkyl halides are treated with

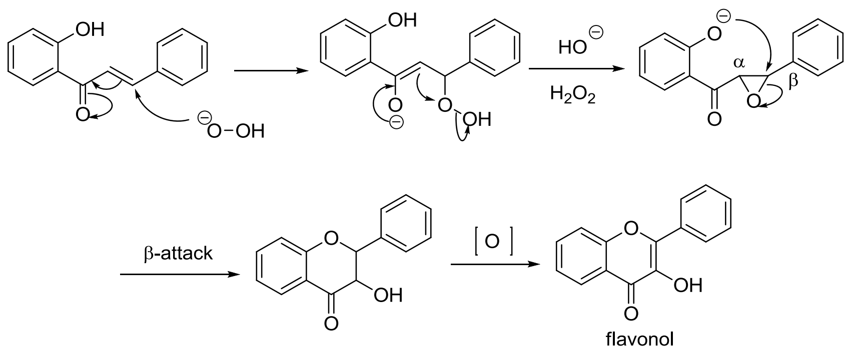
sodium to form a new carbon–carbon bond, is no longer considered synthetically useful, although *the aldol reaction* that Wurtz discovered in 1872 has become a staple in organic synthesis. Alexander P. Borodin is also credited with the discovery of the aldol reaction together with Wurtz. In 1872 he announced to the Russian Chemical Society the discovery of a new by-product in aldehyde reactions with properties like that of an alcohol, and he noted similarities with compounds already discussed in publications by Wurtz from the same year.

2. Nielsen, A. T.; Houlihan, W. J. *Org. React.* **1968,** *16*, 1–438. (Review).
3. Still, W. C.; McDonald, J. H., III. *Tetrahedron Lett*. **1980,** *21*, 1031–1034.
4. Mukaiyama, T. *Org. React.* **1982,** *28*, 203–331. (Review).
5. Mukaiyama, T.; Kobayashi, S. *Org. React.* **1994,** *46*, 1–103. (Review on tin(II) enolates).
6. Johnson, J. S.; Evans, D. A. *Acc. Chem. Res*. **2000,** *33*, 325–335. (Review).
7. Denmark, S. E.; Stavenger, R. A. *Acc. Chem. Res*. **2000,** *33*, 432–440. (Review).
8. Yang, Z.; He, Y.; Vourloumis, D.; Vallberg, H.; Nicolaou, K. C. *Angew. Chem. Int. Ed.* **1997,** *36*, 166–168.
9. Mahrwald, R. (ed.) *Modern Aldol Reactions,* Wiley–VCH: Weinheim, Germany, **2004**. (Book).
10. Desimoni, G.; Faita, G.; Piccinini, F.; Toscanini, M. *Eur. J. Org. Chem*. **2006,** 5228–5230.
11. Guillena, G.; Najera, C.; Ramon, D. J. *Tetrahedron: Asymmetry* **2007,** *18*, 2249–2293. (Review on enantioselective direct aldol reaction using organocatalysis.)
12. Doherty, S.; Knight, J. G.; McRae, A.; Harrington, R. W.; Clegg, W. *Eur. J. Org. Chem*. **2008,** 1759–1766.
13. O'Brien, E. M.; Morgan, B. J.; Kozlowski, M. C. *Angew. Chem. Int. Ed.* **2008,** *47*, 6877–6880.
14. Trost, B. M.; Brindle, C. S. *Chem. Soc. Rev.* **2010,** *39*, 1600–1632. (Review).
15. Gazaille, J. A.; Abramite, J. A.; Sammakia, T. *Org. Lett.* **2012,** *14*, 178–181.
16. Esumi, T.; Yamamoto, C.; Tsugawa, Y.; Toyota, M.; Asakawa, Y.; Fukuyama Y. *Org. Lett.* **2013,** *15*, 1898–1901.

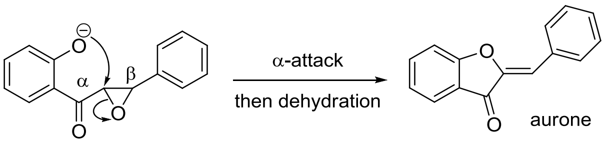
Algar–Flynn–Oyamada Reaction

Conversion of 2′-hydroxychalcones to 2-aryl-3-hydroxy-4*H*-1-benzopyran-4-ones (flavonols) by an oxidative cyclization.

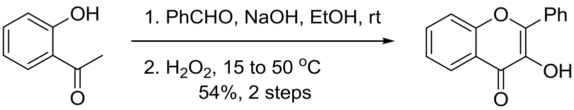




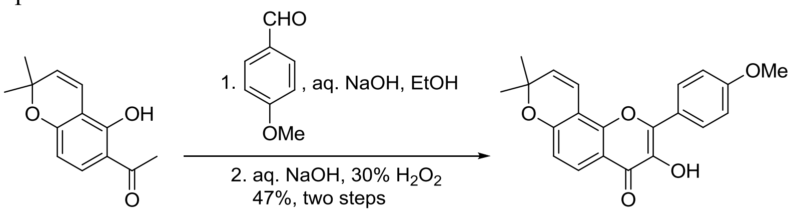
A side reaction:



Example 1[5]



Example 2[5]



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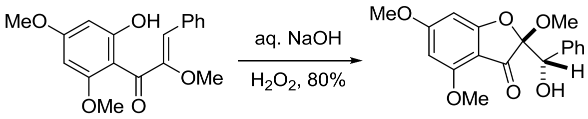
Example 3, The side reaction dominated to give the aurone derivative[9]



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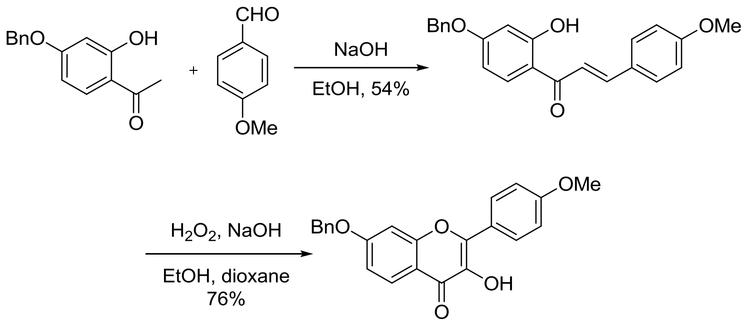
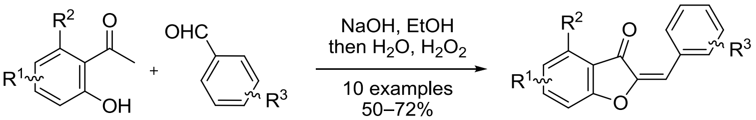


Example 5, The side recation dominated to give the aurone derivative[13]

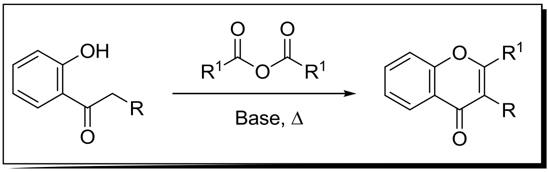


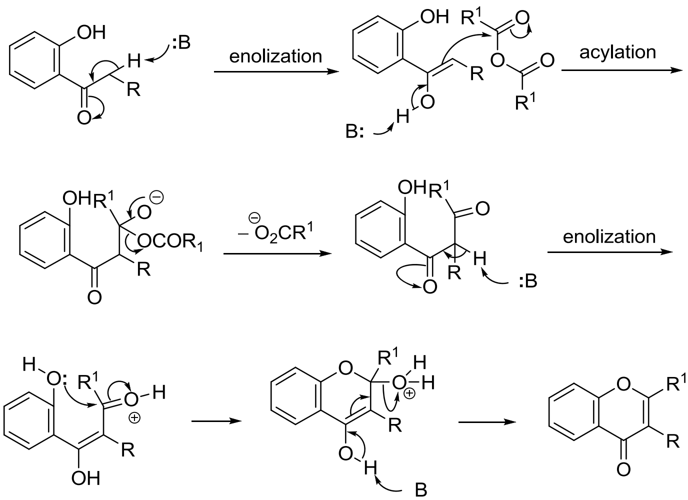
References

1. Algar, J.; Flynn, J. P. *Proc. Roy. Irish Acad.* **1934,** *B42*, 1–8. Algar and Flynn were Irish chemists.
2. Oyamada, T. *J. Chem. Soc. Jpn* **1934,** *55*, 1256–1261.
3. Oyamada, T. *Bull. Chem. Soc. Jpn.* **1935,** *10*, 182–186.
4. Wheeler, T. S. *Record Chem. Progr.* **1957,** *18*, 133–161. (Review).
5. Smith, M. A.; Neumann, R. M.; Webb, R. A. *J. Heterocycl. Chem.* **1968,** *5*, 425–426.
6. Wagner, H.; Farkas, L. In *The Flavonoids*; Harborne, J. B.; Mabry, T. J.; Mabry H., Eds.; Academic Press: New York, **1975,** *1,* pp 127–213. (Review).
7. Wollenweber, E. In *The Flavonoids: Advances in Research*; Harborne, J. B.; Mabry, T. J., Eds; Chapman and Hall: New York, **1982,** pp 189–259. (Review).
8. Wollenweber, E. In *The Flavonoids: Advances in Research since 1986*; Harborne, J. B., Ed.; Chapman and Hall: New York, **1994,** pp 259–335. (Review).
9. Bennett, M.; Burke, A. J.; O'Sullivan, W. I. *Tetrahedron* **1996,** *52*, 7163–7178.
10. Bohm, B. A.; Stuessy, T. F. *Flavonoids of the Sunflower Family (Asteraceae)*; Springer-Verlag: New York, **2000**. (Review).
11. Limberakis, C. *Algar–Flynn–Oyamada Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 496–503. (Review).
12. Li, Z.; Ngojeh, G.; DeWitt, P.; Zheng, Z.; Chen, M.; Lainhart, B.; Li, V.; Felpo, P. *Tetrahedron Lett*. **2008,** *49*, 7243–7245.
13. Zhao, X.; Liu, J.; Xie, Z.; Li, Y. *Synthesis* **2012,** *44,* 2217–2224.

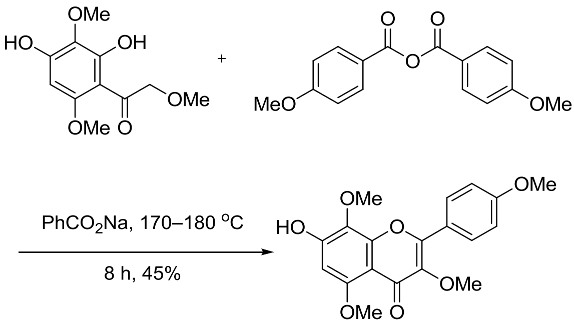
Allan–Robinson reaction

Synthesis of flavones or isoflavones by the treatment of of *o*-hydroxyaryl ketones with aromatic aldehydes in the presence of a base. *Cf.* Kostanecki reaction.

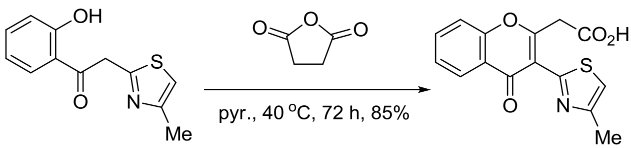




Example 1[6]



Example 2, Non-aromatic anhydride[9]



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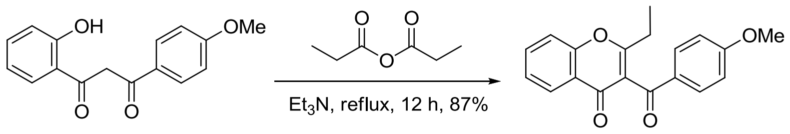
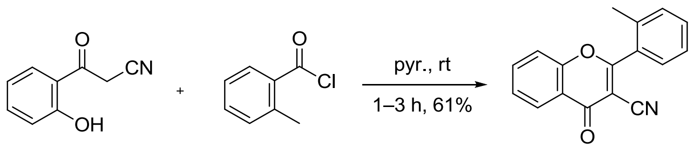
DOI 10.1007/978-3-319-03979-4_4, © Springer International Publishing Switzerland 2014

Example 3, Non-aromatic anhydride[10]



Example 4, Acid chloride in place of anhydride[10]

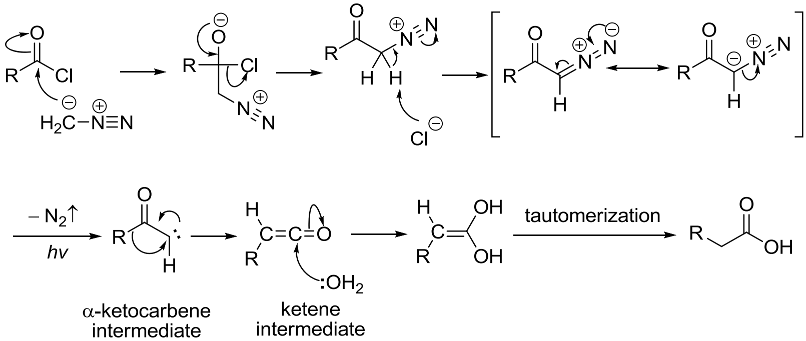


References

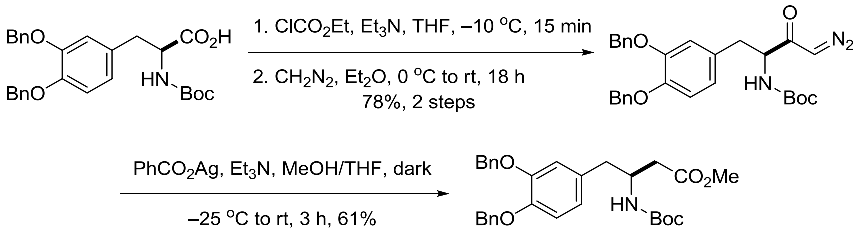
1. Allan, J.; Robinson, R. *J. Chem. Soc.* **1924,** *125*, 2192–2195. Robert Robinson (United Kingdom, 1886–1975) won the Nobel Prize in Chemistry in 1947 for his studies on alkaloids. However, Robinson himself considered his greatest contribution to science was that he founded the qualitative theory of electronic mechanisms in organic chemistry. Robinson, along with Lapworth (a friend) and Ingold (a rival), pioneered the arrow pushing approach to organic reaction mechanism. Robinson was also an accomplished pianist. James Allan, his student, also coauthored another important paper with Robinson on the relative directive powers of groups for aromatic substitution.
2. Széll, T.; Dózsai, L.; Zarándy, M.; Menyhárth, K. *Tetrahedron* **1969,** *25*, 715–724.
3. Wagner, H.; Maurer, I.; Farkas, L.; Strelisky, J. *Tetrahedron* **1977,** *33*, 1405–1409.
4. Dutta, P. K.; Bagchi, D.; Pakrashi, S. C. *Indian J. Chem., Sect. B* **1982,** *21B*, 1037–1038.
5. Patwardhan, S. A.; Gupta, A. S. *J. Chem. Res., (S)* **1984,** 395.
6. Horie, T.; Tsukayama, M.; Kawamura, Y.; Seno, M. *J. Org. Chem.* **1987,** *52*, 4702–4709.
7. Horie, T.; Tsukayama, M.; Kawamura, Y.; Yamamoto, S. *Chem. Pharm. Bull.* **1987,** *35*, 4465–4472.
8. Horie, T.; Kawamura, Y.; Tsukayama, M.; Yoshizaki, S. *Chem. Pharm. Bull.* **1989,** *37*, 1216–1220.
9. Poyarkov, A. A.; Frasinyuk, M. S.; Kibirev, V. K.; Poyarkova, S. A. *Russ. J. Bioorg. Chem.* **2006,** *32*, 277–279.
10. Peng, C.-C.; Rushmore, T.; Crouch, G. J.; Jones, J. P. *Bioorg. Med. Chem. Lett.* **2008,** *16*, 4064–4074.
11. Levchenko, K. S.; Semenova, I. S.; Yarovenko, V. N.; Shmelin, P. S.; Krayushkin, M. M. *Tetrahedron Lett.* **2012,** *53*, 3630–3632;

Arndt–Eistert homologation

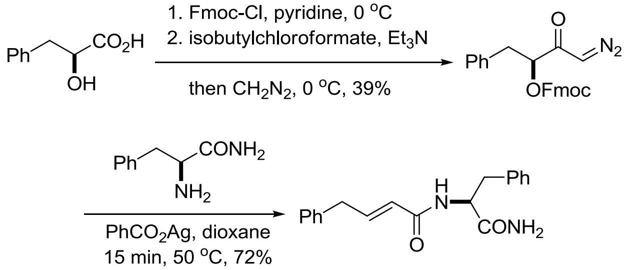
One-carbon homologation of carboxylic acids using diazomethane.



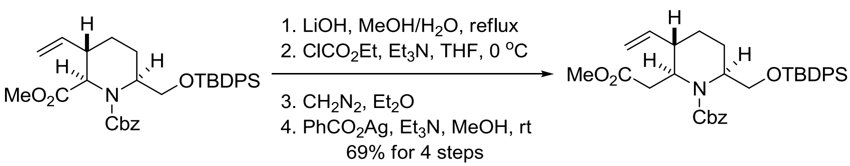
Example 1[7]



Example 2, An interesting variation[9]



Example 3[10]



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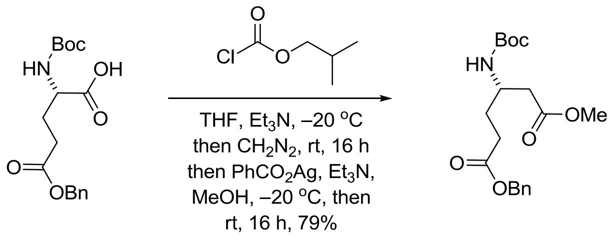
Example 4[10]

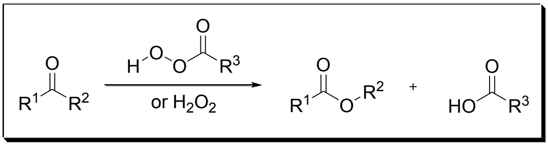


References

1. Arndt, F.; Eistert, B. *Ber.* **1935,** *68*, 200–208. Fritz Arndt (1885–1969) was born in Hamburg, Germany. He discovered the Arndt–Eistert homologation at the University of Breslau where he extensively investigated the synthesis of diazomethane and its reactions with aldehydes, ketones, and acid chlorides. Fritz Arndt's chain-smoking of cigars ensured that his presence in the laboratories was always well advertised. Bernd Eistert (1902–1978), born in Ohlau, Silesia, was Arndt's Ph.D. student. Eistert later joined I. G. Farbenindustrie, which became BASF after the Allies broke up the conglomerate following WWII.
2. Podlech, J.; Seebach, D. *Angew. Chem. Int. Ed.* **1995,** *34*, 471–472.
3. Matthews, J. L.; Braun, C.; Guibourdenche, C.; Overhand, M.; Seebach, D. In *Enantioselective Synthesis of β-Amino Acids* Juaristi, E. ed.; Wiley-VCH: Weinheim, Germany, **1996,** pp 105–126. (Review).
4. Katritzky, A. R.; Zhang, S.; Fang, Y. *Org. Lett.* **2000,** *2*, 3789–3791.
5. Vasanthakumar, G.-R.; Babu, V. V. S. *Synth. Commun.* **2002,** *32*, 651–657.
6. Chakravarty, P. K.; Shih, T. L.; Colletti, S. L.; Ayer, M. B.; Snedden, C.; Kuo, H.; Tyagarajan, S.; Gregory, L.; Zakson-Aiken, M.; Shoop, W. L.; Schmatz, D. M.; Wyvratt, M. J.; Fisher, M. H.; Meinke, P. T. *Bioorg. Med. Chem. Lett.* **2003,** *13*, 147–150.
7. Gaucher, A.; Dutot, L.; Barbeau, O.; Hamchaoui, W.; Wakselman, M.; Mazaleyrat, J.-P. *Tetrahedron: Asymmetry* **2005,** *16*, 857–864.
8. Podlech, J. In *Enantioselective Synthesis of β-Amino Acids (2nd Edn.)* Wiley: Hoboken, NJ, **2005,** pp 93–106. (Review).
9. Spengler, J.; Ruiz-Rodriguez, J.; Burger, K.; Albericio, F. *Tetrahedron Lett.* **2006,** *47*, 4557–4560.
10. Toyooka, N.; Kobayashi, S.; Zhou, D.; Tsuneki, H.; Wada, T.; Sakai, H.; Nemoto, H.; Sasaoka, T.; Garraffo, H. M.; Spande, T. F.; Daly, J. W. *Bioorg. Med. Chem. Lett.* **2007,** *17*, 5872–5875.
11. Fuchter, M. J. *Arndt–Eistert Homologation*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 336–349. (Review).
12. Saavedra, C. J.; Boto, A.; Hernández, R. *Org. Lett.* **2012,** *14*, 3542–3545.

Baeyer–Villiger oxidation

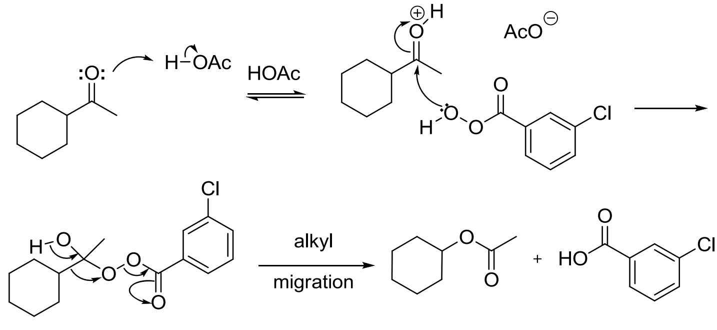
General scheme:



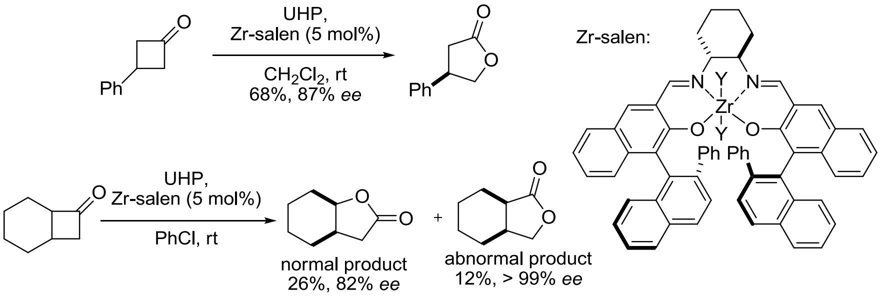
The most electron-rich alkyl group (more substituted carbon) migrates first. The general migration order: tertiary alkyl > cyclohexyl > secondary alkyl > benzyl > phenyl > primary alkyl > methyl >> H.

For substituted aryls:

p-MeO-Ar > *p*-Me-Ar > *p*-Cl-Ar > *p*-Br-Ar > *p*-O_2N-Ar

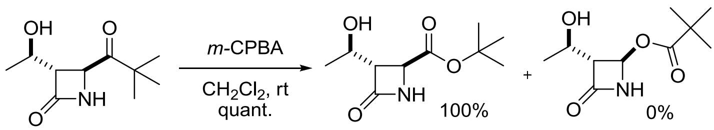


Example 1[4]



UHP = Urea-hydrogen peroxide complex

Example 2, Chemoselective over lactam[5]



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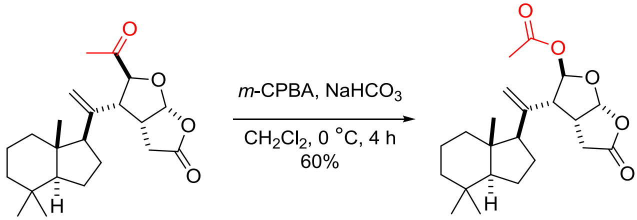
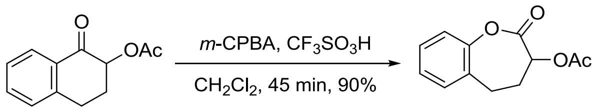
DOI 10.1007/978-3-319-03979-4_6, © Springer International Publishing Switzerland 2014

Example 3, Chemoselective over lactone[6]



Example 4, Chemoselective over ester[8]

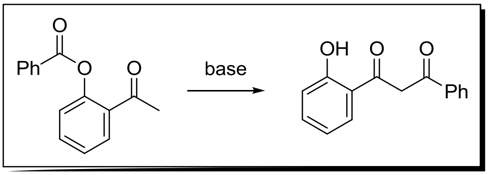


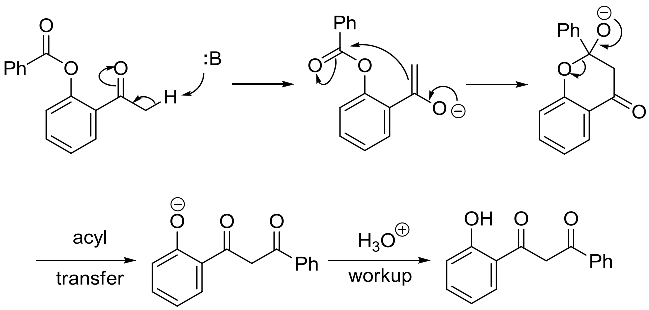
References

1. v. Baeyer, A.; Villiger, V. *Ber.* **1899,** *32*, 3625–3633. Adolf von Baeyer (1835–1917) was one of the most illustrious organic chemists in history. He contributed to many areas of the field. The Baeyer–Drewson indigo synthesis made possible the commercialization of synthetic indigo. Another one of Baeyer's claim of fame is his synthesis of barbituric acid, named after his then girlfriend, Barbara. Baeyer's real joy was in his laboratory and he deplored any outside work that took him away from his bench. When a visitor expressed envy that fortune had blessed so much of Baeyer's work with success, Baeyer retorted dryly: "Herr Kollege, I experiment more than you." As a scientist, Baeyer was free of vanity. Unlike other scholastic masters of his time (Liebig for instance), he was always ready to acknowledge ungrudgingly the merits of others. Baeyer's famous greenish-black hat was a part of his perpetual wardrobe and he had a ritual of tipping his hat when he admired novel compounds. Adolf von Baeyer received the Nobel Prize in Chemistry in 1905 at age seventy. His apprentice, Emil Fischer, won it in 1902 when he was fifty, three years before his teacher. Victor Villiger (1868–1934), born in Switzerland, went to Munich and worked with Adolf von Baeyer for eleven years.
2. Krow, G. R. *Org. React.* **1993,** *43*, 251–798. (Review).
3. Renz, M.; Meunier, B. *Eur. J. Org. Chem.* **1999,** *4*, 737–750. (Review).
4. Wantanabe, A.; Uchida, T.; Ito, K.; Katsuki, T. *Tetrahedron Lett.* **2002,** *43*, 4481–4485.
5. Laurent, M.; Ceresiat, M.; Marchand-Brynaert, J. *J. Org. Chem.* **2004,** *69*, 3194–3197.
6. Brady, T. P.; Kim, S. H.; Wen, K.; Kim, C.; Theodorakis, E. A. *Chem. Eur. J.* **2005,** *11*, 7175–7190.
7. Curran, T. T. *Baeyer–Villiger Oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 160–182. (Review).
8. Demir, A. S.; Aybey, A. *Tetrahedron* **2008,** *64*, 11256–11261.
9. Zhou, L.; Liu, X.; Ji, J.; Zhang, Y.; Hu, X.; Lin, L.; Feng, X. *J. Am. Chem. Soc.* **2012,** *134*, 17023–17026. (Desymmetrization and Kinetic Resolution).
10. Itoh, Y.; Yamanaka, M.; Mikami, K. *J. Org. Chem.* **2013,** *78*, 146–153.

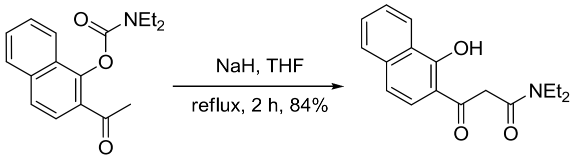
Baker–Venkataraman rearrangement

Base-catalyzed acyl transfer reaction that converts α-acyloxyketones to β-diketones.

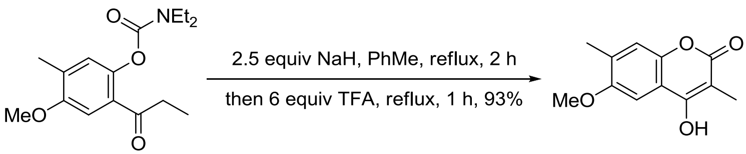




Example 1, Carbamoyl Baker–Venkataraman rearrangement[5]



Example 2, Carbamoyl Baker–Venkataraman rearrangement, followed by cyclization[6]



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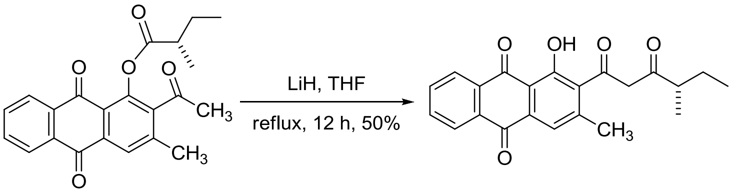
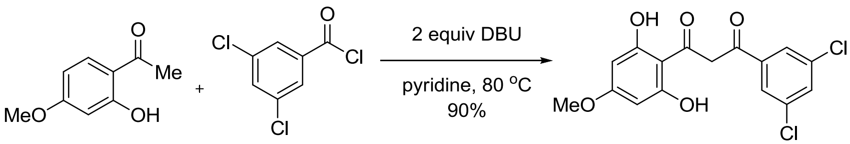
DOI 10.1007/978-3-319-03979-4_7,

Example 3, Baker–Venkataraman rearrangement[9]



Example 4, Baker–Venkataraman rearrangement[10]

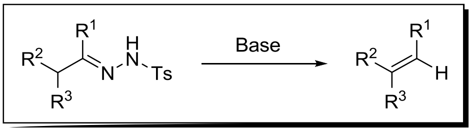


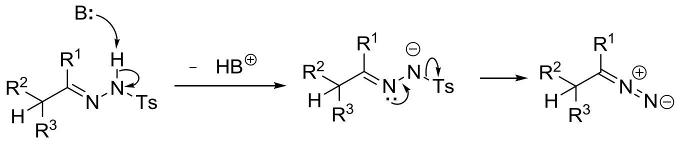
References

1. Baker, W. *J. Chem. Soc.* **1933,** 1381–1389. Wilson Baker (1900–2002) was born in Runcorn, England. He studied chemistry at Manchester under Arthur Lapworth and at Oxford under Robinson. In 1943, Baker was the first to confirm that penicillin contained sulfur, of which Robinson commented: "This is a feather in your cap, Baker." Baker began his independent academic career at University of Bristol. He retired in 1965 as the Head of the School of Chemistry. Baker was a well-known chemist centenarian, spending 47 years in retirement!
2. Mahal, H. S.; Venkataraman, K. *J. Chem. Soc.* **1934,** 1767–1771. K. Venkataraman studied under Robert Robinson Manchester. He returned to India and later arose to be the Director of the National Chemical Laboratory at Poona.
3. Kraus, G. A.; Fulton, B. S.; Wood, S. H. *J. Org. Chem.* **1984,** *49*, 3212–3214.
4. Reddy, B. P.; Krupadanam, G. L. D. *J. Heterocycl. Chem.* **1996,** *33*, 1561–1565.
5. Kalinin, A. V.; da Silva, A. J. M.; Lopes, C. C.; Lopes, R. S. C.; Snieckus, V. *Tetrahedron Lett.* **1998,** *39*, 4995–4998.
6. Kalinin, A. V.; Snieckus, V. *Tetrahedron Lett.* **1998,** *39*, 4999–5002.
7. Thasana, N.; Ruchirawat, S. *Tetrahedron Lett*. **2002,** *43*, 4515–4517.
8. Santos, C. M. M.; Silva, A. M. S.; Cavaleiro, J. A. S. *Eur. J. Org. Chem*. **2003,** 4575–4585.
9. Krohn, K.; Vidal, A.; Vitz, J.; Westermann, B.; Abbas, M.; Green, I. *Tetrahedron: Asymmetry* **2006,** *17*, 3051–3057.
10. Yu, Y.; Hu, Y.; Shao, W.; Huang, J.; Zuo, Y.; Huo, Y.; An, L.; Du, J.; Bu, X. *E. J. Org. Chem*. **2011,** 4551–4563.

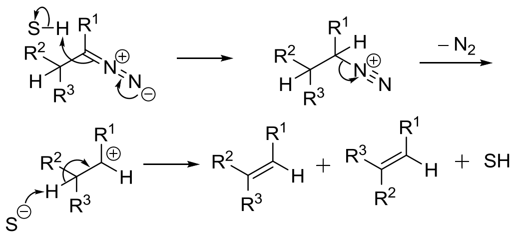
Bamford–Stevens reaction

The Bamford−Stevens reaction and the Shapiro reaction share a similar mechanistic pathway. The former uses a base such as Na, NaOMe, LiH, NaH, $NaNH_2$, heat, *etc.*, whereas the latter employs bases such as alkyllithiums and Grignard reagents. As a result, the Bamford−Stevens reaction furnishes more-substituted olefins as the thermodynamic products, while the Shapiro reaction generally affords less-substituted olefins as the kinetic products.

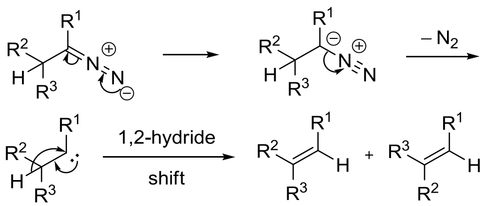




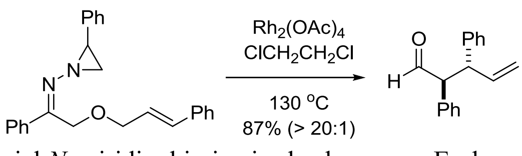
In protic solvent (S–H):



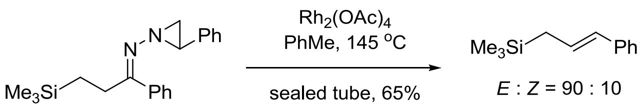
In aprotic solvent:



Example 1, Tandem Bamford–Stevens/thermal aliphatic Claisen rearrangement sequence[6]



The starting material *N*-aziridinyl imine is also known as Eschenmoser hydrazone.
Example 2, Thermal Bamford–Stevens[6]



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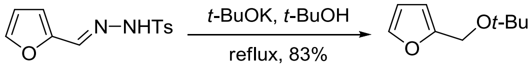
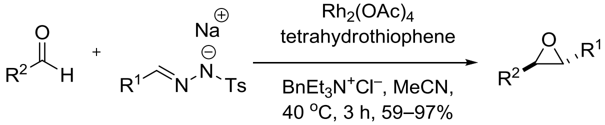
DOI 10.1007/978-3-319-03979-4_8, © Springer International Publishing Switzerland 2014

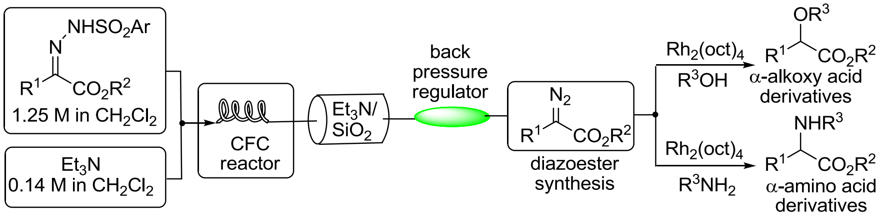
Example 3[7]



Example 4[8]



Example 5, Diazoesters from arylsulfonylhydrazones by means of in-flow Bamford-Stevens reactions[13]



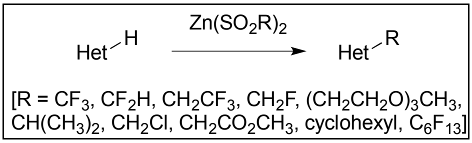
CFC = Continuous-Flow Centrifugation

References

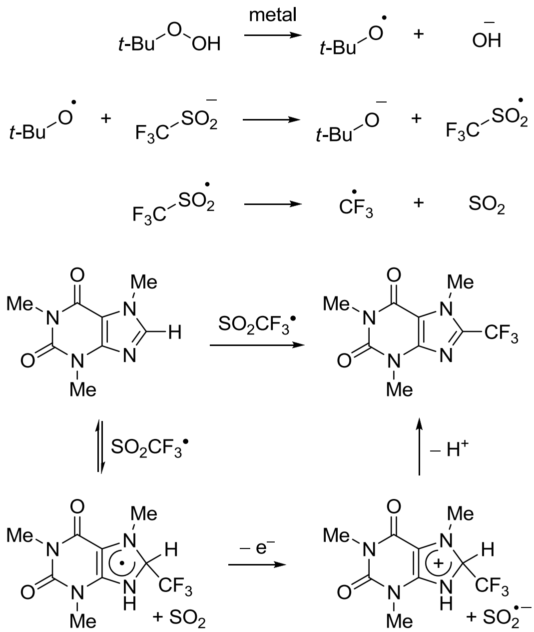
1. Bamford, W. R.; Stevens, T. S. M. *J. Chem. Soc.* **1952,** 4735–4740. Thomas Stevens (1900–2000), another chemist centenarian, was born in Renfrew, Scotland. He and his student W. R. Bamford published this paper at the University of Sheffield, UK. Stevens also contributed to another name reaction, the McFadyen–Stevens reaction.
2. Felix, D.; Müller, R. K.; Horn, U.; Joos, R.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1972,** *55*, 1276–1319.
3. Shapiro, R. H. *Org. React.* **1976,** *23*, 405–507. (Review).
4. Adlington, R. M.; Barrett, A. G. M. *Acc. Chem. Res.* **1983,** *16*, 55–59. (Review on the Shapiro reaction).
5. Chamberlin, A. R.; Bloom, S. H. *Org. React.* **1990,** *39*, 1–83. (Review).
6. Sarkar, T. K.; Ghorai, B. K. *J. Chem. Soc., Chem. Commun*. **1992,** *17,* 1184–1185.
7. Chandrasekhar, S.; Rajaiah, G.; Chandraiah, L.; Swamy, D. N. *Synlett* **2001,** 1779–1780.
8. Aggarwal, V. K.; Alonso, E.; Hynd, G.; Lydon, K. M.; Palmer, M. J.; Porcelloni, M.; Studley, J. R. *Angew. Chem. Int. Ed.* **2001,** *40*, 1430–1433.
9. May, J. A.; Stoltz, B. M. *J. Am. Chem. Soc.* **2002,** *124*, 12426–12427.
10. Zhu, S.; Liao, Y.; Zhu, S. *Org. Lett.* **2004,** *6*, 377–380.
11. Baldwin, J. E.; Bogdan, A. R.; Leber, P. A.; Powers, D. C. *Org. Lett.* **2005,** *7*, 5195–5197.
12. Humphries, P. *Bamford–Stevens Reaction*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 642–652. (Review).
13. Bartrum, H. E.; Blakemore, D. C.; Moody, C. J.; Hayes, C. J. *Chem. Eur. J.* **2011,** *17*, 9586–9589.

Baran reagents

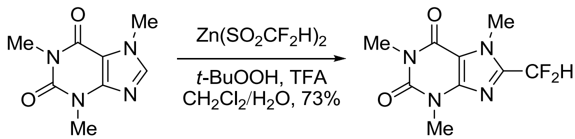
Zinc bis(alkanesulfinate) salts, which permit direct C−H functionalization of heteroarenes. Several of these reagents are now commercially available.[6,7]



A proposed mechanism for CF_3 radical generation is shown below.[5] Two regimes of differing reaction rates have been observed, and this tentative mechanism is still under study.[10]



Example 1, Difluoromethylation of caffeine[6]



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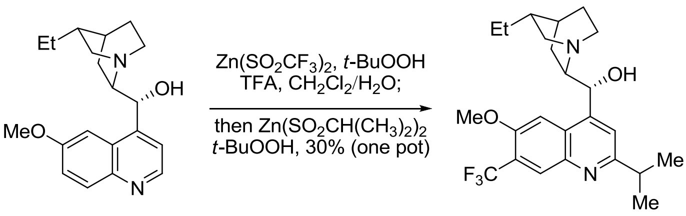
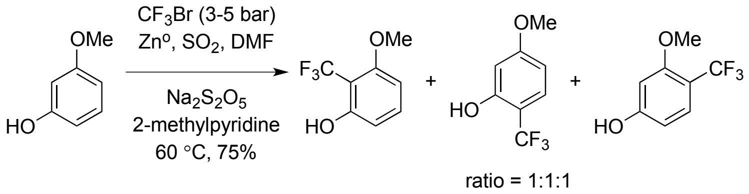
DOI 10.1007/978-3-319-03979-4_9, © Springer International Publishing Switzerland 2014

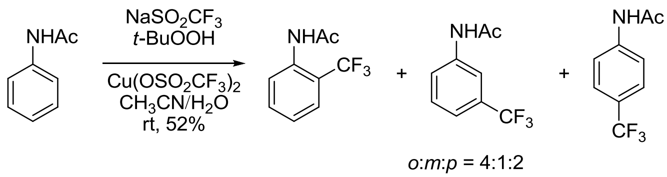
Example 2, sequential functionalization of dihydroquinine[7]



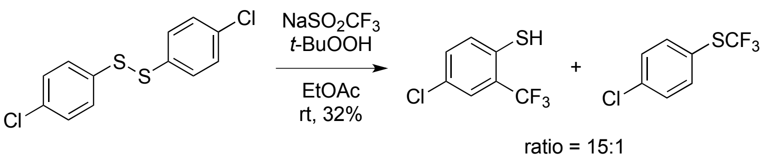
Cf. Example 3[1]



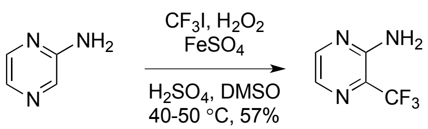
Cf. Example 4, use of Langlois reagent (sodium trifluoromethanesulfinate)[2]



Cf. Example 5[3]



Cf. Example 6, Yamakawa's group[4]



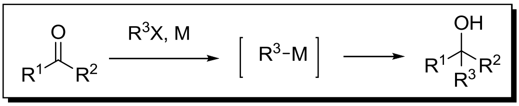
References

1. Tordeux, M.; Langlois, B.; Wakselman, C. *J. Chem. Soc., Perkin Trans. 1* **1990,**

2293–2299.
2. Langlois, B. R.; Laurent, E.; Roidot, N. *Tetrahedron Lett.* **1991,** *32*, 7525–7528.
3. Clavel, J. L.; Langlois, B.; Laurent, E.; Roidot, N. *Phosphorus, Sulfur, and Silicon* **1991,** *58*, 463–466.
4. Kino, T.; Nagase, Y.; Ohtsuka, Y.; Yamamoto, K.; Uraguchi, D.; Tokuhisa, K.; Yamakawa, T. *J. Fluorine Chem.* **2010,** *131*, 98–105.
5. Ji, Y.; Brueckl, T.; Baxter, R. D.; Fujiwara, Y.; Seiple, I. B.; Su, S.; Blackmond, D. G.; Baran, P. S. *Proc. Natl. Acad. Sci. U. S. A.* **2011,** *108*, 14411–14415. Phil S. Baran is currently a Professor in the Department of Chemistry at The Scripps Research Institute and Member of The Skaggs Institute for Chemical Biology. He was born in New Jersey in 1977, received his B.S. in chemistry from NYU in 1997, his Ph.D. at The Scripps Research Institute in 2001 (NSF fellow with K.C. Nicolaou), and from 2001–2003 he was an NIH postdoctoral fellow at Harvard in the laboratory of E. J. Corey. He has published over 120 scientific articles (H-Factor = 40) and has recently released a book in heterocyclic chemistry. His laboratory is focused on the invention of new reactions of broad utility and synthesizing complex natural products in a scalable, economic fashion. He recently won the John D. and Catharine T. MacArthur award.
6. Fujiwara, Y.; Dixon, J. A.; Rodriguez, R. A.; Baxter, R. D.; Dixon, D. D.; Collins, M. R.; Blackmond, D. G.; Baran, P. S. *J. Am. Chem. Soc.* **2012,** *134*, 1494–1497.
7. Fujiwara, Y.; Dixon, J. A.; O'Hara, F.; Funder, E. D.; Dixon, D. D.; Rodriguez, R. A.; Baxter, R. D.; Herle, B.; Sach, N.; Collins, M. R.; Ishihara, Y.; Baran, P. S. *Nature* **2012,** *492*, 95–99.
8. Zhou, Q.; Ruffoni, A.; Gianatassio, R.; Fujiwara, Y.; Sella, E.; Shabat, D.; Baran, P. S. *Angew. Chem. Int. Ed.* **2013,** *52,* 3949–3952
9. O'Hara, F.; Baxter, R. D.; O'Brien, A. G.; Collins, M. R.; Dixon, J. A.; Fujiwara, Y.; Ishihara, Y.; Baran, P. S. *Nature Protocols* **2013,** *8*, 1042–1047.
10. Baxter, R. D.; Blackmond, D. G. *Tetrahedron* **2013,** *69*, 5604–5608.
11. O'Hara, F.; Blackmond, D. G.; Baran, P. S. *J. Am. Chem. Soc.* **2013**, *135*, 12122–12134.

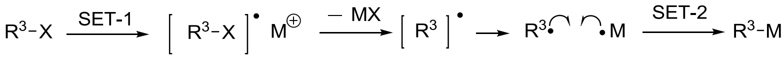
Barbier reaction

The Barbier reaction is an organic reaction between an alkyl halide and a carbonyl group as an electrophilic substrate in the presence of magnesium, aluminium, zinc, indium, tin or its salts. The reaction product is a primary, secondary or tertiary alcohol. *Cf.* Grignard reaction.



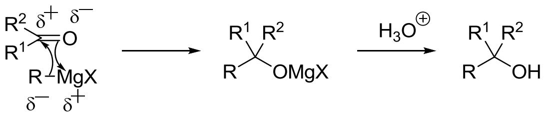
According to conventional wisdom,[3] the organometallic intermediate (M = Mg, Li, Sm, Zn, La, *etc.*) is generated *in situ*, which is intermediately trapped by the carbonyl compound. However, recent experimental and theoretical studies seem to suggest that the Barbier coupling reaction goes through a single electron transfer (SET) pathway.

Generation of the organometallic intermediate *in situ*:

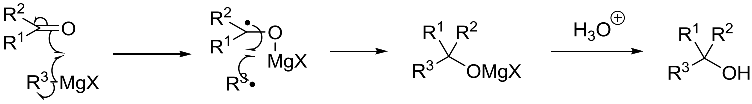


SET = single electron transfer

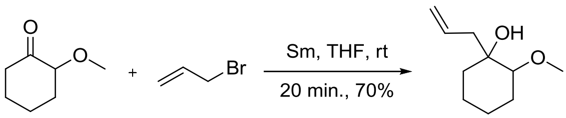
Ionic mechanism,



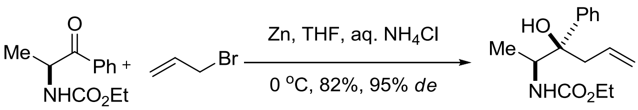
Single electron transfer (SET) mechanism:



Example 1[6]



Example 2[9]



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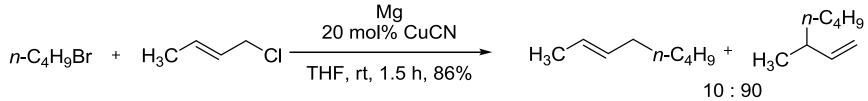
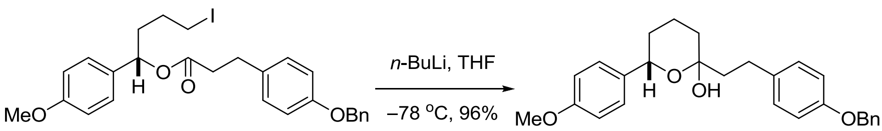
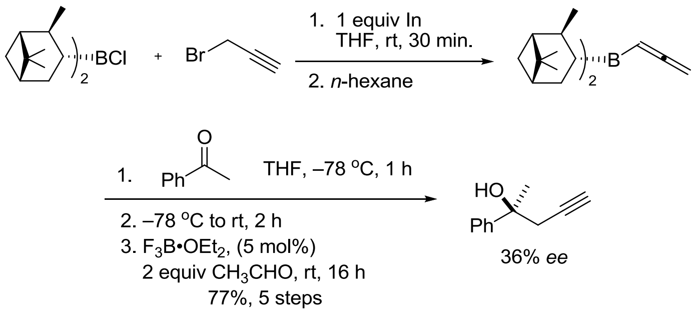
Example 3[10]



Example 4[11]



Example 5, The following whole sequence of 5 steps can also be carried out in one-pot[12]

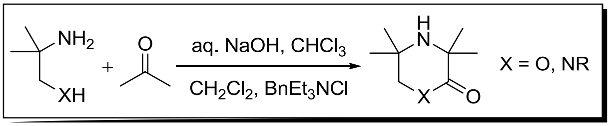


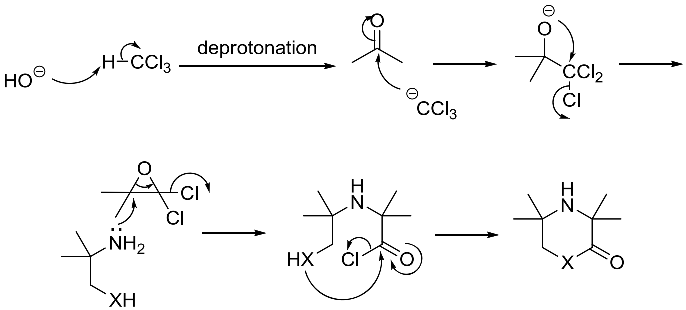
References

1. Barbier, P. *C. R. Hebd. Séances Acad. Sci.* **1899,** *128,* 110–111. Phillippe Barbier (1848–1922) was born in Luzy, Nièvre, France. He studied terpenoids using zinc and magnesium. Barbier suggested the use of magnesium to his student, Victor Grignard, who later discovered the Grignard reagent and won the Nobel Prize in 1912.
2. Grignard, V. *C. R. Hebd. Séances Acad. Sci.* **1900,** *130,* 1322–1324.
3. Moyano, A.; Pericás, M. A.; Riera, A.; Luche, J.-L. *Tetrahedron Lett.* **1990,** *31*, 7619–7622. (Theoretical study).
4. Alonso, F.; Yus, M. *Rec. Res. Dev. Org. Chem.* **1997,** *1*, 397–436. (Review).
5. Russo, D. A. *Chem. Ind.* **1996,** *64*, 405–409. (Review).
6. Basu, M. K.; Banik, B. *Tetrahedron Lett.* **2001,** *42*, 187–189.
7. Sinha, P.; Roy, S. *Chem. Commun.* **2001,** 1798–1799.
8. Lombardo, M.; Gianotti, K.; Licciulli, S.; Trombini, C. *Tetrahedron* **2004,** *60*, 11725–11732.
9. Resende, G. O.; Aguiar, L. C. S.; Antunes, O. A. C. *Synlett* **2005,** 119–120.
10. Erdik, E.; Kocoglu, M. *Tetrahedron Lett.* **2007,** *48*, 4211–4214.
11. Takeuchi, T.; Matsuhashi, M.; Nakata, T. *Tetrahedron Lett.* **2008,** *49*, 6462–6465.
12. Hirayama, L. C.; Haddad, T. D.; Oliver, A. G.; Singaram, B. *J. Org. Chem.* **2012,** *77*, 4342–4353.
13. Aslam, N. A.; Babu, S. A.; Sudha, A. J.; Yasuda, M.; Baba, A. *Tetrahedron* **2013,** *69*, 6598–6611.

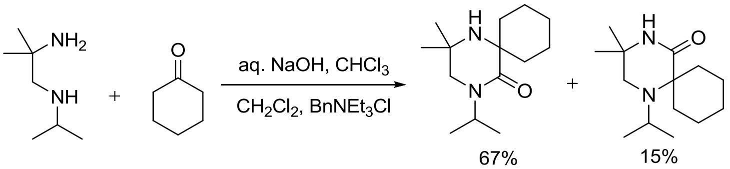
Bargellini reaction

Synthesis of hindered morpholinones or piperazinones from ketones (such as acetone) and 2-amino-2-methyl-1-propanol or 1,2-diaminopropanes.

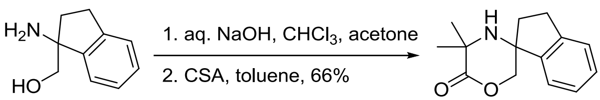




Example 1[2]



Example 2[4]



References

1. Bargellini, G. *Gazz. Chim. Ital.* **1906,** *36*, 329–337.
2. Lai, J. T. *J. Org. Chem.* **1980,** *45*, 754.
3. Lai, J. T. *Synthesis* **1981,** 754; **1984,** 122; **1984,** 124.
4. Rychnovsky, S. D.; Beauchamp, T.; Vaidyanathan, R.; Kwan, T. *J. Org. Chem.* **1998,** *63*, 6363–6374.
5. Butcher, K. J.; Hurst, J. *Tetrahedron Lett.* **2009,** *50*, 2497–2500.
6. Rohman, M. R.; Myrboh, B. *Tetrahedron Lett.* **2010,** *50*, 4772–4775.
7. Snowden, T. S. *ARKIVOC* **2012,** *(ii)*, 24–40. (Review).

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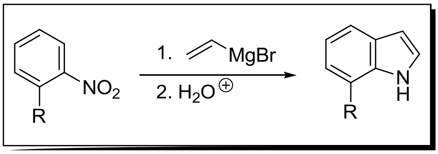
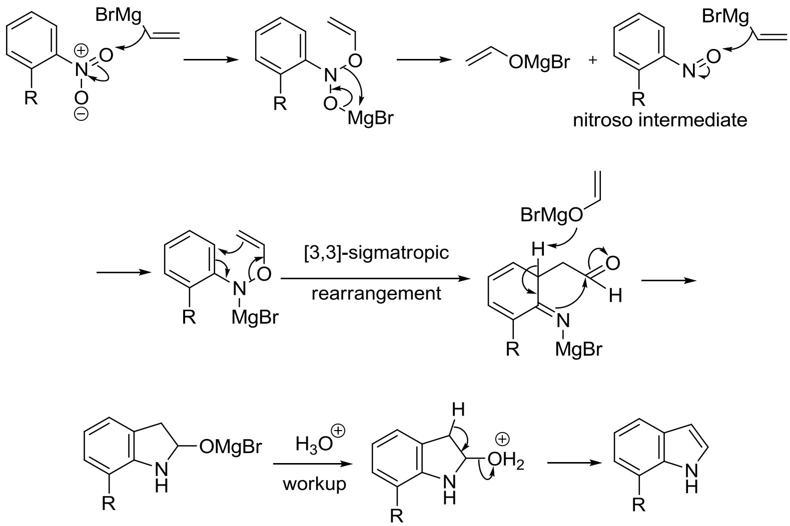
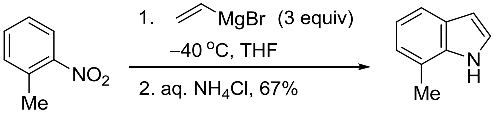
Bartoli indole synthesis

7-Substituted indoles from the reaction of *ortho*-substituted nitroarenes and vinyl Grignard reagents.

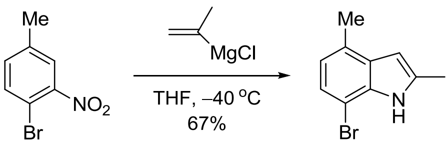




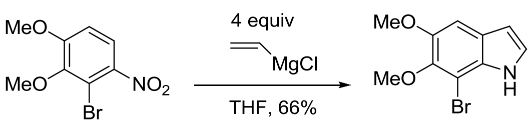
Example 1[3]



Example 2[6]



Example 3[10]



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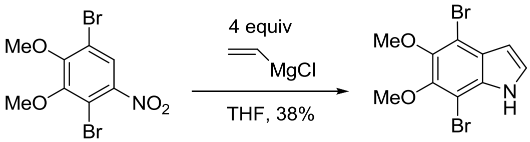
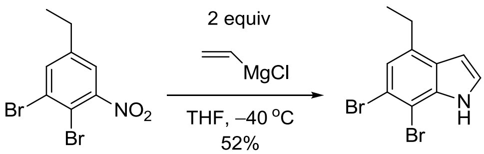
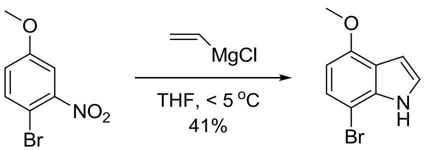
DOI 10.1007/978-3-319-03979-4_12,



Example 4[11]



Example 5[12]

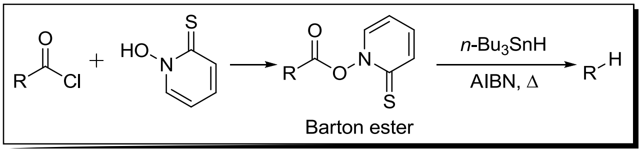


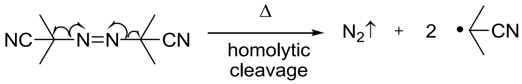
References

1. Bartoli, G.; Leardini, R.; Medici, A.; Rosini, G. *J. Chem. Soc., Perkin Trans. 1* **1978,** 692–696. Giuseppe Bartoli is a professor at the Università di Bologna, Italy.
2. Bartoli, G.; Bosco, M.; Dalpozzo, R.; Todesco, P. E. *J. Chem. Soc., Chem. Commun.* **1988,** 807–805.
3. Bartoli, G.; Palmieri, G.; Bosco, M.; Dalpozzo, R. *Tetrahedron Lett.* **1989,** *30*, 2129–2132.
4. Bosco, M.; Dalpozzo, R.; Bartoli, G.; Palmieri, G.; Petrini, M. *J. Chem. Soc., Perkin Trans. 2* **1991,** 657–663. Mechanistic studies.
5. Bartoli, G.; Bosco, M.; Dalpozzo, R.; Palmieri, G.; Marcantoni, E. *J. Chem. Soc., Perkin Trans. 1* **1991,** 2757–2761.
6. Dobbs, A. *J. Org. Chem*. **2001,** *66*, 638–641.
7. Garg, N. K.; Sarpong, R.; Stoltz, B. M. *J. Am. Chem. Soc.* **2002,** *124,* 13179–13184.
8. Li, J.; Cook, J. M. *Bartoli Indole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Corey, E. J. Eds.; Wiley: Hoboken, NJ, **2005,** pp 100–103. (Review).
9. Dalpozzo, R.; Bartoli, G. *Current Org. Chem.* **2005,** *9*, 163–178. (Review).
10. Huleatt, P. B.; Choo, S. S.; Chua, S.; Chai, C. L. L. *Tetrahedron Lett.* **2008,** *49*, 5309–5311.
11. Buszek, K. R.; Brown, N.; Luo, D. *Org. Lett.* **2009,** *11*, 201–204.
12. Grant, S. W.; Gallagher, T. F.; Bobko, M. A.; Duquenne, C.; Axten, J. M. *Tetrahedron Lett.* **2011,** *52*, 3376–3378.
13. Chandrasoma, N.; Brown, N.; Brassfield, A.; Nerurkar, A.; Suarez, S.; Buszek, K. R. *Tetrahedron Lett.* **2013,** *54,* 913–917.

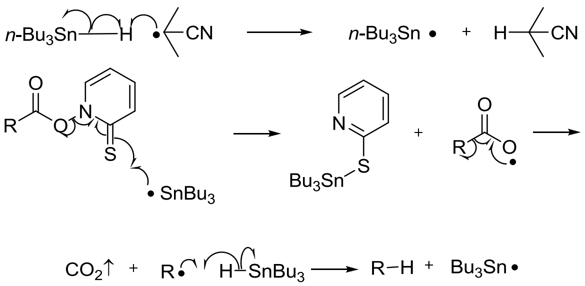
Barton radical decarboxylation

Radical decarboxylation of the carboxylic acids.

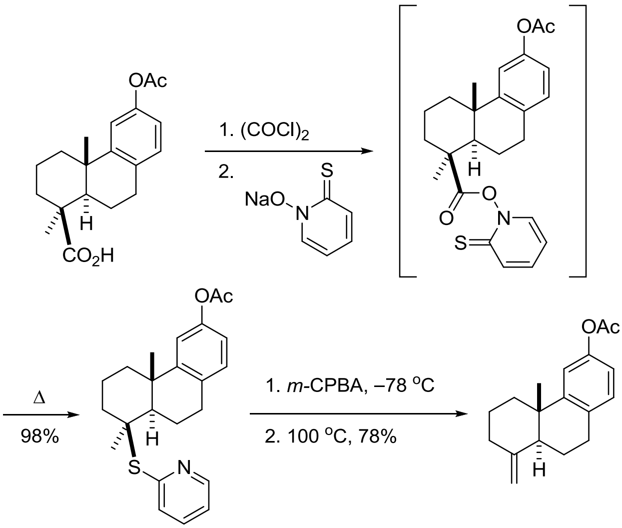




AIBN = 2,2′-azobisisobutyronitrile



Example 1, Tin hydride not used and elimination occurs via thioether intermediate[3]



Example 2[6]

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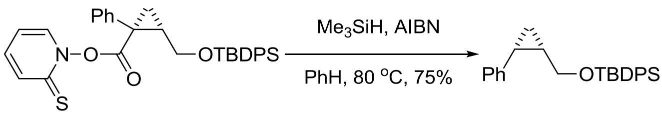
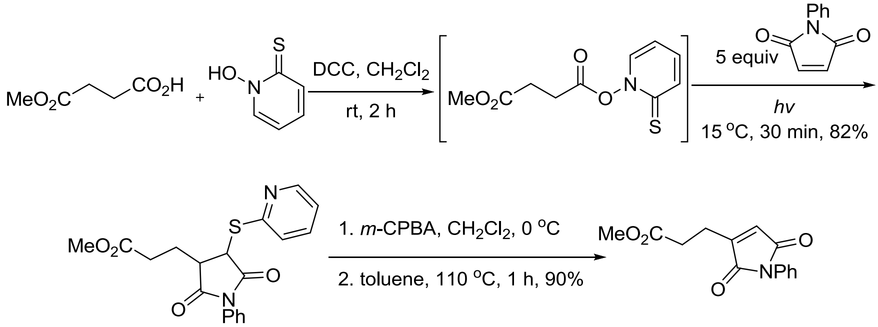
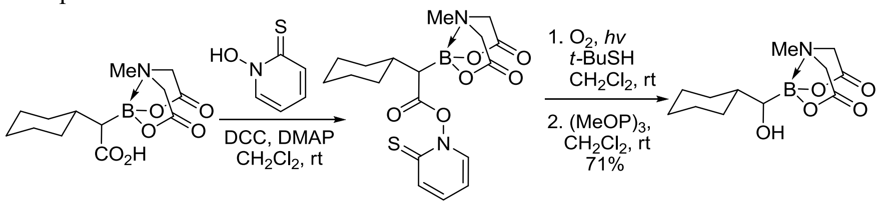


Example 3[9]



Example 4[11]

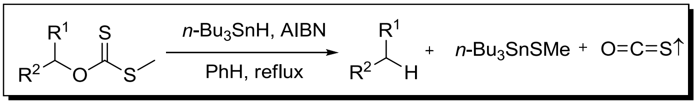


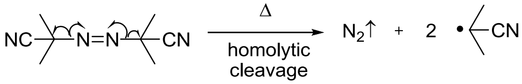
References

1. Barton, D. H. R.; Crich, D.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1983,** 939–941. Sir Derek Barton (United Kingdom, 1918–1998) studied under Ian Heilbron at Imperial College in his youth. He taught in England, France and the US. Barton won the Nobel Prize in Chemistry in 1969 for development of the concept of conformation. He passed away in his office at the University of Texas A&M in 1998.
2. Barton, D. H. R.; Zard, S. Z. *Pure Appl. Chem.* **1986,** *58*, 675–684. (Review).
3. Cochane, E. J.; Lazer, S. W.; Pinhey, J. T.; Whitby, J. D. *Tetrahedron Lett.* **1989,** *30*, 7111–7114.
4. Barton, D. H. R. *Aldrichimica Acta* **1990,** *23*, 3. (Review).
5. Crich, D.; Hwang, J.-T.; Yuan, H. *J. Org. Chem.* **1996,** *61*, 6189–6198.
6. Yamaguchi, K.; Kazuta, Y.; Abe, H.; Matsuda, A.; Shuto, S. *J. Org. Chem.* **2003,** *68*, 9255–9262.
7. Zard, S. Z. *Radical Reactions in Organic Synthesis* Oxford University Press: Oxford, UK, **2003**. (Book).
8. Carry, J.-C.; Evers, M.; Barriere, J.-C.; Bashiardes, G.; Bensoussan, C.; Gueguen, J.-C.; Dereu, N.; Filoche, B.; Sable, S.; Vuilhorgne, M.; Mignani, S. *Synlett* **2004,** 316–320.
9. Brault, L.; Denance, M.; Banaszak, E.; El Maadidi, S.; Battaglia, E.; Bagrel, D.; Samadi, M. *Eur. J. Med. Chem.* **2007,** *42*, 243–247.
10. Guthrie, D. B.; Curran, D. P. *Org. Lett.* **2009,** *11*, 249–251.
11. He, Z.; Trinchera, P.; Adachi, S.; St. Denis, J. D.; Yudin, A. K. *Angew. Chem. Int. Ed.* **2012,** *51*, 11092–11096.

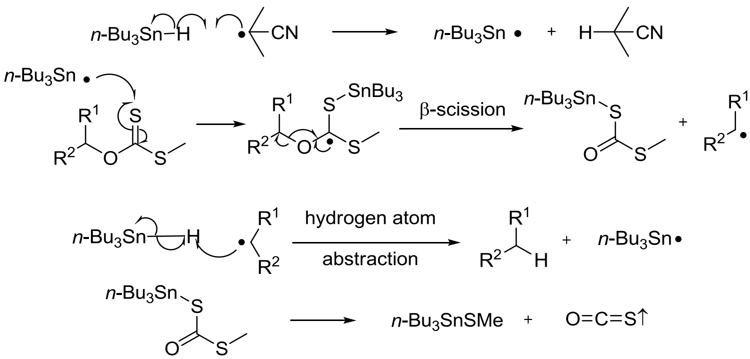
Barton–McCombie deoxygenation

Deoxygenation of alcohols by means of radical scission of their corresponding thiocarbonyl derivatives.

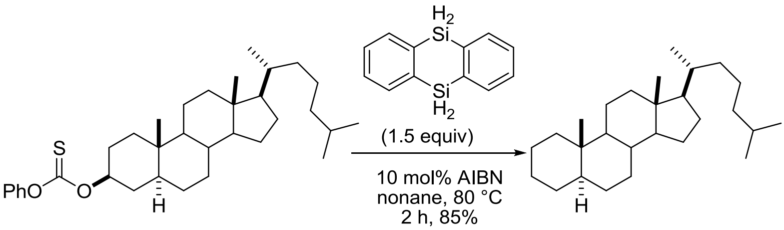




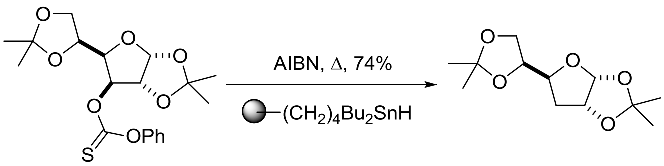
AIBN = 2,2′-azobisisobutyronitrile



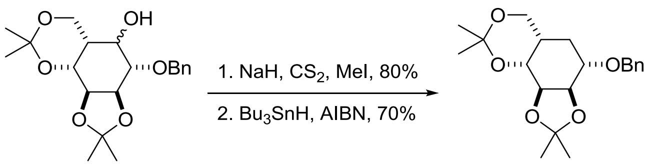
Example 1[2]



Example 2[6]



Example 3[10]



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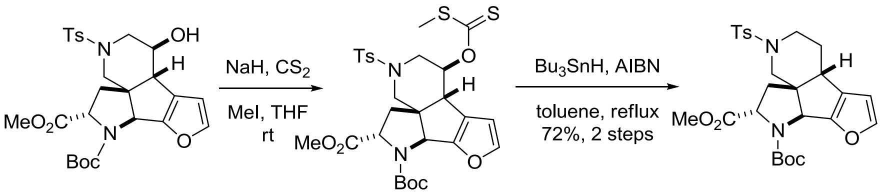
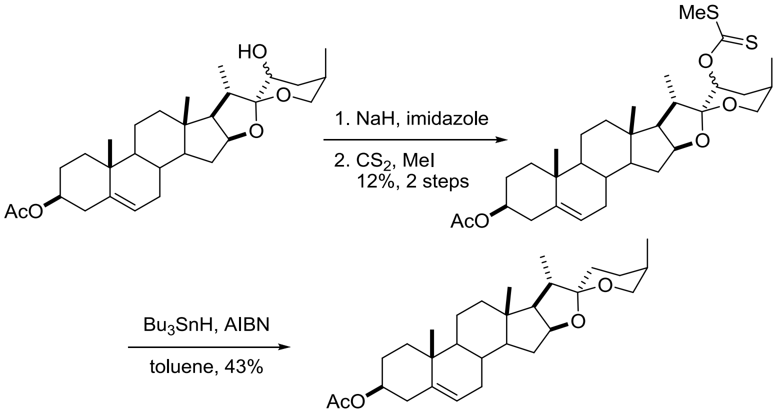
DOI 10.1007/978-3-319-03979-4_14,

Example 4[11]



Example 5[13]

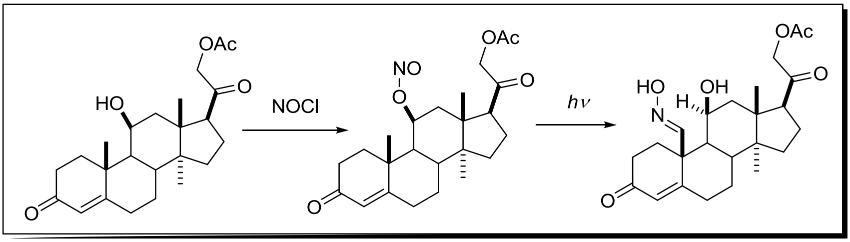


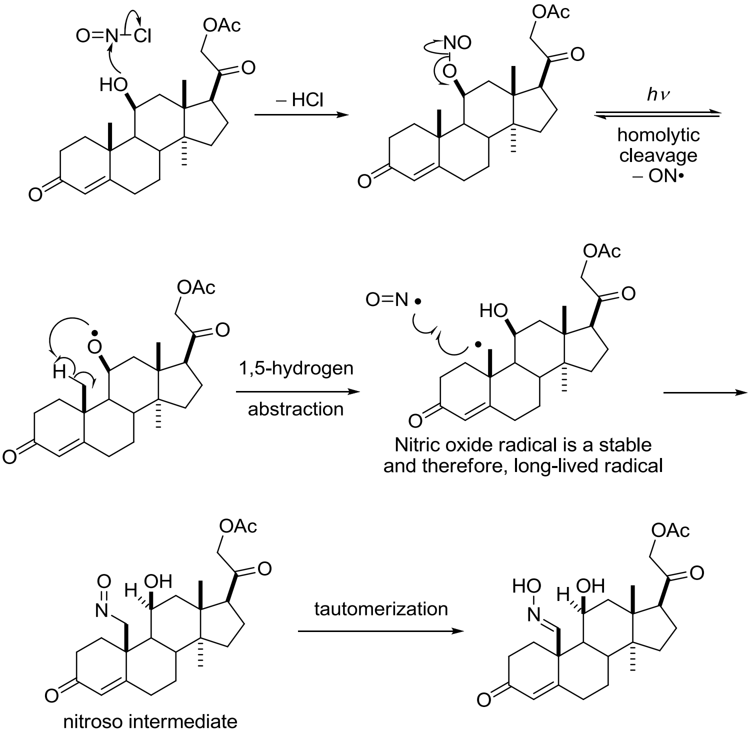
References

1. Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975,** 1574–1585. Stuart McCombie, a Barton student, worked at Schering–Plough for many years, but is now retired after the company was bought by Merck.
2. Gimisis, T.; Ballestri, M.; Ferreri, C.; Chatgilialoglu, C.; Boukherroub, R.; Manuel, G. *Tetrahedron Lett.* **1995,** *36*, 3897–3900.
3. Zard, S. Z. *Angew. Chem. Int. Ed.* **1997,** *36*, 673–685.
4. Lopez, R. M.; Hays, D. S.; Fu, G. C. *J. Am. Chem. Soc*. **1997,** *119*, 6949–6950.
5. Hansen, H. I.; Kehler, J. *Synthesis* **1999,** 1925–1930.
6. Boussaguet, P.; Delmond, B.; Dumartin, G.; Pereyre, M. *Tetrahedron Lett*. **2000,** *41*, 3377–3380.
7. Cai, Y.; Roberts, B. P. *Tetrahedron Lett*. **2001,** *42*, 763–766.
8. Clive, D. L. J.; Wang, J. *J. Org. Chem.* **2002,** *67*, 1192–1198.
9. Rhee, J. U.; Bliss, B. I.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2003,** *125*, 1492–1493.
10. Gómez, A. M.; Moreno, E.; Valverde, S.; López, J. C. *Eur. J. Org. Chem.* **2004,** 1830–1840.
11. Deng, H.; Yang, X.; Tong, Z.; Li, Z.; Zhai, H. *Org. Lett.* **2008,** *10,* 1791–1793.
12. Mancuso, J. *Barton–McCombie deoxygenation*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 614–632. (Review).
13. McCombie, S. W.; Motherwell, W. B.; Tozer, M. J. *The Barton–McCombie Reaction,* In *Org. React.* **2012,** *77,* pp 161–591. (Review).
14. Jastrzebska, I.; Gorecki, M.; Frelek, J.; Santillan, R.; Siergiejczyk, L.; Morzycki, J. W. *J. Org. Chem.* **2012,** *77,* 11257–11269.

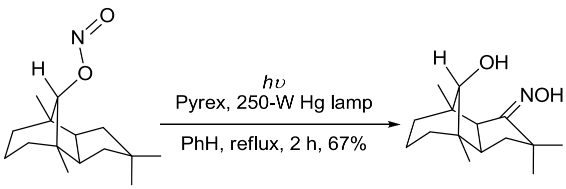
Barton nitrite photolysis

Photolysis of a nitrite ester to a γ-oximino alcohol.





Example 1[2]



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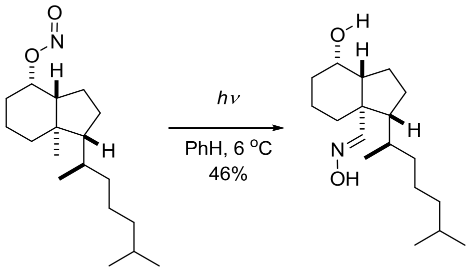
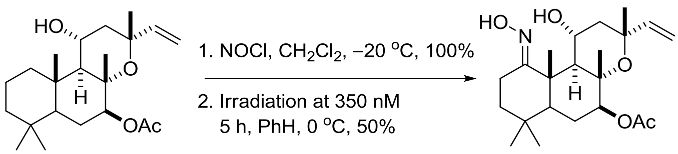
DOI 10.1007/978-3-319-03979-4_15,

Example 2[6]



Example 3[7]

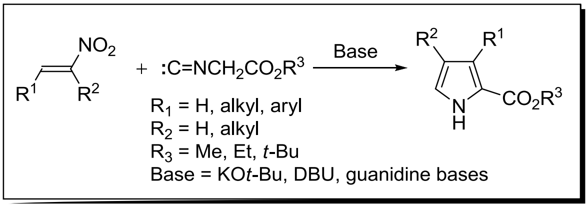


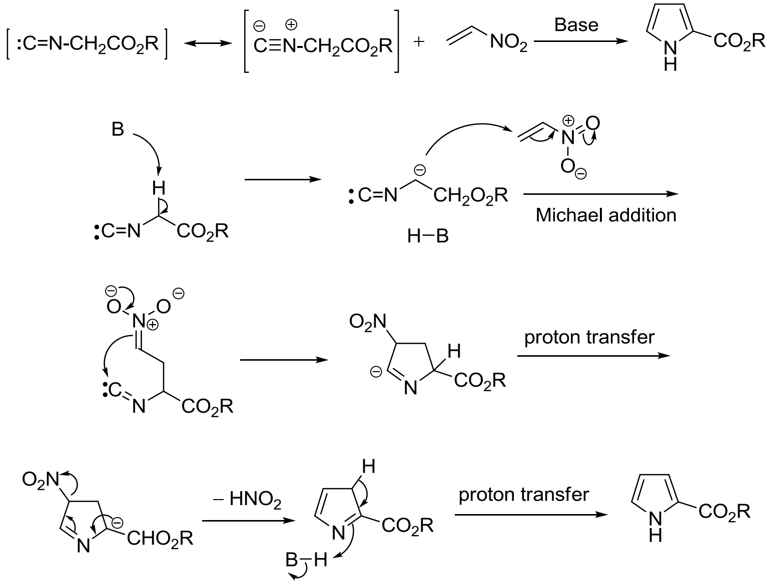
References

1. (a) Barton, D. H. R.; Beaton, J. M.; Geller, L. E.; Pechet, M. M. *J. Am. Chem. Soc.* **1960,** *82*, 2640–2641. In 1960, Derek Barton took a "vacation" in Cambridge, Massachusetts; he worked in a small research institute called the Research Institute for Medicine and Chemistry. In order to make the adrenocortical hormone aldosterol, Barton invented the Barton nitrite photolysis by simply writing down on a piece of paper what he thought would be an ideal process. His skilled collaborator, Dr. John Beaton, was able to reduce it to practice. They were able to make 40 to 50 g of aldosterol at a time when the total world supply was only about 10 mg. Barton considered it his most satisfying piece of work. (b) Barton, D. H. R.; Beaton, J. M. *J. Am. Chem. Soc.* **1960,** *82*, 2641−2641. (c) Barton, D. H. R.; Beaton, J. M. *J. Am. Chem. Soc.* **1961,** *83*, 4083−4089. (d) Barton, D. H. R.; Lier, E. F.; McGhie, J. M. *J. Chem. Soc., (C)* **1968,** 1031−1040.
2. Nickon, A; Iwadare, T.; McGuire, F. J.; Mahajan, J. R; Narang, S. A.; Umezawa, B. *J. Am. Chem. Soc.* **1970,** *92*, 1688–1696.
3. Barton, D. H. R.; Hesse, R. H.; Pechet, M. M.; Smith, L. C. *J. Chem. Soc., Perkin Trans. 1* **1979,** 1159−1165.
4. Barton, D. H. R. *Aldrichimica Acta* **1990,** *23*, 3−10. (Review).
5. Majetich, G.; Wheless, K. *Tetrahedron* **1995,** *51*, 7095–7129. (Review).
6. Sicinski, R. R.; Perlman, K. L.; Prahl, J.; Smith, C.; DeLuca, H. F. *J. Med. Chem.* **1996,** *22,* 4497–4506.
7. Anikin, A.; Maslov, M.; Sieler, J.; Blaurock, S.; Baldamus, J.; Hennig, L.; Findeisen, M.; Reinhardt, G.; Oehme, R.; Welzel, P. *Tetrahedron* **2003,** *59*, 5295–5305.
8. Suginome, H. *CRC Handbook of Organic Photochemistry and Photobiology* 2nd edn.; **2004**, 102/1−102/16. (Review).
9. Hagan, T. J. *Barton nitrite photolysis*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 633−647. (Review).

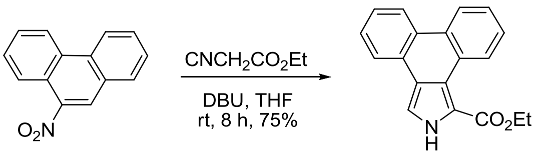
Barton–Zard reaction

Base-induced reaction of nitroalkenes with alkyl α-isocyanoacetates to afford pyrroles.





Example 1[5]



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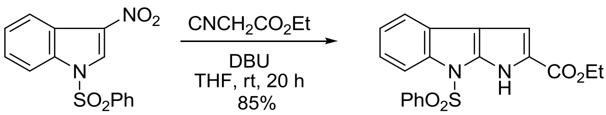

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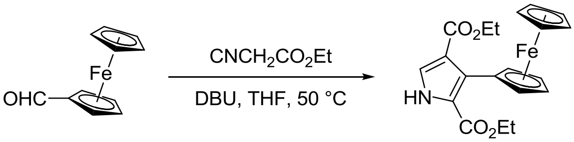
DOI 10.1007/978-3-319-03979-4_16, © Springer International Publishing Switzerland 2014

Example 3, A Barton–Zard reaction on a ferrocene ring[12]

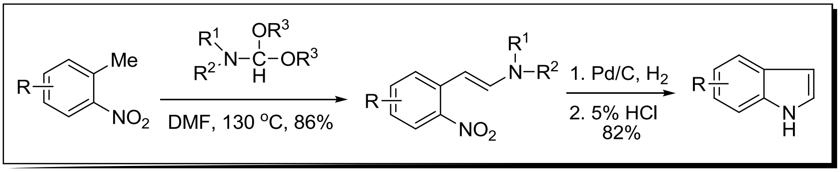


References

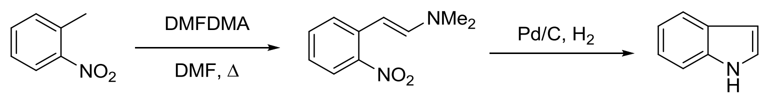
1. Barton, D. H. R.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1985,** 1098–1100. Samir Z. Zard, a Barton student, emigrated from Lebanon to the UK in 1975. He is a professor at CNRS and École Polytechnique in France.
2. van Leusen, A. M.; Siderius, H.; Hoogenboom, B. E.; van Leusen, D. *Tetrahedron Lett.* **1972,** 5337–5340.
3. Barton, D. H. R.; Kervagoret, J.; Zard, S. Z. *Tetrahedron* **1990,** *46*, 7587-5340.
4. Sessler, J. L.; Mozaffari, A.; Johnson, M. R. *Org. Synth.* **1991,** *70*, 68-78.
5. Ono, N.; Hironaga, H.; Ono, K.; Kaneko, S.; Murashima, T.; Ueda, T.; Tsukamura, C.; Ogawa, T. *J. Chem. Soc., Perkin Trans. 1* **1996,** 417–423.
6. Murashima, T.; Fujita, K.; Ono, K.; Ogawa, T.; Uno, H.; Ono, N. *J. Chem. Soc., Perkin Trans. 1* **1996,** 1403–1407.
7. Pelkey, E. T.; Chang, L.; Gribble, G. W. *Chem. Commun.* **1996,** 1909–1910.
8. Fumoto, Y.; Uno, H.; Tanaka, K.; Tanaka, M.; Murashima, T.; Ono, N. *Synthesis* **2001,** 399–402.
9. Lash, T. D.; Werner, T. M.; Thompson, M. L.; Manley, J. M. *J. Org. Chem.* **2001,** *66*, 3152–3159.
10. Ferreira, V. F.; de Souza, M. C. B. V.; Cunha, A. C.; Pereira, L. O. R.; Ferreira, M. L. G. *Org. Prep. Proc. Int.* **2001,** *33*, 411–454. (Review).
11. Gribble, G. W. *Barton–Zard Reaction* in *Name Reactions in Heterocyclic Chemistry*, Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 70–78. (Review).
12. Guillon, J.; Mouray, E.; Moreau, S.; Mullié, C.; Forfar, I.; Desplat, V.; Belisle-Fabre, S.; Pinaud, N.; Ravanello, F.; Le-Naour, A.; Léger, J. M.; Gosmann, G.; Jarry, C.; Déléris, G.; Sonnet, P.; Grellier, P. *E. J. Med. Chem.* **2011,** *46*, 2310–2326.

Batcho–Leimgruber indole synthesis

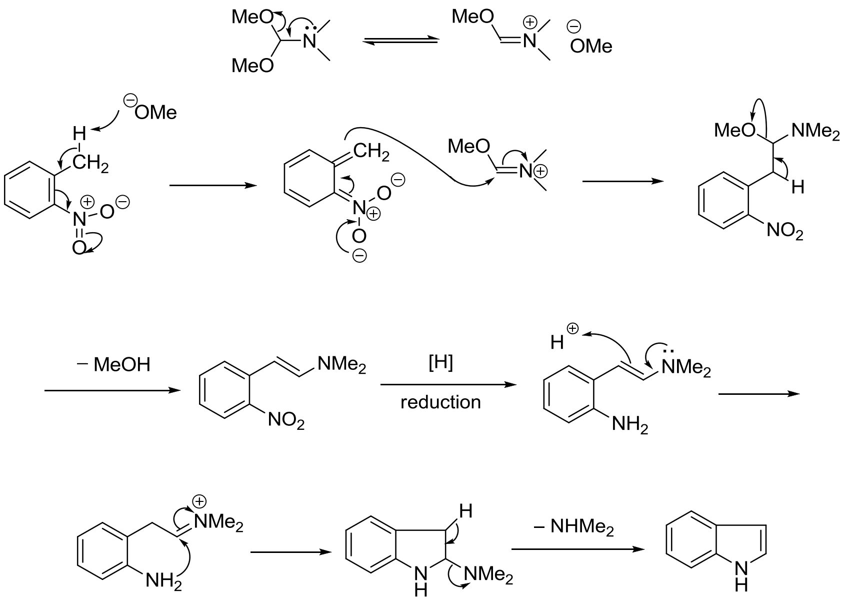
Condensation of *o*-nitrotoluene derivatives with formamide acetals, followed by reduction of the *trans*-β-dimethylamino-2-nitrostyrene to furnish indole derivatives.



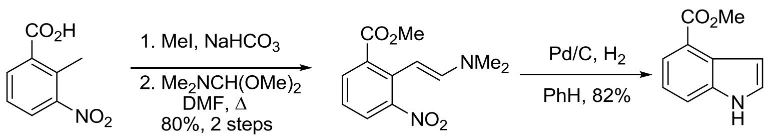
Example 1[4]



DMFDMA = *N,N*-dimethylformamide dimethyl acetal, $Me_2NCH(OMe)_2$



Example 2[4]



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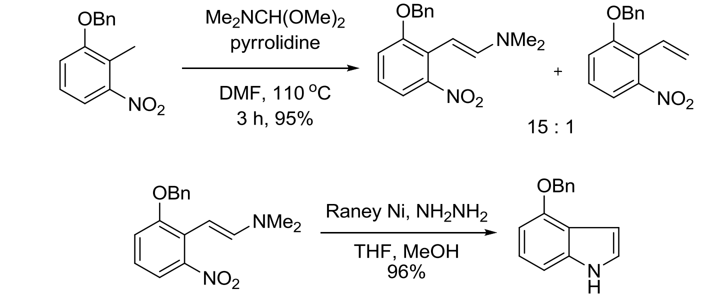
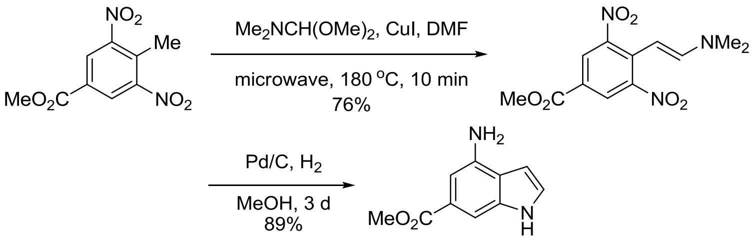
DOI 10.1007/978-3-319-03979-4_17, © Springer International Publishing Switzerland 2014

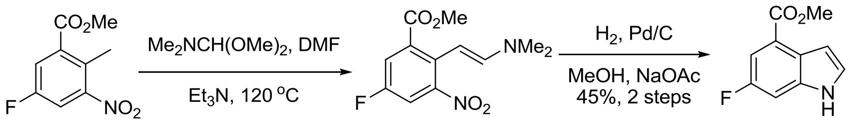
Example 3[5]



Example 4[10]



Example 5[12]

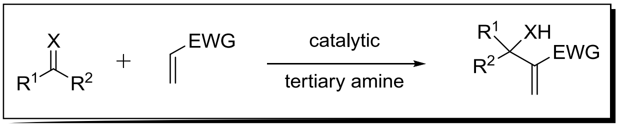


References

1. Leimgruber, W.; Batcho, A. D. *Third International Congress of Heterocyclic Chemistry*: Japan, **1971**. Both Andrew D. Batcho and Willy Leimgruber were chemists at Hoffmann-La Roche in Nutley, NJ, a site that was closed in 2012.
2. Leimgruber, W.; Batcho, A. D. USP 3732245 (1973).
3. Sundberg, R. J. *The Chemistry of Indoles*; Academic Press: New York & London, **1970**. (Review).
4. Kozikowski, A. P.; Ishida, H.; Chen, Y.-Y. *J. Org. Chem.* **1980,** *45*, 3350–3352.
5. Batcho, A. D.; Leimgruber, W. *Org. Synth.* **1985,** *63*, 214–225.
6. Clark, R. D.; Repke, D. B. *Heterocycles* **1984,** *22*, 195–221. (Review).
7. Moyer, M. P.; Shiurba, J. F.; Rapoport, H. *J. Org. Chem.* **1986,** *51*, 5106–5110.
8. Siu, J.; Baxendale, I. R.; Ley, S. V. *Org. Biomol. Chem*. **2004,** *2*, 160–167.
9. Li, J.; Cook, J. M. *Batcho–Leimgruber Indole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 104–109. (Review).
10. Braun, H. A.; Zall, A.; Brockhaus, M.; Schütz, M.; Meusinger, R.; Schmidt, B. *Tetrahedron Lett*. **2007,** *48*, 7990–7993.
11. Leze, M.-P.; Palusczak, A.; Hartmann, R. W.; Le Borgne, M. *Bioorg. Med. Chem. Lett*. **2008,** *18*, 4713–4715.
12. Gillmore, A. T.; Badland, M.; Crook, C. L.; Castro, N. M.; Critcher, D. J.; Fussell, S. J.; Jones, K. J.; Jones, M. C.; Kougoulos, E.; Mathew, J. S.; et al. *Org. Process Res. Dev*. **2012,** *16*, 1897–1904.

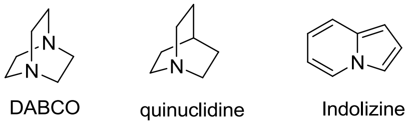
Baylis–Hillman reaction

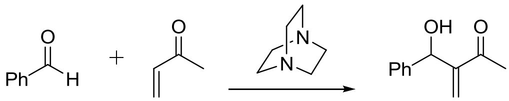
Also known as the Morita–Baylis–Hillman reaction. It is a carbon–carbon bond-forming transformation of an electron-poor alkene with a carbon electrophile. Electron-poor alkenes include acrylic esters, acrylonitriles, vinyl ketones, vinyl sulfones, and acroleins. On the other hand, carbon electrophiles may be aldehydes, α-alkoxycarbonyl ketones, aldimines, and Michael acceptors.
General scheme:

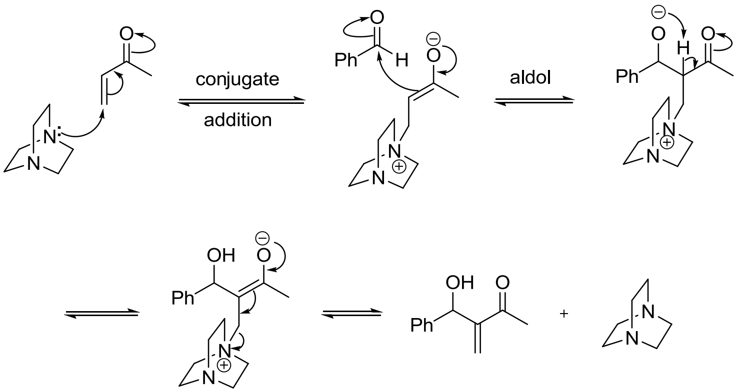


X = O, NR_2, EWG = CO_2R, COR, CHO, CN, SO_2R, SO_3R, $PO(OEt)_2$, $CONR_2$, $CH_2{=}CHCO_2Me$

Catalytic tertiary amines:







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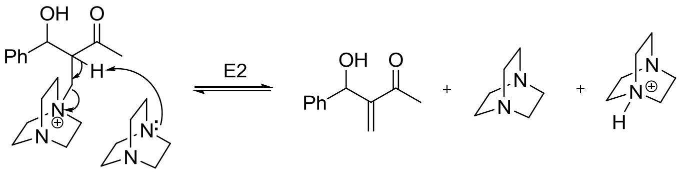
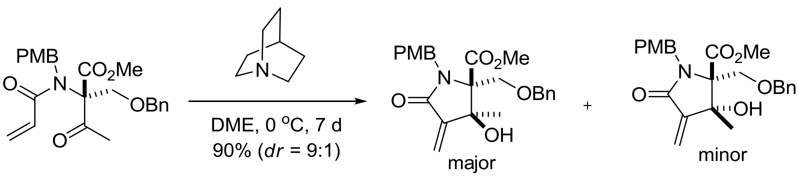
DOI 10.1007/978-3-319-03979-4_18,

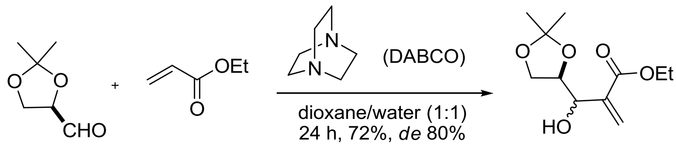
E2 (bimolecular elimination) mechanism is also operative here:



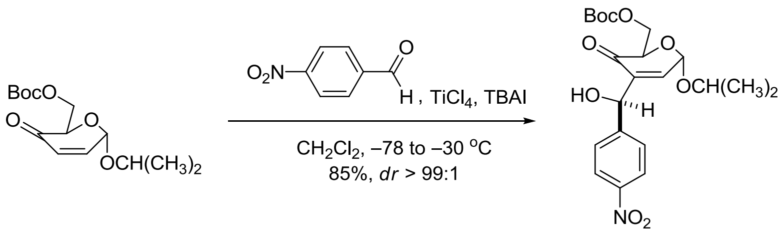
Example 1, Intramolecular Baylis–Hillman reaction[6]



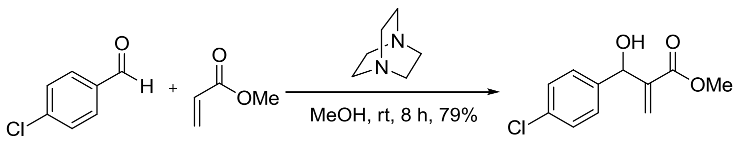
Example 2[7]



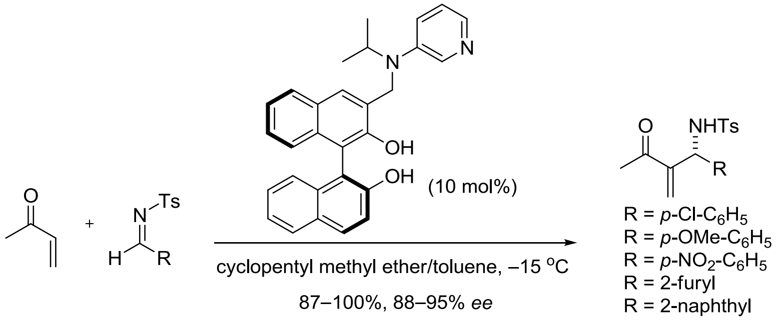
Example 3[8]



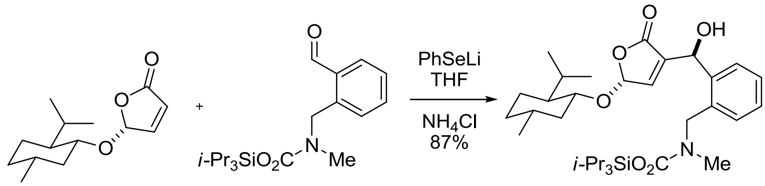
Example 4[9]



Example 5[10]



Example 6[13]

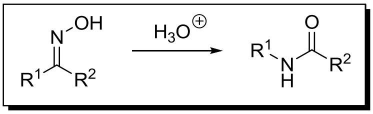


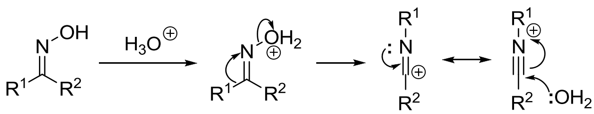
References

1. Baylis, A. B.; Hillman, M. E. D. Ger. Pat. 2,155,113, (**1972**). Both Anthony B. Baylis and Melville E. D. Hillman were chemists at Celanese Corp. USA.
2. Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996,** *52*, 8001–8062. (Review).
3. Ciganek, E. *Org. React.* **1997,** *51,* 201–350. (Review).
4. Wang, L.-C.; Luis, A. L.; Agapiou, K.; Jang, H.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2002,** *124*, 2402–2403.
5. Frank, S. A.; Mergott, D. J.; Roush, W. R. *J. Am. Chem. Soc.* **2002,** *124*, 2404–2405.
6. Reddy, L. R.; Saravanan, P.; Corey, E. J. *J. Am. Chem. Soc.* **2004,** *126*, 6230–6231.
7. Krishna, P. R.; Narsingam, M.; Kannan, V. *Tetrahedron Lett.* **2004,** *45*, 4773–4775.
8. Sagar, R,; Pant, C. S.; Pathak, R.; Shaw, A. K. *Tetrahedron* **2004,** *60*, 11399–11406.
9. Mi, X.; Luo, S.; Cheng, J.-P. *J. Org. Chem.* **2005,** *70*, 2338–2341.
10. Matsui, K.; Takizawa, S.; Sasai, H. *J. Am. Chem. Soc.* **2005,** *127*, 3680–3681.
11. Price, K. E.; Broadwater, S. J.; Jung, H. M.; McQuade, D. T. *Org. Lett.* **2005,** *7*, 147–150. A novel mechanism involving a hemiacetal intermediate is proposed.
12. Limberakis, C. *Morita–Baylis–Hillman Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 350–380. (Review).
13. Cheng, P.; Clive, D. L. J. *J. Org. Chem.* **2012,** *77*, 3348–3364.
14. Chandrasoma, N.; Brown, N.; Brassfield, A.; Nerurkar, A.; Suarez, S.; Buszek, K. R. *Tetrahedron Lett.* **2013,** *54,* 913–917.

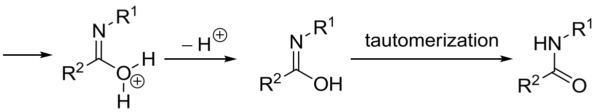
Beckmann rearrangement

Acid-mediated isomerization of oximes to amides.
In protic acid:

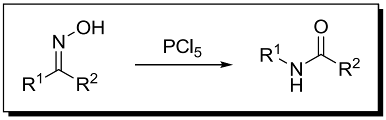


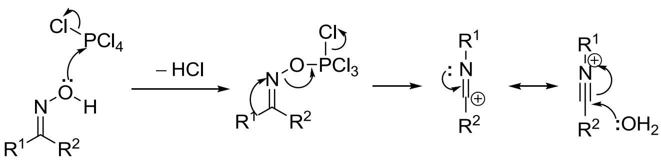


the substituent *trans* to the leaving group migrates

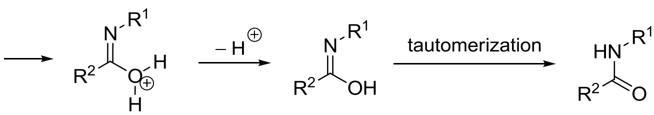


With PCl_5:

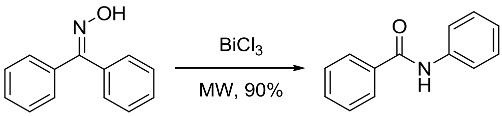




Again, the substituent *trans* to the leaving group migrates



Example 1, Microwave (MW) reaction[3]



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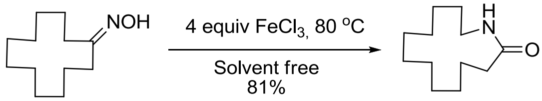
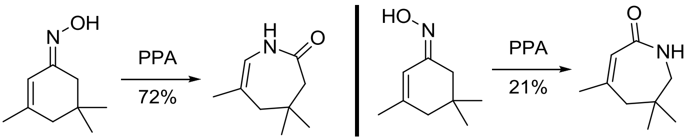
Example 2[4]

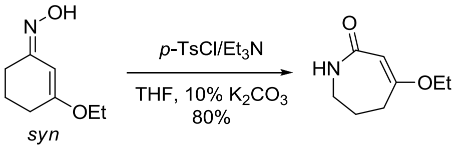


Example 3[6]

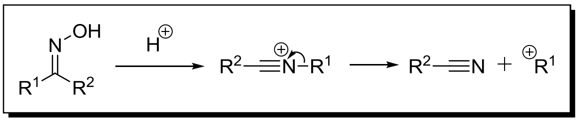


PPA = **p**oly**p**hosphoric **a**cid

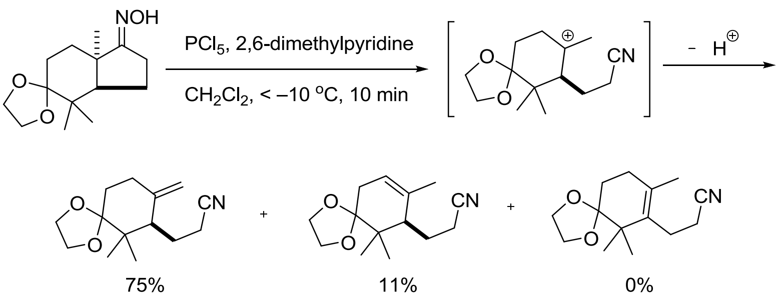
Example 4[8]



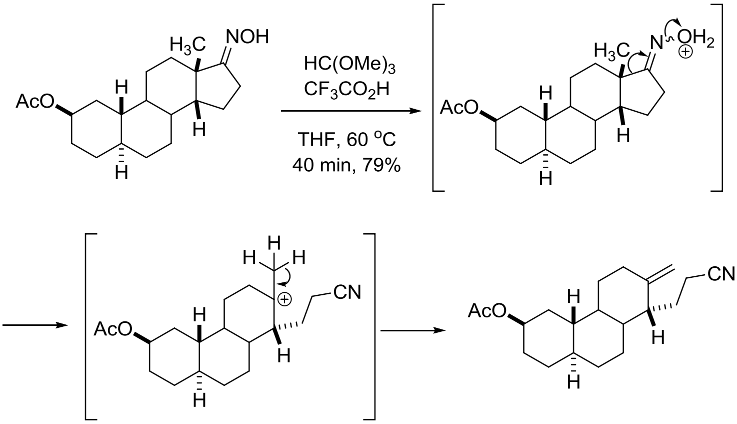
Abnormal Beckmann rearrangement is when the migrating fragment (e.g., R^1) departs from the intermediate, leaving a nitrile as a stable product.



Example 1[9]



Example 2[10]

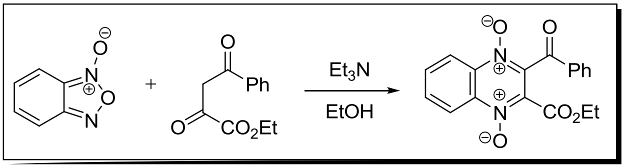


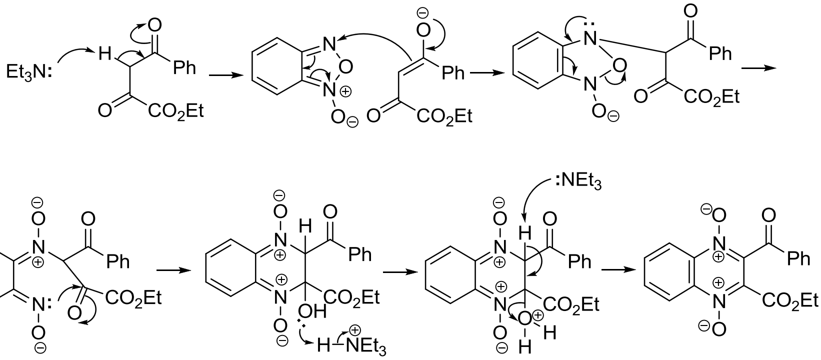
References

1. Beckmann, E. *Chem. Ber.* **1886,** *89*, 988. Ernst Otto Beckmann (1853−1923) was born in Solingen, Germany. He studied chemistry and pharmacy at Leipzig. In addition to the Beckmann rearrangement of oximes to amides, his name is associated with the Beckmann thermometer, used to measure freezing and boiling point depressions to determine molecular weights. 
2. Gawley, R. E. *Org. React.* **1988,** *35*, 1–420. (Review).
3. Thakur, A. J.; Boruah, A.; Prajapati, D.; Sandhu, J. S. *Synth. Commun.* **2000,** *30*, 2105–2011.
4. Khodaei, M. M.; Meybodi, F. A.; Rezai, N.; Salehi, P. *Synth. Commun.* **2001,** *31*, 2047–2050.
5. Torisawa, Y.; Nishi, T.; Minamikawa, J.-i. *Bioorg. Med. Chem. Lett.* **2002,** *12*, 387–390.
6. Hilmey, D. G.; Paquette, L. A. *Org. Lett.* **2005,** *7*, 2067–2069.
7. Fernández, A. B.; Boronat, M.; Blasco, T.; Corma, A. *Angew. Chem. Int. Ed.* **2005,** *44*, 2370–2373.
8. Collison, C. G.; Chen, J.; Walvoord, R. *Synthesis* **2006,** 2319–2322.
9. Cao, L.; Sun, J.; Wang, X.; Zhu, R.; Shi, H.; Hu, Y. *Tetrahedron* **2007,** *63*, 5036–5041.
10. Wang, C.; Rath, N. P.; Covey, D. F. *Tetrahedron* **2007,** *63*, 7977–7984.
11. Kumar, R. R.; Vanitha, K. A.; Balasubramanian, M. *Beckmann Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 274–292. (Review).
12. Faraldos, J. A.; Kariuki, B. M.; Coates, R. M. *Org. Lett.* **2011,** *13*, 836–839.
13. Tian, B.-X.; An, N.; Deng, W.-P.; Eriksson, L. A. **2013,** *15*, 6782–6785.

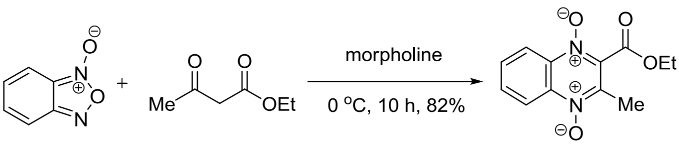
Beirut reaction

Synthesis of quinoxaline-1,4-dioxides from benzofurazan oxide.

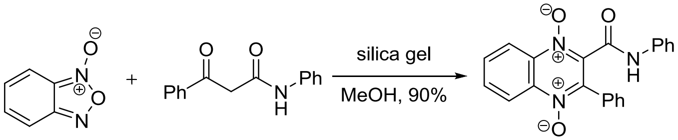




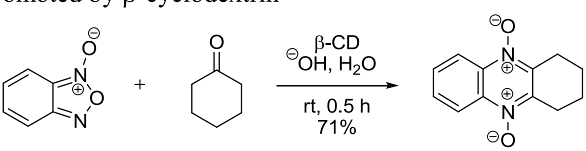
Example 1[3]



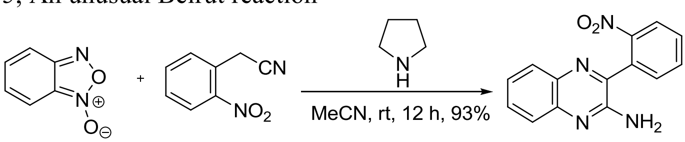
Example 2[7]



Example 4, Promoted by β-cyclodextrin[11]



Example 5, An unusual Beirut reaction[12]



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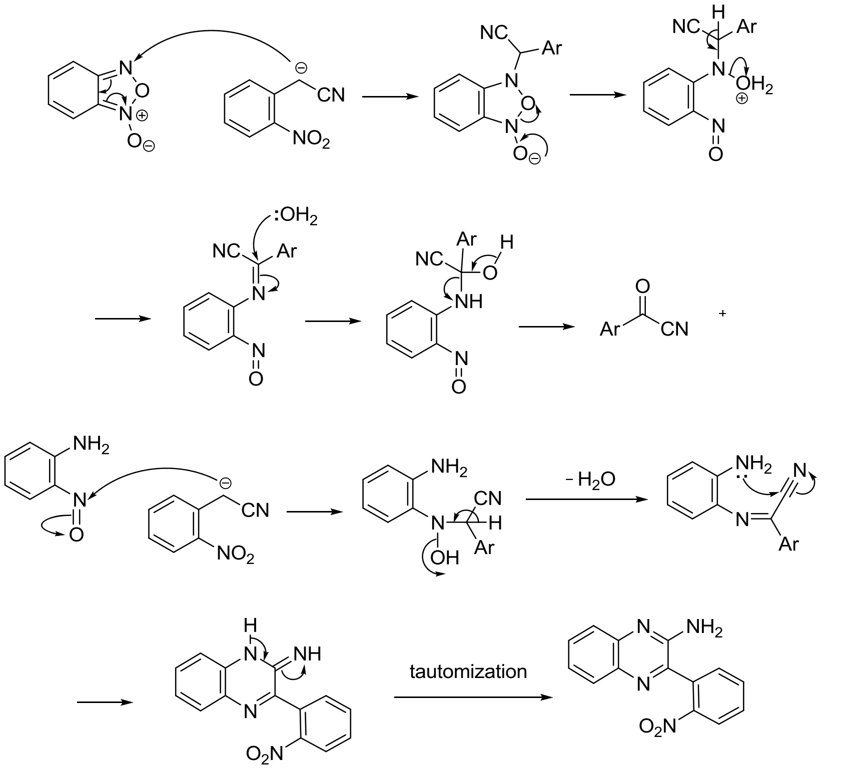
DOI 10.1007/978-3-319-03979-4_20, © Springer International Publishing Switzerland 2014

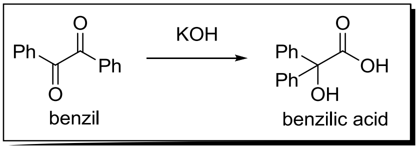


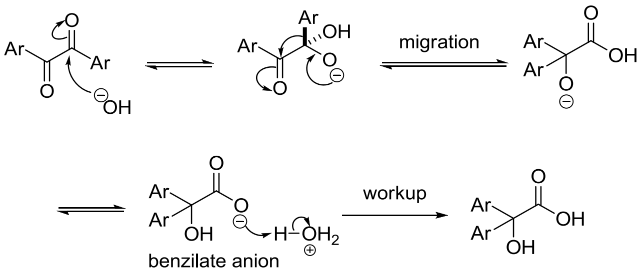
References

1. Haddadin, M. J.; Issidorides, C. H. *Heterocycles* **1976,** *4*, 767–816. The authors named the reaction after the city where it was discovered, Beirut, the capital of Lebanon.
2. Gaso, A.; Boulton, A. J. In *Advances in Heterocyclic Chem.;* Vol. 29, Katritzky, A. R.; Boulton, A. J., eds.; Academic Press Inc.: New York, **1981,** 251. (Review).
3. Vega, A. M.; Gil, M. J.; Fernández-Alvarez, E. *J. Heterocycl. Chem.* **1984,** *21*, 1271.
4. Atfah, A.; Hill, J. *J. Chem. Soc., Perkin Trans. 1* **1989,** 221–224.
5. Haddadin, M. J.; Issidorides, C. H. *Heterocycles* **1993,** *35*, 1503–1525.
6. El-Abadelah, M. M.; Nazer, M. Z.; El-Abadla, N. S.; Meier, H. *Heterocycles* **1995,** *41*, 2203–2219.
7. Takabatake, T.; Miyazawa, T.; Kojo, M.; Hasegawa, M. *Heterocycles* **2000,** *53*, 2151–2162.
8. Panasyuk, P. M.; Mel'nikova, S. F.; Tselinskii, I. V. *Russ. J. Org. Chem.* **2001,** *37*, 892.
9. Turker, L.; Dura, E. *Theochem* **2002,** *593*, 143–147.
10. Tinsley, J. M. *Beirut Reaction* in *Name Reactions in Heterocyclic Chemistry*, Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 504–509. (Review).
11. Sun, T.; Zhao, W.-J.; Hao, A.-Y.; Sun, L.-Z. *Synthesis* **2011,** *41*, 3097–3105.
12. Haddadin, M. J.; El-Khatib, M.; Shoker, T. A.; Beavers, C. M.; Olmstead, M. M.; Fettinger, J. C.; Farber, K. M.; Kurth, M. J. *J. Org. Chem.* **2011,** *76*, 8421–8427.

Benzilic acid rearrangement

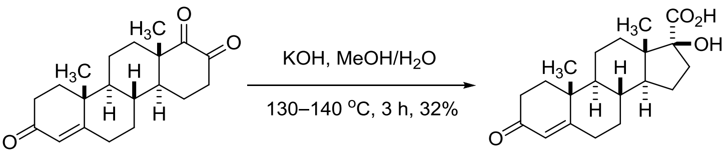
Rearrangement of benzil to benzilic acid *via* aryl migration.



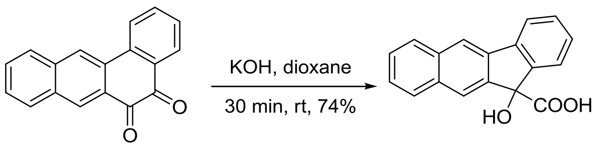


Final deprotonation (before workup) of the carboxylate to afford the benzilate anion drives the reaction forward.

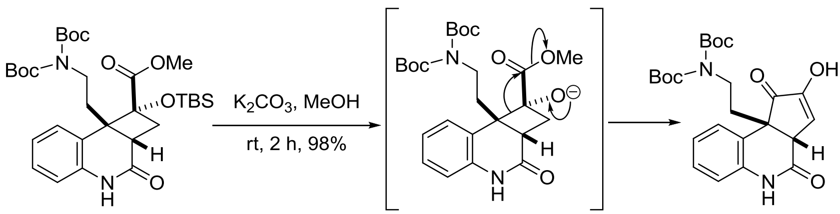
Example 1[3]



Example 2[6]



Example 3, Retro-benzilic acid rearrangement[7]



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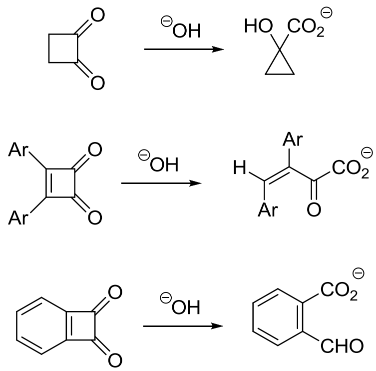
DOI 10.1007/978-3-319-03979-4_21, © Springer International Publishing Switzerland 2014

Example 4, Cyclobutane-1,2-diones (Computational Chemistry)[9]

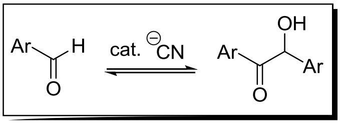


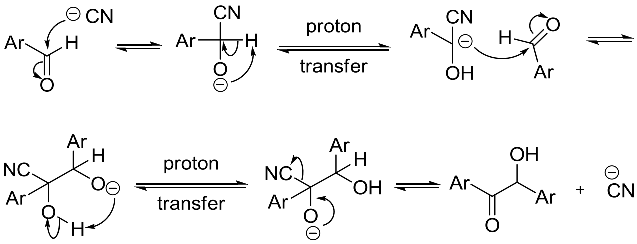
References

1. Liebig, J. *Justus Liebigs Ann. Chem.* **1838,** 27. Justus von Liebig (1803−1873) pursued his Ph.D. in organic chemistry in Paris under the tutelage of Joseph Louis Gay-Lussac (1778−1850). He was appointed the Chair of Chemistry at Giessen University, which incited a furious jealousy amongst several of the professors already working there because he was so young. Fortunately, time would prove the choice was a wise one for the department. Liebig would soon transform Giessen from a sleepy university to a mecca of organic chemistry in Europe. Liebig is now considered the father of organic chemistry. Many classic name reactions were published in the journal that still bears his name, *Justus Liebigs Annalen der Chemie.*[2]
2. Zinin, N. *Justus Liebigs Ann. Chem.* **1839,** *31*, 329.
3. Georgian, V.; Kundu, N. *Tetrahedron* **1963,** *19*, 1037−1049.
4. Robinson, J. M.; Flynn, E. T.; McMahan, T. L.; Simpson, S. L.; Trisler, J. C.; Conn, K. B. *J. Org. Chem.* **1991,** *56*, 6709−6712.
5. Fohlisch, B.; Radl, A.; Schwetzler-Raschke, R.; Henkel, S. *Eur. J. Org. Chem.* **2001,** 4357–4365.
6. Patra, A.; Ghorai, S. K.; De, S. R.; Mal, D. *Synthesis* **2006,** *15*, 2556–2562.
7. Selig, P.; Bach, T. *Angew. Chem. Int. Ed.* **2008,** *47*, 5082–5084.
8. Kumar, R. R.; Balasubramanian, M. *Benzilic Acid Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 395–405. (Review).
9. Sultana, N.; Fabian, W. M. F. *Beilstein J. Org. Chem.* **2013,** *9,* 594–601.

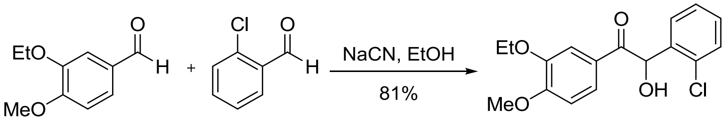
Benzoin condensation

Cyanide-catalyzed condensation of aryl aldehyde to benzoin. Now cyanide is mostly replaced by thiazolium salts or *N*-heterocyclic carbenes. *Cf.* Stetter reaction.

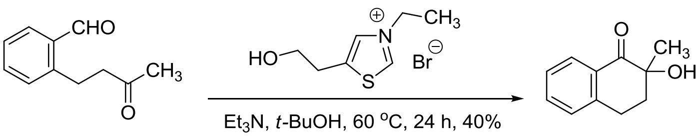




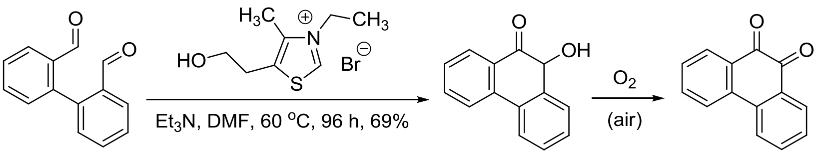
Example 1[2]



Example 2[7]



Example 3[7]



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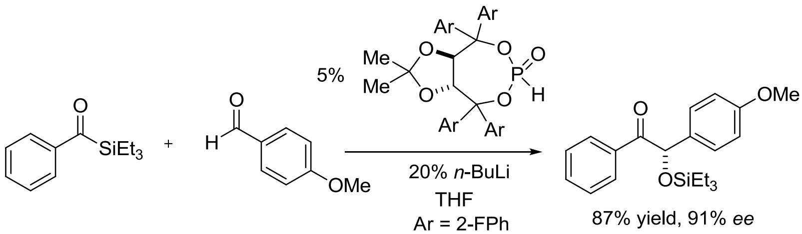
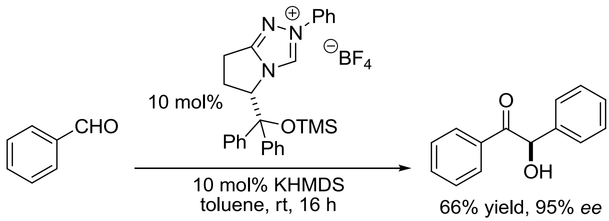
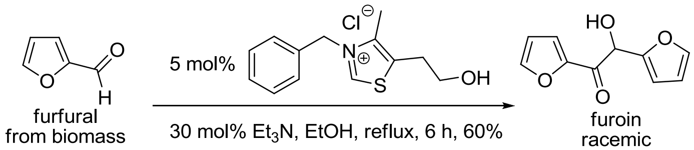
Example 4, With Brook rearrangement[9]



Example 5[10]



Example 6[12]

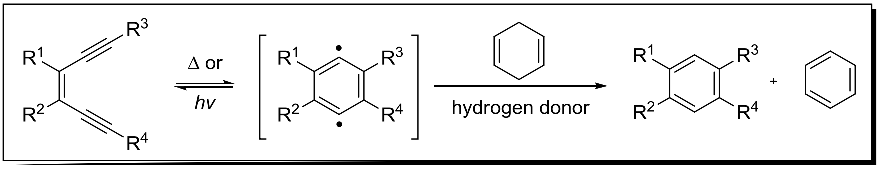


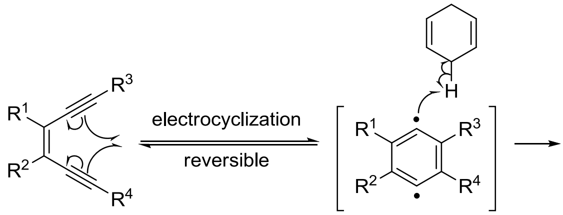
References

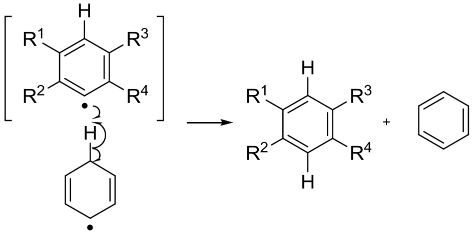
1. Lapworth, A. J. *J. Chem. Soc.* **1903,** *83*, 995–1005. Arthur Lapworth (1872–1941) was born in Scotland. He was a figure in the development of the modern view of mechanisms of organic reactions. Lapworth investigated the benzoin condensation at the Chemical Department, The Goldsmiths' Institute, New Cross, UK.
2. Buck, J. S.; Ide, W. S. *J. Am. Chem. Soc.* **1932,** *54*, 3302–3309.
3. Ide, W. S.; Buck, J. S. *Org. React.* **1948,** *4*, 269–304. (Review).
4. Stetter, H.; Kuhlmann, H. *Org. React.* **1991,** *40*, 407–496. (Review).
5. White, M. J.; Leeper, F. J. *J. Org. Chem.* **2001,** *66*, 5124–5131.
6. Hachisu, Y.; Bode, J. W.; Suzuki, K. *J. Am. Chem. Soc.* **2003,** *125*, 8432–8433.
7. Enders, D.; Niemeier, O. *Synlett* **2004,** 2111–2114.
8. Johnson, J. S. *Angew. Chem. Int. Ed.* **2004,** *43*, 1326–1328. (Review).
9. Linghu, X.; Potnick, J. R.; Johnson, J. S. *J. Am. Chem. Soc.* **2004,** *126*, 3070–3071.
10. Enders, D.; Han, J. *Tetrahedron: Asymmetry* **2008,** *19*, 1367–1371.
11. Cee, V. J. *Benzoin Condensation*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 381–392. (Review).
12. Kabro, A.; Escudero-Adan, E. C.; Grushin, V. V.; van Leeuwen, P. W. N. M. *Org. Lett.* **2012,** *14*, 4014–4017.

Bergman cyclization

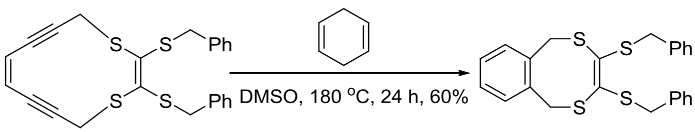
Formation of a substituted benzene through 1,4-benzenediyl diradical formation from enediyne *via* electrocyclization.



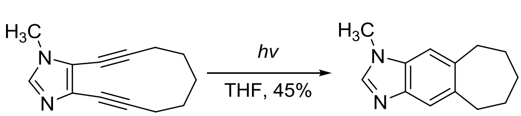




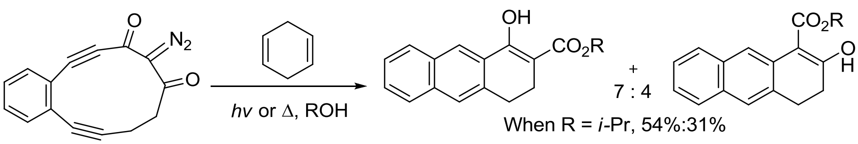
Example 1[6]



Example 2[7]



Example 3, Wolff rearrangement followed by Bergman cyclization[8]



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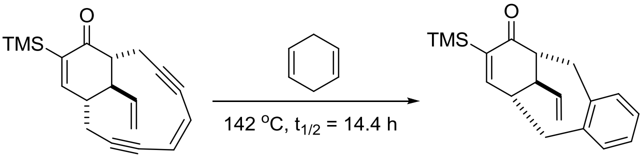
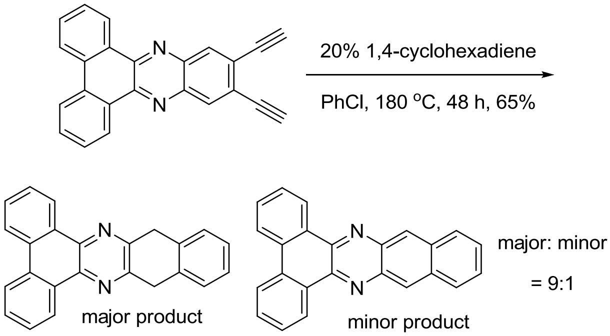
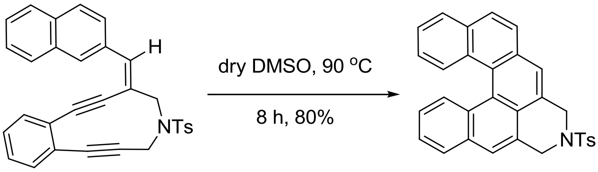
Example 4[10]



Example 5[12]



Example 5[13]

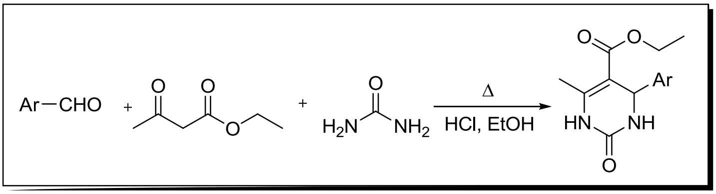


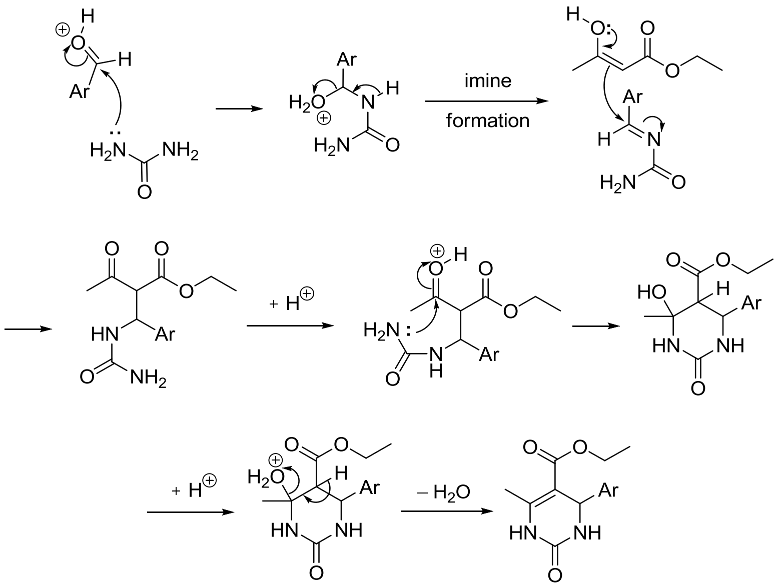
References

1. Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972,** *94*, 660–661. Robert G. Bergman (1942–) is a professor at the University of California, Berkeley. His discovery of the Bergman cyclization was completed far in advance of the discovery of ene-diyne's anti-cancer properties.
2. Bergman, R. G. *Acc. Chem. Res.* **1973,** *6*, 25–31. (Review).
3. Myers, A. G.; Proteau, P. J.; Handel, T. M. *J. Am. Chem. Soc.* **1988,** *110*, 7212–7214.
4. Yus, M.; Foubelo, F. *Rec. Res. Dev. Org. Chem.* **2002,** *6*, 205–280. (Review).
5. Basak, A.; Mandal, S.; Bag, S. S. *Chem. Rev.* **2003,** *103*, 4077–4094. (Review).
6. Bhattacharyya, S.; Pink, M.; Baik, M.-H.; Zaleski, J. M. *Angew. Chem. Int. Ed.* **2005,** *44*, 592–595.
7. Zhao, Z.; Peacock, J. G.; Gubler, D. A.; Peterson, M. A. *Tetrahedron Lett.* **2005,** *46*, 1373–1375.
8. Karpov, G. V.; Popik, V. V. *J. Am. Chem. Soc.* **2007,** *129*, 3792–3793.
9. Kar, M.; Basak, A. *Chem. Rev.* **2007,** *107*, 2861–2890. (Review).
10. Lavy, S.; Pérez-Luna, A.; Kündig, E. P. *Synlett* **2008,** 2621–2624.
11. Pandithavidana, D. R.; Poloukhtine, A.; Popik, V. V. *J. Am. Chem. Soc.* **2009,** *131*, 351–356.
12. Spence, J. D.; Rios, A. C.; Frost, M. A.; etc. *J. Org. Chem.* **2012,** *77*, 10329–10339.
13. Roy, S.; Basak, A. *Tetrahedron* **2013,** *69*, 2184–2192.

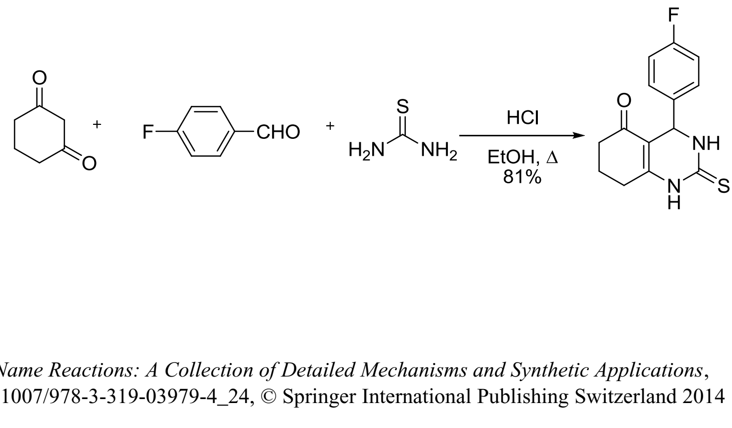
Biginelli reaction

Also known as Biginelli pyrimidone synthesis. One-pot condensation of an aromatic aldehyde, urea, and β-dicarbonyl compound in acidic ethanolic solution and expansion of such a condensation thereof. It belongs to a class of transformations called multicomponent reactions (MCRs).





Example 1[4]



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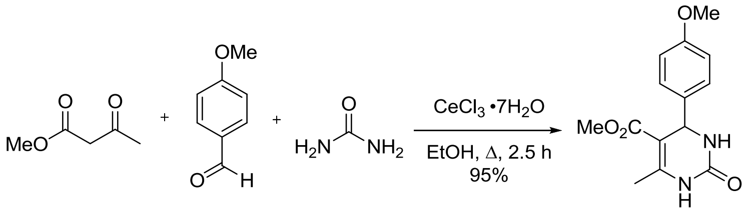
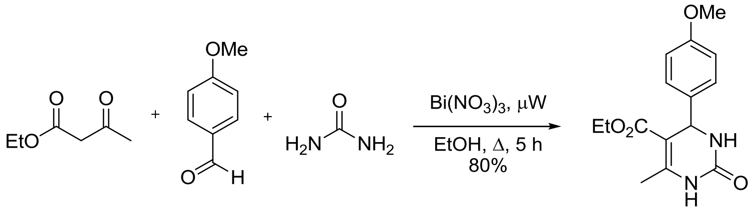
DOI 10.1007/978-3-319-03979-4_24,

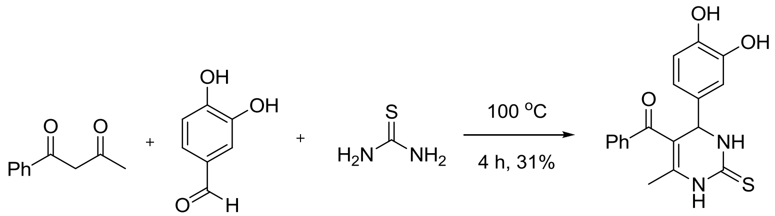
Example 2[5]



Example 3, Microwave-induced Biginelli condensation[9]



Example 3[10]



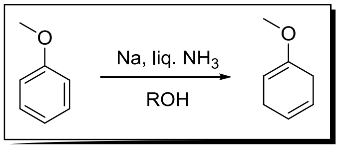
References

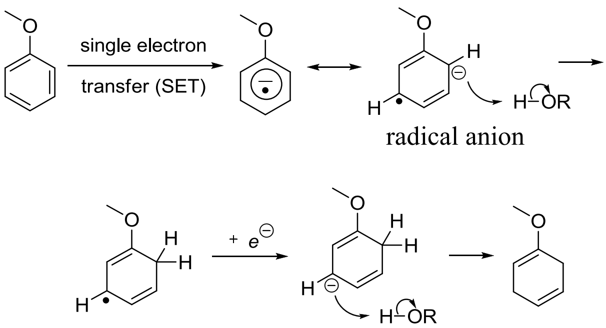
1. Biginelli, P. *Ber.* **1891,** *24*, 1317. Pietro Biginelli was at Lab. chim. della Sanita pubbl. in Roma, Italy when this paper was published.
2. Kappe, C. O. *Tetrahedron* **1993,** *49*, 6937–6963. (Review).
3. Kappe, C. O. *Acc. Chem. Res.* **2000,** *33*, 879–888. (Review).
4. Kappe, C. O. *Eur. J. Med. Chem.* **2000,** *35*, 1043–1052. (Review).
5. Ghorab, M. M.; Abdel-Gawad, S. M.; El-Gaby, M. S. A. *Farmaco* **2000,** *55*, 249–255.
6. Bose, D. S.; Fatima, L.; Mereyala, H. B. *J. Org. Chem.* **2003,** *68*, 587–590.
7. Kappe, C. O.; Stadler, A. *Org. React.* **2004,** *68*, 1–116. (Review).
8. Limberakis, C. *Biginelli Pyrimidone Synthesis* In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 509–520. (Review).
9. Banik, B. K.; Reddy, A. T.; Datta, A.; Mukhopadhyay, C. *Tetrahedron Lett.* **2007,** *48*, 7392–7394.
10. Wang, R.; Liu, Z.-Q. *J. Org. Chem.* **2012,** *77*, 3952–3958.
11. Fuchs, D.; Nasr-Esfahani, M.; Diab, L.; Šmejkal, T.; Breit, B. *Synlett* **2013,** ***24,*** 1657–1662.
12. Liberto, N. A.; de Paiva Silva, S.; de Fátima, Â.; Fernandes, S. A. *Tetrahedron* **2013,** ***69,*** 8245–8249.

Birch reduction

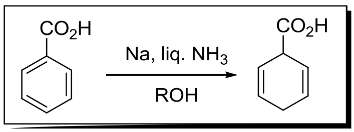
The Birch reduction is the 1,4-reduction of aromatics to their corresponding cyclohexadienes by alkali metals (Li, K, Na) dissolved in liquid ammonia in the presence of an alcohol.

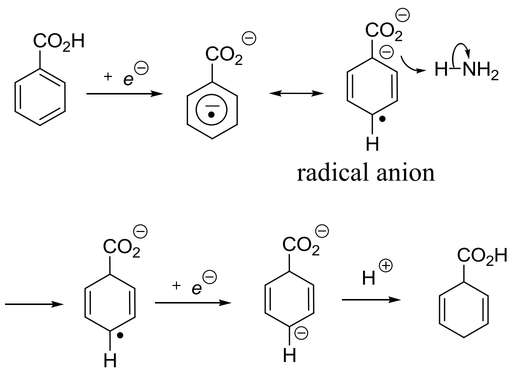
Benzene ring bearing an electron-donating substituent:





Benzene ring with an electron-withdrawing substituent:





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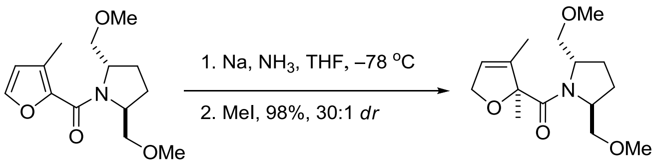
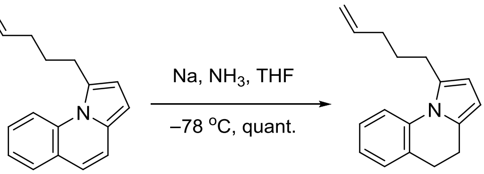
DOI 10.1007/978-3-319-03979-4_25,

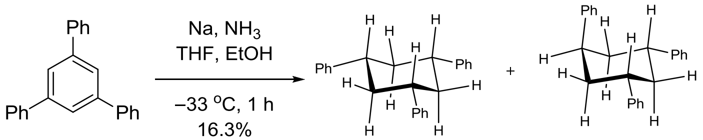
Example 1, Birch reductive alkylation[4]



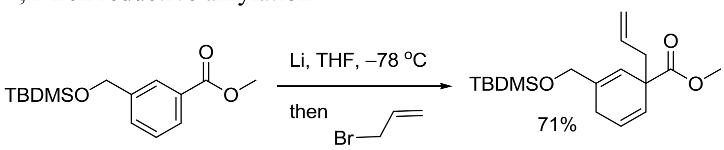
Example 2[7]



Example 3, Fully reduced products[8]



Example 4, Birch reductive alkylation[9]

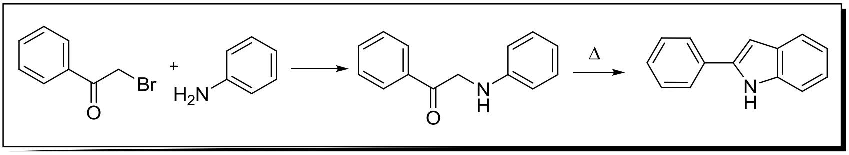


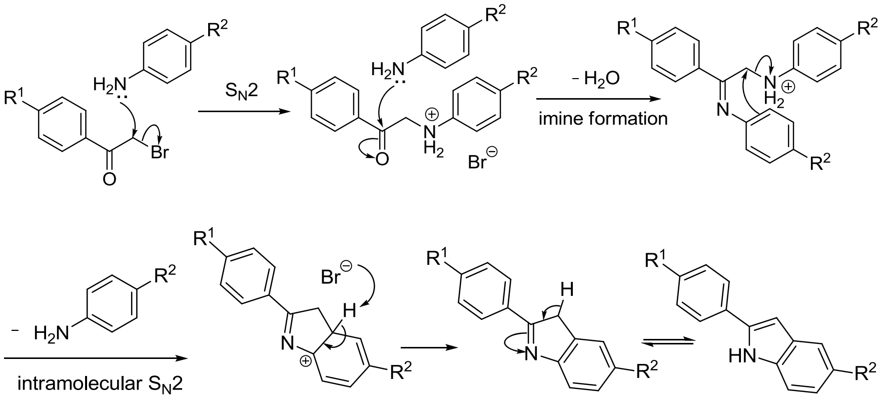
References

1. Birch, A. J. *J. Chem. Soc.* **1944,** 430–436. Arthur Birch (1915−1995), an Australian, developed the "Birch reduction" at Oxford University during WWII in Robert Robinson's laboratory. The Birch reduction was instrumental to the discovery of the birth control pills and many other drugs.
2. Rabideau, P. W.; Marcinow, Z. *Org. React.* **1992,** *42*, 1−334. (Review).
3. Birch, A. J. *Pure Appl. Chem.* **1996,** *68*, 553−556. (Review).
4. Donohoe, T. J.; Guillermin, J.-B.; Calabrese, A. A.; Walter, D. S. *Tetrahedron Lett.* **2001,** *42*, 5841−5844.
5. Pellissier, H.; Santelli, M. *Org. Prep. Proced. Int.* **2002,** *34*, 611−642. (Review).
6. Subba Rao, G. S. R. *Pure Appl. Chem.* **2003,** *75*, 1443−1451. (Review).
7. Kim, J. T.; Gevorgyan, V. *J. Org. Chem.* **2005,** *70*, 2054–2059.
8. Gealis, J. P.; Müller-Bunz, H.; Ortin, Y.; Condell, M.; Casey, M.; McGlinchey, M. J. *Chem. Eur. J.* **2008,** *14*, 1552–1560.
9. Fretz, S. J.; Hadad, C. M.; Hart, D. J.; Vyas, S.; Yang, D. *J. Org. Chem.* **2013,** *78*, 83–92.

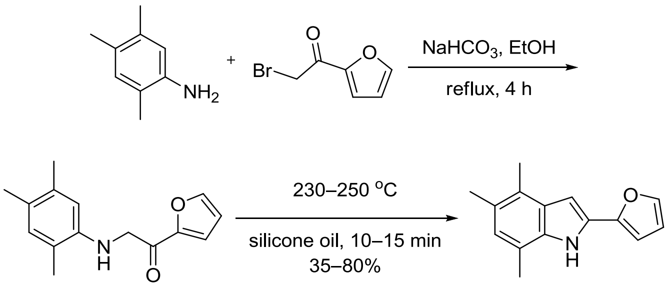
Bischler–Möhlau indole synthesis

The Bischler–Möhlau indole synthesis, also known as the Bischler indole synthesis, refers to the synthesis of 2-arylindoles from the cyclization of α-arylamino-ketones and excess anilines.

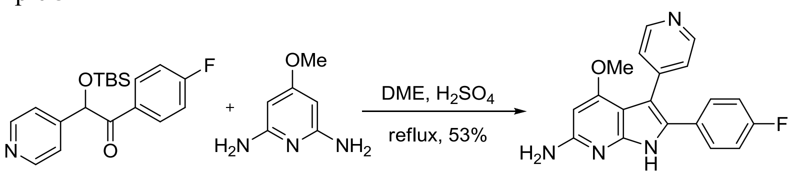




Example 1[5]



Example 3[9]



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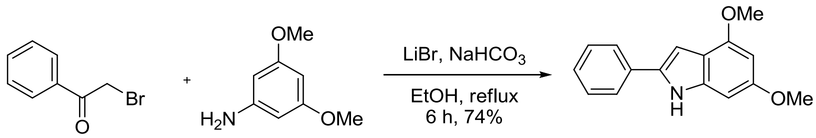
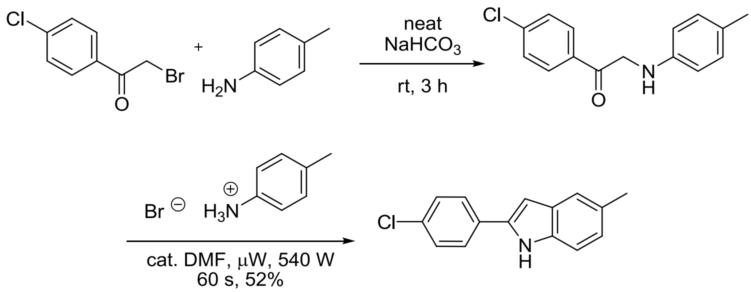
DOI 10.1007/978-3-319-03979-4_26,

Example 4[10]



Example 5, Microwave-assisted, solvent-free Bischler indole synthesis[11]

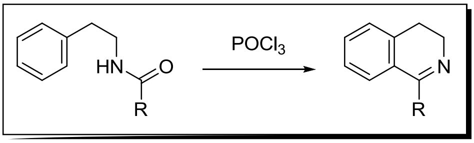


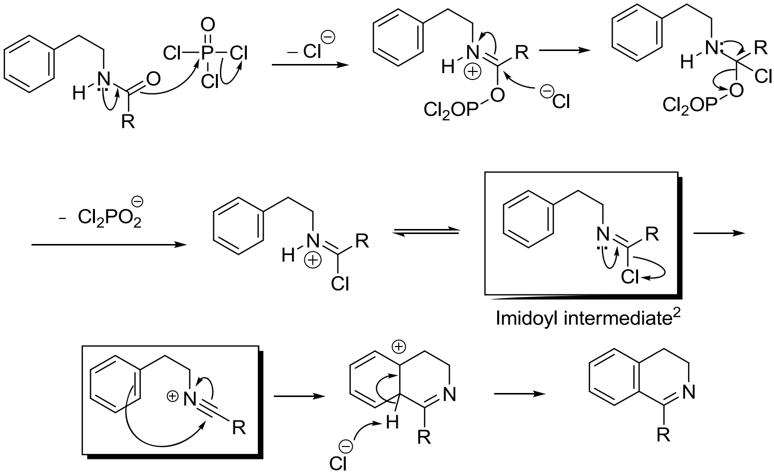
References

1. Möhlau, R. *Ber.* **1881,** *14*, 171–175. Möhlau, a German chemist, worked extensively in the dye industry.
2. Bischler, A.; Fireman, P. *Ber.* **1893,** *26*, 1346–1349. Augustus Bischler (1865–1957) was born in Southern Russia. He studied in Zurich with Arthur Hantzsch. He discovered the Bischler–Napieralski reaction while studying alkaloids at Basel Chemical Works, Switzerland with his coworker, B. Napieralski.
3. Sundberg, R. J. *The Chemistry of Indoles;* Academic Press: New York, **1970,** pp 164. (Book).
4. Buu-Hoï, N. P.; Saint-Ruf, G.; Deschamps, D.; Bigot, P. *J. Chem. Soc. (C)* **1971,** 2606–2609.
5. Houlihan, W. J., Ed.; *The Chemistry of Heterocyclic Compounds, Indoles (Part 1),* Wiley: New York, **1972**. (Book).
6. Bigot, P.; Saint-Ruf, G.; Buu-Hoï, N. P. *J. Chem. Soc., Perkin 1* **1972,** 2573–2576.
7. Bancroft, K. C. C.; Ward, T. J. *J. Chem. Soc., Perkin 1* **1974,** 1852–1858.
8. Coïc, J. P.; Saint-Ruf, G.; Brown, K. *J. Heterocycl. Chem.* **1978,** *15*, 1367–1371.
9. Henry, J. R.; Dodd, J. H. *Tetrahedron Lett.* **1998,** *39*, 8763–8764.
10. Pchalek, K.; Jones, A. W.; Wekking, M. M. T.; Black, D. S. C. *Tetrahedron* **2005,** *61*, 77–82.
11. Sridharan, V.; Perumal, S.; Avendaño, C.; Menéndez, J. C. *Synlett* **2006,** 91–95.
12. Zhang, J. *Bischler–Möhlau Indole Synthesis*, In *Name Reactions in Heterocyclic Chemistry II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2011,** pp 84–90. (Review).

Bischler–Napieralski reaction

Dihydroisoquinolines from β-phenethylamides in refluxing phosphorus oxychloride.

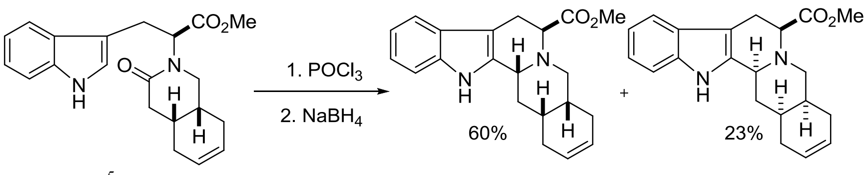




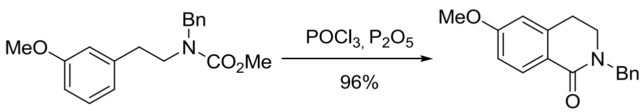
Imidoyl intermediate[2]

Nitrilium salt intermediate[2]

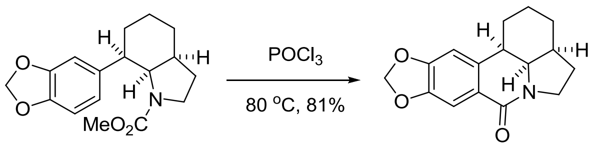
Example 1[3]



Example 2[5]



Example 3[7]



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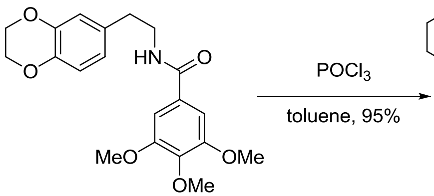
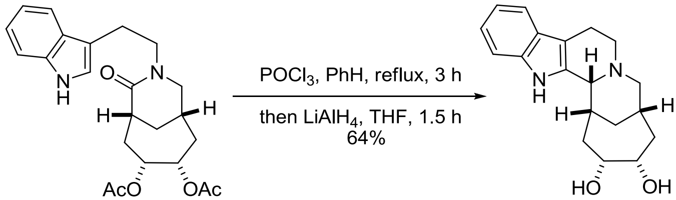
DOI 10.1007/978-3-319-03979-4_27, © Springer International Publishing Switzerland 2014

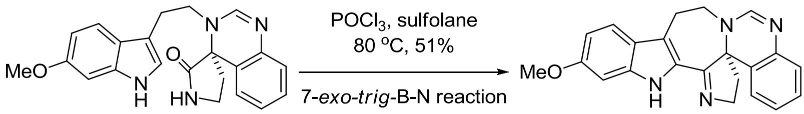
Example 4[8]



Example 5[10]



Example 6, An unprecedented Bischler–Napieralski reaction[12]

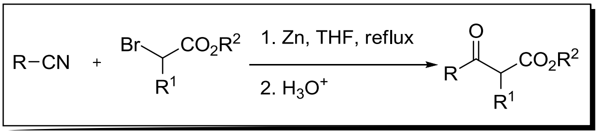


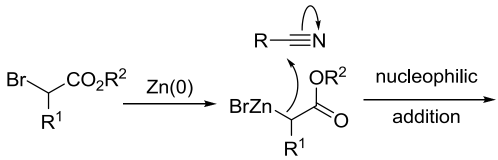
References

1. Bischler, A.; Napieralski, B. *Ber.* **1893,** *26*, 1903–1908. Augustus Bischler discovered the Bischler–Napieralski reaction while studying alkaloids at Basel Chemical Works, Switzerland with his coworker, B. Napieralski. Bernard Napieralski was affiliated with the University of Zurich.
2. Mechanistic studies: (a) Fodor, G.; Gal, J.; Phillips, B. A. *Angew. Chem. Int. Ed. Engl.* **1972,** *11*, 919–920. (b) Nagubandi, S.; Fodor, G. *J. Heterocycl. Chem.* **1980,** *17*, 1457–1463. (c) Fodor, G.; Nagubandi, S. *Tetrahedron* **1980,** *36*, 1279–1300.
3. Aubé, J.; Ghosh, S.; Tanol, M. *J. Am. Chem. Soc.* **1994,** *116*, 9009–9018.
4. Sotomayor, N.; Domínguez, E.; Lete, E. *J. Org. Chem*. **1996,** *61*, 4062–4072.
5. Wang, X.-j.; Tan, J.; Grozinger, K. *Tetrahedron Lett.* **1998,** *39*, 6609–6612.
6. Ishikawa, T.; Shimooka, K.; Narioka, T.; Noguchi, S.; Saito, T.; Ishikawa, A.; Yamazaki, E.; Harayama, T.; Seki, H.; Yamaguchi, K. *J. Org. Chem*. **2000,** *65*, 9143–9151.
7. Banwell, M. G.; Harvey, J. E.; Hockless, D. C. R., Wu, A. W. *J. Org. Chem.* **2000,** *65*, 4241–4250.
8. Capilla, A. S.; Romero, M.; Pujol, M. D.; Caignard, D. H.; Renard, P. *Tetrahedron* **2001,** *57*, 8297–8303.
9. Wolfe, J. P. *Bischler–Napieralski Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 376–385. (Review).
10. Ho, T.-L.; Lin, Q.-x. *Tetrahedron* **2008,** *64*, 10401–10405.
11. Csomós, P.; Fodor, L.; Bernáth, G.; Csámpai, A.; Sohár, P. *Tetrahedron* **2009,** *65*, 1475–1480.
12. Buyck, T.; Wang, Q.; Zhu, J. *Org. Lett.* **2012,** *14*, 1338–1341.

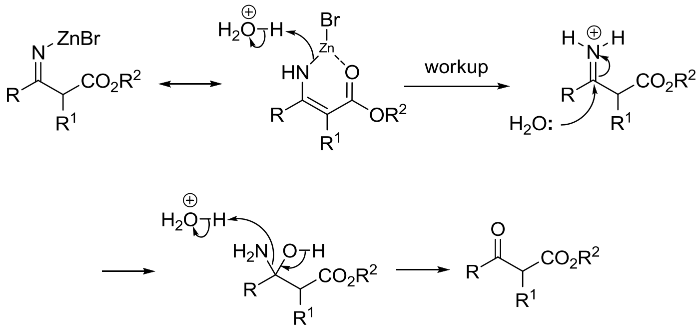
Blaise reaction

β-Ketoesters from nitriles, α-haloesters and Zn. *Cf.* Reformatsky reaction.

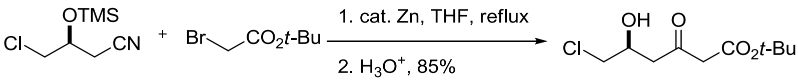




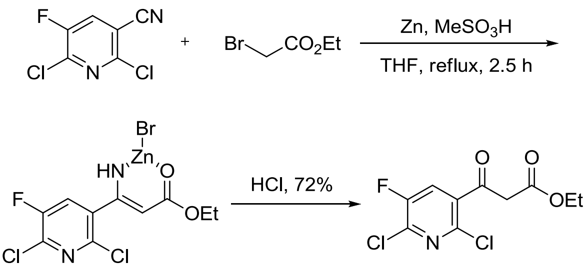
The Zn enolate itself is a *C*-enolate (in the crystal form), but for the reaction to occur, it equilibrates back into an *O*-enolate



Example 1, Preparation of the statin side chain[5]



Example 2[6]



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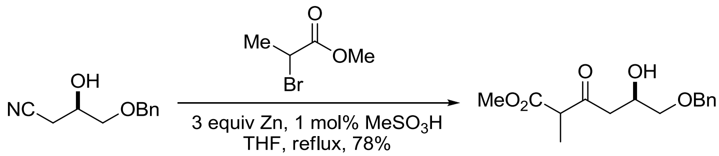
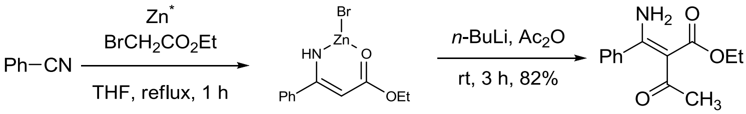
DOI 10.1007/978-3-319-03979-4_28,

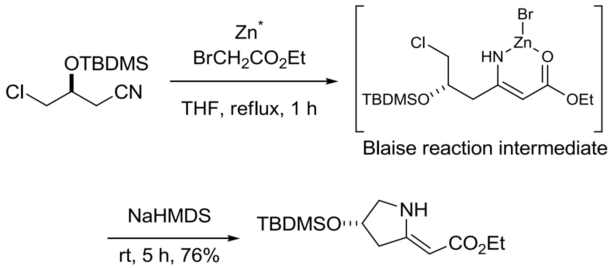
Example 3[7]



Example 4, Chemoselective tandem acylation of a Blaise reaction intermediate[9]



Example 5, Chemoselective intramolecular alkylation of Blaise reaction intermediate[10]

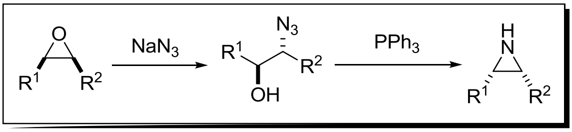


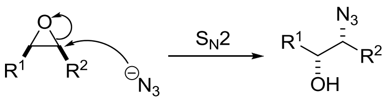
References

1. (a) Blaise, E. E. *C. R. Hebd. Seances Acad. Sci.* **1901,** *132*, 478–480. (b) Blaise, E. E. *C. R. Hebd. Seances Acad. Sci.* **1901,** *132*, 978–980. Blaise was at Institut Chimique de Nancy, France.
2. Beard, R. L.; Meyers, A. I. *J. Org. Chem*. **1991,** *56*, 2091–2096.
3. Deutsch, H. M.; Ye, X.; Shi, Q.; Liu, Z.; Schweri, M. M. *Eur. J. Med. Chem*. **2001,** *36,* 303–311.
4. Creemers, A. F. L.; Lugtenburg, J. *J. Am. Chem. Soc.* **2002,** *124*, 6324–6334.
5. Shin, H.; Choi, B. S.; Lee, K. K.; Choi, H.-w.; Chang, J. H.; Lee, K. W.; Nam, D. H.; Kim, N.-S. *Synthesis* **2004,** 2629–2632.
6. Choi, B. S.; Chang, J. H.; Choi, H.-w.; Kim, Y. K.; Lee, K. K.; Lee, K. W.; Lee, J. H.; Heo, T.; Nam, D. H.; Shin, H. *Org. Proc. Res. Dev*. **2005,** *9*, 311–313.
7. Pospíšil, J.; Markó, I. E. *J. Am. Chem. Soc.* **2007,** *129*, 3516–3517.
8. Rao, H. S. P.; Rafi, S.; Padmavathy, K. *Tetrahedron* **2008,** *64*, 8037–8043. (Review).
9. Chun, Y. S.; Lee, S.-g.; Ko, Y. O.; Shin, H. *Chem. Commun.* **2008,** 5098–5100.
10. Kim, J. H.; Shin, H.; Lee, S.-g. *J. Org. Chem*. **2012,** *77*, 1560–1565.
11. Chun, Y. S.; Xuan, Z.; Kim, J. H.; Lee, S.-g. *Org. Lett.* **2013,** *15*, 3162–3165.

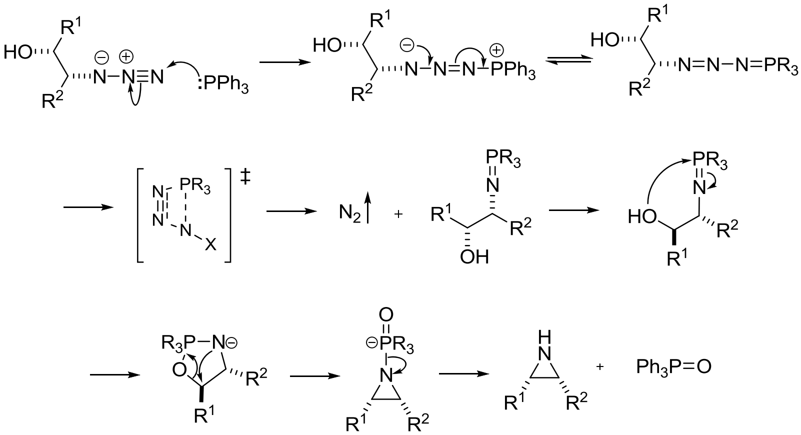
Blum–Ittah aziridine synthesis

Ring opening of oxiranes using azide followed by PPh_3 reduction of the intermediate azido alcohol to give the corresponding aziridines. *Cf.* Staudinger reduction.

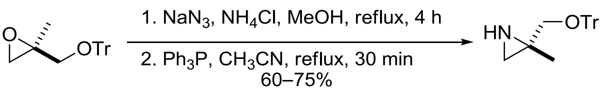




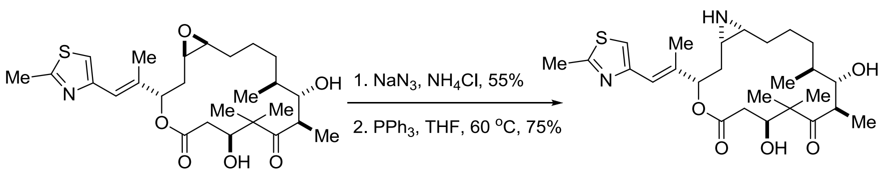
Regardless of the regioselectivity of the S_N2 reaction of the azide, the ultimate stereochemical outcome for the aziridine is the same.



Example 1[3]



Example 2[4]



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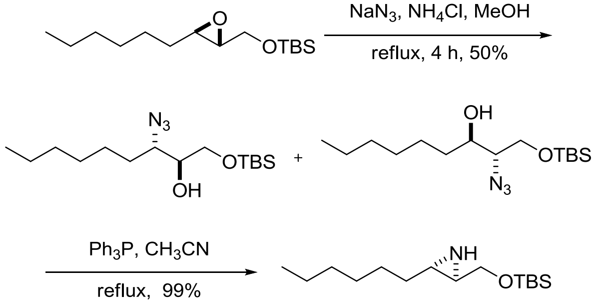
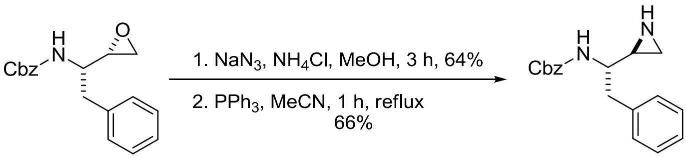
DOI 10.1007/978-3-319-03979-4_29, © Springer International Publishing Switzerland 2014

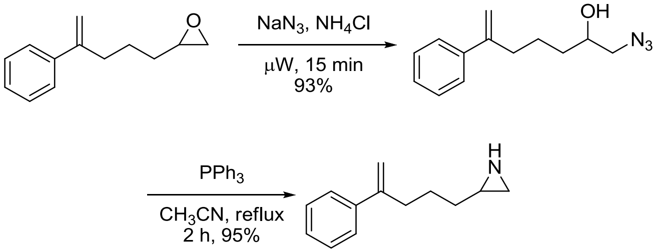
Example 3[6]



Example 4[8]



Example 5[9]

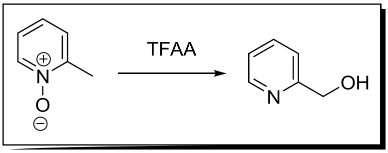


References

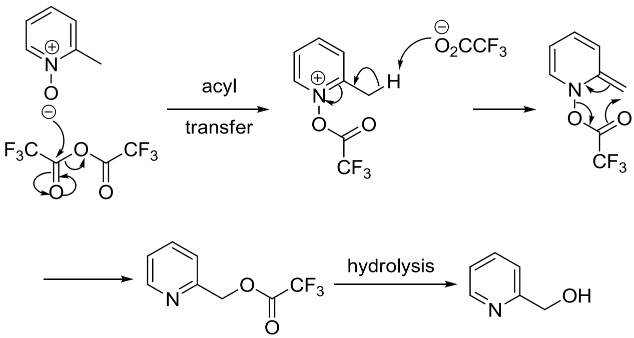
1. Ittah, Y.; Sasson, Y.; Shahak, I.; Tsaroom, S.; Blum, J. *J. Org. Chem.* **1978,** *43*, 4271–4273. Jochanan Blum is a professor at The Hebrew University in Jerusalem, Israel.
2. Tanner, D.; Somfai, P. *Tetrahedron Lett.* **1987,** *28*, 1211–1214.
3. Wipf, P.; Venkatraman, S.; Miller, C. P. *Tetrahedron Lett.* **1995,** *36*, 3639–3642.
4. Regueiro-Ren, A.; Borzilleri, R. M.; Zheng, X.; Kim, S.-H.; Johnson, J. A.; Fairchild, C. R.; Lee, F. Y. F.; Long, B. H.; Vite, G. D. *Org. Lett.* **2001,** *3*, 2693–2696.
5. Fürmeier, S.; Metzger, J. O. *Eur. J. Org. Chem.* **2003,** 649–659.
6. Oh, K.; Parsons, P. J.; Cheshire, D. *Synlett* **2004,** 2771–2775.
7. Serafin, S. V.; Zhang, K.; Aurelio, L.; Hughes, A. B.; Morton, T. H. *Org. Lett.* **2004,** *6*, 1561–1564.
8. Torrado, A. *Tetrahedron Lett.* **2006,** *47*, 7097–7100.
9. Pulipaka, A. B.; Bergmeier, S. C. *J. Org. Chem.* **2008,** *73*, 1462–1467.
10. Richter, J. M. *Blum aziridine synthesis*, In *Name Reactions in Heterocyclic Chemistry II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2011,** pp 2–10. (Review).

Boekelheide reaction

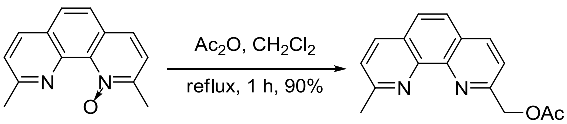
Treatment of 2-methylpyridine *N*-oxide with trifluoroacetic anhydride, or acetic anhydride gives rise to 2-hydroxymethylpyridine.



TFAA: trifluoroacetic anhydride



Example 1[4]



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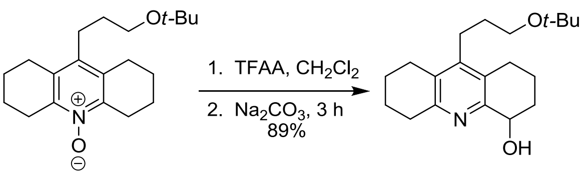
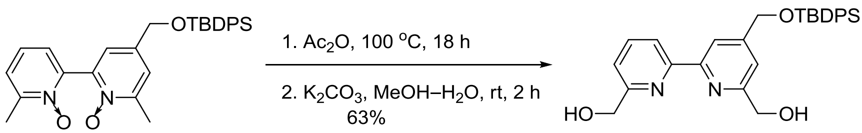


Example 3, Double Boekelheide reaction[8]



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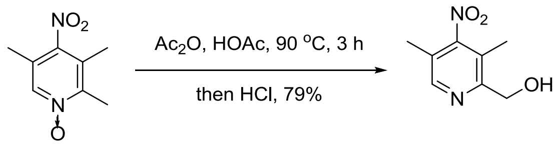
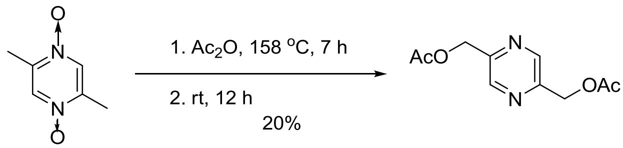
DOI 10.1007/978-3-319-03979-4_30, © Springer International Publishing Switzerland 2014

Example 4[9]



Example 5, Double Boekelheide reaction[10]

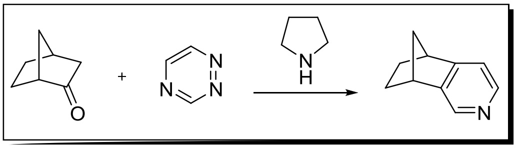


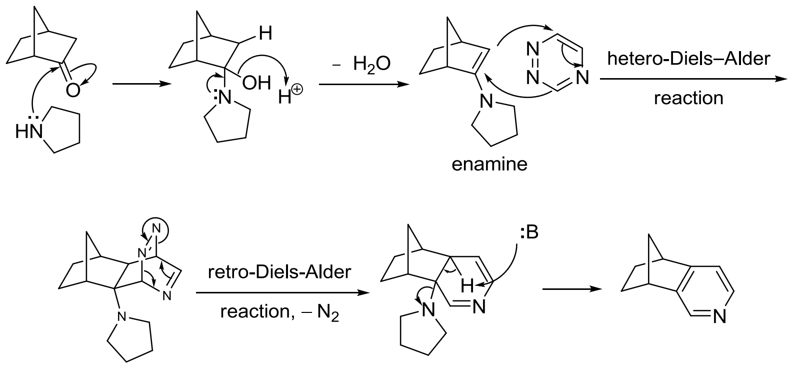
References

1. Boekelheide, V.; Linn, W. J. *J. Am. Chem. Soc.* **1954,** *76*, 1286–1291. Virgil Boekelheide (1919–2003) was a professor at the University of Oregon.
2. Boekelheide, V.; Harrington, D. L. *Chem. Ind.* **1955,** 1423–1424.
3. Katritzky, A. R.; Lagowski, J. M. *Chemistry of the Heterocylic N-Oxides,* Academic Press: NY, **1971**. (Review).
4. Newkome, G. R.; Theriot, K. J.; Gupta, V. K.; Fronczek, F. R.; Baker, G. R. *J. Org. Chem.* **1989,** *54*, 1766–1769.
5. Katritzky, A. R.; Lam, J. N. *Heterocycles* **1992,** *33*, 1011–1049. (Review).
6. Fontenas, C.; Bejan, E.; Haddou, H. A.; Balavoine, G. G. A. *Synth. Commun.* **1995,** *25*, 629–633.
7. Galatsis, P. *Boekelheide Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 340–349. (Review).
8. Havas, F.; Danel, M.; Galaup, C.; Tisnès, P.; Picard, C. *Tetrahedron Lett.* **2007,** *48*, 999–1002.
9. Dai, L.; Fan, D.; Wang, X.; Chen, Y. *Synth. Commun.* **2008,** *38*, 576–582.
10. Das, S. K.; Frey, J. *Tetrahedron Lett.* **2012,** *53*, 3869–3872.

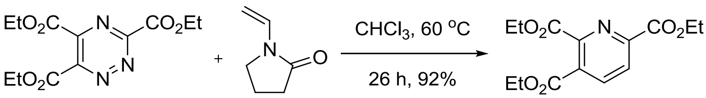
Boger pyridine synthesis

Pyridine synthesis *via* hetero-Diels–Alder reaction of 1,2,4-triazines and dienophiles (e.g., enamine) followed by extrusion of N_2.

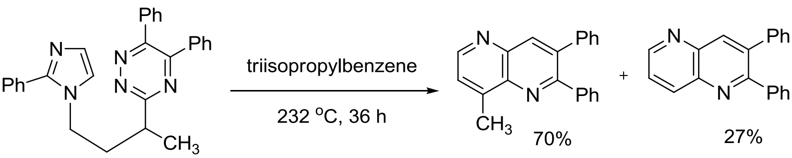




Example 1[3]



Example 2, Intramolecular Boger pyridine synthesis[8]



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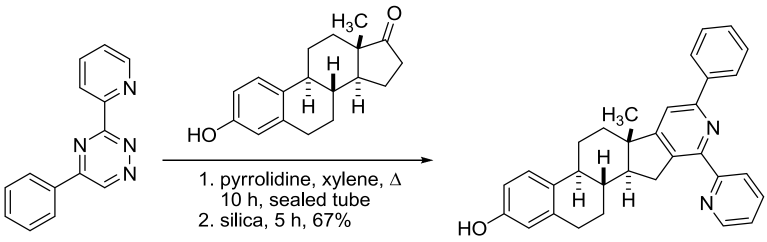
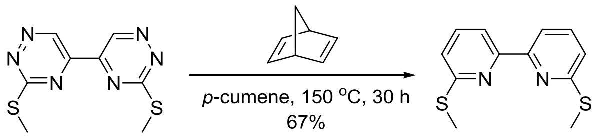
Example 3[10]



Example 4[11]

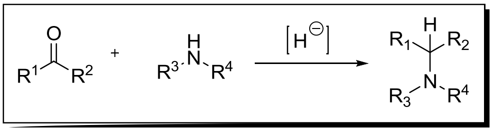


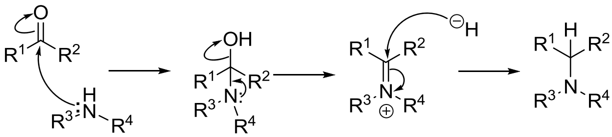
References

1. Boger, D. L.; Panek, J. S. *J. Org. Chem*. **1981,** *46*, 2179–2182. Dale Boger obtained his Ph.D. under E.J. Corey at Harvard University in 1980. He started his independent career at the University of Kansas, moving onto Purdue University, and currently he is a professor at The Scripps Research Institute.
2. Boger, D. L. *Tetrahedron* **1983,** *39*, 2869–2939. (Review).
3. Boger, D. L.; Panek, J. S.; Yasuda, M. *Org. Synth*. **1988,** *66*, 142–150.
4. Boger, D. L. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 5*, 451–512. (Review).
5. Behforouz, M.; Ahmadian, M.*Tetrahedron* **2000,** *56*, 5259–5288. (Review).
6. Buonora, P.; Olsen, J.-C.; Oh, T. *Tetrahedron* **2001,** *57*, 6099–6138. (Review).
7. Jayakumar, S.; Ishar, M. P. S.; Mahajan, M. P. *Tetrahedron* **2002,** *58*, 379–471. (Review).
8. Lahue, B. R.; Lo, S.-M.; Wan, Z.-K.; Woo, G. H. C.; Snyder, J. K. *J. Org. Chem*. **2006,** *69*, 7171–7182.
9. Galatsis, P. *Boger Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 323–339. (Review).
10. Catozzi, N.; Bromley, W. J.; Wasnaire, P.; Gibson, M.; Taylor, R. J. K. *Synlett* **2007,** 2217–2221.
11. Lawecka, J.; Bujnicki, B.; Drabowicz, J.; Rykowski, A. *Tetrahedron Lett.* **2008,** *49*, 719–722.

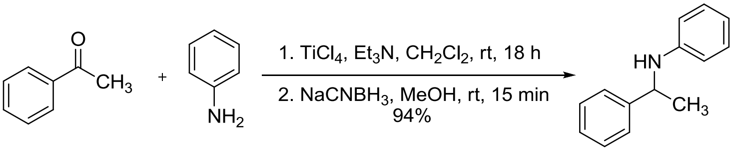
Borch reductive amination

Reduction (often using $NaCNBH_3$) of an imine, formed by condensation of an amine and a carbonyl, to afford the corresponding amine.

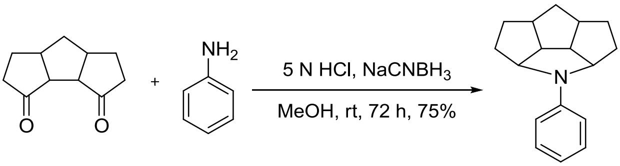




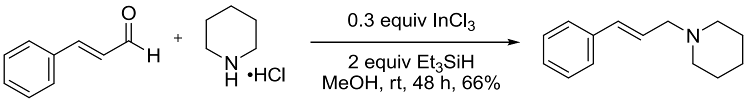
Example 1[4]



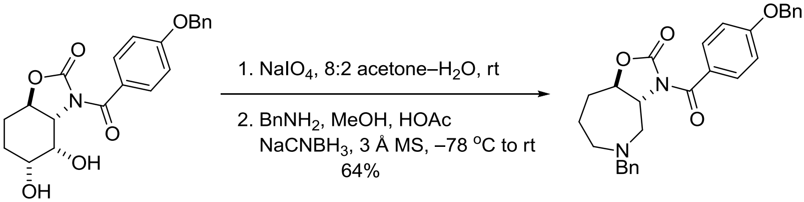
Example 2[5]



Example 3[8]



Example 4[9]



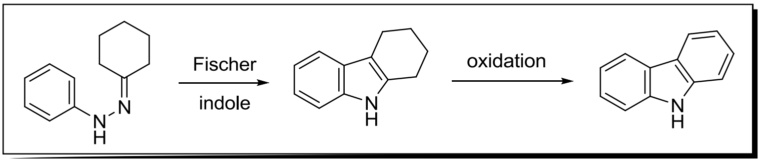
J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_32,

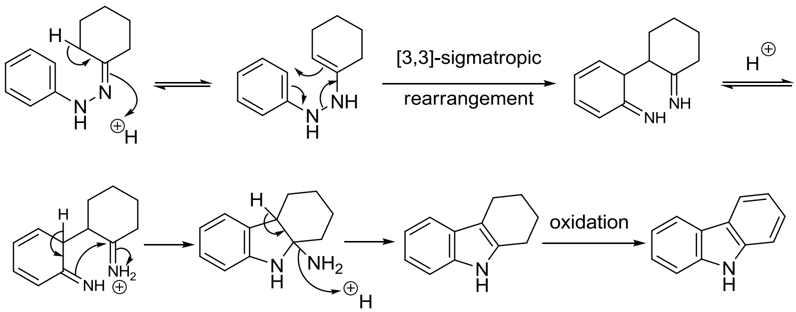
References

1. Borch, R. F., Durst, H. D. *J. Am. Chem. Soc.* **1969,** *91*, 3996–3997. Richard F. Borch, born in Cleveland, Ohio, was a professor at the University of Minnesota.
2. Borch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am. Chem. Soc.* **1971,** *93*, 2897–2904.
3. Borch, R. F.; Ho, B. C. *J. Org. Chem*. **1977,** *42*, 1225–1227.
4. Barney, C. L.; Huber, E. W.; McCarthy, J. R. *Tetrahedron Lett*. **1990,** *31*, 5547–5550.
5. Mehta, G.; Prabhakar, C. *J. Org. Chem*. **1995,** *60*, 4638–4640.
6. Lewin, G.; Schaeffer, C. *Heterocycles* **1998,** *48*, 171–174.
7. Lewin, G.; Schaeffer, C.; Hocquemiller, R.; Jacoby, E.; Léonce, S.; Pierré, A.; Atassi, G. *Heterocycles* **2000,** *53*, 2353–2356.
8. Lee, O.-Y.; Law, K.-L.; Ho, C.-Y.; Yang, D. *J. Org. Chem*. **2008,** *73*, 8829–8837.
9. Sullivan, B.; Hudlicky, T. *Tetrahedron Lett*. **2008,** *49*, 5211–5213.
10. Koszelewski, D.; Lavandera, I.; Clay, D.; Guebitz, G. M.; Rozzell, D.; Kroutil, W. *Angew. Chem. Int. Ed.* **2008,** *47*, 9337–9340.

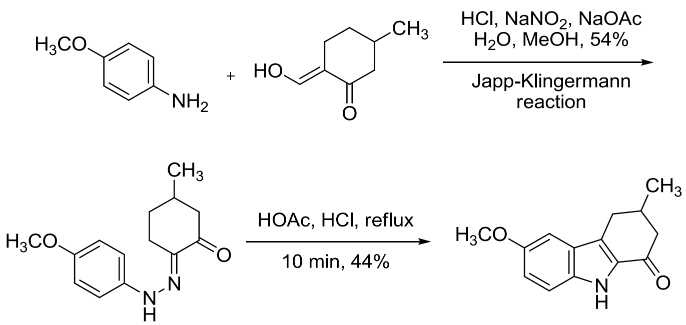
Borsche–Drechsel cyclization

Also known as Borsche carbazole synthesis, is the two-step conversion of phenyl hydrazine and cyclohexanone derivatives to the corresponding carbazole. *Cf.* Fischer indole synthesis.

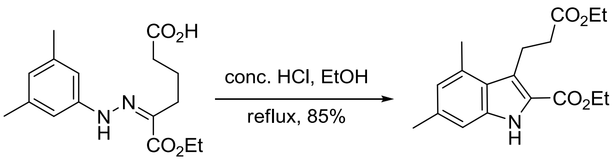




Example 1[6]



Example 2[9]



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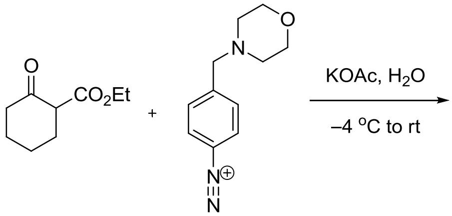
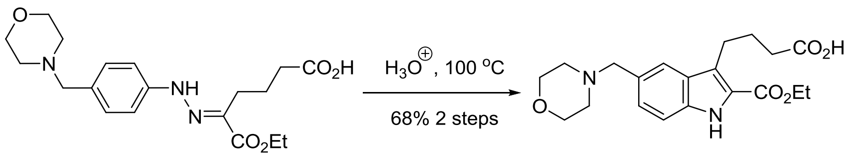
DOI 10.1007/978-3-319-03979-4_33, © Springer International Publishing Switzerland 2014

Example 3[10]



Japp-Klingemann hydrazone synthesis

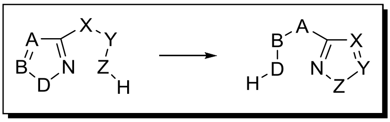


References

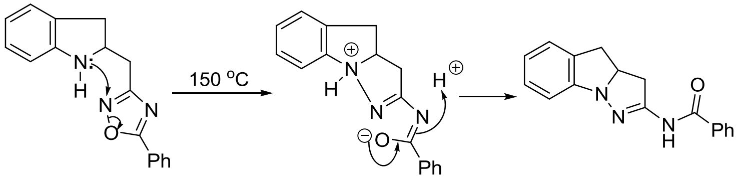
1. Drechsel, E. *J. Prakt. Chem.* **1858,** *38*, 69.
2. Borsche, W.; Feise, M. *Ann.* **1908,** *359*, 49–80. Walther Borsche was a professor at Chemischen Institut, Universität Göttingen, Germany when this paper was published. Borsche was completely devoid of the arrogance shown by many of his contemporaries. Both Borsche and his colleague at Frankfurt, Julius von Braun, suffered under the Nazi regime for their independent minds.
3. Bruck, P. *J. Org. Chem.* **1970,** *35,* 2222–2227.
4. Gazengel, J.-M.; Lancelot, J.-C.; Rault, S.; Robba, M. *J. Heterocycl. Chem.* **1990,** *27,* 1947–1951.
5. Abramovitch, R. A.; Bulman, A. *Synlett* **1992,** 795–796.
6. Lin, G.; Zhang, A. *Tetrahedron* **2000,** *56,* 7163–7171.
7. Ergun, Y.; Bayraktar, N.; Patir, S.; Okay, G. *J. Heterocycl. Chem.* **2000,** *37,* 11–14.
8. Rebeiro, G. L.; Khadilkar, B. M. *Synthesis* **2001,** 370–372.
9. Takahashi, K.; Kasai, M.; Ohta, M.; Shoji, Y.; Kunishiro, K.; Kanda, M.; Kurahashi, K.; Shirahase, H. *J. Med. Chem.* **2008,** *51,* 4823–4833.
10. Pete, B. *Tetrahedron Lett.* **2008,** *49,* 2835–2838.
11. Fultz, M. W. *Borsche–Drechsel Cyclization*, In *Name Reactions in Heterocyclic Chemistry II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2011,** pp 91–101. (Review).

Boulton–Katritzky rearrangement

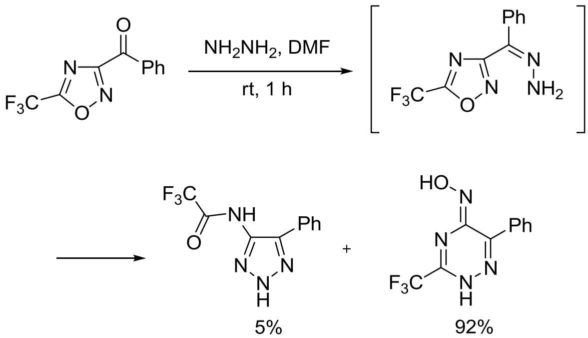
Rearrangement of one five-membered heterocycle into another under thermolysis.



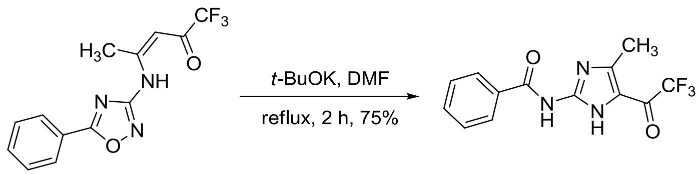
Example 1[4]



Example 2, Hydrazinolysis[7]



Example 4[3]



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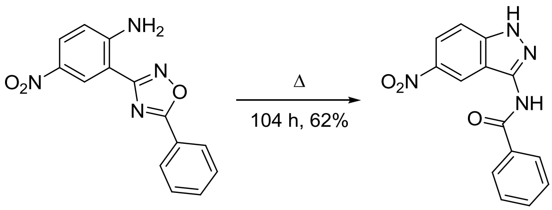
DOI 10.1007/978-3-319-03979-4_34,

Example 5[12]

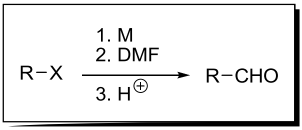


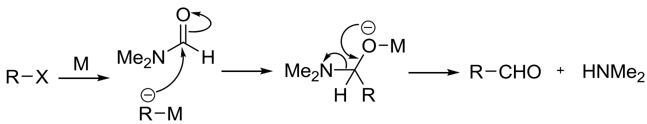
References

1. Boulton, A. J.; Katritzky, A. R.; Majid Hamid, A. *J. Chem. Soc. (C)* **1967,** 2005–2007. Alan Katritzky, a professor at the University of Florida, is best known for his series *Advances of Heterocyclic Chemistry*, now in its 107th volume.
2. Ruccia, M.; Vivona, N.; Spinelli, D. *Adv. Heterocycl. Chem.* **1981,** *29*, 141–169. (Review).
3. Vivona, N.; Buscemi, S.; Frenna, V.; Gusmano, C. *Adv. Heterocyl. Chem.* **1993,** *56*, 49–154. (Review).
4. Katayama, H.; Takatsu, N.; Sakurada, M.; Kawada, Y. *Heterocycles* **1993,** *35*, 453–459.
5. Rauhut, G. *J. Org. Chem*. **2001,** *66*, 5444–5448.
6. Crampton, M. R.; Pearce, L. M.; Rabbitt, L. C. *J. Chem. Soc., Perkin Trans. 2* **2002,** 257–261.
7. Buscemi, S.; Pace, A.; Piccionello, A. P.; Macaluso, G.; Vivona, N.; Spinelli, D.; Giorgi, G. *J. Org. Chem.* **2005,** *70*, 3288–3291.
8. Pace, A.; Pibiri, I.; Piccionello, A. P.; Buscemi, S.; Vivona, N.; Barone, G. *J. Org. Chem.* **2007,** *64*, 7656–7666.
9. Piccionello, A. P.; Pace, A.; Buscemi, S.; Vivona, N.; Pani, M. *Tetrahedron* **2008,** *64*, 4004–4010.
10. Pace, A.; Pierro, P.; Buscemi, S.; Vivona, N.; Barone, G. *J. Org. Chem.* **2009,** *74*, 351–358.
11. Corbett M. T.; Mullins, R. J. *Boulton–Katritzky rearrangement*, In *Name Reactions in Heterocyclic Chemistry II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2011,** pp 527–538. (Review).
12. Ott, G. R.; Anzalone, A. V. *Synlett* **2011,** 3018–3022.

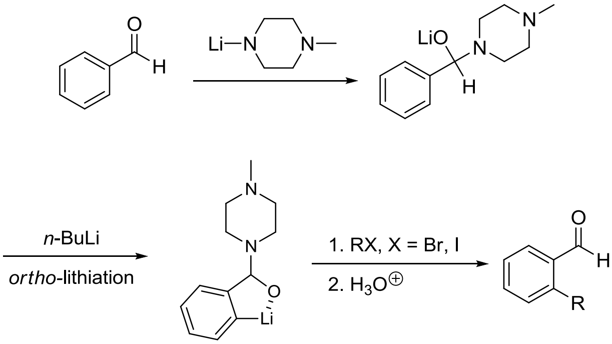
Bouveault aldehyde synthesis

Formylation of an alkyl or aryl halide to the homologous aldehyde by transformation to the corresponding organometallic reagent then addition of DMF (M = Li, Mg, Na, and K).

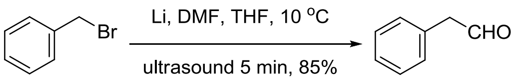




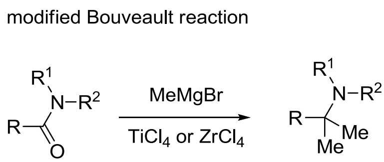
Comins modification:[4]



Example 1[3]



Example 2, A modified Bouveault reaction[7]



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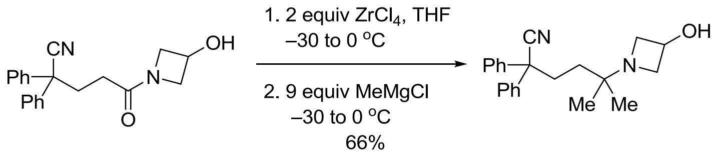
DOI 10.1007/978-3-319-03979-4_35, © Springer International Publishing Switzerland 2014

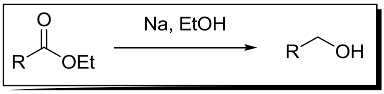


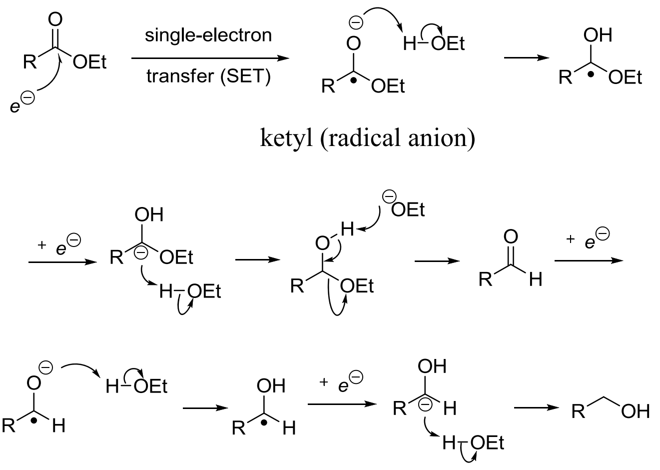
References

1. Bouveault, L. *Bull. Soc. Chim. Fr.* **1904,** *31*, 1306–1322, 1322–1327. Louis Bouveault (1864–1909) was born in Nevers, France. He devoted his short yet very productive life to teaching and to working in science.
2. Sicé, J. *J. Am. Chem. Soc*. **1953,** *75*, 3697–3700.
3. Pétrier, C.; Gemal, A. L.; Luche, J.-L. *Tetrahedron Lett*. **1982,** *23*, 3361–3364.
4. Comins, D. L.; Brown, J. D. *J. Org. Chem*. **1984,** *49*, 1078–1083.
5. Einhorn, J.; Luche, J. L. *Tetrahedron Lett*. **1986,** *27*, 1793–1796.
6. Meier, H.; Aust, H. *J. Prakt. Chem*. **1999,** *341*, 466–471.
7. Dillon, B R.; Roberts, D F.; Entwistle, D A.; Glossop, P A.; Knight, C. J.; Laity, D. A.; James, K.; Praquin, C. F.; Strang, R. S.; Watson, C. A. L. *Org. Process Res. Dev.* **2012,** *16*, 195–203.

Bouveault–Blanc reduction

Also known as the Bouveault reaction. Reduction of esters to the corresponding alcohols using sodium in an alcoholic solvent.





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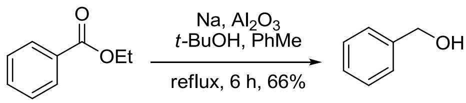

References

1. Bouveault, L.; Blanc, G. *Compt. Rend. Hebd. Seances Acad. Sci.* **1903,** *136*, 1676–1678.
2. Bouveault, L.; Blanc, G. *Bull. Soc. Chim.* **1904,** *31*, 666–672.
3. Rühlmann, K.; Seefluth, H.; Kiriakidis, T.; Michael, G.; Jancke, H.; Kriegsmann, H. *J. Organomet. Chem.* **1971,** *27*, 327–332.
4. Seo, B.-I.; Wall, L. K.; Lee, H.; Buttrum, J. W.; Lewis, D. E. *Synth. Commun.* **1993,** *23*, 15–22.
5. Singh, S.; Dev, S. *Tetrahedron* **1993,** *49*, 10959–10964.
6. Schopohl, M. C.; Bergander, K.; Kataeva, O.; Föehlich, R.; Waldvogel, S. R. *Synthesis* **2003,** 2689–2694.

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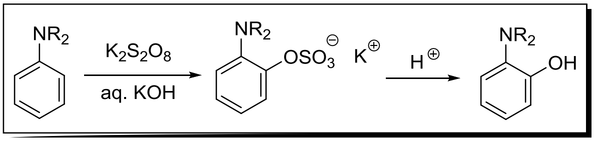
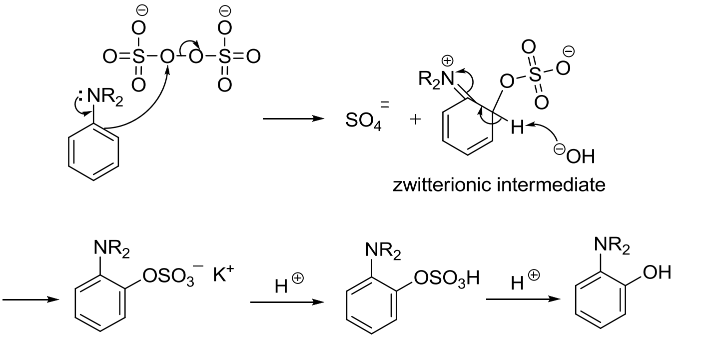
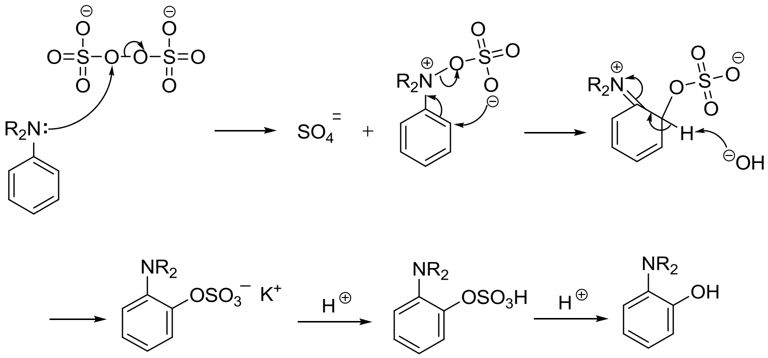
Boyland–Sims oxidation

Oxidation of anilines to phenols using alkaline persulfate.

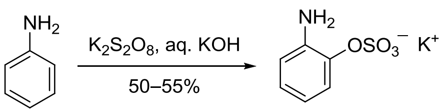




Another pathway is also operative:[9–12]



Example 1[3]



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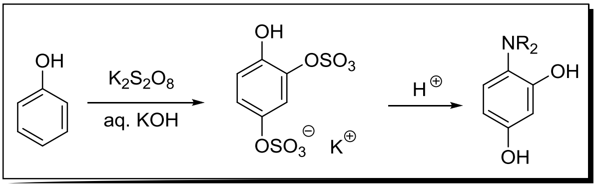
Elbs oxidation

Also known as the Elbs persulfate oxidation,[13–15] it is a variant of the Boyland–Sims oxidation except the substrate is phenol rather than aniline. Its mechanism is similar to that of the Boyland–Sims oxidation.

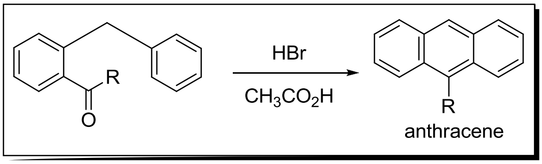


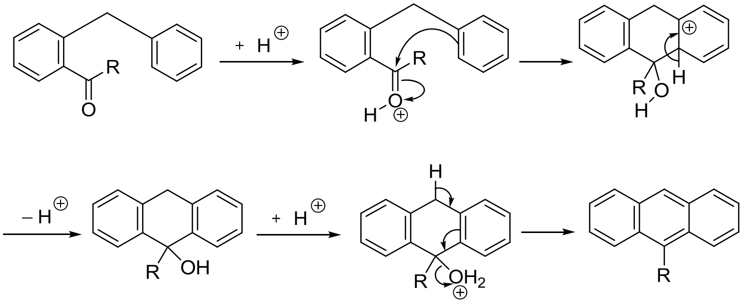
References

1. Boyland, E.; Manson, D.; Sims, P. *J. Chem. Soc.* **1953,** 3623–3628. Eric Boyland and Peter Sims were at the Royal Cancer Hospital in London, UK.
2. Boyland, E.; Sims, P. *J. Chem. Soc.* **1954,** 980–985.
3. Behrman, E. J. *J. Am. Chem. Soc.* **1967,** *89*, 2424–2428.
4. Behrman, E. J.; Behrman, D. M. *J. Org. Chem.* **1978,** *43*, 4551–4552.
5. Srinivasan, C.; Perumal, S.; Arumugam, N. *J. Chem. Soc., Perkin Trans. 2* **1985,** 1855–1858.
6. Behrman, E. J. *Org. React.* **1988,** *35,* 421–511. (Review).
7. Behrman, E. J. *J. Org. Chem.* **1992,** *57*, 2266–2270.
8. Behrman, E. J. *Beilstein J. Org. Chem.* **2006,** *2,* 22.
9. Behrman, E. J. *Chem. Educator* **2010,** *15*, 392–393.
10. Behrman, E. J. *J. Phys. Chem.* **2011,** *115*, 7863–7864.
11. Marjanović, B.; Juranić, I.; Ćiric-Marjanović, G. *J. Phys. Chem.* **2011,** *115*, 3536–3550.
12. Marjanović, B.; Juranić, I.; Ćiric-Marjanović, G. *J. Phys. Chem.* **2011,** *115*, 7865–7868.
13. Elbs, K. *J. Prakt. Chem.* **1893,** *48,* 179–185.
14. Watson, K. G.; Serban, A. *Aust. J. Chem.* **1995,** *48*, 1503–1509.
15. Dai, K.; Wen, Q.; Liu, X.; Chen, S. *Faming Zhuanli Shenqing* CN102408401 (**2012**).

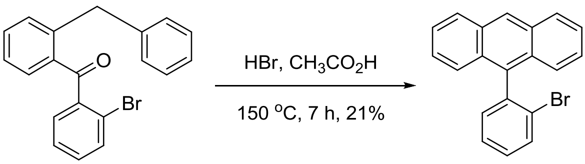
Bradsher reaction

The intramolecular Bradsher cyclization refers to the acid-catalyzed aromatic cyclodehydration of *ortho*-acyl diarylmethanes to form anthracenes. On the other hand, the intermolecular Bradsher cycloaddition often involves the Diels–Alder reaction of a pyridium with a vinyl ether or vinyl sulfide.

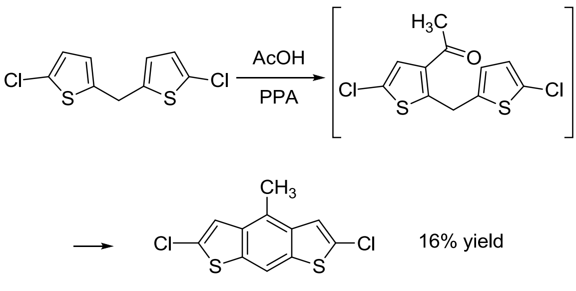




Example 1, Intramolecular Bradsher reaction[2]



Example 2, Intramolecular Bradsher reaction[5]



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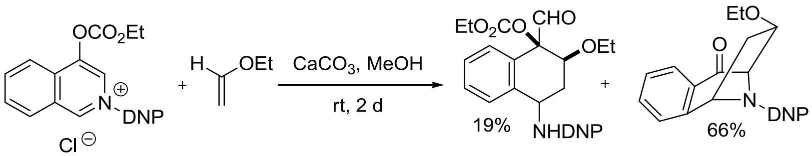
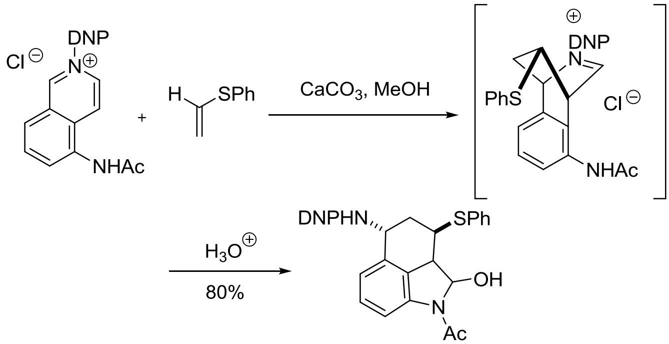
DOI 10.1007/978-3-319-03979-4_38, © Springer International Publishing Switzerland 2014

Example 3, Intermolecular Bradsher cycloaddition[8]



DNP = dinitrophenyl

Example 4, Intermolecular Bradsher cycloaddition[11]



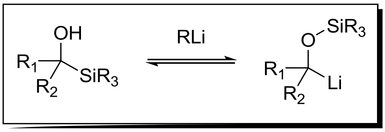
References

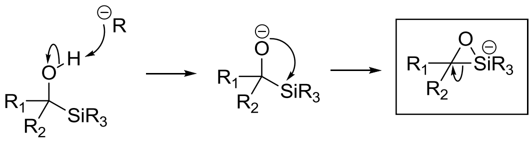
1. (a) Bradsher, C. K. *J. Am. Chem. Soc.* **1940,** *62*, 486–488. Charles K. Bradsher was born in Petersburg, VA in 1912. After his Ph.D. under Louis F. Fieser at Harvard and postdoctoral training with R. C. Fuson, he became a professor at Duke University. (b) Bradsher, C. K.; Smith, E. S. *J. Am. Chem. Soc.* **1943,** *65*, 451–452. (c) Bradsher, C. K.; Vingiello, F. A. *J. Org. Chem*. **1948,** *13*, 786–789. (d) Bradsher, C. K.; Sinclair, E. F. *J. Org. Chem*. **1957,** *22*, 79–81.
2. Vingiello, F. A.; Spangler, M. O. L.; Bondurant, J. E. *J. Org. Chem*. **1960,** *25*, 2091–2094.
3. Brice, L. K.; Katstra, R. D. *J. Am. Chem. Soc*. **1960,** *82*, 2669–2670.
4. Saraf, S. D.; Vingiello, F. A. *Synthesis* **1970,** 655.
5. Ahmed, M.; Ashby, J.; Meth-Cohn, O. *J. Chem. Soc., Chem. Commun.* **1970,** 1094–1095.
6. Ashby, J.; Ayad, M.; Meth-Cohn, O. *J. Chem. Soc., Perkin Trans. 1* **1974,** 1744–1747.
7. Bradsher, C. K. *Chem. Rev.* **1987,** *87*, 1277–1297. (Review).
8. Nicolas, T. E.; Franck, R. W. *J. Org. Chem*. **1995,** *60*, 6904–6911.
9. Magnier, E.; Langlois, Y. *Tetrahedron Lett*. **1998,** *39*, 837–840.
10. Urban, D.; Duval, E.; Langlois, Y. *Tetrahedron Lett*. **2000,** *41*, 9251–9256.
11. Soll, C. E.; Franck, R. W. *Heterocycles* **2006,** *70*, 531–540.
13. Mondal, M.; Kerrigan, N. J. *Bradsher Reaction,* In *Name Reactions for Carbocyclic Ring Formations,* Li, J. J., Ed.; Wiley: Hoboken, NJ, **2010,** pp 251–266. (Review).

Brook rearrangement

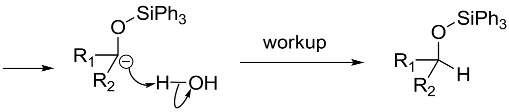
Rearrangement of α-silyl oxyanions to α-silyloxy carbanions *via* a reversible process involving a pentacoordinate silicon intermediate is known as the [1,2]-Brook rearrangement, or [1,2]-silyl migration.

[1,2]-Brook rearrangement

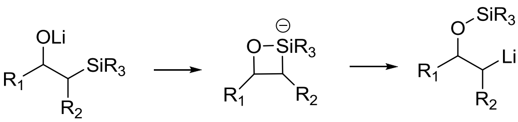




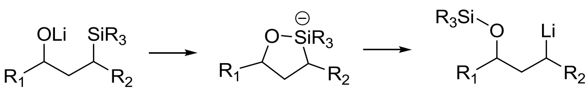
pentacoordinate silicon intermediate



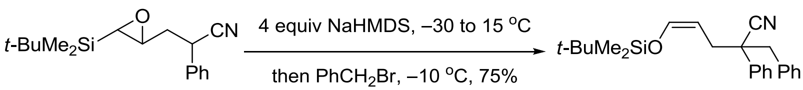
[1,3]-Brook rearrangement



[1,4]-Brook rearrangement



Example 1[6]



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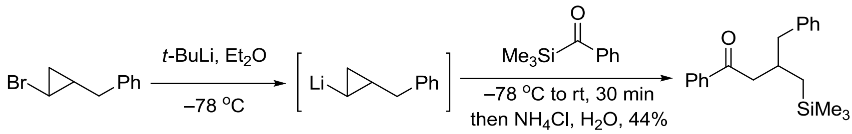
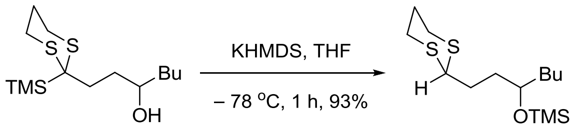
DOI 10.1007/978-3-319-03979-4_39, © Springer International Publishing Switzerland 2014

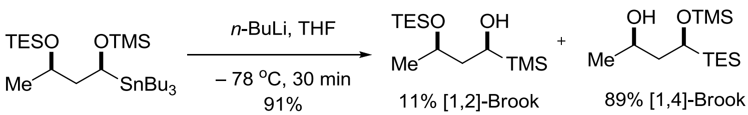
Example 2, [1,2]-Brook rearrangement followed by a retro-[1,5]-Brook rearrangement[8]



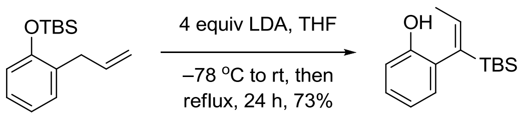
Example 3, [1,5]-Brook rearrangement[9]



Example 4, Retro-[1,4]-Brook rearrangement[10]



Example 5, Retro-Brook rearrangement[12]

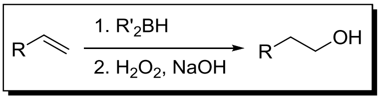


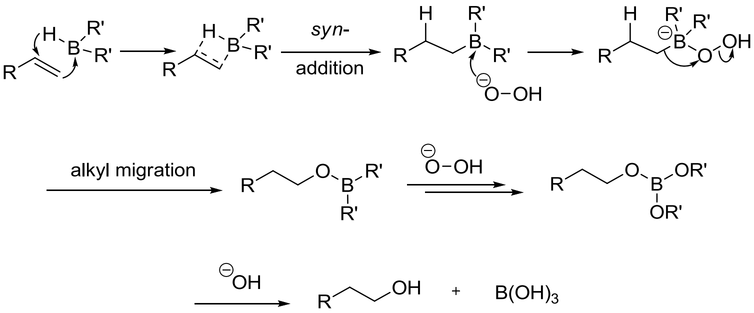
References

1. Brook, A. G. *J. Am. Chem. Soc.* **1958,** *80*, 1886–1889. Adrian G. Brook (1924–) was born in Toronto, Canada. He was a professor in Lash Miller Chemical Laboratories, University of Toronto, Canada.
2. Brook, A. G. *Acc. Chem. Res.* **1974,** *7*, 77–84. (Review).
3. Bulman Page, P. C.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990,** *19*, 147–195. (Review).
4. Fleming, I.; Ghosh, U. *J. Chem. Soc., Perkin Trans. 1* **1994,** 257–262.
5. Moser, W. H. *Tetrahedron* **2001,** *57*, 2065–2084. (Review).
6. Okugawa, S.; Takeda, K. *Org. Lett.* **2004,** *6*, 2973–2975.
7. Matsumoto, T.; Masu, H.; Yamaguchi, K.; Takeda, K. *Org. Lett.* **2004,** *6*, 4367–4369.
8. Clayden, J.; Watson, D. W.; Chambers, M. *Tetrahedron* **2005,** *61*, 3195–3203.
9. Smith, A. B., III; Xian, M.; Kim, W.-S.; Kim, D.-S. *J. Am. Chem. Soc.* **2006,** *128*, 12368–12369.
10. Mori, Y.; Futamura, Y.; Horisaki, K. *Angew. Chem. Int. Ed.* **2008,** *47*, 1091–1093.
11. Greszler, S. N.; Johnson, J. S. *Org. Lett.* **2009,** *11*, 827–830.
12. He, Y.; Hu, H.; Xie, X.; She, X. *Tetrahedron* **2013,** *69*, 559–563.

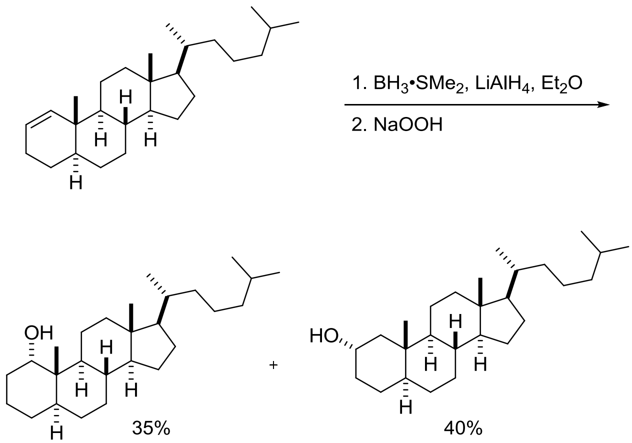
Brown hydroboration

Addition of boranes to olefins followed by alkalinic oxidation of the organoborane adducts to afford alcohols. Regiochemistry is anti-Markovnikov's rule.

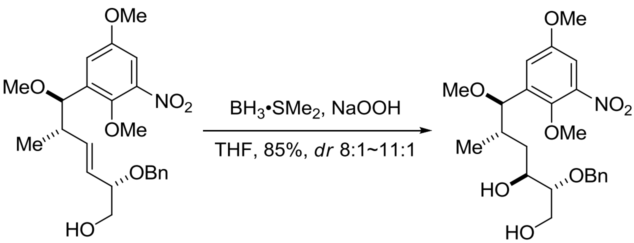




Example 1[2]



Example 2[7]



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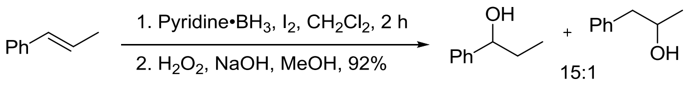
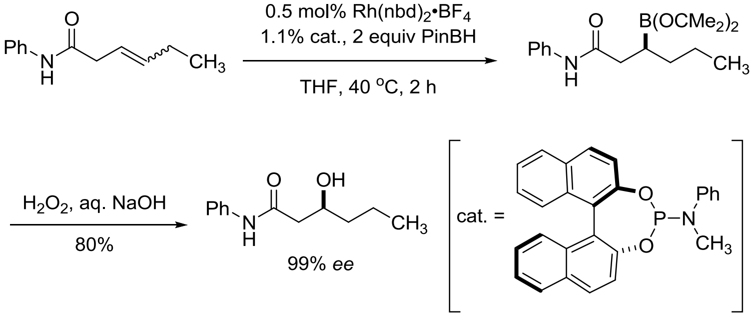
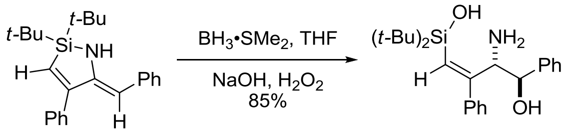
Example 3[8]



Example 4, Asymmetric hydroboration[10]



Example 5[11]

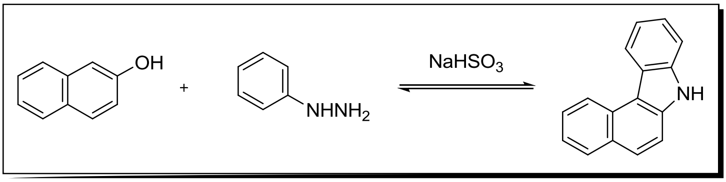


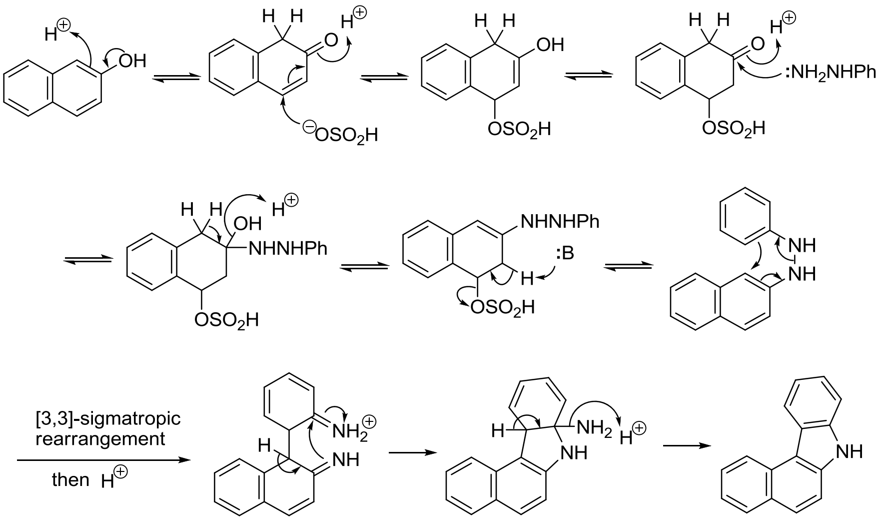
References

1. Brown, H. C.; Tierney, P. A. *J. Am. Chem. Soc.* **1958,** *80*, 1552–1558. Herbert C. Brown (USA, 1912–2004) began his academic career at Wayne State University and moved on to Purdue University where he shared the Nobel Prize in Chemistry in 1981 with Georg Wittig (Germany, 1897–1987) for their development of organic boron and phosphorous compounds.
2. Nussim, M.; Mazur, Y.; Sondheimer, F. *J. Org. Chem*. **1964,** *29*, 1120–1131.
3. Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents,* Academic Press: New York, **1972**. (Book).
4. Brewster, J. H.; Negishi, E. *Science* **1980,** *207*, 44–46. (Review).
5. Fu, G. C.; Evans, D. A.; Muci, A. R. *Advances in Catalytic Processes* **1995,** *1*, 95–121. (Review).
6. Hayashi, T. *Comprehensive Asymmetric Catalysis I–III* **1995,** *1*, 351–364. (Review).
7. Carter K. D.; Panek J. S. *Org. Lett.* **2004,** *6*, 55–57.
8. Clay, J. M.; Vedejs, E. *J. Am. Chem. Soc.* **2005,** *127*, 5766–5767.
9. Clay, J. M. *Brown hydroboration reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 183–188. (Review).
10. Smith, S. M.; Thacker, N. C.; Takacs, J. M. *J. Am. Chem. Soc.* **2008,** *130*, 3734–3735.
11. Anderson, L. L.; Woerpel, K. A. *Org. Lett.* **2009,** *11,* 425–428.
12. Yadav, J. S.; Kavita, A.; Raghavendra Rao, K. V.; Mohapatra, D. K. *Tetrahedron Lett.* **2013,** *54*, 1710–1713.

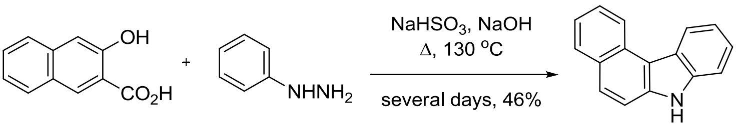
Bucherer carbazole synthesis

Carbazole formation from naphthols and aryl hydrazines promoted by sodium bisulfite. Another variant of the Fischer indole synthesis.

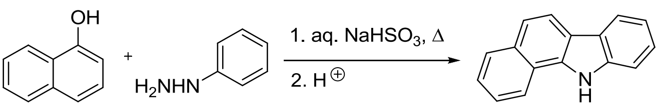




Example 1[2]



Example 2[3]



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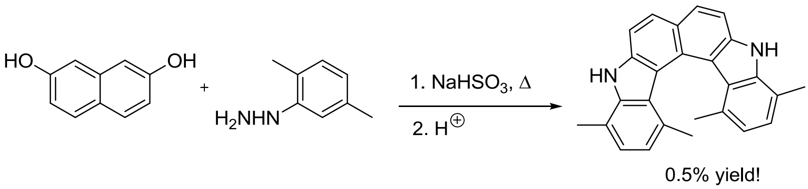
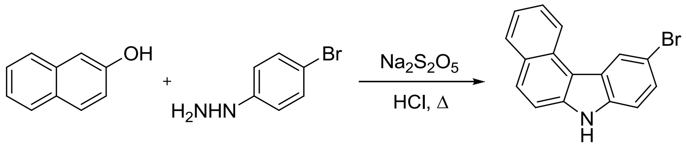
DOI 10.1007/978-3-319-03979-4_41, © Springer International Publishing Switzerland 2014

Example 3[4]



Example 4[7]

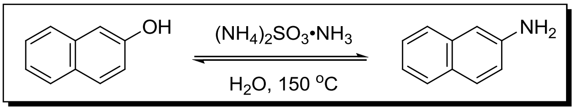


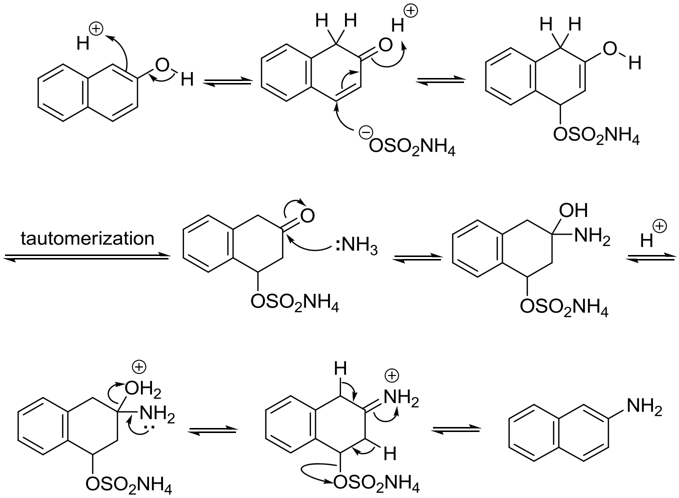
References

1. Bucherer, H. T. *J. Prakt. Chem.* **1904,** *69*, 49–91. Hans Th. Bucherer (1869–1949) was born in Ehrenfeld, Germany. He shuttled between industry and academia all through his career.
2. Bucherer, H. T.; Schmidt, M. *J. Prakt. Chem.* **1909,** *79*, 369–417.
3. Bucherer, H. T.; Sonnenburg, E. F. *J. Prakt. Chem.* **1909,** *81*, 1–48.
4. Drake, N. L. *Org. React.* **1942,** *1*, 105–128. (Review).
5. Seeboth, H. *Angew. Chem. Int. Ed.* **1967,** *6*, 307–317. (Review).
6. Robinson, B. *The Fischer Indole Synthesis*, Wiley-Interscience, New York, **1982**. (Book).
7. Hill, J. A.; Eaddy, J. F. *J. Labelled Compd. Radiopharm.* **1994,** *34*, 697–706.
8. Pischel, I.; Grimme, S.; Kotila, S.; Nieger, M.; Vögtle, F. *Tetrahedron: Asymmetry* **1996,** *7*, 109–116.
9. Moore, A. J. *Bucherer Carbazole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 110–115. (Review).

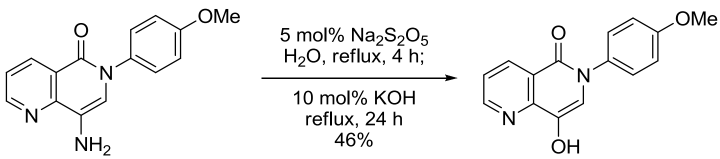
Bucherer reaction

Transformation of β-naphthols to β-naphthylamines using ammonium sulfite.

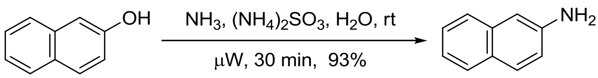




Example 1, Retro-Bucherer reaction[6]



Example 2, Although the classic Bucherer reaction requires high temperatures, it may be carried out at room temperature with the aid of microwave (150 Watts):[7]



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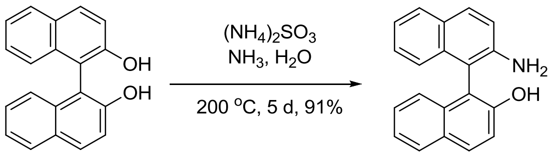
DOI 10.1007/978-3-319-03979-4_42,

Example 3[8]

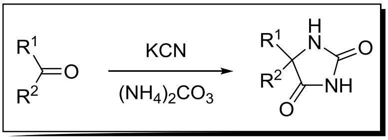


References

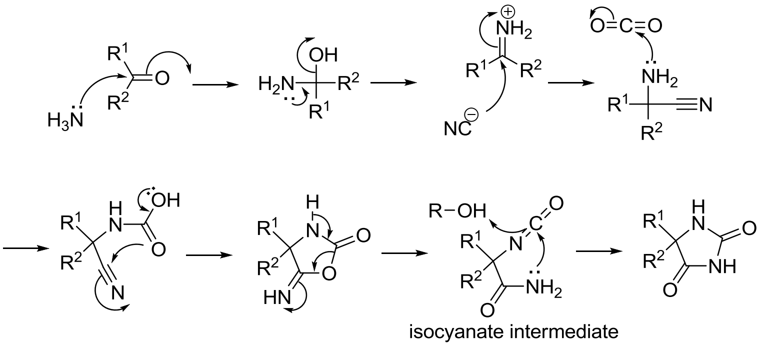
1. Bucherer, H. T. *J. Prakt. Chem.* **1904,** *69*, 49–91.
2. Drake, N. L. *Org. React.* **1942,** *1*, 105–128. (Review).
3. Gilbert, E. E. *Sulfonation and Related Reactions* Wiley: New York, **1965,** p 166. (Review).
4. Seeboth, H. *Angew. Chem. Int. Ed.* **1967,** *6*, 307–317.
5. Gruszecka, E.; Shine, H. J. *J. Labelled Compd. Radiopharm.* **1983,** *20*, 1257–1264.
6. Belica, P. S.; Manchand, P. S. *Synthesis* **1990,** 539–540.
7. Canete, A.; Melendrez, M. X.; Saitz, C.; Zanocco, A. L. *Synth. Commun.* **2001,** *31,* 2143–2148.
8. Körber, K.; Tang, W.; Hu, X.; Zhang, X. *Tetrahedron Lett*. **2002,** *43*, 7163–7165.
9. Deady, L. W.; Devine, S. M. *Tetrahedron* **2006,** *62*, 2313–2320.
10. Budzikiewicz, H. *Mini-Reviews Org. Chem*. **2006,** *3*, 93–97. (Review).
11. Yu, J.; Zhang, P.i; Wu, J.; Shang, Z. *Tetrahedron Lett.* **2013,** *54*, 3167–3170.

Bucherer–Bergs reaction

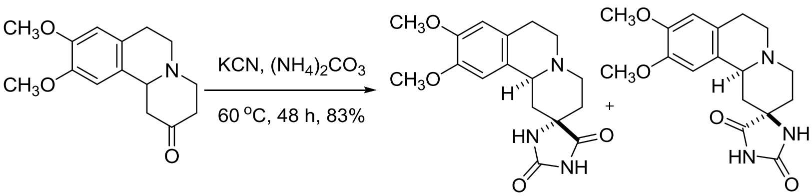
Formation of hydantoins from carbonyl compounds with potassium cyanide (KCN) and ammonium carbonate [$(NH_4)_2CO_3$] or from cyanohydrins and ammonium carbonate. It belongs to the category of multiple component reactions (MCRs).



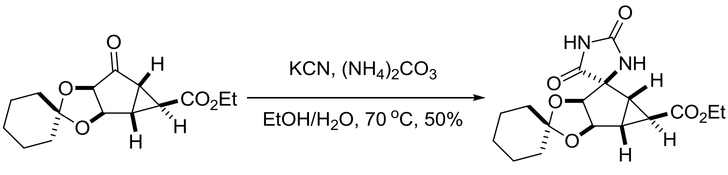
$$(NH_4)_2CO_3 = 2\ NH_3 + CO_2 + H_2O$$



Example 1[5]



Example 2[6]



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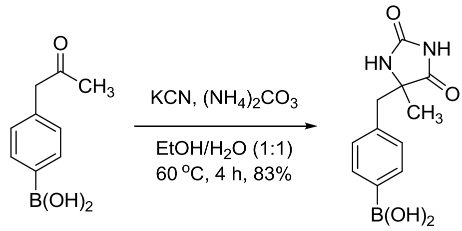
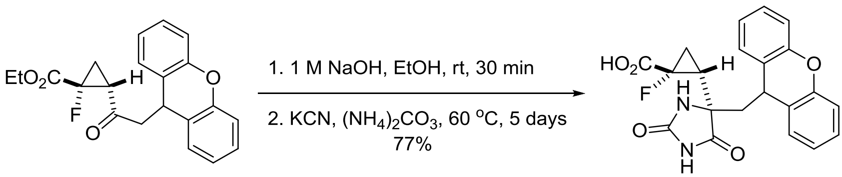
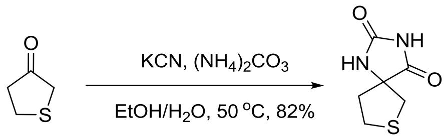
Example 3[7]



Example 4[9]



Example 5[11]

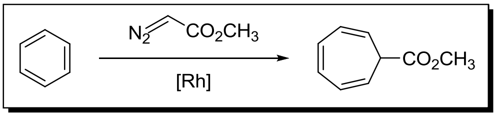


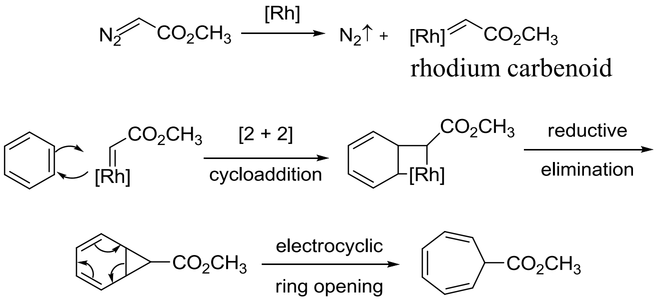
References

1. Bergs, H. Ger. Pat. 566, 094, **1929**. Hermann Bergs worked at I. G. Farben in Germany.
2. Bucherer, H. T., Steiner, W. *J. Prakt. Chem.* **1934,** *140*, 291–316. (Mechanism).
3. Ware, E. *Chem. Rev.* **1950,** *46,* 403–470. (Review).
4. Wieland, H. In *Houben–Weyl's Methoden der organischen Chemie*, Vol. XI/2, **1958,** p 371. (Review).
5. Menéndez, J. C.; Díaz, M. P.; Bellver, C.; Söllhuber, M. M. *Eur. J. Med. Chem.* **1992,** *27*, 61–66.
6. Domínguez, C.; Ezquerra, A.; Prieto, L.; Espada, M.; Pedregal, C. *Tetrahedron: Asymmetry* **1997,** *8*, 511–514.
7. Zaidlewicz, M.; Cytarska, J.; Dzielendziak, A.; Ziegler-Borowska, M. *ARKIVOC* **2004,** *iii,* 11–21.
8. Li, J. J. *Bucherer–Bergs Reaction*. In *Name Reactions in Heterocyclic Chemistry*, Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 266–274. (Review).
9. Sakagami, K.; Yasuhara, A.; Chaki, S.; Yoshikawa, R.; Kawakita, Y.; Saito, A.; Taguchi, T.; Nakazato, A. *Bioorg. Med. Chem.* **2008,** *16*, 4359–4366.
10. Wuts, P. G. M.; Ashford, S. W.; Conway, B.; Havens, J. L.; Taylor, B.; Hritzko, B.; Xiang, Y.; Zakarias, P. S. *Org. Proc. Res. Dev.* **2009,** *13*, 331–335.
11. Oba, M.; Shimabukuro, A.; Ono, M.; Doi, M.; Tanaka, M. *Tetrahedron: Asymmetry* **2013,** *24*, 464–467.

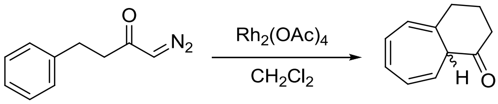
Büchner ring expansion

Reaction of a phenyl ring with a diazoacetic ester to give a cyclohepta-2,4,6-trienecarboxylic acid ester. Intramolecular Büchner reaction is more useful in synthesis. *Cf.* Pfau–Platter azulene synthesis.

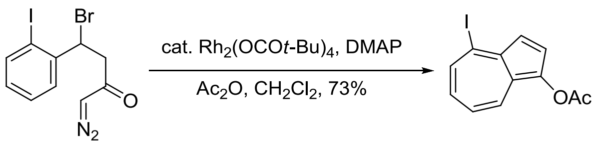




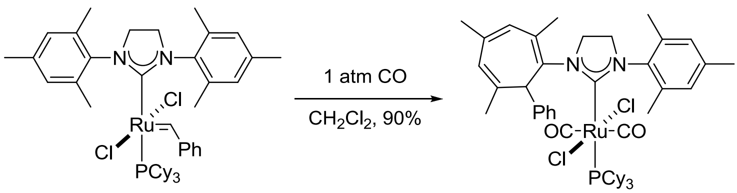
Example 1, Intramolecular Büchner reaction[7]



Example 2, Intramolecular Büchner reaction[8]



Example 3, An intramolecular Büchner reaction within the Grubbs' catalyst![9]



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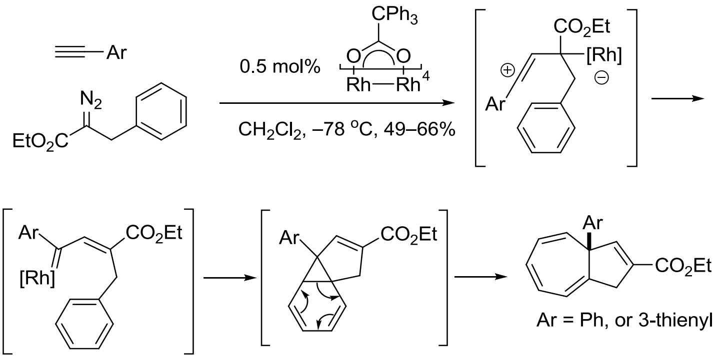
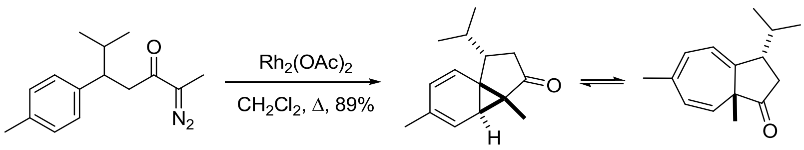
Example 4[10]



Example 5[12]

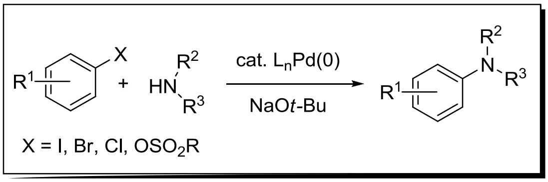


References

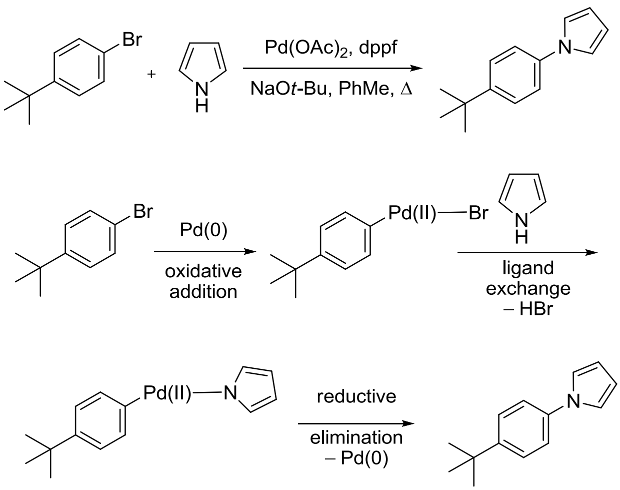
1. Büchner, E. *Ber.* **1896,** *29*, 106–109. Eduard Büchner (1860–1917) won Nobel Prize in 1907 for his work on fermentation. His name is imortalized with the Büchner funnels that we still use daily in organic laboratories.
2. von E. Doering, W.; Knox, L. H. *J. Am. Chem. Soc.* **1957,** *79*, 352–356.
3. Marchard, A. P.; Brockway, N. M. *Chem. Rev.* **1974,** *74*, 431–469. (Review).
4. Anciaux, A. J.; Demoncean, A.; Noels, A. F.; Hubert, A. J.; Warin, R.; Teyssié, P. *J. Org. Chem.* **1981,** *46*, 873–876.
5. Duddeck, H.; Ferguson, G.; Kaitner, B.; Kennedy, M.; McKervey, M. A.; Maguire, A. R. *J. Chem. Soc., Perkin Trans. 1* **1990,** 1055–1063.
6. Doyle, M. P.; Hu, W.; Timmons, D. J. *Org. Lett.* **2001,** *3*, 933–935.
7. Manitto, P.; Monti, D.; Speranza, G. *J. Org. Chem.* **1995,** *60*, 484–485.
8. Crombie, A. L; Kane, J. L., Jr.; Shea, K. M.; Danheiser, R. L. *J. Org. Chem.* **2004,** *69*, 8652–8667.
9. Galan, B. R.; Gembicky, M.; Dominiak, P. M.; Keister, J. B.; Diver, S. T. *J. Am. Chem. Soc.* **2005,** *127*, 15702–15703.
10. Panne, P.; Fox, J. M. *J. Am. Chem. Soc.* **2007,** *129*, 22–23.
11. Gomes, A. T. P. C.; Leão, R. A. C.; Alonso, C. M. A.; Neves, M. G. P. M. S.; Faustino, M. A. F.; Tomé, A. C.; Silva, A.M. S.; Pinheiro, S.; de Souza, M. C. B. V.; Ferreira, V. F.; Cavaleiro, J. A. S. *Helv. Chim. Acta* **2008,** *91*, 2270–2283.
12. Foley, D. A.; O'Leary, P.; Buckley, N. R.; Lawrence, S. E.; Maguire, A. R. *Tetrahedron* **2013,** *69*, 1778–1794.

Buchwald–Hartwig amination

The Buchwald–Hartwig amination is an exceedingly general method for generating an aromatic amine from an aryl halide or an aryl sulfonates. The key feature of this methodology is the use of catalytic palladium modulated by various electron-rich ligands. Strong bases, such as sodium *tert*-butoxide, are essential for catalyst turnover.

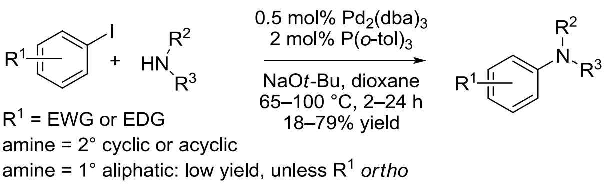


Mechanism:



The catalytic cycle is shown on the next page.

Example 1[3]



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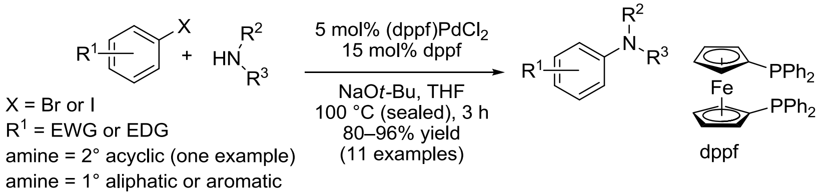
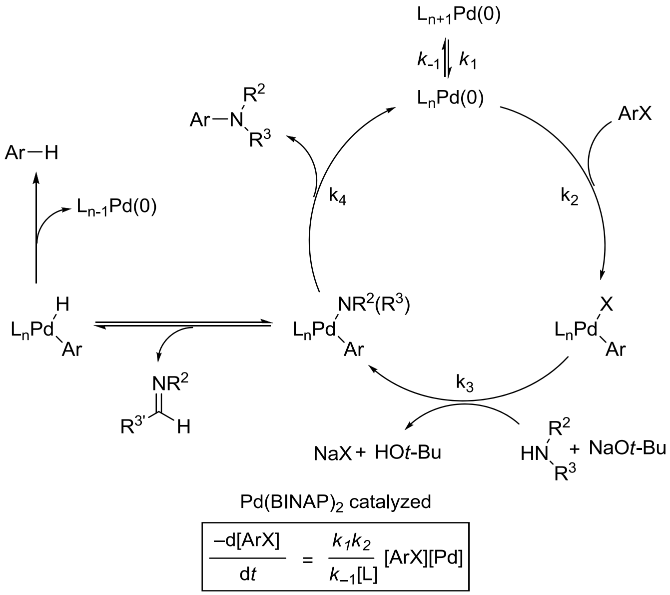
DOI 10.1007/978-3-319-03979-4_45,

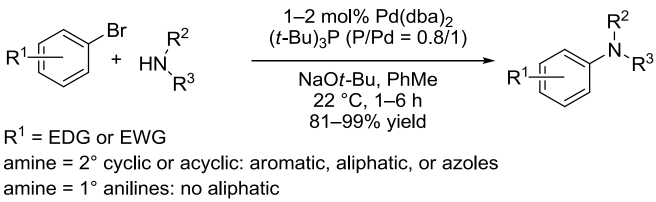
Example 2[4]



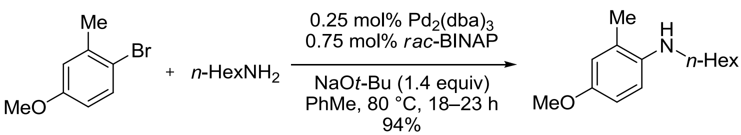
Catalytic cycle:



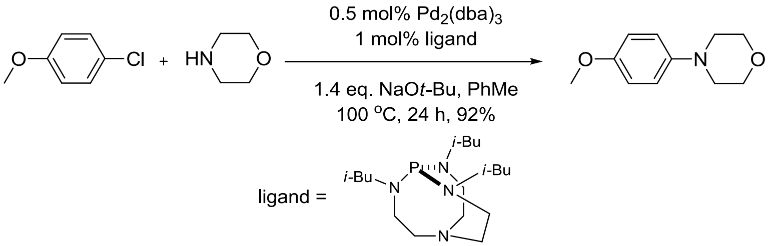
Example 3, Room temperature Buchwald–Hartwig amination[9]



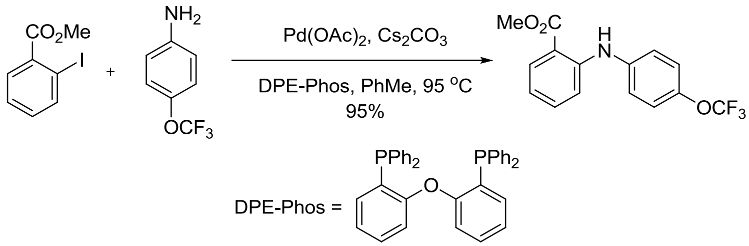
Example 4[10]



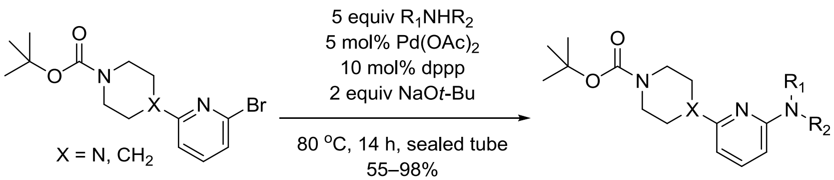
Example 5[11]



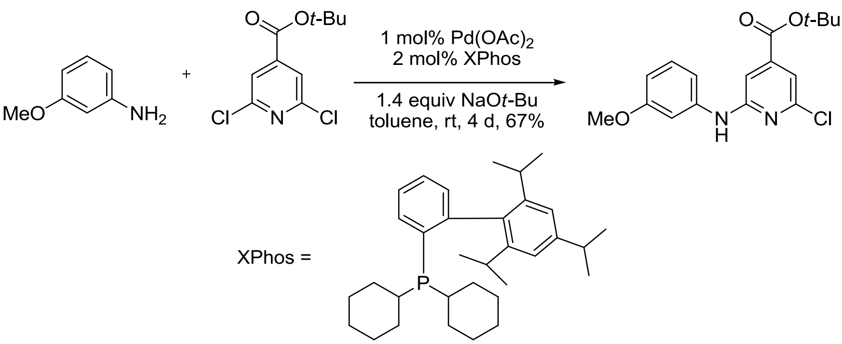
Example 6[12]



Example 7, Amination of volatile amines[14]



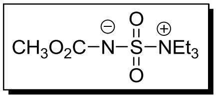
Example 8[15]



References

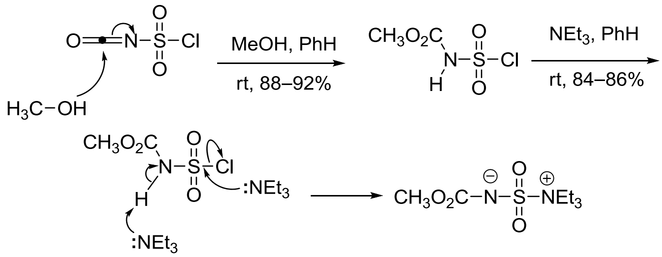
1. (a) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994,** *116*, 5969–5970. John Hartwig earned his Ph.D. at the University of California-Berkeley in 1990 under the guidance of Robert Bergman and Richard Anderson. He moved from Yale University to the University of Illinois at Urbana-Champaign in 2006 and moved from UI-UC to UC Berkeley in 2011. Hartwig and Buchwald independently discovered this chemistry. (b) Mann, G.; Hartwig, J. F. *J. Org. Chem.* **1997,** *62*, 5413–5418. (c) Mann, G.; Hartwig, J. F. *Tetrahedron Lett.* **1997,** *38*, 8005–8008.
2. (a) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994,** *116*, 7901–7902. Stephen Buchwald received his Ph.D. in 1982 under Jeremy Knowles at Harvard University. He is currently a professor at MIT. (b) Palucki, M.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996,** *118*, 10333–10334.
3. Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996,** *61*, 1133–1135.
4. Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996,** *118*, 7217–7218.
5. Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998,** *31*, 805–818. (Review).
6. Hartwig, J. F. *Acc. Chem. Res.* **1998,** *31*, 852–860. (Review).
7. Frost, C. G.; Mendonça, P. *J. Chem. Soc., Perkin Trans. 1* **1998,** 2615–2624. (Review).
8. Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999,** *576*, 125–146. (Review).
9. Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999,** *64*, 5575–5580.
10. Wolfe, J. P.; Buchwald, S. L. *Org. Syn.* **2002,** *78*, 23–30.
11. Urgaonkar, S.; Verkade, J. G. *J. Org. Chem.* **2004,** *69*, 9135–9142.
12. Csuk, R.; Barthel, A.; Raschke, C. *Tetrahedron* **2004,** *60*, 5737–5750.
13. Janey, J. M. *Buchwald–Hartwig amination,* In *Name Reactions for Functional Group Transformations*; Li, J. J., Corey, E. J. Eds.; Wiley: Hoboken, NJ, **2007,** pp 564–609. (Review).
14. Li, J. J.; Wang, Z.; Mitchell, L. H. *J. Org. Chem.* **2007,** *72,* 3606–3607.
15. Lorimer, A. V.; O'Connor, P. D.; Brimble, M. A. *Synthesis* **2008,** 2764–2770.
16. Nodwell, M.; Pereira, A.; Riffell, J. L.; Zimmerman, C.; Patrick, B. O.; Roberge, M.; Andersen, R. J. *J. Org. Chem.* **2009,** *74,* 995–1006.
17. Witt, A.; Teodorovic, P.; Linderberg, M.; Johansson, P.; Minidis, A. *Org. Process Res. Dev.* **2013,** *17*, 672–678.
18. Raders, S. M.; Moore, J. N.; et al. *Org. Chem.* **2013,** *78,* 4649–4664.

Burgess reagent

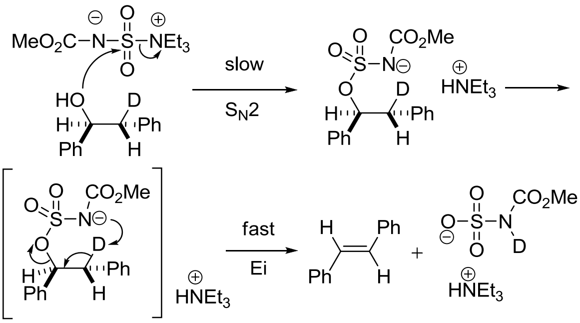


The Burgess reagent [methyl N-(triethylammoniumsulfonyl)carbamate], a neutral, white crystalline solid, is efficient at generating olefins from secondary and tertiary alcohols where the first-order thermolytic Ei (during the elimination—the two groups leave at about the same time and bond to each other concurrently) mechanism prevails.

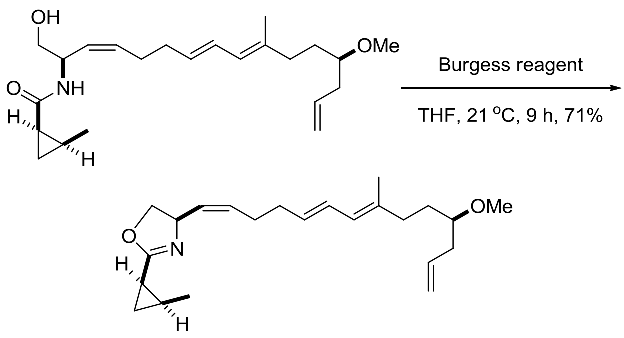
Preparation[2]



Mechanism of dehydration[5]



Example 1, On primary alcohols, the hydroxyl group does not eliminate but rather undergoes substitution[3]



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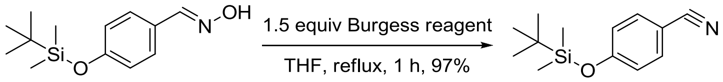
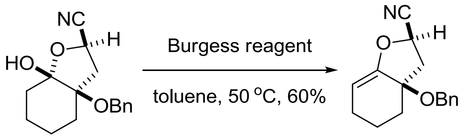
DOI 10.1007/978-3-319-03979-4_46, © Springer International Publishing Switzerland 2014

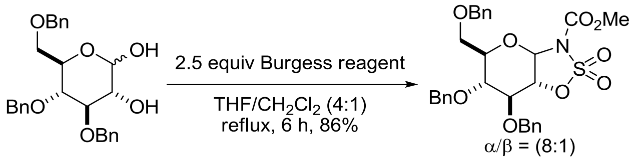
Example 2[6]



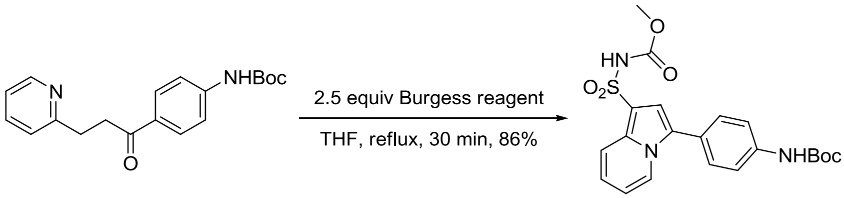
Example 3[7]



Example 4[8]



Example 5, Cyclodehydration followed by a novel carbamoylsulfonylation[10]



References

1 (a) Atkins, G. M., Jr.; Burgess, E. M. *J. Am. Chem. Soc.* **1968,** *90*, 4744–4745. (b) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A., Jr. *J. Am. Chem. Soc*. **1970,** *92*, 5224–5226. (c) Atkins, G. M., Jr.; Burgess, E. M. *J. Am. Chem. Soc*. **1972,** *94*, 6135–6141. (d) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Org. Chem*. **1973,** *38*, 26–31.

2 (a) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A.; Williams, W. M. *Org. Synth. Coll. Edn*. **1987,** *6*, 788–791. (b) Duncan, J. A.; Hendricks, R. T.; Kwong, K. S. *J. Am. Chem. Soc.* **1990,** *112*, 8433–8442.

3 Wipf, P.; Xu, W. *J. Org. Chem*. **1996,** *61*, 6556–6562.

4 Lamberth, C. *J. Prakt. Chem*. **2000,** *342*, 518–522. (Review).

5 Khapli, S.; Dey, S.; Mal, D. J. *Indian Inst. Sci*. **2001,** *81*, 461–476. (Review).

6 Miller, C. P.; Kaufman, D. H. *Synlett* **2000,** *8*, 1169–1171.

7 Keller, L.; Dumas, F.; D'Angelo, J. *Eur. J. Org. Chem.* **2003,** 2488–2497.

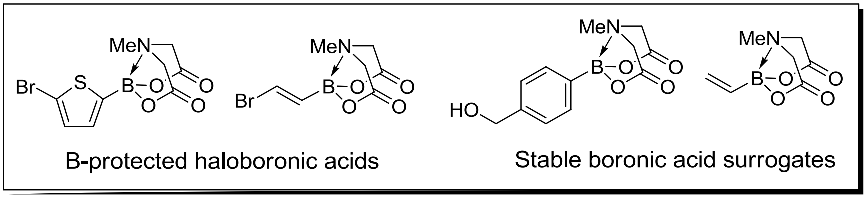
8 Nicolaou, K. C.; Snyder, S. A.; Longbottom, D. A.; Nalbandian, A. Z.; Huang, X. *Chem. Eur. J.* **2004,** *10*, 5581–5606.

9 Holsworth, D. D. *The Burgess Dehydrating Reagent*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 189–206. (Review).

10 Li, J. J.; Li, J. J.; Li, J.; et al. *Org. Lett.* **2008,** *10*, 2897–2900.

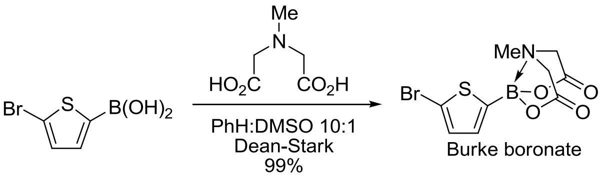
11 Werner, L.; Wernerova, M.; Hudlicky, T. et al. *Adv. Synth. Catal*. **2012,** *354*, 2706–2712.

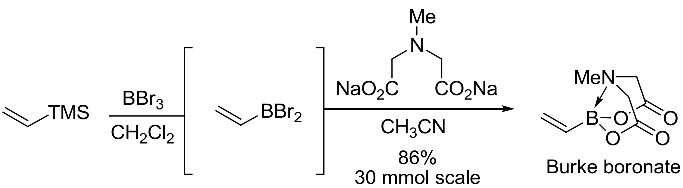
Burke boronates



Burke boronates can serve as B-protected haloboronic acids for a wide variety of applications in iterative cross-coupling.[1–6] The corresponding boronic acids can be liberated using mild aqueous bases such as NaOH or $NaHCO_3$.[1–4] Burke boronates are also compatible with many synthetic reagents, enabling the synthesis of complex boronic acids from simple B-containing starting materials.[3,6] They can also serve as stable building blocks for cross-coupling, i.e., under aqueous basic conditions, the corresponding boronic acid is released and coupled in situ.[2,3,7] Moreover, Burke boronates are highly crystalline, monomeric, free-flowing solids that are indefinitely stable to benchtop storage under air and compatible with silica gel chromatography.[1–3,6]

Preparation:[1,2,4,6,]





Alternatively, many of these building blocks are now commercially available.

Example 1[2]
A wide range of selective couplings can be performed at the halide terminus of a B-protected haloboronic acid.

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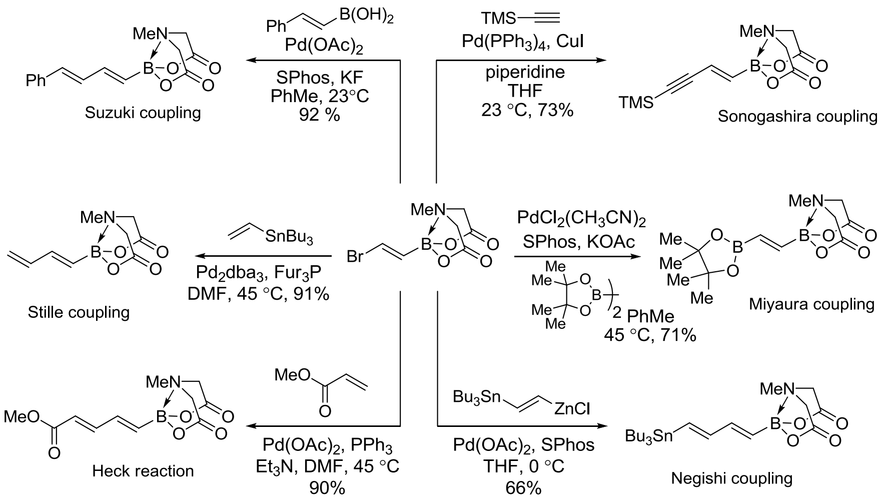
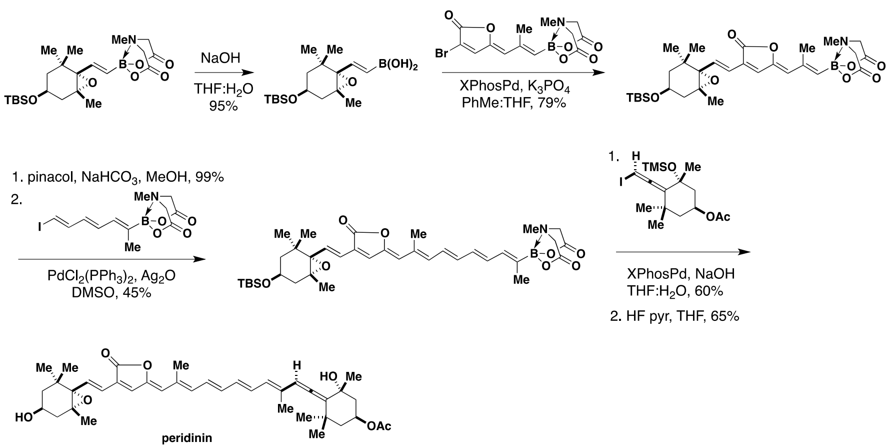
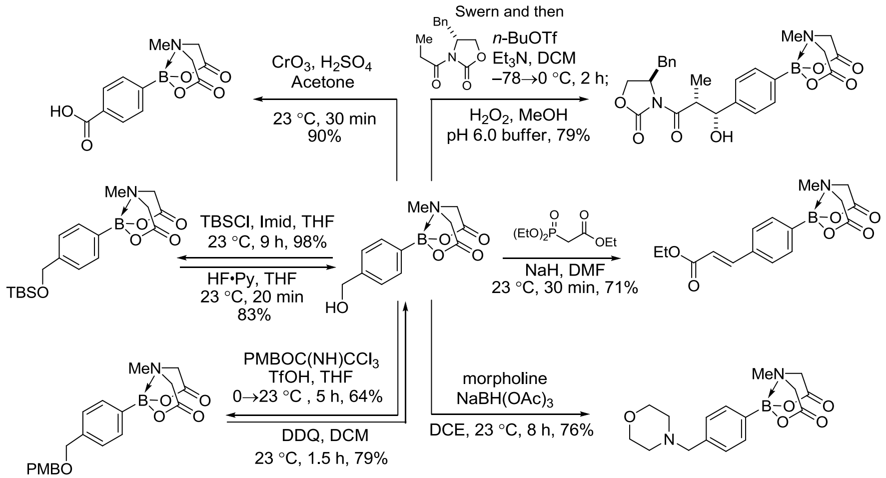
DOI 10.1007/978-3-319-03979-4_47, © Springer International Publishing Switzerland 2014



Example 2[9,10]
Small molecule natural products and their derivatives can be prepared via iterative cross-coupling with B-protected haloboronic acids.

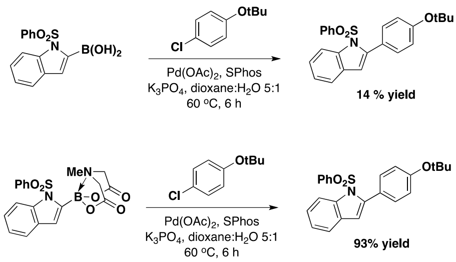


Example 3[3]
Burke boronates are stable to a wide range of synthetic reagents, including acids, non-aqueous bases, oxidants, reductants, electrophiles, and soft nucleophiles. This reagent compatibility enables multistep synthesis of complex boranes from simple boron-containing starting materials.



Example 4[7,8]

Burke boronates can be used directly in cross-couplings as shelf-stable surrogates for unstable boronic acids via slow-release cross-coupling.

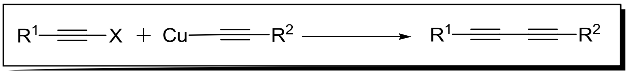


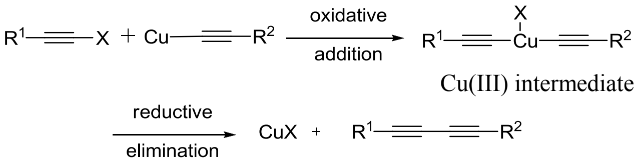
References

1. Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 6716–6717.
2. Lee, S. J., Gray, K. C., Paek, J. S., Burke, M. D. *J. Am. Chem. Soc.* **2008**, *130*, 466–468.
3. Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2008**, *130*, 14084–14085.
4. Ballmer, S. G.; Gillis, E. P.; Burke, M. D. *Org. Synth.* **2009**, 86, 344–359.
5. Gillis, E. P.; Burke, M. D. *Aldrichimica Acta* **2009**, *42*, 17–27.
6. Uno, B. E.; Gillis, E. P.; Burke, M. D. *Tetrahedron* **2009**, *65,* 3130–3138.
7. Knapp, D. M.; Gillis, E. P., Burke, M. D. *J. Am. Chem. Soc*. **2009,** *131*, 6961–6963.
8. Dick, G. R.; Woerly, E. M.; Burke, M. D. *Angew. Chem. Int. Ed.* **2012**, *51,* 2667–2672.
9. Woerly, E. M.; Cherney, A. H.; Davis, E. K.; Burke, M. D. *J. Am. Chem. Soc.* **2010**, *132*, 6941–6943.
10. Gray, K. C.; Palacios, D. S.; Dailey, I.; Endo, M. M.; Uno, B. E.; Wilcock, B. C.; Burke, M. D. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 2234–2239.

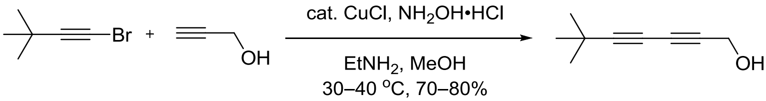
Cadiot–Chodkiewicz coupling

Bis-acetylene synthesis from alkynyl halides and alkynyl copper reagents. *Cf.* Castro–Stephens reaction.

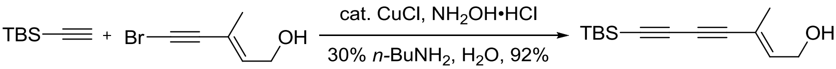




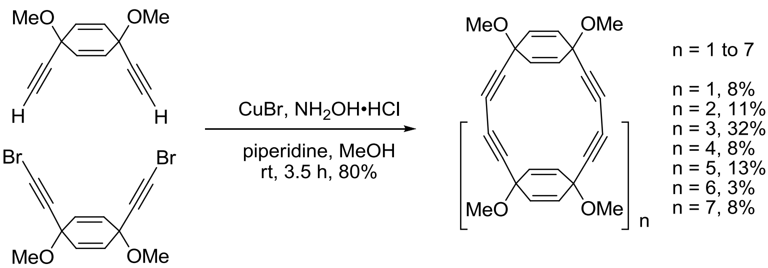
Example 1[3]



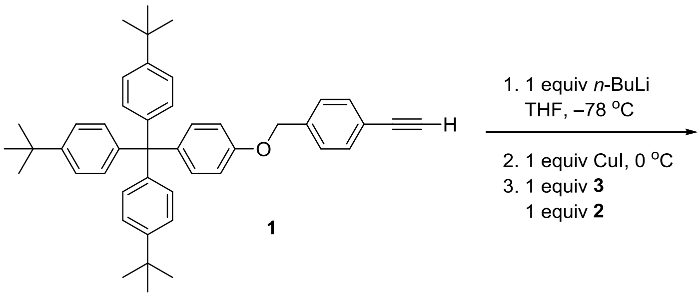
Example 2[7]



Example 3[9]



Example 4, Cadiot–Chodkiewicz active template synthesis of rotaxanes and switchable molecular shuttles with weak intercomponent interactions[10]



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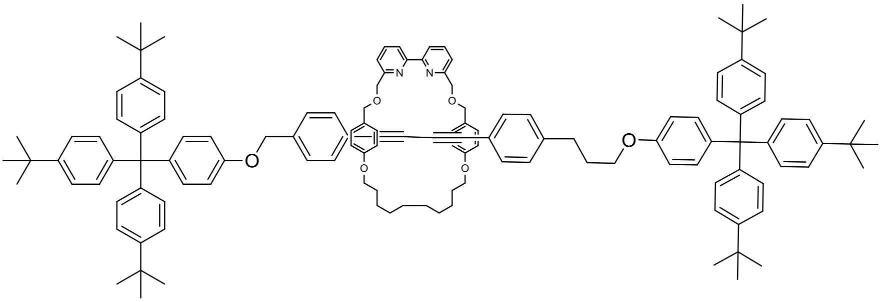
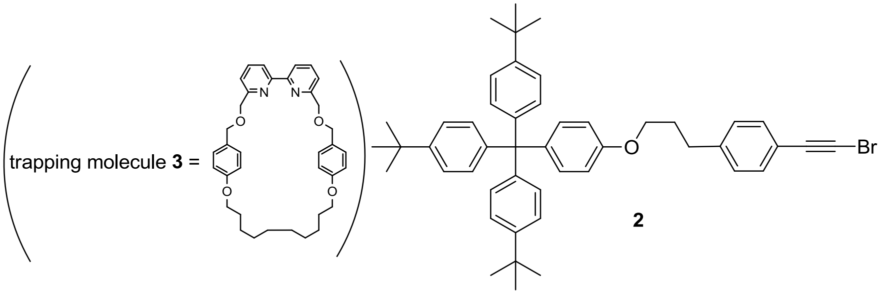




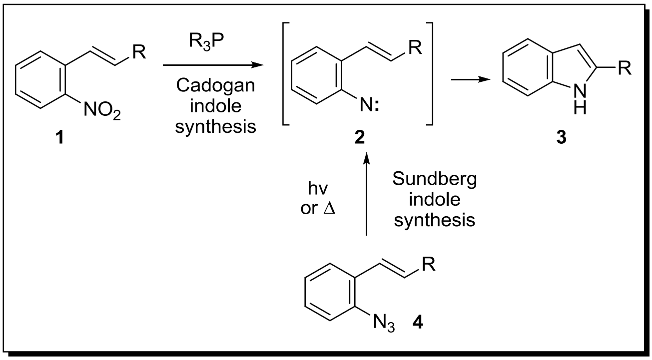
2

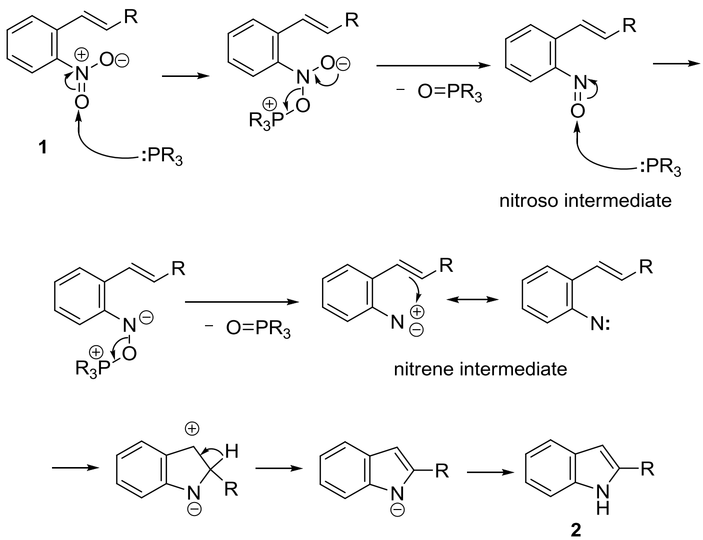
References

1. Chodkiewicz, W.; Cadiot, P. *C. R. Hebd. Seances Acad. Sci.* **1955,** *241*, 1055–1057. Both Paul Cadiot (1923–) and Wladyslav Chodkiewicz (1921–) are French chemists.
2. Cadiot, P.; Chodkiewicz, W. In *Chemistry of Acetylenes;* Viehe, H. G., ed.; Dekker: New York, **1969,** 597–647. (Review).
3. Gotteland, J.-P.; Brunel, I.; Gendre, F.; Désiré, J.; Delhon, A.; Junquéro, A.; Oms, P.; Halazy, S. *J. Med. Chem.* **1995,** *38*, 3207–3216.
4. Bartik, B.; Dembinski, R.; Bartik, T.; Arif, A. M.; Gladysz, J. A. *New J. Chem.* **1997,** *21*, 739–750.
5. Montierth, J. M.; DeMario, D. R.; Kurth, M. J.; Schore, N. E. *Tetrahedron* **1998,** *54*, 11741–11748.
6. Negishi, E.-i.; Hata, M.; Xu, C. *Org. Lett.* **2000,** *2*, 3687–3689.
7. Marino, J. P.; Nguyen, H. N. *J. Org. Chem.* **2002,** *67*, 6841–6844.
8. Utesch, N. F.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **2004,** *87*, 698–718.
9. Bandyopadhyay, A.; Varghese, B.; Sankararaman, S. *J. Org. Chem.* **2006,** *71*, 4544–4548–4548.
10. Berna, J.; Goldup, S. M.; Lee, A.-L.; Leigh, D. A.; Symes, M. D.; Teobaldi, G.; Zerbetto, F. *Angew. Chem. Int. Ed.* **2008,** *47*, 4392–4396.
11. Glen, P. E.; O’Neill, J. A. T.; Lee, A.-L. *Tetrahedron* **2013,** *69*, 57–68.

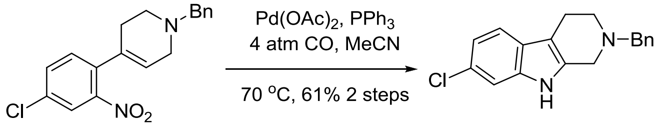
Cadogan–Sundberg indole synthesis

The Cadogan reaction refers to the deoxygenation of *o*-nitrostyrenes **1** or *o*-nitrostilbenes with trialkyl phosphite or trialkylphosphine and subsequent cyclization of the resulting intermediate nitrene **2** to form indoles **3**. The Sundberg indole synthesis refers to the synthesis of indoles **3** via either thermolysis or irradiation of *o*-azidostyrene **4** via the intermediacy of nitrene **2**.





Example 1, Söderberg's modified conditions to prepare indole[3]



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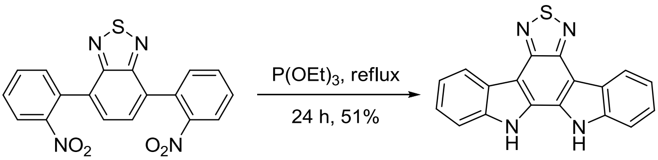
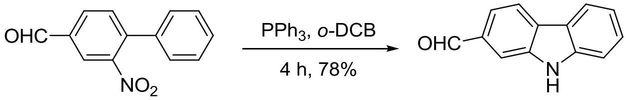
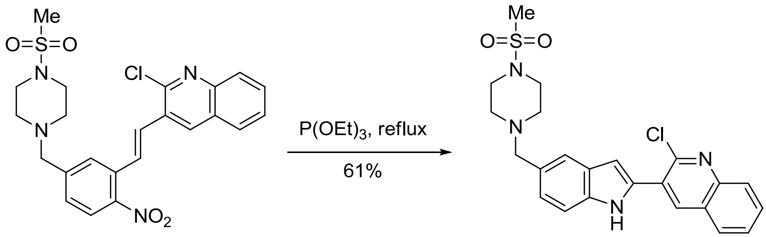
Example 2[4]



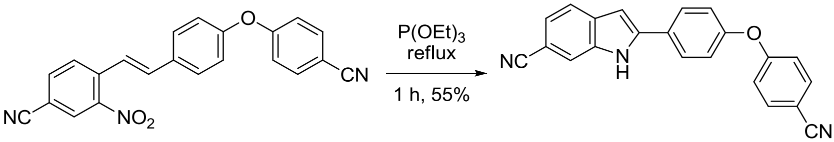
Example 3[5]



Example 4[6]



Example 5[7]

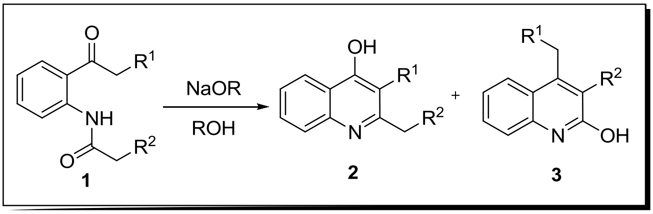


References

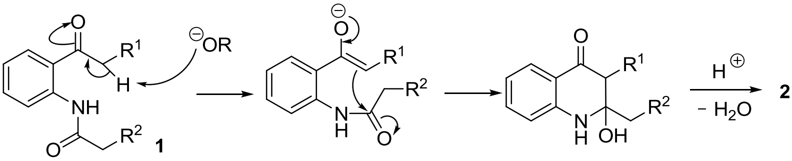
1 Cadogan, J. I. G.; Cameron-Wood, M. *Proc. Chem. Soc.* **1962,** 361.
2 Sundberg, R. J. *J. Org. Chem.* **1965,** *30*, 3604–3610.
3 Scott, T. L.; Söderberg, B. C. G. *Tetrahedron Lett.* **2002,** *43*, 1621–1624.
4 Kuethe, J. T.; Wong, A.; Qu, C.; Smitrovich, J.; Davies, I. W.; Hughes, D. L. *J. Org. Chem.* **2005,** *70,* 2555–2567.
5 Freeman, A. W.; Urvoy, M.; Criswell, M. E. *J. Org. Chem.* **2005,** *70,* 5014–5019.
6 Balaji, G.; Shim, W. L.; Parameswaran, M.; Valiyaveettil, S. *Org. Lett.* **2009,** *11,* 4450–4453.
7 Li, B.; Pai, R.; Cardinale, S. C.; Butler, M. M.; Peet, N. P.; Moir, D. T.; Bavari, S.; Bowlin, T. L. *J. Med. Chem.* **2010,** *53,* 2264–2276.

Camps quinoline synthesis

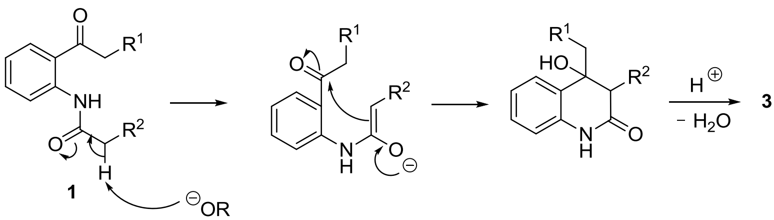
Base-catalyzed intramolecular condensation of a 2-acetamido acetophenone (**1**) to a 2-(and possibly 3)-substituted-quinolin-4-ol (**2**), a 4-(and possibly 3)-substituted-quinolin-2-ol (**3**), or a mixture.



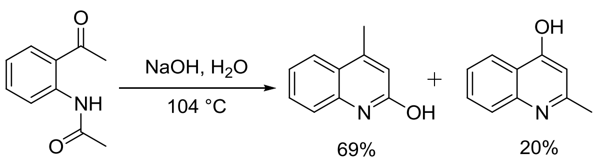
Pathway A:



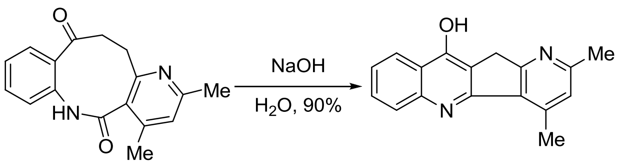
Pathway B:



Example 1[1]



Example 2[6]



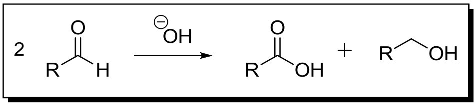
J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_50, © Springer International Publishing Switzerland 2014

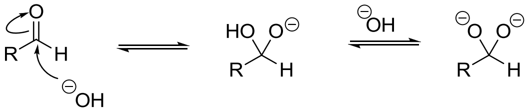
References

1. (a) Camps, R. *Chem. Ber.* **1899,** *32*, 3228–3234. Rudolf Camps worked under Professor Engler from 1899 to 1902 at the Technische Hochschule in Karlsruhe, Germany. (b) Camps, R. *Arch. Pharm.* **1899,** *237*, 659–691.
2. Elderfield, R. C.; Todd, W. H.; Gerber, S. *Heterocyclic Compounds* Vol. 6, Elderfield, R. C., ed.; Wiley and Sons, New York, **1957,** 576. (Review).
3. Clemence, F.; LeMartret, O.; Collard, J. *J. Heterocycl. Chem.* **1984,** *21*, 1345–1353.
4. Hino, K.; Kawashima, K.; Oka, M.; Nagai, Y.; Uno, H.; Matsumoto, J. *Chem. Pharm. Bull.* **1989,** *37*, 110–115.
5. Witkop, B.; Patrick, J. B.; Rosenblum, M. *J. Am. Chem. Soc.* **1951,** *73*, 2641–2647.
6. Barret, R.; Ortillon, S.; Mulamba, M.; Laronze, J. Y.; Trentesaux, C.; Lévy, J. *J. Heterocycl. Chem.* **2000,** *37*, 241–244.
7. Pflum, D. A. *Camps Quinolinol Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 386–389. (Review).

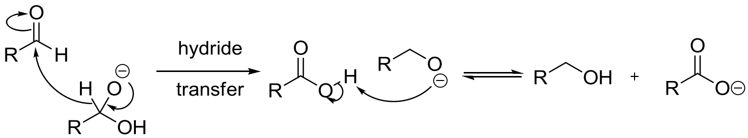
Cannizzaro reaction

Redox reaction between aromatic aldehydes, formaldehyde or other aliphatic aldehydes without α-hydrogen. Base is used to afford the corresponding alcohols and carboxylic acids.



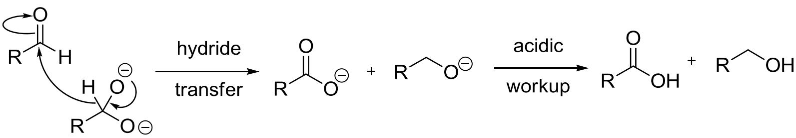


Pathway A:

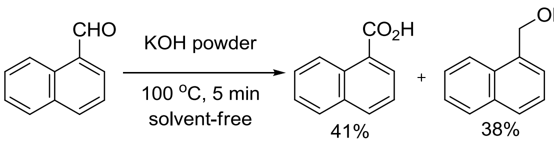


Final deprotonation of the carboxylic acid drives the reaction forward.

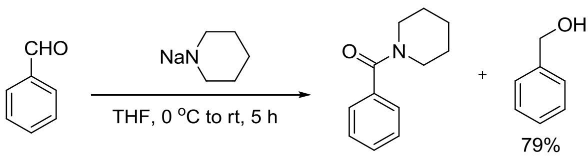
Pathway B:



Example 1[4]



Example 2[6]



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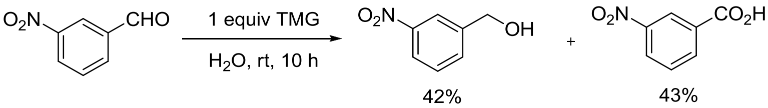
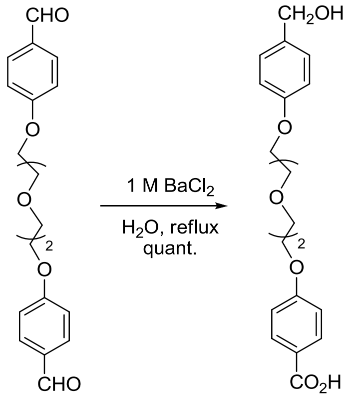
DOI 10.1007/978-3-319-03979-4_51, © Springer International Publishing Switzerland 2014

Example 3[8]



TMG = 1,1,3,3-tetramethylguanidine

Example 4, Desymmetrization by intramolecular Cannizzaro reaction[9]

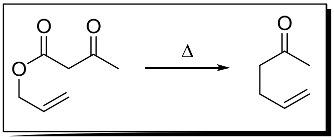


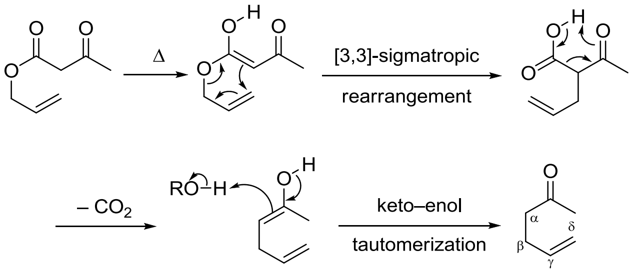
References

1. Cannizzaro, S. *Ann.* **1853,** *88*, 129–130. Stanislao Cannizzaro (1826–1910) was born in Palermo, Sicily, Italy. In 1847, he had to escape to Paris for participating in the Sicilian Rebellion. Upon his return to Italy, he discovered benzyl alcohol synthesis by the action of potassium hydroxide on benzaldehyde. Political interests brought Cannizzaro to the Italian Senate and he later became its vice president.
2. Geissman, T. A. *Org. React.* **1944,** *1*, 94–113. (Review).
3. Russell, A. E.; Miller, S. P.; Morken, J. P. *J. Org. Chem.* **2000,** *65*, 8381–8383.
4. Yoshizawa, K.; Toyota, S.; Toda, F. *Tetrahedron Lett.* **2001,** *42*, 7983–7985.
5. Reddy, B. V. S.; Srinvas, R.; Yadav, J. S.; Ramalingam, T. *Synth. Commun.* **2002,** *32*, 219–223.
6. Ishihara, K.; Yano, T. *Org. Lett.* **2004,** *6*, 1983–1986.
7. Curini, M.; Epifano, F.; Genovese, S.; Marcotullio, M. C.; Rosati, O. *Org. Lett.* **2005,** *7*, 1331–1333.
8. Basavaiah, D.; Sharada, D. S.; Veerendhar, A. *Tetrahedron Lett.* **2006,** *47*, 5771–5774.
9. Ruiz-Sanchez, A. J.; Vida, Y.; Suau, R.; Perez-Inestrosa, E. *Tetrahedron* **2008,** *64*, 11661–11665.
10. Yamabe, S.; Yamazaki, S. *Org. Biomol. Chem.* **2009,** *7*, 951–961.
11. Shen, M.-G.; Shang, S.-B.; Song, Z.-Q.; Wang, D.; Rao, X.-P.; Gao, H.; Liu, H. *J. Chem. Res.* **2013,** *37*, 51–52.

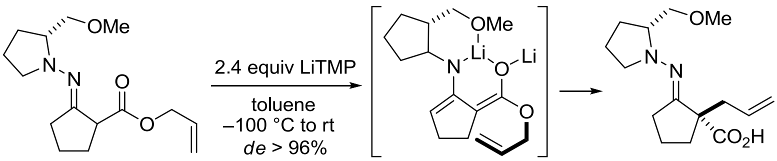
Carroll rearrangement

Thermal rearrangement of β-ketoesters followed by decarboxylation to yield γ-unsaturated ketones *via* anion-assisted Claisen rearrangement. It is a variant of the Claisen rearrangement.

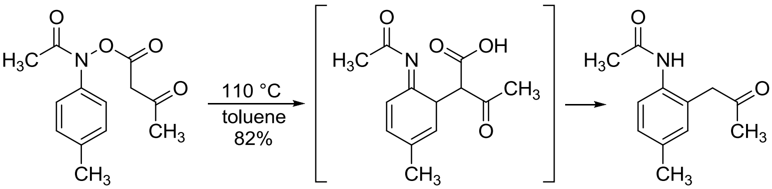




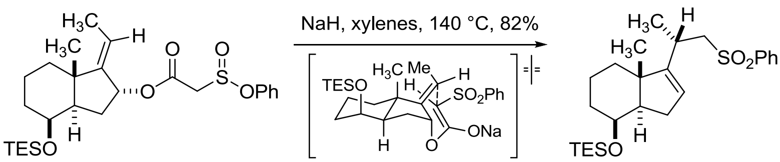
Example 1, Asymmetric Carroll rearrangement[4,5]



Example 2, Hetero-Carroll rearrangement[6]



Example 3[7]



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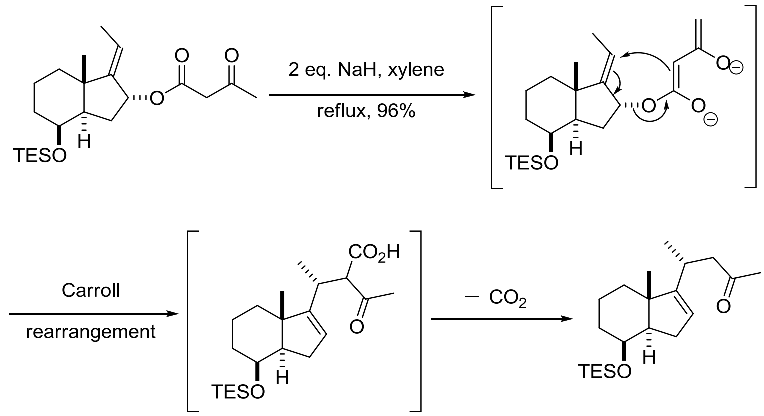
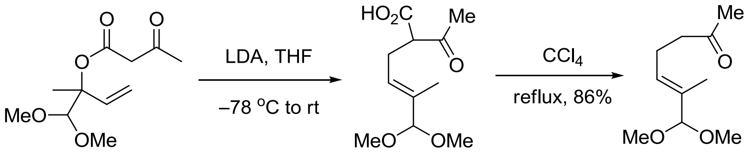
DOI 10.1007/978-3-319-03979-4_52,

Example 4, Similar to Example 3[7]



Example 5[8]

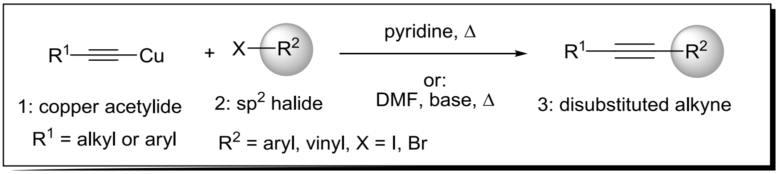


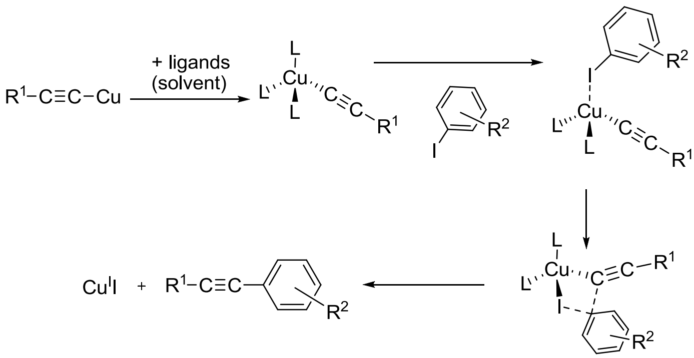
References

1. (a) Carroll, M. F. *J. Chem. Soc.* **1940,** 704–706. Michael F. Carroll worked at A. Boake, Roberts and Co. Ltd., in London, UK. (b) Carroll, M. F. *J. Chem. Soc.* **1941,** 507–511.
2. Ziegler, F. E. *Chem. Rev.* **1988,** *88*, 1423–1452. (Review).
3. Echavarren, A. M.; Mendosa, J.; Prados, P.; Zapata, A. *Tetrahedron Lett.* **1991,** *32*, 6421–6424.
4. Enders, D.; Knopp, M.; Runsink, J.; Raabe, G. *Angew. Chem. Int. Ed.* **1995,** *34*, 2278–2280.
5. Enders, D.; Knopp, M. *Tetrahedron* **1996,** *52*, 5805–5818.
6. Coates, R. M.; Said, I. M. *J. Am. Chem. Soc.* **1977,** *99*, 2355–2357.
7. Hatcher, M. A.; Posner, G. H. *Tetrahedron Lett*. **2002,** *43*, 5009–5012.
8. Jung, M. E.; Duclos, B. A. *Tetrahedron Lett*. **2004,** *45*, 107–109.
9. Defosseux, M.; Blanchard, N.; Meyer, C.; Cossy, J. *J. Org. Chem.* **2004,** *69*, 4626–4647.
10. Williams, D. R.; Nag, P. P. *Claisen and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 33–87. (Review).
11. Naruse, Y.; Todo, Y.; Shiomi, M. *Tetrahedron Lett*. **2011,** *52*, 4456–4460.
12. Abe, H.; Sato, A.; Kobayashi, T.; Ito, H. *Org. Lett*. **2013,** *15*, 1298–1301.

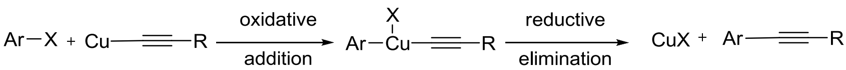
Castro–Stephens coupling

Aryl–acetylene synthesis, *Cf.* Cadiot–Chodkiewicz coupling and Sonogashira coupling. The Castro–Stephens coupling uses stoichiometric copper, whereas the Sonogashira variant uses catalytic palladium and copper.



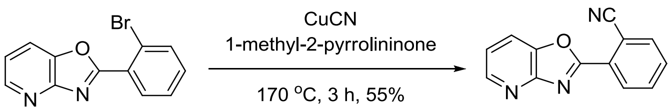


An alternative mechanism similar to that of the Cadiot–Chodkiewicz coupling:

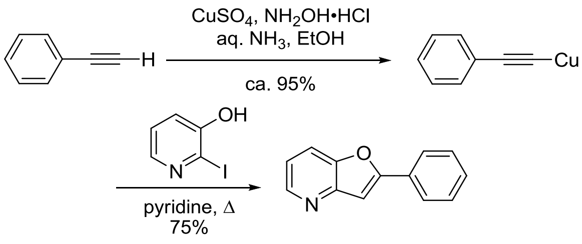


Cu(III) intermediate

Example 1, A variant, also known as the Rosenmund–von Braun synthesis of aryl nitriles[2]

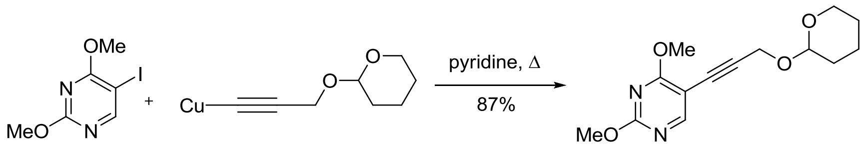


Example 2[4]

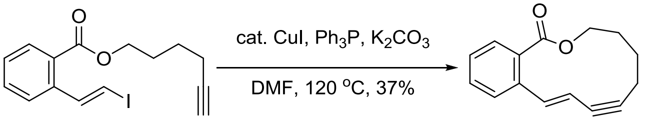


J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_53,

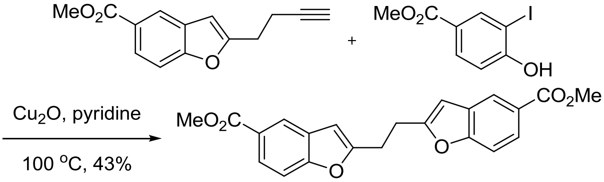
Example 3[5]



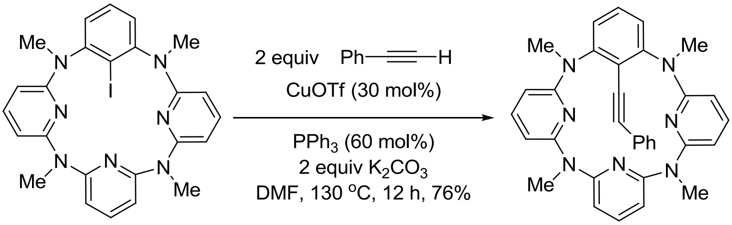
Example 4[8]



Example 5, *In situ* Castro–Stephens reaction[10]



Example 6[13]



References

1. (a) Castro, C. E.; Stephens, R. D. *J. Org. Chem.* **1963,** *28*, 2163. Castro and Stephens worked in the Department of Nematology and Chemistry at University of California, Riverside. (b) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963,** *28*, 3313–3315.
2. Clark, R. L.; Pessolano, A. A.; Witzel, B.; Lanza, T.; Shen, T. Y.; Van Arman, C. G.; Risley, E. A. *J. Med. Chem.* **1978,** *21*, 1158–1162.
3. Staab, H. A.; Neunhoeffer, K. *Synthesis* **1974,** 424.
4. Owsley, D.; Castro, C. *Org. Synth.* **1988,** *52*, 128–131.
5. Kundu, N. G.; Chaudhuri, L. N. *J. Chem. Soc., Perkin Trans 1* **1991,** 1677–1682.
6. Kabbara, J.; Hoffmann, C.; Schinzer, D. *Synthesis* **1995,** 299–302.
7. White, J. D.; Carter, R. G.; Sundermann, K. F.; Wartmann, M. *J. Am. Chem. Soc.* **2001,** *123*, 5407–5413.
8. Coleman, R. S.; Garg, R. *Org. Lett.* **2001,** *3*, 3487–3490.
9. Rawat, D. S.; Zaleski, J. M. *Synth. Commun.* **2002,** *32*, 1489–1494.
10. Bakunova, A.; Bakunov, S.; Wenzler, T.; Barszcz, T.; Werbovetz, K.; Brun, R.; Hall, J.; Tidwell, R. *J. Med. Chem.* **2007,** *50*, 5807–5823.
11. Gray, D. L. *Castro–Stephens coupling*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 212–235. (Review).
12. Wang, Z.-L.; Zhao, L.; Wang, M.-X. *Org. Lett.* **2012,** *14*, 1472–1475.

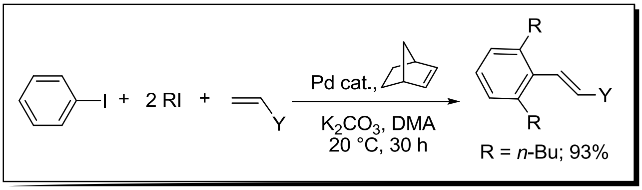
C−H activation

The C−H activation reaction is a reaction that cleaves a carbon–hydrogen bond. Here the carbon–hydrogen bond is mostly referred to unactivated carbon–hydrogen bonds.

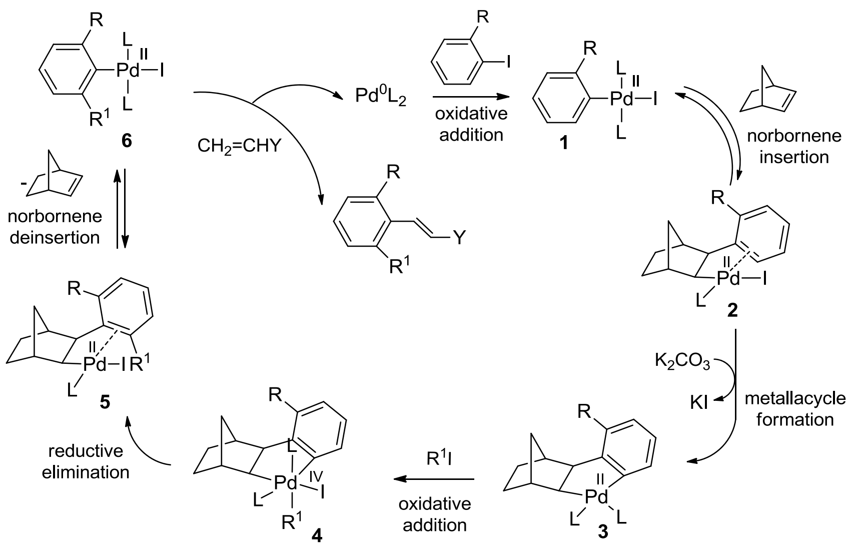
Catellani reaction

Selective *ortho*-alkylation and -arylation of aryl iodides can be achieved by the cooperative catalytic action of palladium and norbornene.[1] The first reported case was the *ortho*-dialkylation of aryl iodides, followed by Heck reaction.[2] Here an aryl iodide with free *o*-positions reacts with an aliphatic iodide and a terminal olefin in the presence of palladium/norbornene as catalyst and a base, to give a 2,6-substituted vinylarene. Analogously, an aryl iodide with one substituted *o*-position leads to a vinylarene containing two different *ortho* groups.[3]

Example 1, A three-component reaction allowing the construction of three adjacent C–C bonds through C–I and C–H activation.[2]



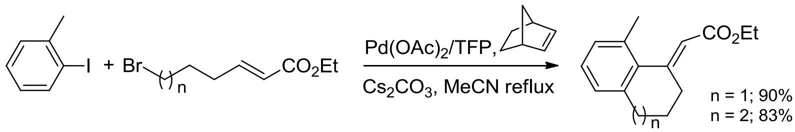
Mechanism for the reaction of an *o*-substitued aryl iodide: Pd(0), Pd(II) and Pd(IV) intermediates and catalytic role of palladium and norbornene.[1–3]



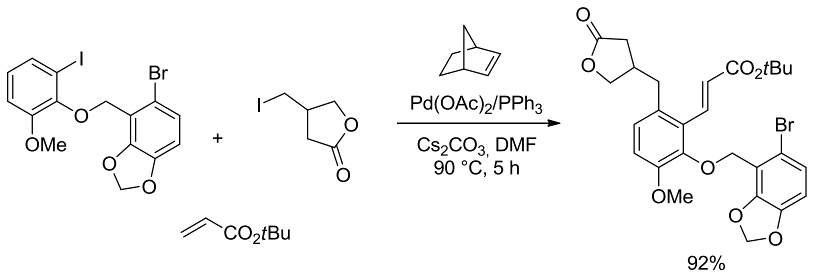
J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_54, © Springer International Publishing Switzerland 2014

The mechanism involves initial oxidative addition of an *o*-substituted aryl iodide to Pd(0) followed by a stereoselective norbornene insertion leading to the *cis*,*exo* complex **2**. β-Hydrogen elimination is prevented by geometric constraints, and a five-membered palladacycle (**3**) readily forms through intramolecular C–H activation. Oxidative addition of an alkyl iodide to **3** affords a Pd(IV) intermediate (**4**) which undergoes reductive elimination by selective migration of the alkyl moiety onto the aromatic ring to form **5**. Norbornene deinsertion occurs spontaneously at this point, likely due to steric hindrance, giving 2,6-disubstituted phenylpalladium(II) species (**6**) which finally react with the terminal olefin to liberate the organic product and Pd(0). Alternatively the sequence can be terminated by other well-known reactions of the aryl-Pd bond such as the Suzuki or Sonogashira couplings, hydrogenolysis, amination, or cyanation. The described methodology can also be extended to ring-forming reactions.[1e] Thus, the reaction is very versatile and offers countless possibilities for building up many types of functionalized aromatic compounds.

Example 2, The synthesis of fused aromatic compounds through final intramolecular Heck reaction was first reported by the Lautens group.[4,1e]

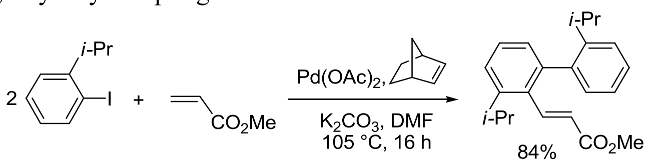


Example 3, The high tolerance to functional groups enabled a key step to the synthesis of a precursor of (+)-linoxepin by Lautens.[5]

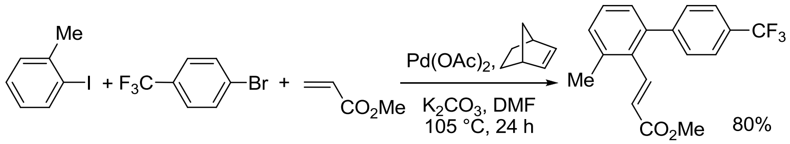


ortho-Arylation of an aryl iodide leading to the construction of a biaryl moiety is also possible, provided that the starting aryl iodide bears an *ortho* substituent. The *o*-substituent in palladacycles of type **3** is essential for selectively directing the attack of an aryl halide onto the aromatic site (*ortho* effect).[1,6]

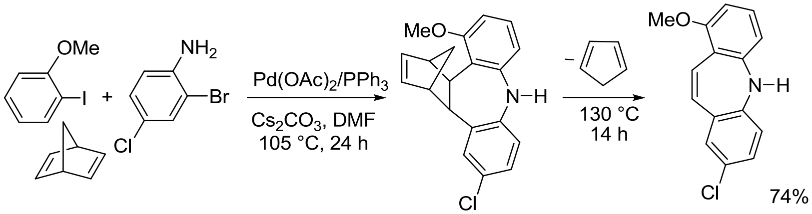
Example 4, Aryl-aryl coupling combined with Heck reaction.[7]



Example 5. The non symmetrical coupling of an aryl iodide bearing an *o*-electron-donating group, an aryl bromide containing an electron-withdrawing substituent, and a terminal olefin illustrates the importance of correctly tuning the electronic properties of the two aryl halides for selectivity control.[8]



Example 6 shows that internal chelation to Pd(IV)[9] can cancel the *ortho* effect.[10]

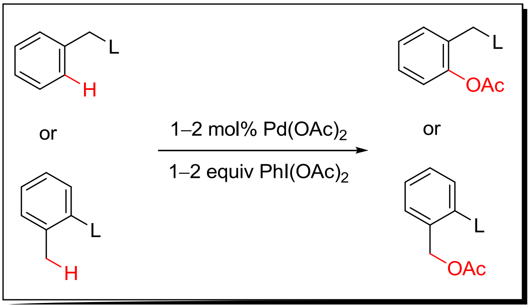


References

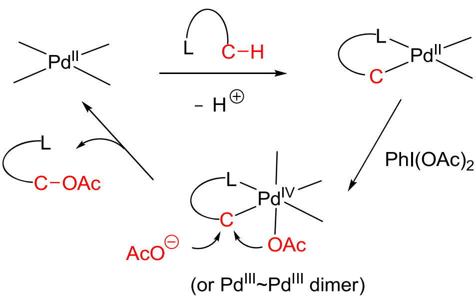
1. (a) Tsuji, J. Palladium Reagents and Catalysts – New Perspective for the 21st Century, 2004, John Wiley & Sons, pp. 409–416. (b) Catellani, M. *Synlett* **2003**, 298–313. (c) Catellani, M. *Top. Organomet. Chem.* **2005**, *14*, 21–53. (d) Catellani M.; Motti E.; Della Ca' N. *Acc. Chem. Res.* **2008**, *41*, 1512–1522. (e) Martins, A.; Mariampillai, B.; Lautens, M. *Top Curr Chem* **2010**, *292*, 1–33. (f) Chiusoli, G. P.; Catellani, M.; Costa, M.; Motti, E.; Della Ca', N.; Maestri, G. *Coord. Chem. Rev.* **2010**, *254*, 456–469.
2. (a) Catellani, M.; Frignani, F.; Rangoni, A. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 119–122. (b) Catellani, M.; Fagnola, M. C. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2421–2422.
3. Catellani, M;. Cugini, F. *Tetrahedron*, **1999**, *55*, 6595–6602.
4. (a) Lautens, M.; Piguel, S.; Dahlmann, M. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 1045–1046. (b) Lautens, M.; Paquin, J.-F.; Piguel, S. *J. Org. Chem.* **2001**, *66*, 8127–8134. (c) Lautens, M.; Paquin, J.-F.; Piguel, S. *J. Org. Chem.* **2002**, *67*, 3972–3974.
5. Weinstabl, H.; Suhartono, M.; Qureshi, Z.; Lautens, M. *Angew. Chem. Int. Ed.* **2013**, *125*, 5413–5416.
6. Maestri, G.; Motti, E.; Della Ca', N.; Malacria, M.; Derat, E.; Catellani, M. *J. Am. Chem. Soc.* **2011**, *133*, 8574–8585.
7. Motti, E.; Ippomei, G.; Deledda, S.; Catellani, M. *Synthesis* **2003**, 2671–2678.
8. Faccini, F.; Motti, E.; Catellani, M. *J. Am. Chem. Soc.* **2004**, *126*, 78–79.
9. Vicente, J.; Arcas, A.; Juliá-Hernández, F.; Bautista, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 6896–6899.
10. Della Ca', N.; Maestri, G.; Malacria, M.; Derat, E.; Catellani, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 12257–12261.

Sanford reaction

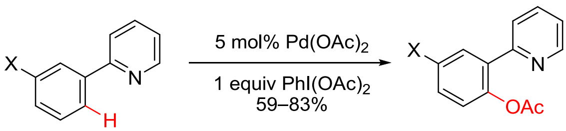
C–H acetoxylations using directing groups L, such as pyridine and pyrimidine.[1,6]



Catalytic Cycle for Ligand-Directed C–H Acetoxylation:[2]

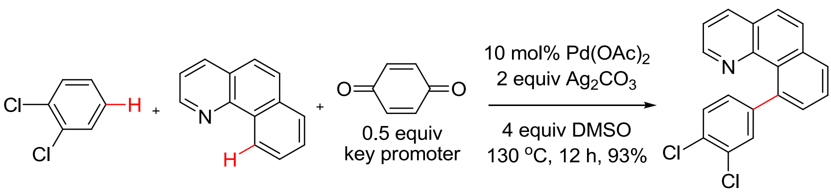


Example 1.[3]



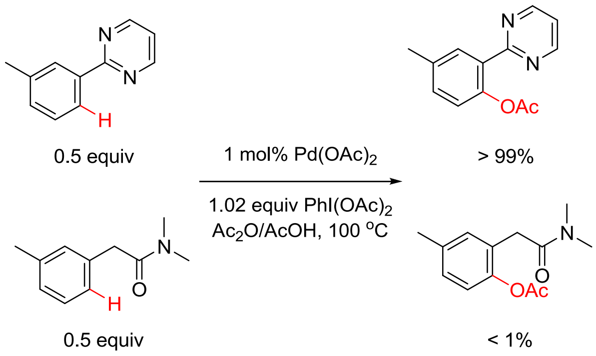
X = OMe, OMOM, Me, Br, F, CF_3, Ac, oxime, NO_2,
regioselectivity: 6:1 to > 20:1

Example 2.[5]

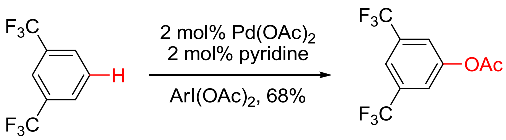


Single regioisomer

Example 3, Directing Group Ability in Palladium-Catalyzed C–H Bond Functionalization.[6]



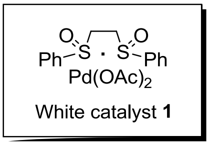
Example 4.[10]



References

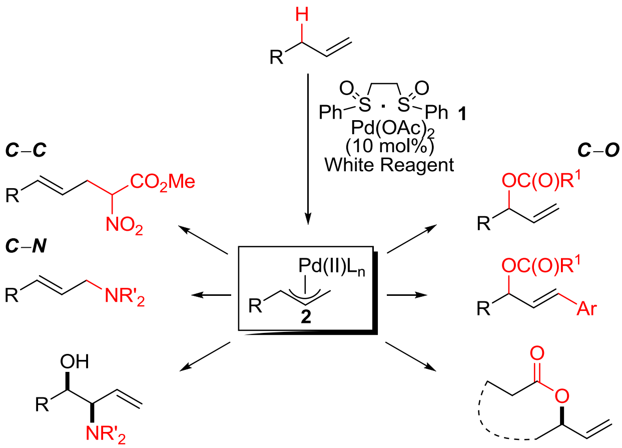
1. Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004,** *126*, 2300–2301. Melanie S. Sanford was born in New Bedford, MA, in 1975. She received a B.S. and M.S. in chemistry from Yale University in 1996 before obtaining her Ph.D. at California Institute of Technology with Professor Robert Grubbs in 2001. She then completed postdoctoral studies at Princeton University working with Professor John Groves. In 2003, she joined the faculty of the University of Michigan where she is currently the Moses Gomberg Collegiate Professor of Chemistry as well as Arthur F. Thurnau Professor of Chemistry. Her research program focuses on the development of new catalysts and catalytic transformations for applications in the synthesis of useful organic molecules.
2. Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005,** *127*, 7330–7331.
3. Kalyani, D.; Sanford, M. S. *Org. Lett.* **2005,** *7*, 4149–4152.
4. Hull, K. L.; Lanni, E. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2006,** *128*, 14047–14047. (Mechanistic insight).
5. Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2007,** *129*, 11904–11905.
6. Desai, L. V.; Stowers, K. J.; Sanford, M. S. *J. Am. Chem. Soc.* **2008,** *130*, 13285–13293.
7. Stowers, K. J.; Sanford, M. S. *Org. Lett.* **2009,** *11*, 4584–4587. (Mechanistic insight).
8. Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010,** *110*, 1147–1169. (Review).
9. Lyons, T. W.; Hull, K. L.; Sanford M. S. *J. Am. Chem. Soc.* **2011,** *133*, 4455–4464. (Regioselectivity).
10. Emmert, M. H.; Cook, A. K.; Xie, Y. J.; Sanford, M. S. *Angew. Chem. Int. Ed.* **2011,** *50*, 9409–9412.
11. Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012,** *45*, 936–946. (Review).

White catalyst



The White catalyst **1** is a highly versatile, commercially-available catalyst for allylic C–H oxidation which allows for the construction of useful C–O, C–N, and C–C bonds directly from relatively inert allylic C–H bonds (Figure 1).[1–11] The White catalyst enables novel and predictable disconnections for the synthesis of complex molecules which can streamline their synthesis.[2,4,7,8] Widely available α-olefins undergo intra- and intermolecular C–H oxidation with remarkably high levels of chemo-, regio-, and stereoselectivity. Mechanistic studies provide evidence that the White catalyst promotes allylic C–H cleavage to generate π-allylpalladium intermediate **2** which can then be functionalized with an oxygen, nitrogen or carbon nucleophile (Figure 1).[3]

Figure 1



Common organic functionality such as Lewis basic phenol **3**,[3] acid-labile acetal **4**,[8] highly reactive aryl triflate **6**,[11] and depsipeptide **5**[5] are well-tolerated under the mild reaction conditions (Figure 2). In all cases the products are isolated as one regioisomer and olefin isomer after column purification.

Current state-of-the-art methods for constructing C–N bonds rely on functional group interconversions or C–C bond forming reactions using preoxidized materials. Allylic amination using the White catalyst can streamline the synthesis of nitrogen-containing molecules by reducing the functional group manipulations necessary for working with oxygenated intermediates. Allylic C–H amination was used to synthesize (–)-**8**, an intermediate in the synthesis of *L*-acosamine derivative **9** (Figure 3A).[7] The C–H amination route to (–)-**8** proceeded in half the total number of steps, no functional group manipulations, and comparable overall yield to the alternative C–O to C–N bond-forming route. Intermolecular C–H amination has also led to the construction of (+)-deoxynegamycin analogue **12** in five less steps and improved overall yield compared to the alternative route relying on C–O substitution (Figure 3B).[8]

Figure 2

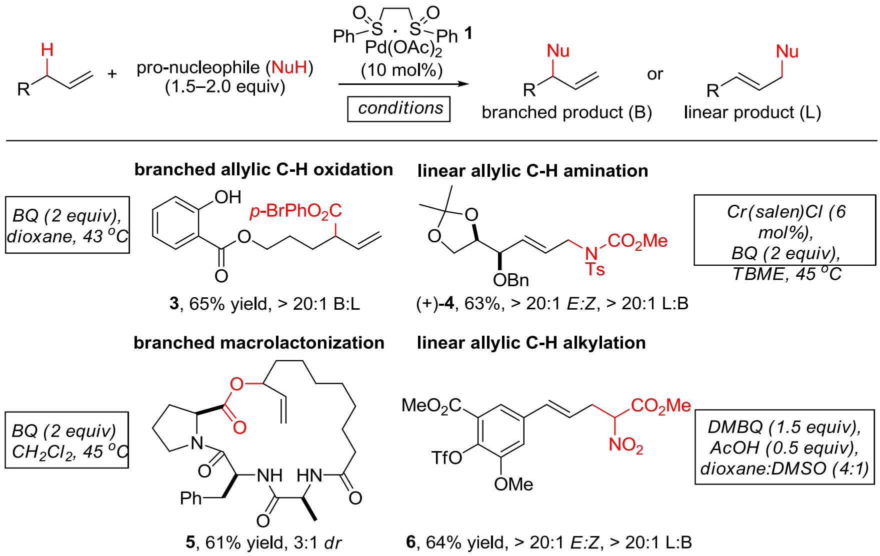
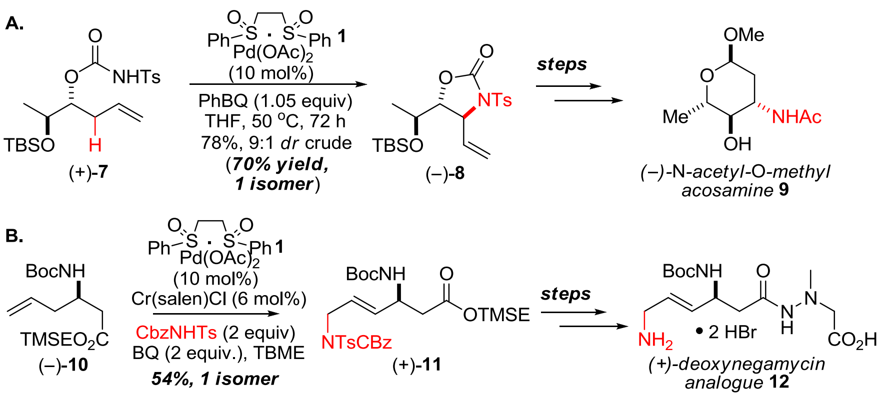
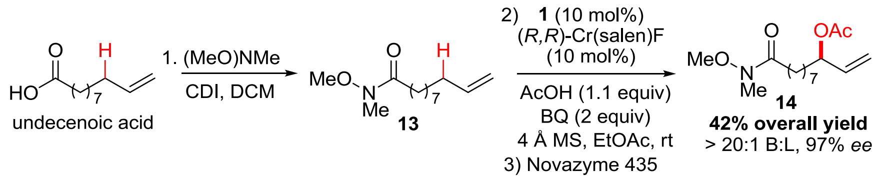


Figure 3



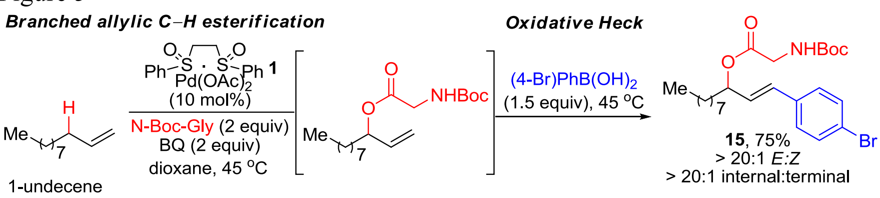
Similarly, allylic C–H oxidation can streamline the construction of oxygenated compounds by reducing functional group manipulations necessary for working with bisoxygenated intermediates. For example, a chiral allylic C–H oxidation/enzymatic resolution sequence furnished bisoxygenated compound **14** in 97% *ee* and in 42% overall yield in just 3 steps from a commercially available monooxygenated precursor, 11-undecenoic acid (Figure 4).[10] Alternative routes to similar molecules require protection/deprotection sequences and use a kinetic resolution giving a maximum of 50% yield.

Figure 4



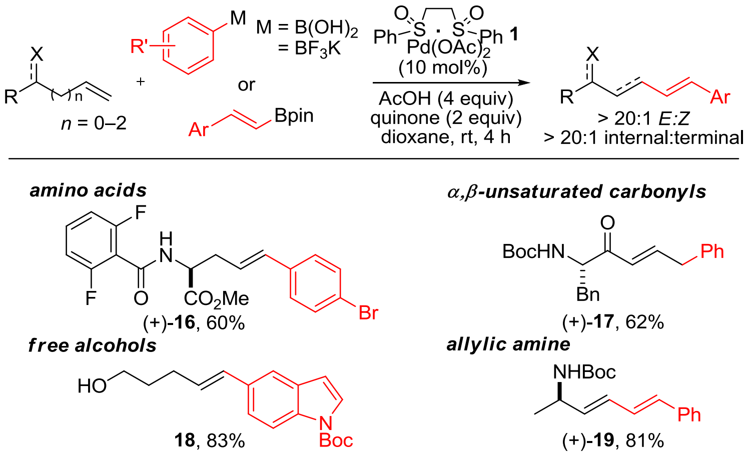
In addition to allylic C–H oxidation, the White catalyst also catalyzes intermolecular Heck arylations.[6] Notably, the arylation uses electronically *unbiased* α-olefins and aryl boronic acids and occurs under acidic, oxidative conditions. A one-pot allylic C–H oxidation/vinylic C–H arylation reaction furnishes *E*-arylated allylic esters with high regio- and stereoselectivities (Figure 5). This three-component coupling can be used to rapidly synthesize densely functionalized products from inexpensive hydrocarbon feedstocks. *N*-Boc glylcine allylic ester **9** was synthesized in one step using commercially available olefin, amino acid, and boronic acid reagents. Compounds similar to **15** have been transformed into medicinally relevant dipeptidyl peptidase IV inhibitors.[6]

Figure 5



Besides the one-pot process described above, the White catalyst catalyzes a chelate-controlled oxidative Heck arylation between a wide range of α-olefins and organoborane compounds in good yields and with excellent regio- and stereoselectivities (Figure 6).[9] Unlike other Heck arylation methods, no Pd–H isomerization is observed under the mild reaction conditions. Aryl boronic acids, styrenylpinacol boronic esters, and aryl potassium trifluoroborates (activated with boric acid) are all compatible with the general reaction conditions.

Figure 6

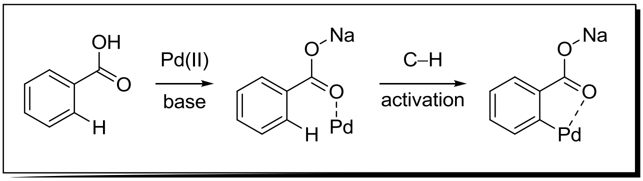


References

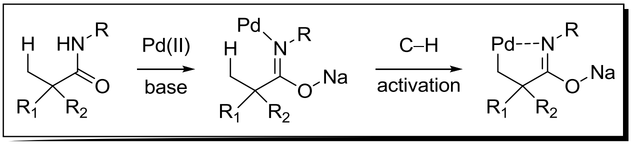
1. Chen, M. S.; White, M. C. *J. Am. Chem. Soc.* **2004,** *126*, 1346–1347. Christina M. White is a professor at the University of Illinois at Urbana-Champagne.
2. Fraunhoffer, K. J.; Bachovchin, D. A.; White, M. C. *Org. Lett.* **2005,** *7*, 223–226.
3. Chen. M. S.; Prabagaran, N.; Labenz, N. A.; White, M. C. *J. Am. Chem. Soc.* **2005,** *127*, 6970–6971.
4. Covell, D. J.; Vermeulen, N. A.; White, M. C. *Angew. Chem. Int. Ed.* **2006,** *45*, 8217–8220.
5. Fraunhoffer, K. J.; Prabagaran, N.; Sirois, L. E.; White, M. C. *J. Am. Chem. Soc.* **2006,** *128*, 9032–9033.
6. Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2006,** *128*, 15076–15077.
7. Fraunhoffer, K. J.; White, M. C. *J. Am. Chem. Soc.* **2007,** *129*, 7274–7276.
8. Reed, S. A.; White, M. C. *J. Am. Chem. Soc.* **2008,** *129*, 3316–3318.
9. Delcamp, J. H.; Brucks, A. P.; White, M. C. *J. Am. Chem. Soc.* **2008,** *129*, 11270–11271.
10. Covell, D. J.; White, M. C. *Angew. Chem. Int. Ed.* **2008,** *47*, 6448–6451.
11. Young, A. J.; White, M. C. *J. Am. Chem. Soc.* **2008,** *129*, 14090–14091.

Yu C−H activation

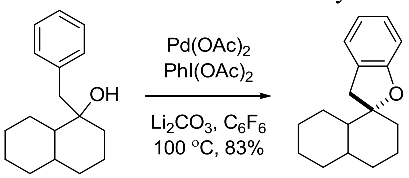
A variety of position-selective or stereoselective C−H activation reactions have been developed by Yu and co-workers.[1,7] These transformations are characterized by the use of a Pd catalyst, an oxidant, often with built-in directing groups and/or optimized ligands that enhance selectivity as well as reaction rate.
Canonical example of sp^2 C−H activation:



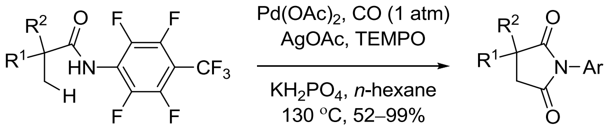
Canonical example of sp^3 C−H activation:



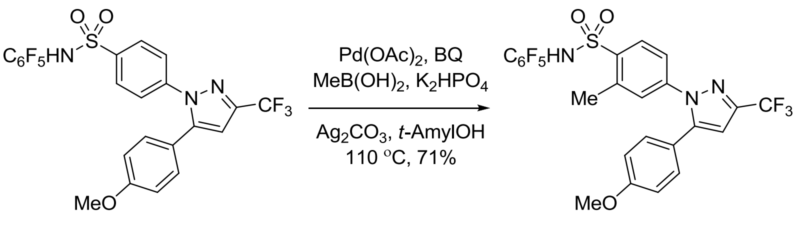
Example 1, Hydroxyl-directed C−H activation/C−O cyclization[2]



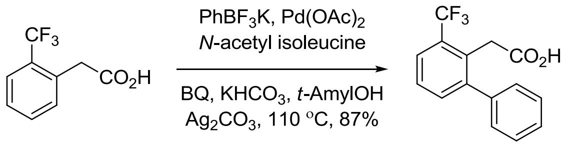
Example 2, Amide-directed sp^3 C−H carbonylation[3]



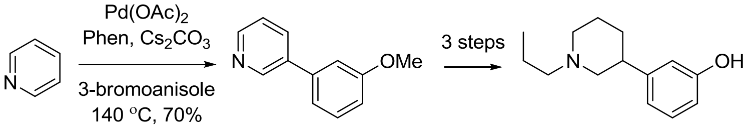
Example 3, Sulfonamide-directed C−H methylation[4]



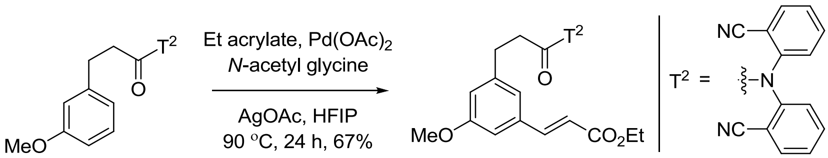
Example 4, *ortho*-Selective C−H arylation of arene[5]



Example 5, C_3-Selective C−H arylation of pyridine[6]



Example 6, *meta*-Selective C−H vinylation of arene[8]

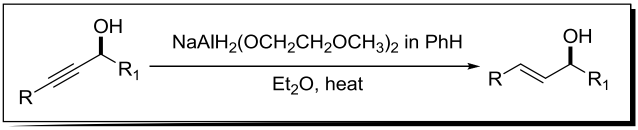


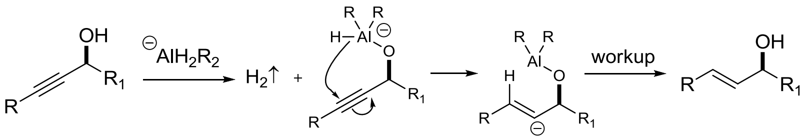
References

1. Wang, D. H.; Engle, K. M.; Shi, B. F.; Yu, J. Q. *Science* **2010,** *327*, 315−319.
2. Wang, X.; Lu, Y.; Dai, H. X.; Yu, J. Q. *J. Am. Chem. Soc.* **2010,** *132*, 12203−12205.
3. Yoo, E. J.; Wasa, M.; Yu, J. Q. *J. Am. Chem. Soc.* **2010,** *132*, 17378−17380.
4. Dai, H. X.; Stepan, A. F.; Plummer, M. S.; Zhang, Y. H.; Yu, J. Q. *J. Am. Chem. Soc.* **2011,** *133*, 7222−7228.
5. Engle, K. M.; Thuy-Boun, P. S.; Dang, M.; Yu, J. Q. *J. Am. Chem. Soc.* **2011,** *133*, 18183−18193.
6. Ye, M.; Gao, G. L.; Edmunds, A. J.; Worthington, P. A.; Morris, J. A.; Yu, J. Q. *J. Am. Chem. Soc.* **2011,** *133*, 19090−19093.
7. Engle, K. M.; Mei, T. S.; Wasa, M.; Yu, J. Q. *Acc. Chem. Res.* **2012,** *45*, 788−802 (Review).
8. Leow, D.; Li, G.; Mei, T. S.; Yu, J. Q. *Nature* **2012,** *486*, 518–522.

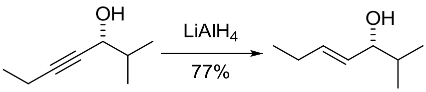
Chan alkyne reduction

Stereoselective reduction of acetylenic alcohols to *E*-allylic alcohols using **s**odium bis(2-**m**ethoxy**e**thoxy)**a**luminum **h**ydride (SMEAH, also known as Red-Al) or $LiAlH_4$.

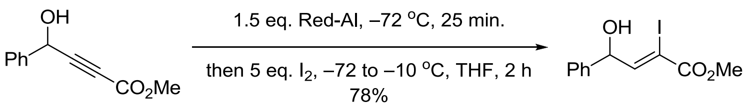




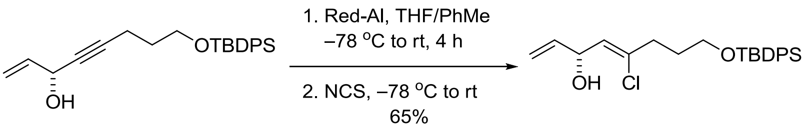
Example 1[3]



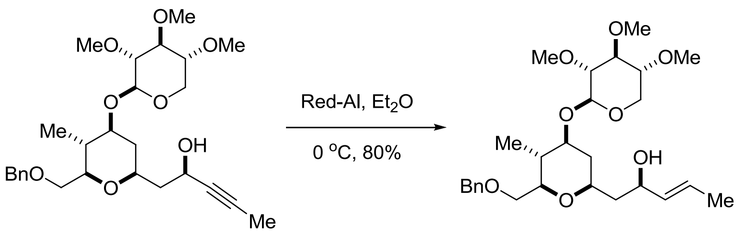
Example 2[4]



Example 3[6]



Example 4[7]



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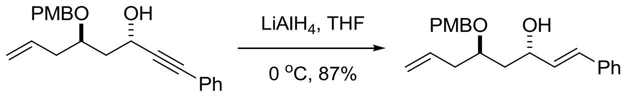
Example 5[8]

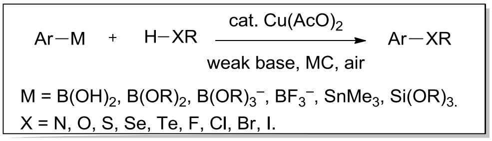


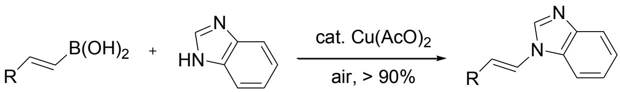
References

1. Chan, K.-K.; Cohen, N.; De Noble, J. P.; Specian, A. C., Jr.; Saucy, G. *J. Org. Chem.* **1976,** *41*, 3497–3505. Ka-Kong Chan was a chemist at Hoffmann–La Roche, Inc. in Nutley, NJ, USA.
2. Blunt, J. W.; Hartshorn, M. P.; Munro, M. H. G.; Soong, L. T.; Thompson, R. S.; Vaughan, J. *J. Chem. Soc., Chem. Commun.* **1980,** 820–821.
3. Midland, M. M.; Gabriel, J. *J. Org. Chem.* **1985,** *50*, 1143–1144.
4. Meta, C. T.; Koide, K. *Org. Lett.* **2004,** *6*, 1785–1787.
5. Yamazaki, T.; Ichige, T.; Kitazume, T. *Org. Lett.* **2004,** *6*, 4073–4076.
6. Xu, S.; Arimoto, H.; Uemura, D. *Angew. Chem. Int. Ed.* **2007,** *46*, 5746–5749.
7. Chakraborty, T. K.; Reddy, V. R.; Gajula, P. K. *Tetrahedron* **2008,** *64*, 5162–5167.
8. Krishna, P. R.; Krishnarao, L.; Reddy, K. L. N. *Beilstein J. Org. Chem*. **2009,** *5*, No. 14.
9. Yadav, J. S.; Krishna, V. H.; Srilatha, A.; Somaiah, R.; Reddy, B. V. S. *Synthesis* **2011,** 3004–3012.
10. Krishna, P. R.; Alivelu, M. *Helv. Chim. Acta* **2011,** *94*, 1102–1107.

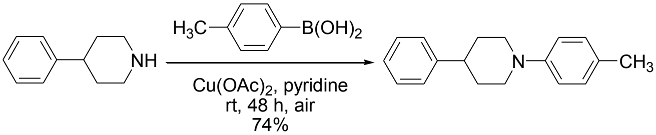
Chan–Lam C–X coupling reaction

Arylation, vinylation and alkylation of a wide range of NH/OH/SH substrates by oxidative cross-coupling with boronic acids in the presence of catalytic cupric acetate, weak base and in air (open-flask chemistry). The reaction works for amides, amines, amidines, anilines, azides, azoles, hydantoins, hydrazines, imides, imines, nitroso, pyrazinones, yridines, purines, pyrimidines, sulfonamides, sulfinates, sulfoximines, ureas, alcohols, phenols, thiols, *etc*. The boronic acids can be replaced with siloxanes, stannanes or other organometalloids. The mild condition of this reaction is an advantage over Buchwald–Hartwig's Pd-catalyzed cross-coupling using halides, though boronic acids are more expensive than halides. The Chan–Lam C–X bond cross-coupling reaction has emerged as a powerful and popular methodogy similar to Suzuki–Miyaura's C–C bond cross-coupling reaction.

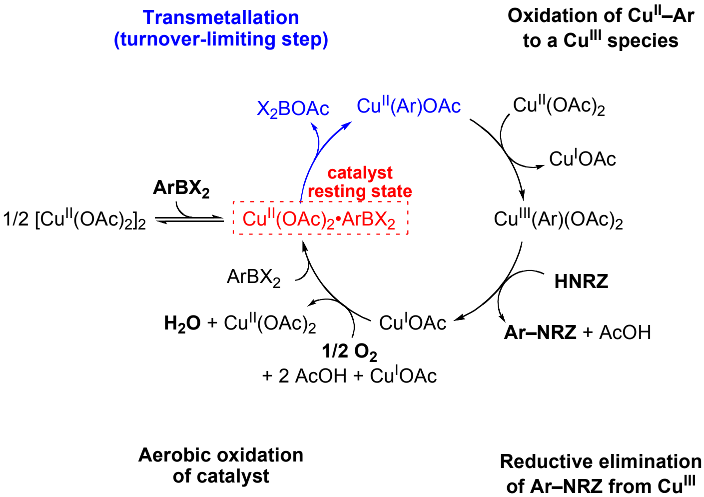




Example 1[1a,d]



Proposed Mechanism:[4]



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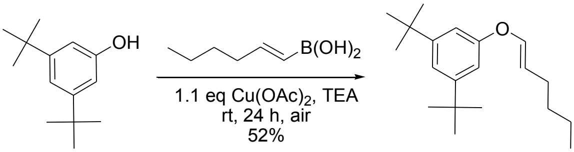
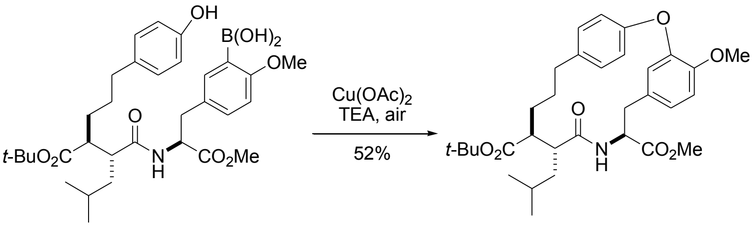
DOI 10.1007/978-3-319-03979-4_56, © Springer International Publishing Switzerland 2014

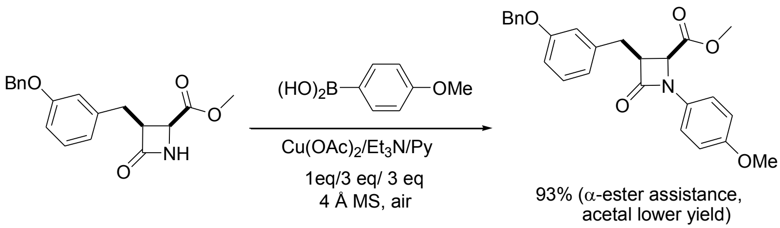
Example 2[5]



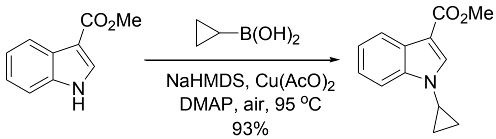
Example 3[6]



Example 4[14]



Example 5[15]



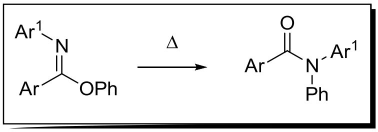
References

1. (a) Chan, D. M. T.; Monaco, K. L.; Wang, R.-P.; Winters, M. P. *Tetrahedron Lett*. **1998**, *39*, 2933–2936. (b) Lam, P. Y. S.; Clark, C. G.; Saubern, S.; Adams, J.; Winters, M. P.; Chan, D. M. T.; Combs, A. *Tet rahedron Lett*. **1998,** *39*, 2941–2949. Dominic Chan is a chemist at DuPont Crop Protection, Wilmington, DE, USA. He did his PhD research with Prof. Barry Trost at the University of Wisconson, Madison. Patrick Lam is a research director at Bristol–Myers Squibb, Princeton, NJ, USA. He was formerly with DuPont Pharmaceuticals Company. He did his PhD research with Prof. Louis Friedrich in the Univeristy of Rochester and Post-doc research with Prof. Michael Jung and the late Prof. Donald Cram in UCLA. (c) Evans, D. A.; Katz, J. L.; West, T. R. *Tetrahedron Lett*. **1998,** *39*, 2937–2940. Prof. Evans' group found out about the discovery of this reaction on a National Organic Symposium poster and be came interested in the *O*-arylation because of his long interest in vancomycin total synthesis. (d) Lam, P. Y. S.; Clark, C. G.; Saubern, S.; Adams, J.; Averill, K. M.; Chan, D. M. T.; Combs, A. *Synlett* **2000,** 674–676. (e) Lam, P. Y. S.; Bonne, D.; Vincent, G.; Clark, C. G.; Combs, A. P. *Tetrahedron Lett*. **2003,** *44*, 1691–1694.

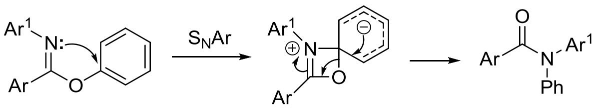
2. Reviews: (a) Qiao, J. X.; Lam, P. Y. S. *Syn*. **2011,** 829–856; (b) Chan, D. M. T.; Lam, P. Y. S., Book chapter in *Boronic Acids* Hall, ed. **2005**, Wiley–VCH, 205–240. (c) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed. Engl.* **2003,** *42*, 5400–5449.
3. Catalytic copper: (a) Lam, P. Y. S.; Vincent, G.; Clark, C. G.; Deudon, S.; Jadhav, P. K. *Tetrahedron Lett.* **2001,** *42*, 3415–3418. (b) Antilla, J. C.; Buch wald, S. L. *Org. Lett.* **2001,** *3*, 2077–2079. (c) Quach, T. D.; Batey, R. A. *Org. Lett.* **2003,** *5*, 4397–4400. (d) Collman, J. P.; Zhong, M. *Org. Lett.* **2000,** *2*, 1233–1236. (e) Lan, J.-B.; Zhang, G.-L.; Yu, X.-Q.; You, J.-S.; Chen, L.; Yan, M.; Xie, R.-G. *Synlett* **2004,** 1095–1097.
4. Mechanism (Part of the mechanistic work from Shannon's lab was funded and in collaboration with BMS: (a) Huffman, L. M.; Stahl, S. S. *J. Am. Chem. Soc*. **2008,** *130*, 9196–9197. (b) King, A. E.; Brunold, T. C.; Stahl, S. S. *J. Am. Chem. Soc*. **2009,** *131*, 5044. (c) King, A. E.; Huffman, L. M.; Casitas, A.; Costas, M.; Ribas, X.; Stahl, S. S. *J. Am. Chem. Soc*. **2010,** *132*, 12068–12073. (d) Casita, A.; King, A. E.; Prella, T.; Costas, M.; Stahl, S. S.; Ribas, X. *J. Chem. Sci*. **2010,** *1*, 326–330.
5. Vinyl boronic acids: Lam, P. Y. S.; Vincent, G.; Bonne, D.; Clark, C. G. *Tetrahe dron Lett*. **2003**, *44*, 4927–4931.
6. Intramolecular: Decicco, C. P.; Song, Y.; Evans, D.A. *Org. Lett.* **2001,** *3*, 1029–1032.
7. Solid phase: (a) Combs, A. P.; Saubern, S.; Rafalski, M.; Lam, P. Y. S. *Tetrahe dron Lett*. **1999,** *40*, 1623–1626. (b) Combs, A. P.; Tadesse, S.; Rafalski, M.; Haque, T. S.; Lam, P. Y. S. *J. Comb. Chem*. **2002,** *4*, 179–182.
8. Boronates/borates: (a) Chan, D. M. T.; Monaco, K. L.; Li, R.; Bonne, D.; Clark, C. G.; Lam, P. Y. S. *Tetrahedron Lett.* **2003,** *44*, 3863–3865. (b) Yu, X. Q.; Yamamoto, Y.; Miyuara, N. *Chem. Asian J.* **2008,** *3*, 1517–1522.
9. Siloxanes: (a) Lam, P. Y. S.; Deudon, S.; Averill, K. M.; Li, R.; He, M. Y.; DeShong, P.; Clark, C. G. *J. Am. Chem. Soc*. **2000**, *122*, 7600–7601. (b) Lam, P. Y. S.; Deudon, S.; Hauptman, E.; Clark, C. G. *Tetrahedron Lett*. **2001,** *42*, 2427–2429.
10. Stannanes: Lam, P. Y. S.; Vincent, G.; Bonne, D.; Clark, C. G. *Tetrahedron Lett*. **2002,** *43*, 3091–3094.
11. Thiols: (a) Herradura, P. S.; Pendora, K. A.; Guy, R. K. *Org. Lett.* **2000,** *2*, 2019–2022. (b) Savarin, C.; Srogl, J.; Liebeskind, L. S. . *Org. Lett.* **2002,** *4*, 4309–4312. (c) Xu, H.-J.; Zhao, Y.-Q.; Feng, T.; Feng, Y.-S. *J. Org. Chem*. **2012,** *77*, 2878–2884.
12. Sulfinates: (a) Beaulieu, C.; Guay. D.; Wang, C.; Evans, D. A. *Tetrahedron Lett*. **2004,** *45*, 3233–3236. (b) Huang, H.; Batey, R. A. *Tetrahedron*. **2007,** *63*, 7667–7672. (c) Kar, A.; Sayyed, L.A.; Lo, W.F.; Kaiser, H.M.; Beller, M.; Tse, M. K. *Org. Lett.* **2007,** *9*, 3405–3408.
13. Sulfoximines: Moessner, C.; Bolm, C. *Org. Lett.* **2005,** *7*, 2667–2669.
14. β-Lactam: Wang, W.; *et al. Bio. Med. Chem. Lett.* **2008,** *18*, 1939–1944.
15. Cyclopropyl boronic acid: Tsuritani, T.; Strotman, N. A.; Yamamoto, Y.; Kawa saki, M.; Yasuda, N.; Mase, T. *Org. Lett.* **2008,** *10*, 1653–1655.
16. Alcohols: Quach, T. D.; Batey, R. A. *Org. Lett.* **2003,** *5*, 1381–1384.
17. Fluorides: (a) Ye, Y.; Sanford, M. S. *J. Am. Chem. Soc*. **2013,** *135*, 4648–4651. (b) Fier, P. S.; Luo, J.; Hartwig, J. F. *J. Am. Chem. Soc*. **2013,** *135*, 2552–2559.

Chapman rearrangement

Thermal aryl rearrangement of *O*-aryliminoethers to amides.

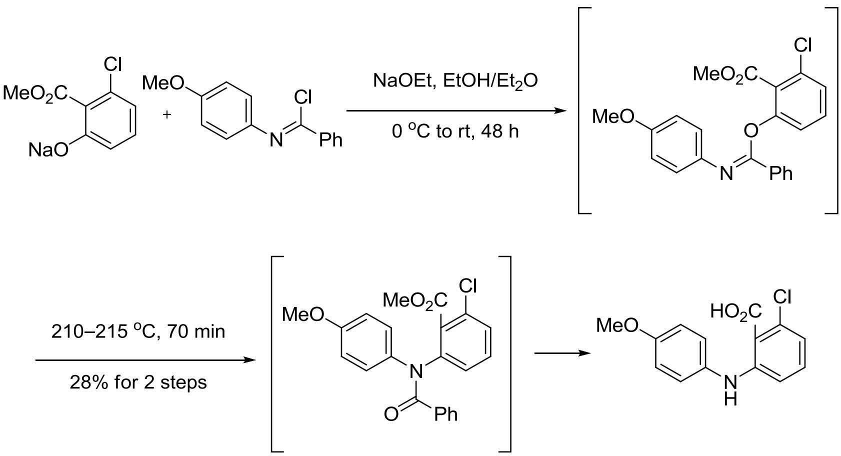


Mechanism:

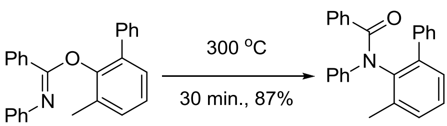


oxazete intermediate

Example 1[2]



Example 2[4]



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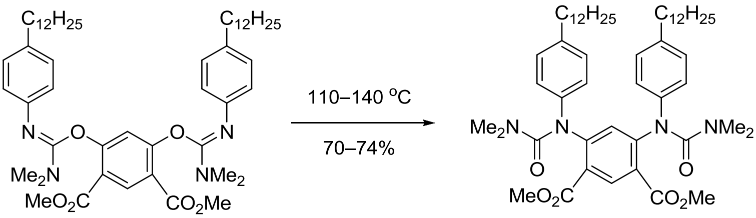
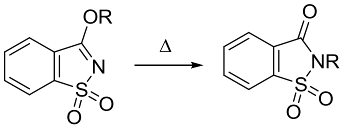
DOI 10.1007/978-3-319-03979-4_57, © Springer International Publishing Switzerland 2014

Example 3, Double Chapman rearrangement[9]



Example 4, Chapman-like thermal rearrangement[11]

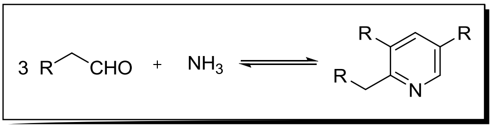


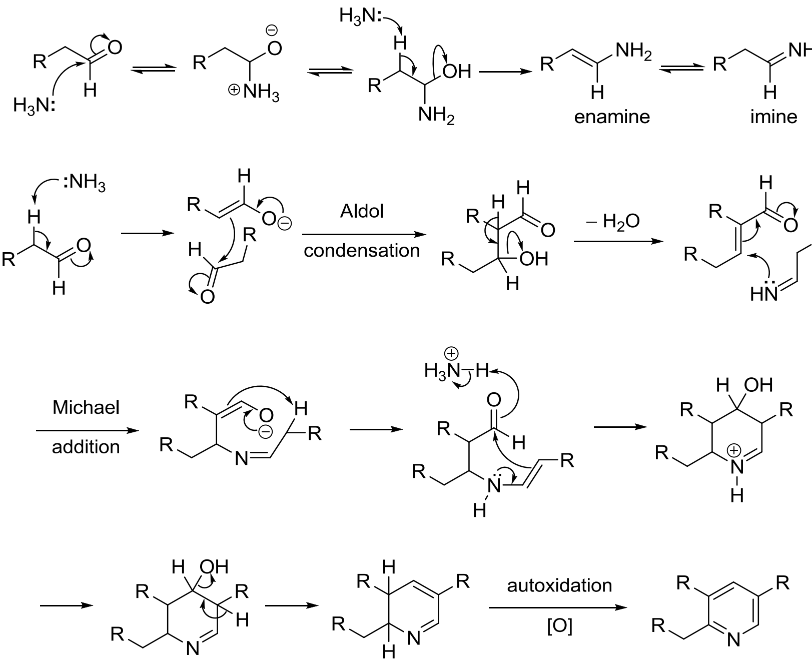
References

1. Chapman, A. W. *J. Chem. Soc.* **1925,** *127*, 1992–1998. Arthur William Chapman was born in 1898 in London, England. He was a Lecturer in Organic Chemistry and later became Registrar of the University of Sheffield from 1944 to 1963.
2. Dauben, W. G.; Hodgson, R. L. *J. Am. Chem. Soc*. **1950,** *72*, 3479–3480.
3. Schulenberg, J. W.; Archer, S. *Org. React.* **1965,** *14*, 1–51. (Review).
4. Relles, H. M. *J. Org. Chem*. **1968,** *33*, 2245–2253.
5. Shawali, A. S.; Hassaneen, H. M. *Tetrahedron* **1972,** *28*, 5903–5909.
6. Kimura, M.; Okabayashi, I.; Isogai, K. *J. Heterocycl. Chem.* **1988,** *25,* 315–320.
7. Farouz, F.; Miller, M. J. *Tetrahedron Lett.* **1991,** *32*, 3305–3308.
8. Dessolin, M.; Eisenstein, O.; Golfier, M.; Prange, T.; Sautet, P. *J. Chem. Soc., Chem. Commun.* **1992,** 132–134.
9. Marsh, A.; Nolen, E. G.; Gardinier, K. M.; Lehn, J. M. *Tetrahedron Lett.* **1994,** *35*, 397–400.
10. Almeida, R.; Gomez-Zavaglia, A.; Kaczor, A.; Cristiano, M. L. S.; Eusebio, M. E. S.; Maria, T. M. R.; Fausto, R. *Tetrahedron* **2008,** *64*, 3296–3305.
11. Noorizadeh, S.; Ozhand, A. *Chin. J. Chem.* **2010,** *28,* 1876–1884.

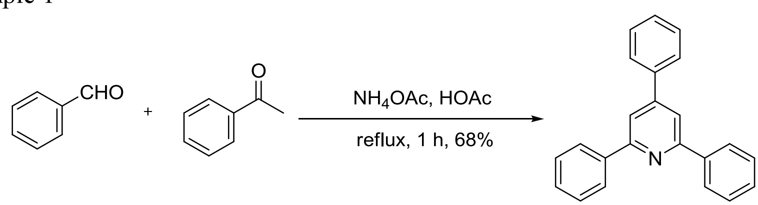
Chichibabin pyridine synthesis

Also known as the Chichibabin reaction. Condensation of aldehydes with ammonia to afford pyridines.

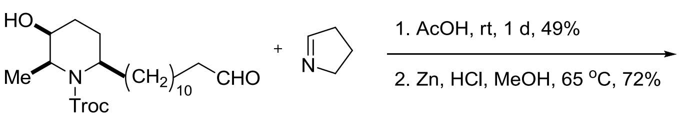




Example 1[4]



Example 2[8]



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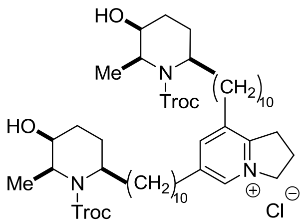
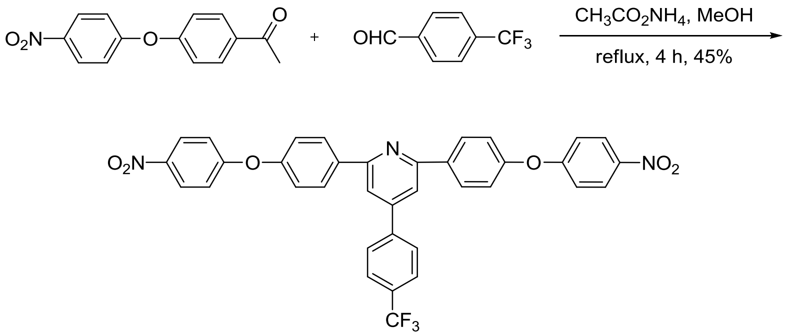
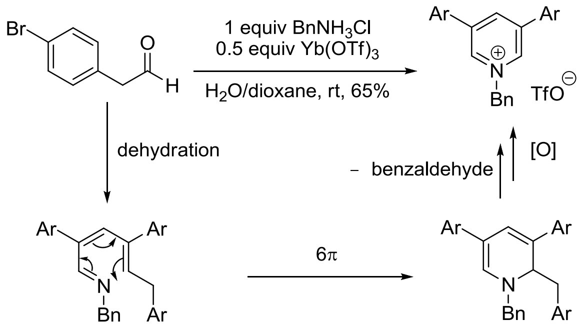
DOI 10.1007/978-3-319-03979-4_58, © Springer International Publishing Switzerland 2014



Example 3[9]



Example 4, An abnormal Chichibabin reaction[10]



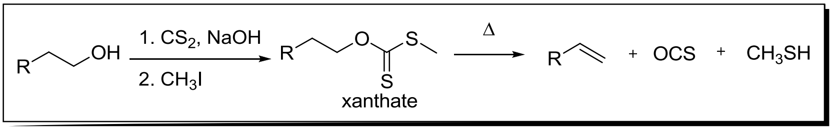
References

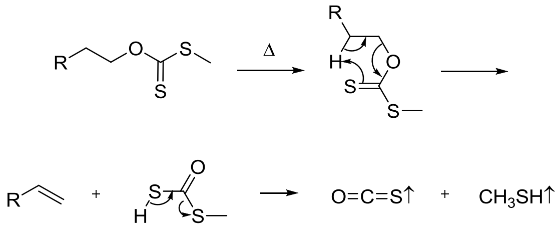
1. Chichibabin, A. E. *J. Russ. Phys. Chem. Soc.* **1906,** *37*, 1229. Alexei E. Chichibabin (1871−1945) was born in Kuzemino, Russia. He was Markovnikov's favorite student. Markovnikov's successor, Zelinsky (of Hell–Volhard–Zelinsky reaction fame) did not want to cooperate with the pupil and gave Chichibabin a negative judgment on his Ph.D. work, earning Chichibabin the nickname "the self-educated man."
2. Sprung, M. M. *Chem. Rev.* **1940,** *40*, 297–338. (Review).
3. Frank, R. L.; Riener, E. F. *J. Am. Chem. Soc.* **1950,** *72*, 4182–4183.
4. Weiss, M. *J. Am. Chem. Soc.* **1952,** *74*, 200–202.
5. Kessar, S. V.; Nadir, U. K.; Singh, M. *Indian J. Chem.* **1973,** *11*, 825−826.

6. Shimizu, S.; Abe, N.; Iguchi, A.; Dohba, M.; Sato, H.; Hirose, K.-I. *Microporous Mesoporous Materials* **1998,** *21*, 447–451.
7. Galatasis, P. *Chichibabin (Tschitschibabin) Pyridine Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 308–309. (Review).
8. Snider, B. B.; Neubert, B. J. *Org. Lett*. **2005,** *7*, 2715–2718.
9. Wang, X.-L.; Li, Y.-F.; Gong, C.-L.; Ma, T.; Yang, F.-C. *J. Fluorine Chem.* **2008,** *129*, 56–63.
10. Burns, N. Z.; Baran, P. S. *Angew. Chem. Int. Ed.* **2008,** *47*, 205–208.
11. Huang, Y.-C.; Wang, K.-L.; Chang, C.-H.; Liao, Y.-A.; Liaw, D.-J.; Lee, K.-R.; Lai, J.-Y. *Macromolecules* **2008,** *46*, 7443–7450.

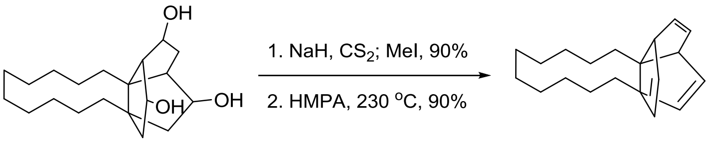
Chugaev elimination

Thermal elimination of xanthates to olefins.

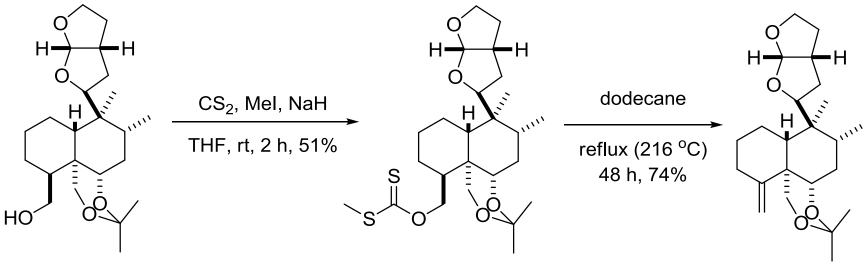




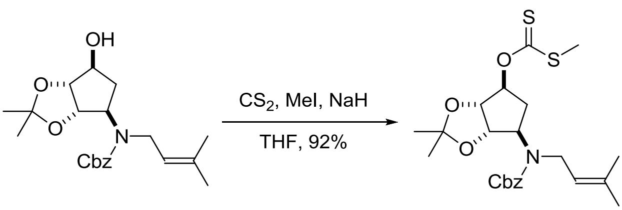
Example 1[4]



Example 2[5]



Example 3, Chugaev *syn*-elimination is followed by an intramolecular ene reaction[6]



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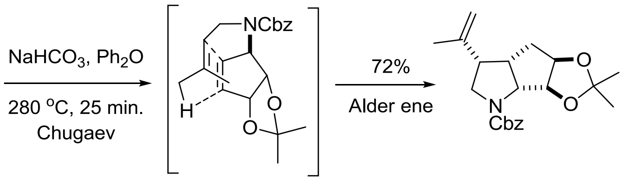
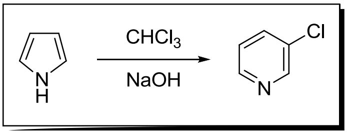


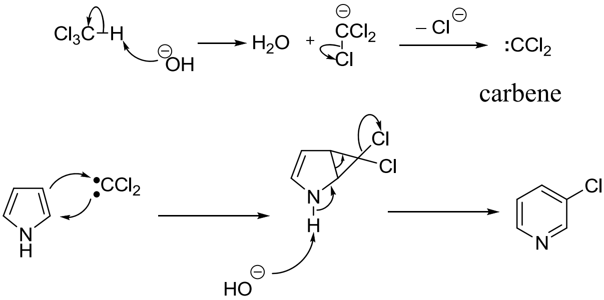
References

1. Chugaev, L. *Ber.* **1899,** *32*, 3332. Lev A. Chugaev (1873−1922) was born in Moscow, Russia. He was a Professor of Chemistry at Petrograd, a position once held by Dimitri Mendeleyev and Paul Walden. In addition to terpenoids, Chugaev also investigated nickel and platinum chemistry. He completely devoted his life to science. The light in Chugaev's study would invariably burn until 4 or 5 a.m.
2. Harano, K.; Taguchi, T. *Chem. Pharm. Bull.* **1975,** *23*, 467–472.
3. Ho, T.-L.; Liu, S.-H. *J. Chem. Soc., Perkin Trans. 1* **1984,** 615–617.
4. Fu, X.; Cook, J. M. *Tetrahedron Lett.* **1990,** *31*, 3409–3412.
5. Meulemans, T. M.; Stork, G. A.; Macaev, F. Z.; Jansen, B. J. M.; de Groot, A. *J. Org. Chem*. **1999,** *64*, 9178–9188.
6. Nakagawa, H.; Sugahara, T.; Ogasawara, K. *Org. Lett*. **2000,** *2*, 3181−3183.
7. Nakagawa, H.; Sugahara, T.; Ogasawara, K. *Tetrahedron Lett*. **2001,** *42*, 4523–4526.
8. Fuchter, M. J. *Chugaev elimination*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 334–342. (Review).
9. Ahmed, S.; Baker, L. A.; Grainger, R. S.; Innocenti, P.; Quevedo, C. E. *J. Org. Chem.* **2008,** *73*, 8116–8119.
10. Tang, P.; Wang, L.; Chen, Q.-F.; Chen, Q.-H.; Jian, X.-X.; Wang, F.-P. *Tetrahedron* **2012,** *68*, 5031–5036.

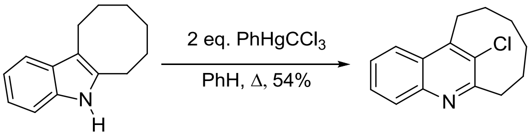
Ciamician–Dennsted rearrangement

Cyclopropanation of a pyrrole with dichlorocarbene generated from $CHCl_3$ and NaOH. Subsequent rearrangement takes place to give 3-chloropyridine.

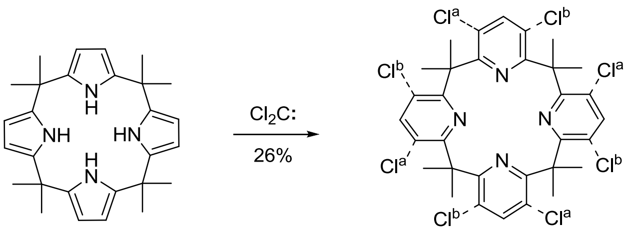




Example 1[4]



Example 2[5]



References

1. Ciamician, G. L.; Dennsted, M. *Ber.* **1881,** *14*, 1153. Giacomo Luigi Ciamician (1857−1922) was born in Trieste, Italy. Ciamician is considered the father of modern organic photochemistry.
2. Wynberg, H. *Chem. Rev.* **1960,** *60*, 169−184. (Review).
3. Wynberg, H. and Meijer, E. W. *Org. React.* **1982,** *28*, 1−36. (Review).
4. Parham, W. E.; Davenport, R. W.; Biasotti, J. B. *J. Org. Chem.* **1970,** *35*, 3775−3779.
5. Král, V.; Gale, P. A.; Anzenbacher, P. Jr.; K. Jursíková; Lynch, V.; Sessler, J. L. *Chem. Comm.* **1998,** 9−10.
6. Pflum, D. A. *Ciamician–Dennsted Rearrangement*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 350–354. (Review).

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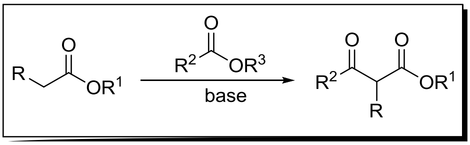
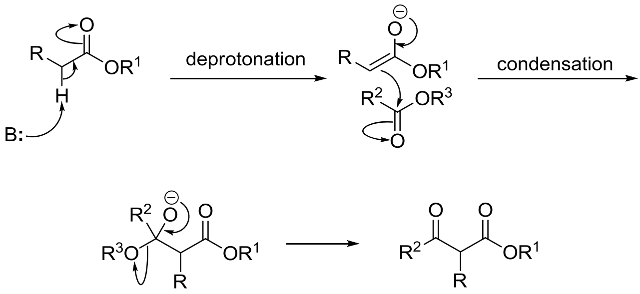
DOI 10.1007/978-3-319-03979-4_60,

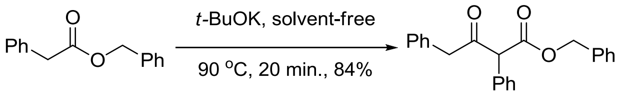
Claisen condensation

Base-catalyzed condensation of esters to afford β-keto esters.

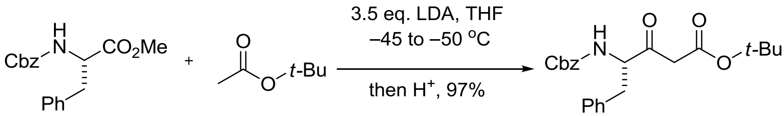




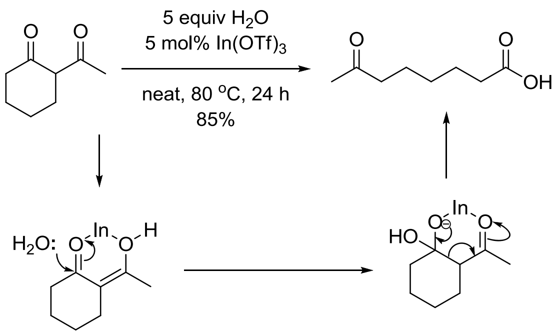
Example 1[4]



Example 2[6]



Example 3, Retro-Claisen condensation[9]



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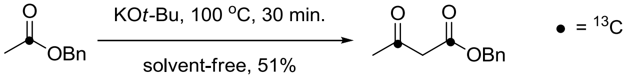
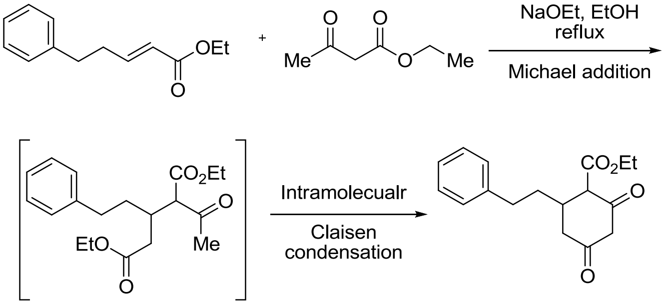
DOI 10.1007/978-3-319-03979-4_61, © Springer International Publishing Switzerland 2014

Example 4, Solvent-free Claisen condensation[10]



Example 5, Intramolecualr Claisen condensation (Dieckmann condensation)[11]

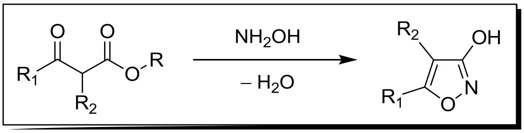


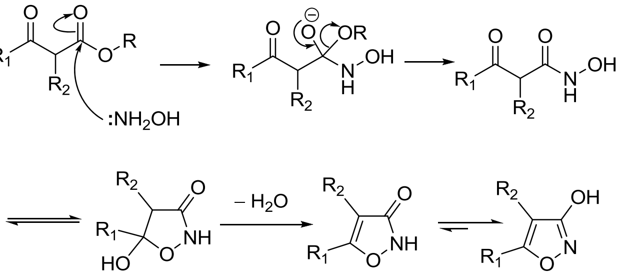
References

1 Claisen, R. L.; Lowman, O. *Ber.* **1887,** *20*, 651. Rainer Ludwig Claisen (1851−1930), born in Cologne, Germany, probably had the best pedigree in the history of organic chemistry. He apprenticed under Kekulé, Wöhler, von Baeyer, and Fischer before embarking on his own independent research.
2 Hauser, C. R.; Hudson, B. E. *Org. React.* **1942,** *1*, 266–302. (Review).
3 Schäfer, J. P.; Bloomfield, J. J. *Org. React.* **1967,** *15*, 1–203. (Review).
4 Yoshizawa, K.; Toyota, S.; Toda, F. *Tetrahedron Lett*. **2001,** *42*, 7983−7985.
5 Heath, R. J.; Rock, C. O. *Nat. Prod. Rep.* **2002,** *19*, 581−596. (Review).
6 Honda, Y.; Katayama, S.; Kojima, M.; Suzuki, T.; Izawa, K. *Org. Lett*. **2002,** *4*, 447–449.
7 Mogilaiah, K.; Reddy, N. V. *Synth. Commun*. **2003,** *33,* 73−78.
8 Linderberg, M. T.; Moge, M.; Sivadasan, S. *Org. Process Res. Dev*. **2004,** *8,* 838−845.
9 Kawata, A.; Takata, K.; Kuninobu, Y.; Takai, K. *Angew. Chem. Int. Ed.* **2007,** *46,* 7793−7795.
10 Iida, K.; Ohtaka, K.; Komatsu, T.; Makino, T.; Kajiwara, M. *J. Labelled Compd. Radiopharm.* **2008,** *51,* 167−169.
11 Song, Y. Y.; He, H. G.; Li, Y.; Deng, Y. *Tetrahedron Lett*. **2013,** *54*, 2658–2660.

Claisen isoxazole synthesis

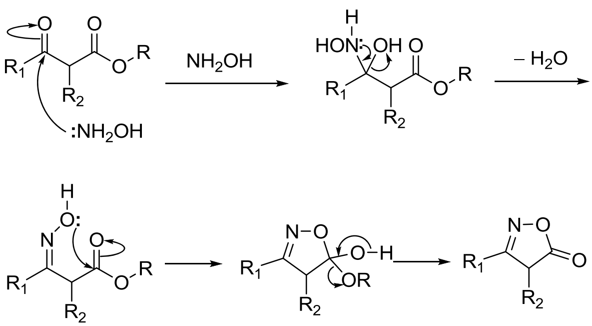
Cyclization of β-keto esters with hydroxylamine to provide 3-hydroxy-isoxazoles (3-isoxazolols).





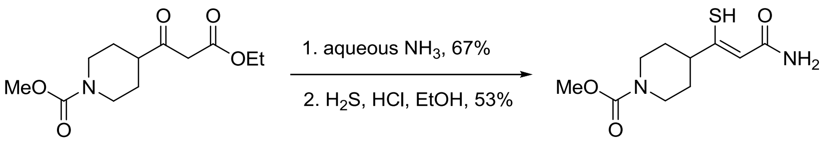
3-isoxazolol

A side reaction:



5-isoxazolone

Example 1, A thio-analog[6]



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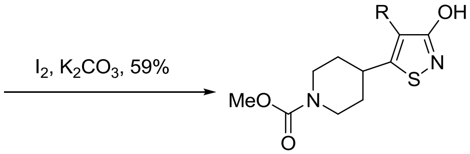
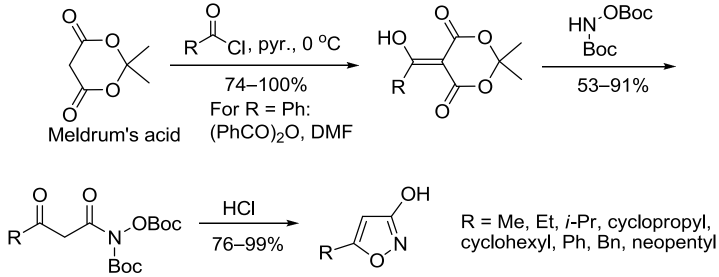
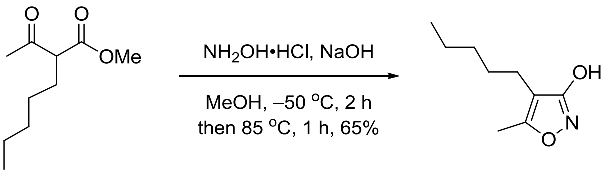
DOI 10.1007/978-3-319-03979-4_62,



Example 2[7]



Example 3[8]

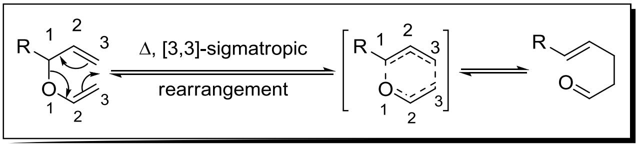


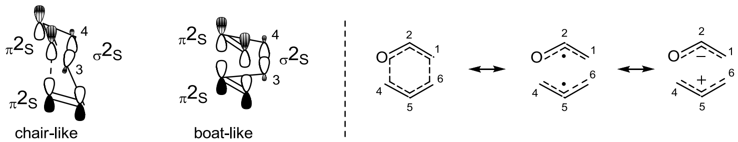
References

1. (a) Claisen, L; Lowman, O. E. *Ber.* **1888,** *21*, 784. (b) Claisen, L.; Zedel, W. *Ber.* **1891,** *24*, 140. (c) Hantzsch, A. *Ber.* **1891,** *24*, 495–506.
2. Barnes, R. A. In *Heterocyclic Compounds*; Elderfield, R. C., Ed.; Wiley: New York, **1957**; *Vol. 5*, p 474ff. (Review).
3. Loudon, J. D. In *Chemistry of Carbon Compounds*; Rodd, E. H., Ed.; Elsevier: Amsterdam, **1957**; Vol. 4a, p. 345ff. (Review).
4. McNab, H. *Chem. Soc. Rev.* **1978,** *7*, 345–358. (Review).
5. Chen, B.-C. *Heterocycles* **1991,** *32*, 529–597. (Review).
6. Frølund, B.; Kristiansen, U.; Brehm, L.; Hansen, A. B.; Krogsgaard-Larsen, K.; Falch, E. *J. Med. Chem.* **1995,** *38*, 3287–3296.
7. Sorensen, U. S.; Falch, E.; Krogsgaard-Larsen, K. *J. Org. Chem.* **2000,** *65*, 1003–1007.
8. Madsen, U.; Bräuner-Osborne, H.; Frydenvang, K.; Hvene, L.; Johansen, T.N.; Nielsen, B.; Sánchez, C.; Stensbøl, T.B.; Bischoff, F.; Krogsgaard-Larsen, K. *J. Med. Chem.* **2001,** *44*, 1051–1059.
9. Brooks, D. A. *Claisen Isoxazole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 220–224. (Review).
10. El Shehry, M. F.; Swellem, R. H.; Abu-Bakr, Sh. M.; El-Telbani, E. M. *Eur. J. Med. Chem.* **2010,** *45*, 4783–4787.

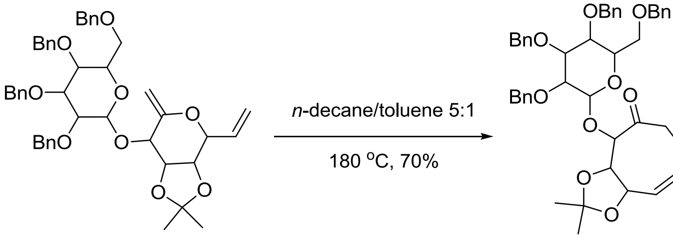
Claisen rearrangements

The Claisen, *para*-Claisen rearrangements, Belluš–Claisen rearrangement; Corey–Claisen, Eschenmoser–Claisen rearrangement, Ireland–Claisen, Kazmaier–Claisen, Saucy–Claisen; orthoester Johnson–Claisen, along with the Carroll rearrangement, belong to the category of *[3,3]-sigmatropic rearrangements*. The Claisen rearrangement is a concerted process and the arrow pushing here is merely illustrative.

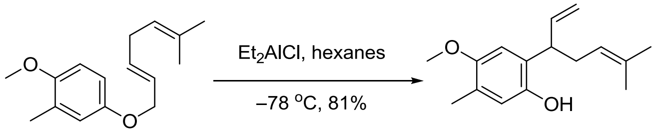




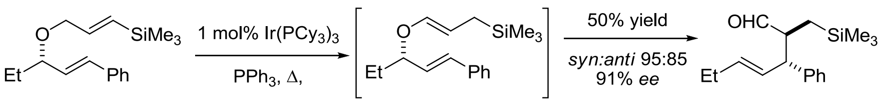
Example 1[7]



Example 2[8]



Example 3[9]



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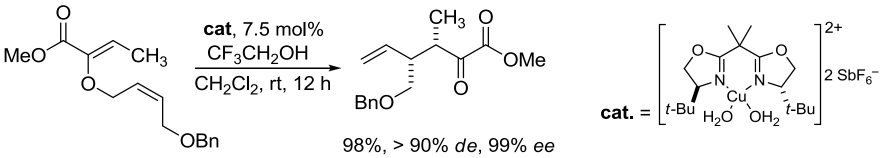
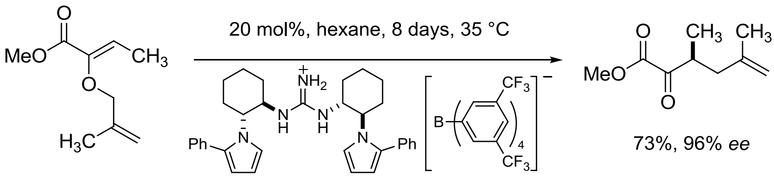
DOI 10.1007/978-3-319-03979-4_63, © Springer International Publishing Switzerland 2014

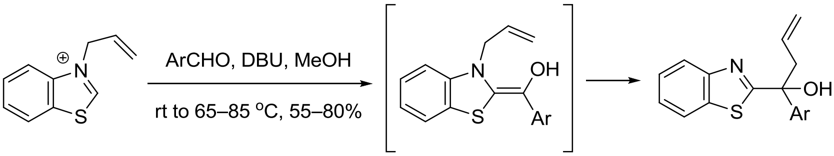
Example 4, Asymmetric Claisen rearrangement[10]



Example 5, Asymmetric Claisen rearrangement[11]



Example 6[13]

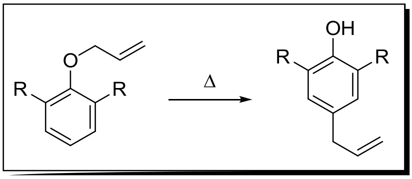


References

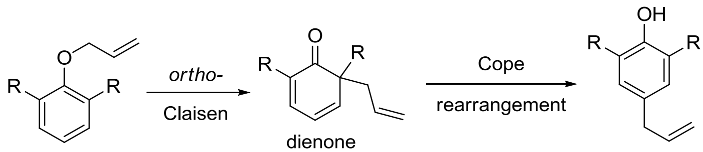
1. Claisen, L. *Ber.* **1912,** *45*, 3157–3166.
2. Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975,** *22*, 1–252. (Review).
3. Wipf, P. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 5*, 827–873. (Review).
4. Ganem, B. *Angew. Chem. Int. Ed.* **1996,** *35*, 937–945. (Review).
5. Ito, H.; Taguchi, T. *Chem. Soc. Rev.* **1999,** *28*, 43–50. (Review).
6. Castro, A. M. M. *Chem. Rev.* **2004,** *104*, 2939–3002. (Review).
7. Jürs, S.; Thiem, J. *Tetrahedron: Asymmetry* **2005,** *16*, 1631−1638.
8. Vyvyan, J. R.; Oaksmith, J. M.; Parks, B. W.; Peterson, E. M. *Tetrahedron Lett.* **2005,** *46*, 2457–2460.
9. Nelson, S. G.; Wang, K. *J. Am. Chem. Soc.* **2006,** *128*, 4232–4233.
10. Körner, M.; Hiersemann, M. *Org. Lett.* **2007,** *9*, 4979–4982.
11. Uyeda, C.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2008,** *130*, 9228–9229.
12. Williams, D. R.; Nag, P. P. *Claisen and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 33–43. (Review).
13. Alwarsh, S.; Ayinuola, K.; Dormi, S. S.; McIntosh, M. C. *Org. Lett.* **2013,** *15*, 3–5.

para-*Claisen rearrangement*

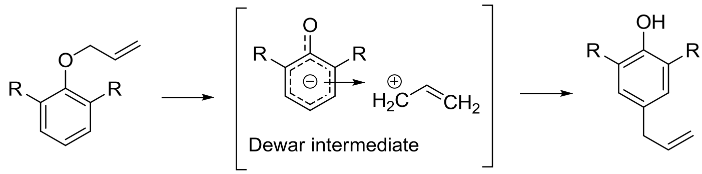
Further rearrangement of the normal *ortho*-Claisen rearrangement product gives the *para*-Claisen rearrangement product.



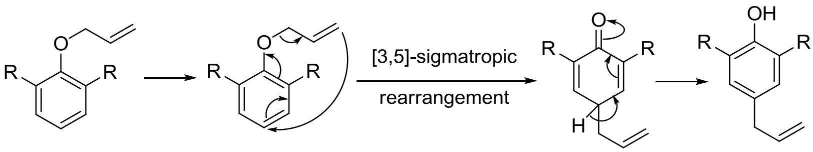
Mechanism 1:



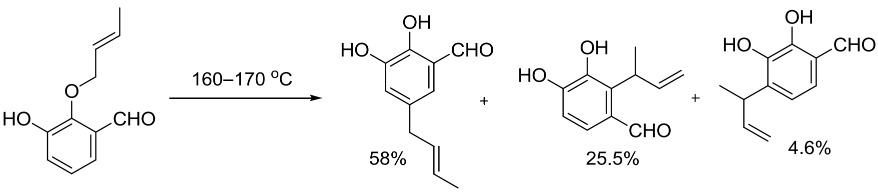
Mechanism 2:



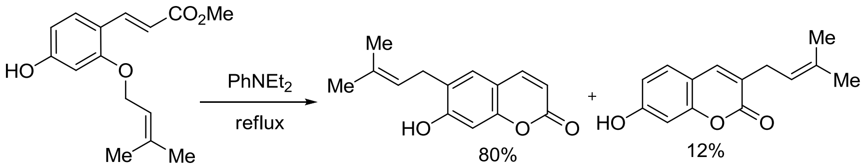
Mechanism 3:



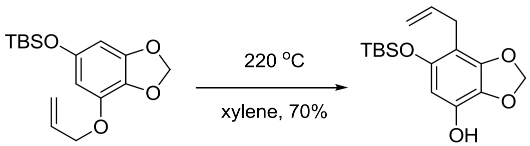
Example 1[6]



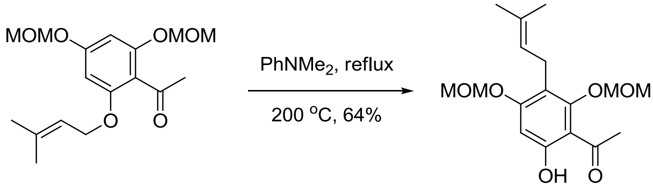
Example 2[7]



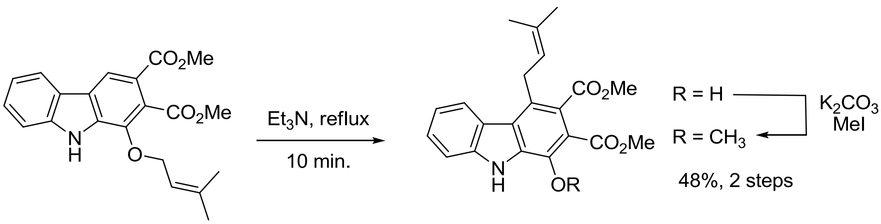
Example 3[8]



Example 4[10]



Example 5[11]



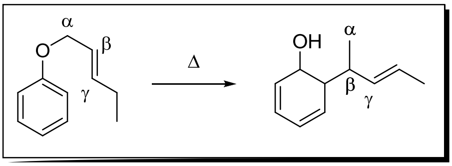
References

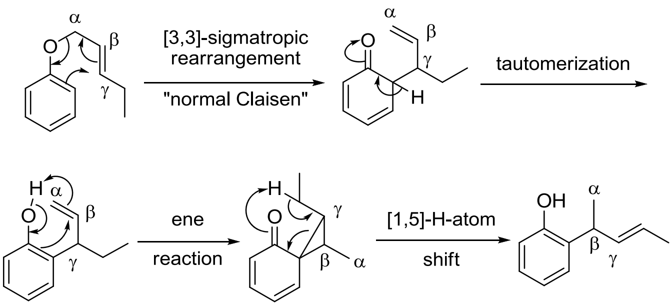
1. Alexander, E. R.; Kluiber, R. W. *J. Am. Chem. Soc.* **1951,** *73*, 4304–4306.
2. Rhoads, S. J.; Raulins, R.; Reynolds, R. D. *J. Am. Chem. Soc.* **1953,** *75*, 2531–2532.
3. Dyer, A.; Jefferson, A.; Scheinmann, F. *J. Org. Chem.* **1968,** *33*, 1259–1261.
4. Murray, R. D. H.; Lawrie, K. W. M. *Tetrahedron* **1979,** *35*, 697–699.
5. Cairns, N.; Harwood, L. M.; Astles, D. P. *J. Chem. Soc., Chem. Commun.* **1986,** 1264–1266.
6. Kilényi, S. N.; Mahaux, J.-M.; van Durme, E. *J. Org. Chem*. **1991,** *56*, 2591–2594.
7. Cairns, N.; Harwood, L. M.; Astles, D. P. *J. Chem. Soc., Perkin Trans. 1* **1994,** 3101–3107.

8. Pettus, T. R. R.; Inoue, M.; Chen, X.-T.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2000,** *122*, 6160–6168.
9. Al-Maharik, N.; Botting, N. P. *Tetrahedron* **2003,** *59*, 4177–4181.
10. Khupse, R. S.; Erhardt, P. W. *J. Nat. Prod*. **2007,** *70*, 1507–1509.
11. Jana, A. K.; Mal, D. *Chem. Commun.* **2010,** *46*, 4411–4413.

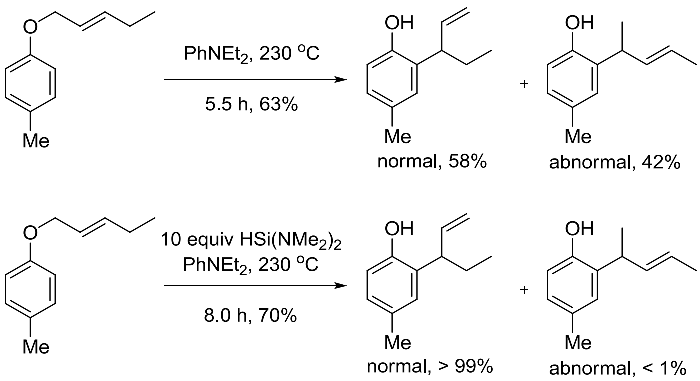
Abnormal Claisen rearrangement

Further rearrangement of the normal Claisen rearrangement product with the β-carbon becoming attached to the ring.

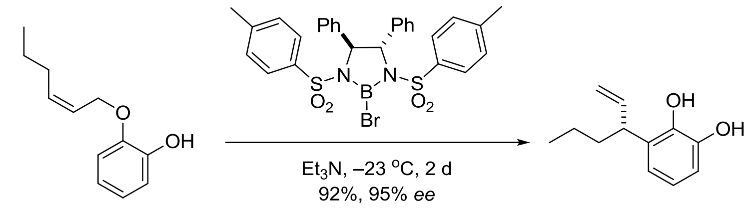




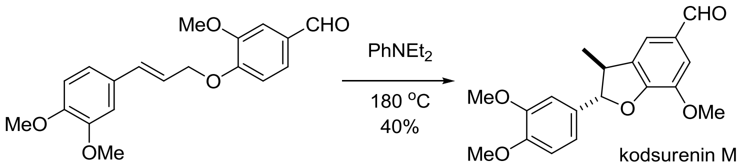
Example 1[3]



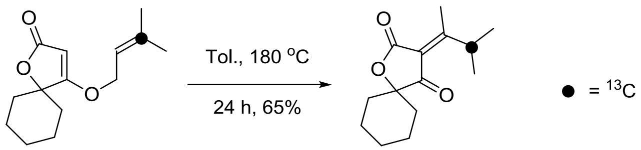
Example 2, Enantioselective aromatic Claisen rearrangement[4]



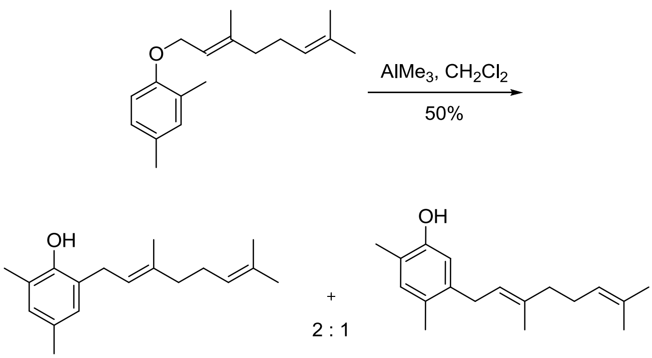
Example 3[5]



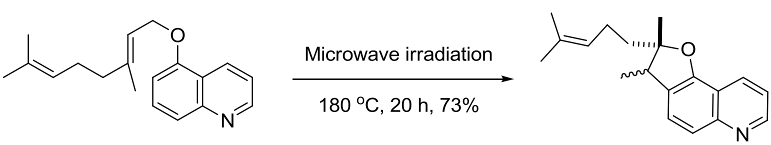
Example 4[6]



Example 5[7]



Example 6[10]

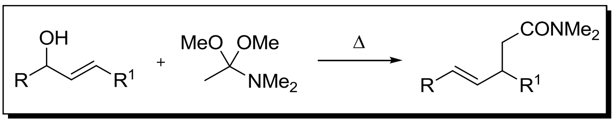


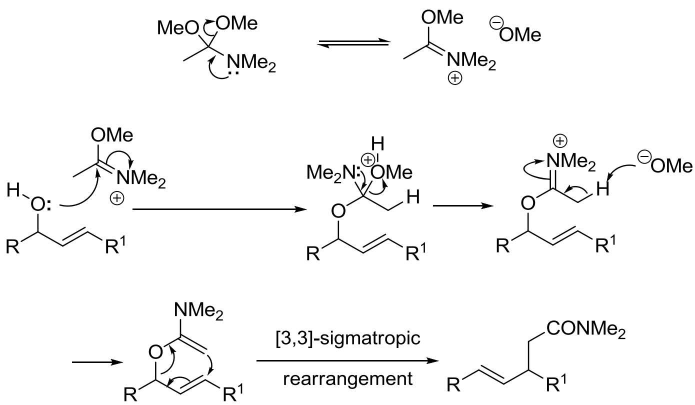
References

1. Hansen, H.-J. In *Mechanisms of Molecular Migrations;* vol. 3, Thyagarajan, B. S., ed.; Wiley-Interscience: New York, **1971,** pp 177–236. (Review).
2. Kilényi, S. N.; Mahaux, J.-M.; van Durme, E. *J. Org. Chem.* **1991,** *56*, 2591–2594.
3. Fukuyama, T.; Li, T.; Peng, G. *Tetrahedron Lett.* **1994,** *35*, 2145–2148.
4. Ito, H.; Sato, A.; Taguchi, T. *Tetrahedron Lett.* **1997,** *38*, 4815–4818.
5. Yi, W. M.; Xin, W. A.; Fu, P. X. *J. Chem. Soc., (S),* **1998,** 168.
6. Schobert, R.; Siegfried, S.; Gordon, G.; Mulholland, D.; Nieuwenhuyzen, M. *Tetrahedron Lett.* **2001,** *42*, 4561–4564.
7. Wipf, P.; Rodriguez, S. *Ad. Synth. Catal.* **2002,** *344*, 434–440.
8. Puranik, R.; Rao, Y. J.; Krupadanam, G. L. D. *Indian J. Chem., Sect. B* **2002,** *41B*, 868–870.
9. Williams, D. R.; Nag, P. P. *Claisen and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 33–87. (Review).
10. Torincsi, M.; Kolonits, P.; Fekete, J.; Novak, L. *Synth.Commun.* **2012,** *42*, 3187–3199.

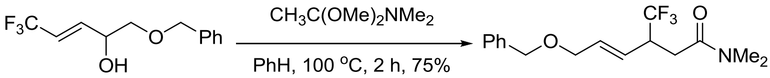
Eschenmoser–Claisen amide acetal rearrangement

[3,3]-Sigmatropic rearrangement of *N,O*-ketene acetals to yield γ,δ-unsaturated amides. Since Eschenmoser was inspired by Meerwein's observations on the interchange of amide, the Eschenmoser–Claisen rearrangement is sometimes known as the Meerwein–Eschenmoser–Claisen rearrangement.

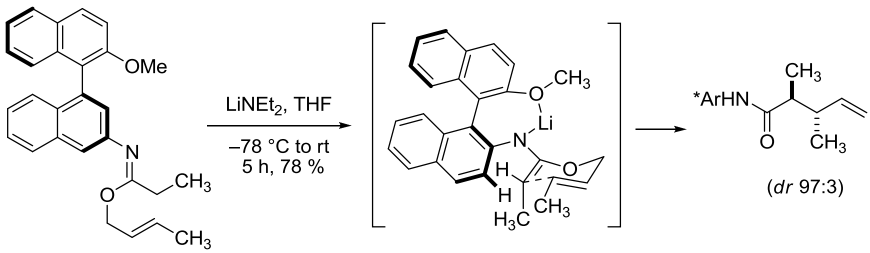




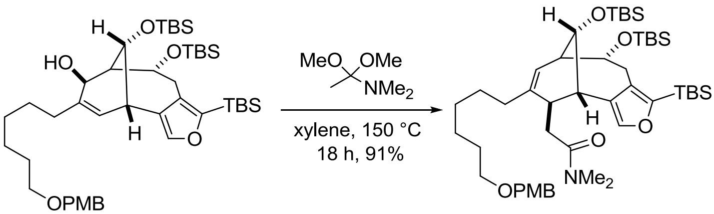
Example 1[4]



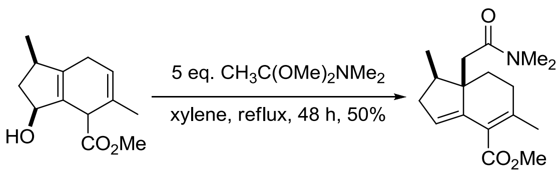
Example 2[5]



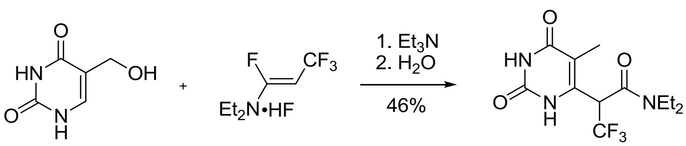
Example 3[6]



Example 4[8]



Example 5[9]



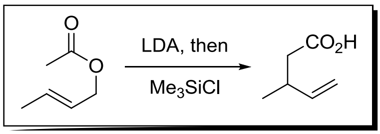
References

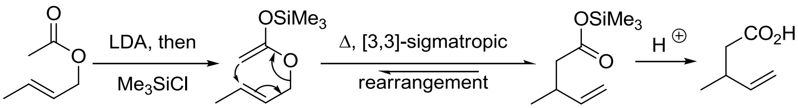
1. Meerwein, H.; Florian, W.; Schön, N.; Stopp, G. *Ann.* **1961,** *641*, 1–39.
2. Wick, A. E.; Felix, D.; Steen, K.; Eschenmoser, A. *Helv. Chim. Acta* **1964,** *47*, 2425–2429. Albert Eschenmoser (Switzerland, 1925–) is known for his work on,

among many others, the monumental total synthesis of Vitamin B_{12} with R. B. Woodward in 1973. He now holds dual appointments at both ETH Zürich and the Scripps Research Institute in La Jolla, CA.
3. Wipf, P. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 5*, 827–873. (Review).
4. Konno, T.; Nakano, H.; Kitazume, T. *J. Fluorine Chem*. **1997,** *86*, 81–87.
5. Metz, P.; Hungerhoff, B. *J. Org. Chem.***1997,** *62*, 4442–4448.
6. Kwon, O. Y.; Su, D. S.; Meng, D. F.; Deng, W.; D'Amico, D. C.; Danishefsky, S. J. *Angew. Chem. Int. Ed.* **1998,** *37*, 1877–1880.
7. Ito, H.; Taguchi, T. *Chem. Soc. Rev*. **1999,** *28*, 43–50. (Review).
8. Loh, T.-P.; Hu, Q.-Y. *Org. Lett*. **2001,** *3*, 279–281.
9. Castro, A. M. M. *Chem. Rev*. **2004,** *104*, 2939–3002. (Review).
10. Williams, D. R.; Nag, P. P. *Claisen and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 60–68. (Review).
11. Walkowiak, J.; Tomas-Szwaczyk, M.; Haufe, G.; Koroniak, H. *J. Fluorine Chem.* **2012,** *143,* 189–197.

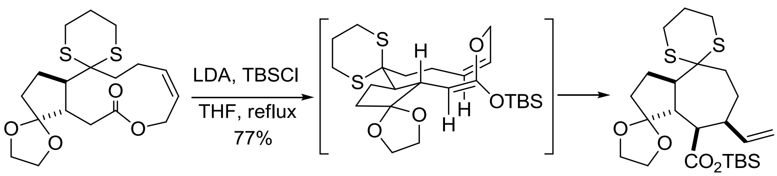
Ireland–Claisen (silyl ketene acetal) rearrangement

Rearrangement of allyl trimethylsilyl ketene acetal, prepared by reaction of allylic ester enolates with trimethylsilyl chloride, to yield γ,δ-unsaturated carboxylic acids. The Ireland–Claisen rearrangement seems to be advantageous to the other variants of the Claisen rearrangement in terms of *E/Z* geometry control and mild conditions.

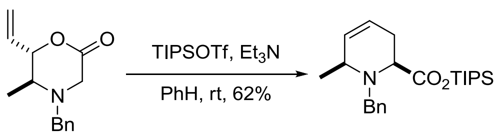




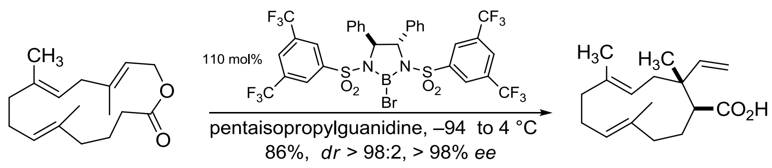
Example 1[2]



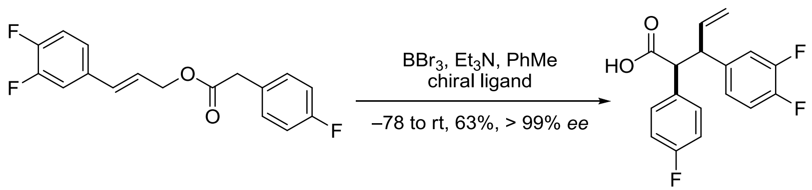
Example 2[3]



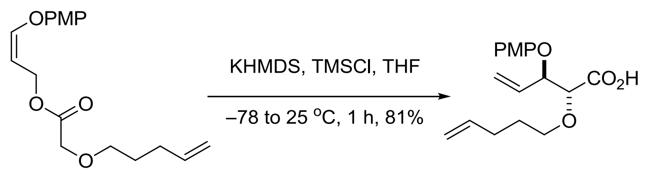
Example 3, Enantioselective ester enolate-Claisen Rearrangement[6]



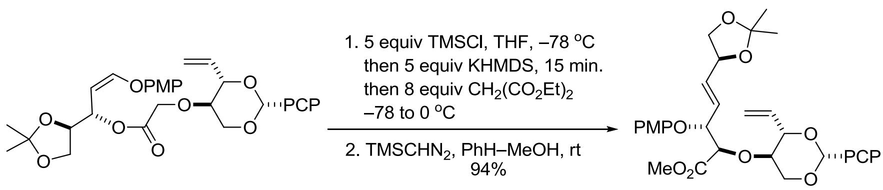
Example 4, A modified Ireland–Claisen rearrangement[8]



Example 5[9]



Example 6, chirality-transferring Ireland-Claisen rearrangement[11]



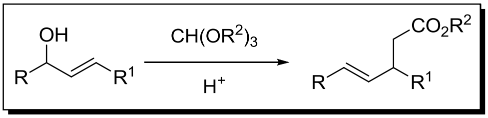
References

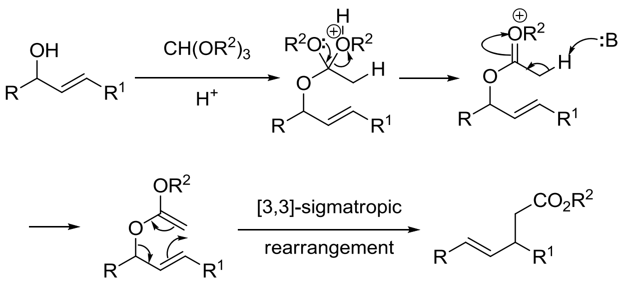
1. Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972,** *94*, 5897–5898. Also *J. Am. Chem. Soc.* **1976,** *98*, 2868–2877. Robert E. Ireland obtained his Ph.D. from William

S. Johnson before becoming a professor at the University of Virginia and later at the California Institute of Technology. He is now retired.
2. Begley, M. J.; Cameron, A. G.; Knight, D. W. *J. Chem. Soc., Perkin Trans. 1* **1986,** 1933–1938.
3. Angle, S. R.; Breitenbucher, J. G. *Tetrahedron Lett.* **1993,** *34*, 3985–3988.
4. Pereira, S.; Srebnik, M. *Aldrichimica Acta* **1993,** *26*, 17–29. (Review).
5. Ganem, B. *Angew. Chem. Int. Ed.* **1996,** *35*, 936–945. (Review).
6. Corey, E.; Kania, R. S. *J. Am. Chem. Soc.* **1996,** *118,* 1229–1230.
7. Chai, Y.; Hong, S.-p.; Lindsay, H. A.; McFarland, C.; McIntosh, M. C. *Tetrahedron* **2002,** *58*, 2905–2928. (Review).
8. Churcher, I.; Williams, S.; Kerrad, S.; Harrison, T.; Castro, J. L.; Shearman, M. S.; Lewis, H. D.; Clarke, E. E.; Wrigley, J. D. J.; Beher, D.; Tang, Y. S.; Liu, W. *J. Med. Chem.* **2003,** *46*, 2275–2278.
9. Fujiwara, K.; Goto, A.; Sato, D.; Kawai, H.; Suzuki, T. *Tetrahedron Lett.* **2005,** *46*, 3465–3468.
10. Williams, D. R.; Nag, P. P. *Claisen and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 45–51. (Review).
11. Nogoshi, K.; Domon, D.; Fujiwara, K.; Kawamura, N.; Katoono, R.; Kawai, H.; Suzuki, T. *Tetrahedron Lett.* **2013,** *54*, 676–680.

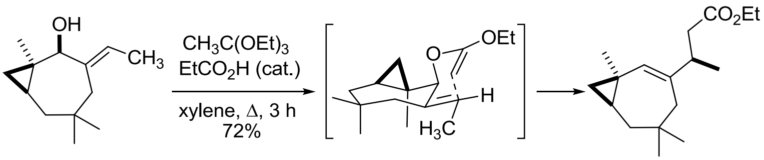
Johnson–Claisen orthoester rearrangement

Heating of an allylic alcohol with an excess of trialkyl orthoacetate in the presence of trace amounts of a weak acid gives a mixed orthoester. Mechanistically, the orthoester loses alcohol to generate the ketene acetal, which undergoes [3,3]-sigmatropic rearrangement to give a γ,δ-unsaturated ester.

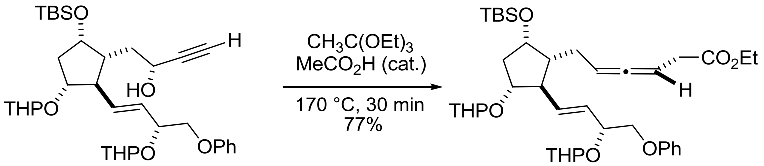




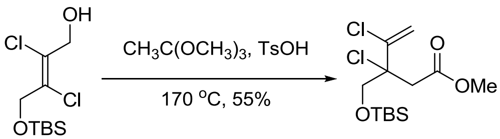
Example 1[2]



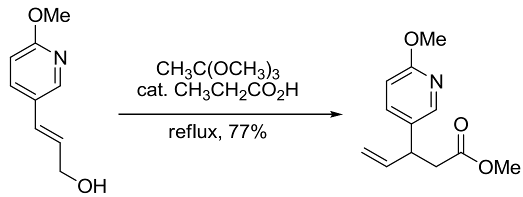
Example 2[3]



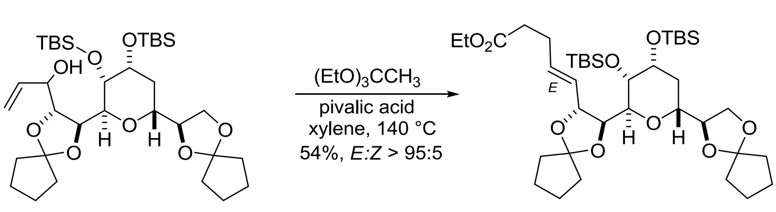
Example 3[4]



Example 4[9]



Example 5[10]



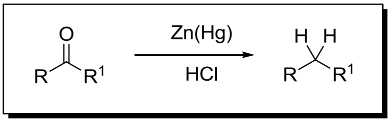
References

1. Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.-t.; Faulkner, D. J.; Peterson, M. R. *J. Am. Chem. Soc.* **1970,** *92*, 741–743. William S. Johnson (1913–1995) was born in New Rochelle, New York. He earned his Ph.D. in only two

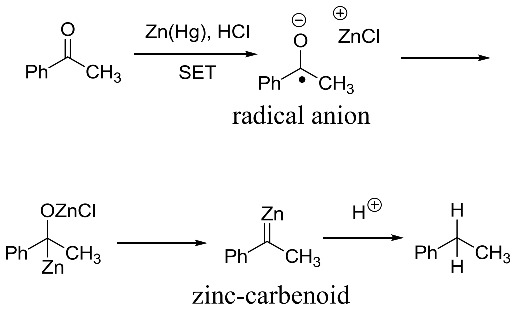
years at Harvard under Louis Fieser. He was a professor at the University of Wisconsin for 20 years before moving to Stanford University, where he was credited with building the modern-day Stanford Chemistry Department.
2. Paquette, L.; Ham, W. H. *J. Am. Chem. Soc.* **1987,** *109*, 3025–3036.
3. Cooper, G. F.; Wren, D. L.; Jackson, D. Y.; Beard, C. C.; Galeazzi, E.; Van Horn, A. R.; Li, T. T. *J. Org. Chem.* **1993,** *58*, 4280–4286.
4. Schlama, T.; Baati, R.; Gouverneur, V.; Valleix, A.; Falck, J. R.; Mioskowski, C. *Angew. Chem. Int. Ed.* **1998,** *37*, 2085–2087.
5. Giardiná, A.; Marcantoni, E.; Mecozzi, T.; Petrini, M. *Eur. J. Org. Chem.* **2001,** 713–718.
6. Funabiki, K.; Hara, N.; Nagamori, M.; Shibata, K.; Matsui, M. *J. Fluorine Chem.* **2003,** *122*, 237–242.
7. Montero, A.; Mann, E.; Herradón, B. *Eur. J. Org. Chem.* **2004,** 3063–3073.
8. Scaglione, J. B.; Rath, N. P.; Covey, D. F. *J. Org. Chem.* **2005,** *70*, 1089–1092.
9. Zartman, A. E.; Duong, L. T.; Fernandez-Metzler, C.; Hartman, G. D.; Leu, C.-T.; Prueksaritanont, T.; Rodan, G. A.; Rodan, S. B.; Duggan, M. E.; Meissner, R. S. *Bioorg. Med. Chem. Lett.* **2005,** *15*, 1647–1650.
10. Hicks, J. D.; Roush, W. R. *Org. Lett.* **2008,** *10*, 681–684.
11. Williams, D. R.; Nag, P. P. *Claisen and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 68–72. (Review).
12. Sydlik, S. A.; Swager, T. M. *Adv. Funct. Mater.* **2013,** *23,* 1873–1882.

Clemmensen reduction

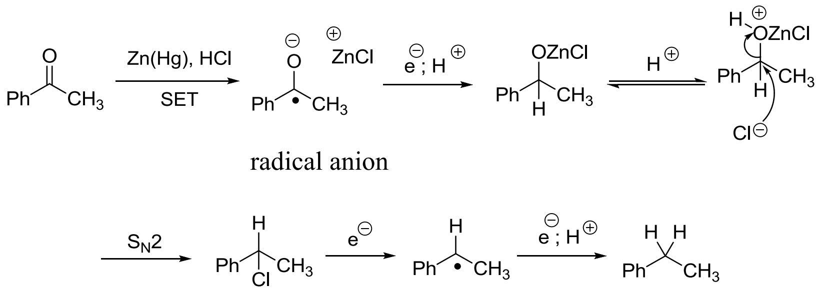
Reduction of aldehydes or ketones to the corresponding methylene compounds using amalgamated zinc in hydrochloric acid.



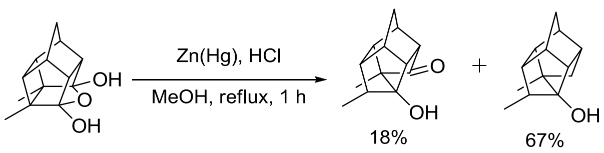
The zinc-carbenoid mechanism:[3]



The radical anion mechanism:

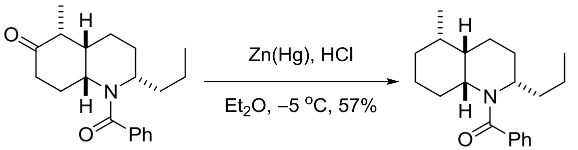


Example 1[5]

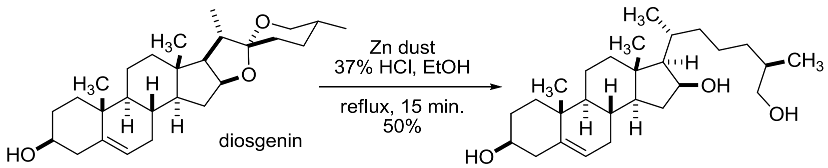


J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_64, © Springer International Publishing Switzerland 2014

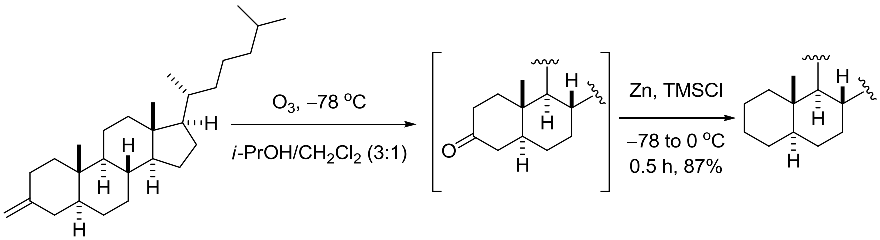
Example 2[6]



Example 3[7]



Example 4[9]

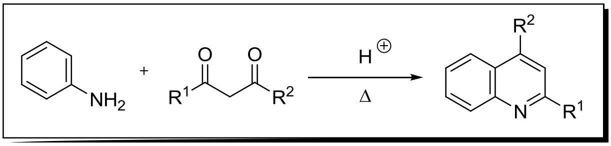


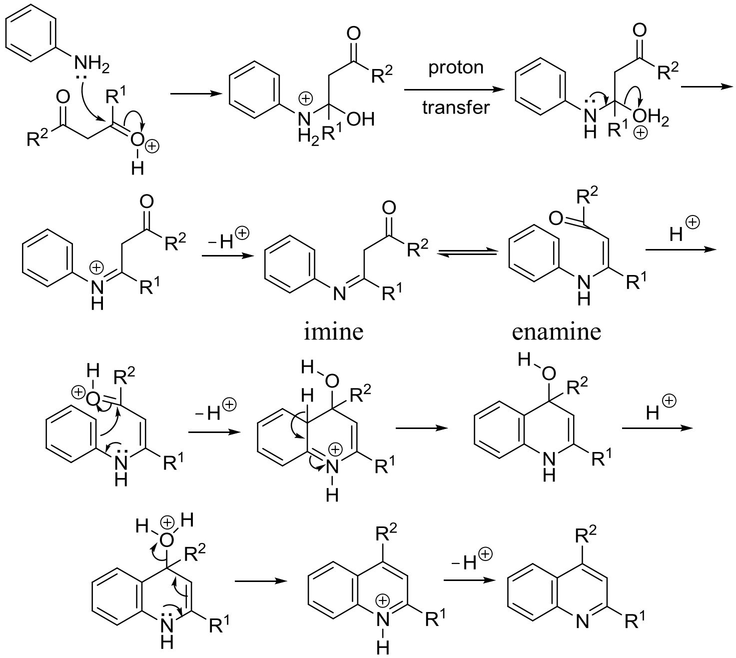
References

1. Clemmensen, E. *Ber.* **1913,** *46*, 1837–1843. Erik C. Clemmensen (1876–1941) was born in Odense, Denmark. He received the M.S. degree from the Royal Polytechnic Institute in Copenhagen. In 1900, Clemmensen immigrated to the United States, and worked at Parke, Davis and Company in Detroit (coincidently, this author's first employer!) as a research chemist for 14 years, where he discovered the reduction of carbonyl compounds with amalgamated zinc. Clemmensen later founded a few chemical companies and was the president of one of them, the Clemmensen Chemical Corporation in Newark, New Jersey.
2. Martin, E. L. *Org. React.* **1942,** *1*, 155–209. (Review).
3. Vedejs, E. *Org. React.* **1975,** *22*, 401–422. (Review).
4. Talpatra, S. K.; Chakrabarti, S.; Mallik, A. K.; Talapatra, B. *Tetrahedron* **1990,** *46*, 6047–6052.
5. Martins, F. J. C.; Viljoen, A. M.; Coetzee, M.; Fourie, L.; Wessels, P. L. *Tetrahedron* **1991,** *47*, 9215–9224.
6. Naruse, M.; Aoyagi, S.; Kibayashi, C. *J. Chem. Soc., Perkin Trans. 1* **1996,** 1113–1124.
7. Alessandrini, L.; et al. *Steroids* **2004,** *69*, 789–794.
8. Dey, S. P.; et al. *J. Indian Chem. Soc.* **2008**, *85*, 717–720.
9. Xu, S.; Toyama, T.; Nakamura, J.; Arimoto, H. *Tetrahedron Let.* **2010,** *51*, 4534–4537.

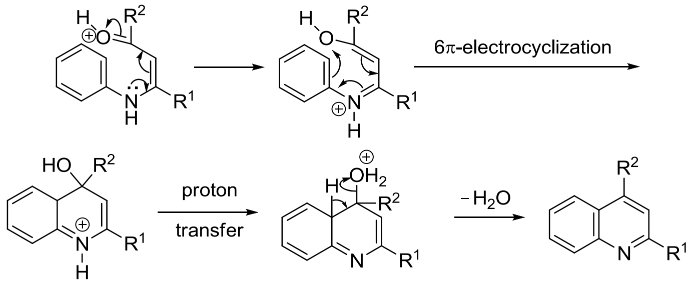
Combes quinoline synthesis

Acid-catalyzed condensation of anilines and β-diketones to assemble quinolines. *Cf.* Conrad–Limpach reaction.



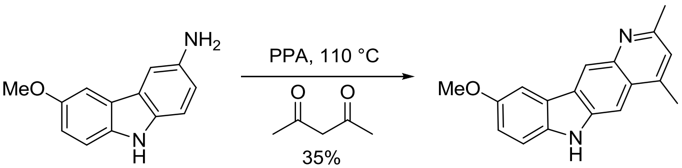


An electrocyclization mechanism is also possible:

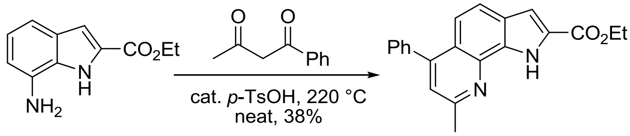


J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_65, © Springer International Publishing Switzerland 2014

Example 1[6]



Example 2[7]

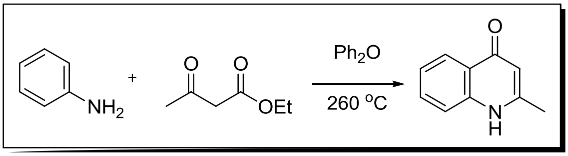


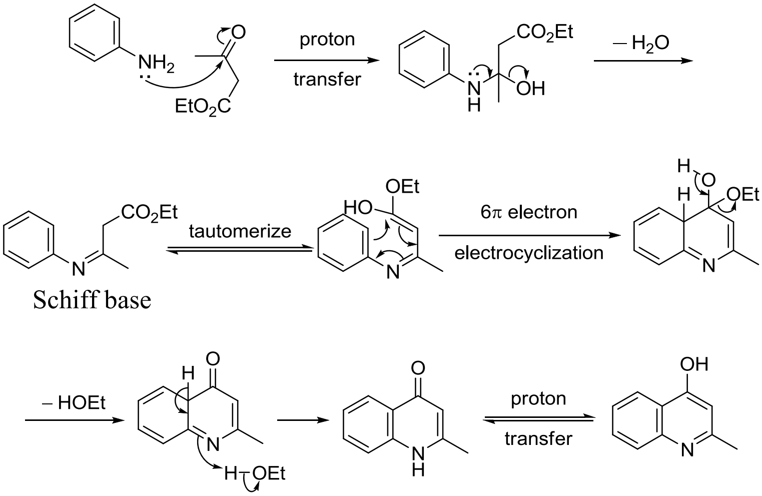
References

1. Combes, A. *Bull. Soc. Chim. Fr.* **1888,** *49*, 89. Alphonse-Edmond Combes (1858–1896) was born in St. Hippolyte-du-Fort, France. He apprenticed with Wurtz at Paris. He also collaborated with Charles Friedel of the Friedel–Crafts reaction fame. He became the president of the French Chemical Society in 1893 at the age of 35. His sudden death shortly after his 38th birthday was a great loss to organic chemistry.
2. Roberts, E. and Turner, E. *J. Chem Soc*. **1927,** 1832–1857. (Review).
3. Elderfield, R. C. In *Heterocyclic Compounds*, Elderfield, R. C., ed.; Wiley: New York, **1952,** vol. 4, 36–38. (Review).
4. Popp, F. D. and McEwen, W. E. *Chem. Rev*. **1958,** *58*, 321–401. (Review).
5. Jones, G. In *Chemistry of Heterocyclic Compounds*, Jones, G., ed.; Wiley & Sons, New York, **1977,** Quinolines *Vol. 32*, pp 119–125. (Review).
6. Alunni-Bistocchi, G.; Orvietani, P., Bittoun, P., Ricci, A.; Lescot, E. *Pharmazie* **1993,** *48*, 817–820.
7. El Ouar, M.; Knouzi, N.; Hamelin, J. *J. Chem. Res. (S)* **1998,** 92–93.
8. Curran, T. T. *Combes Quinoline Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 390–397. (Review).

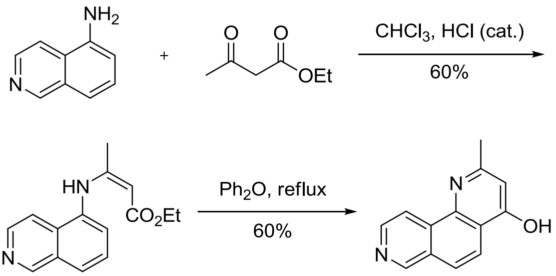
Conrad–Limpach reaction

Thermal or acid-catalyzed condensation of anilines with β-ketoesters leads to quinolin-4-ones. *Cf.* Combes quinoline synthesis.

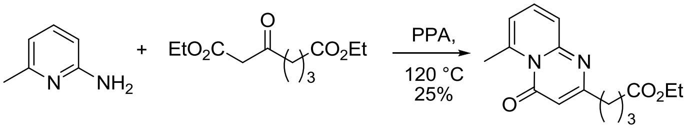




Example 1[3]



Example 2[7]



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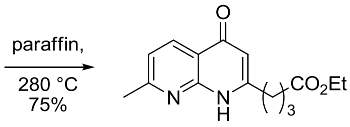
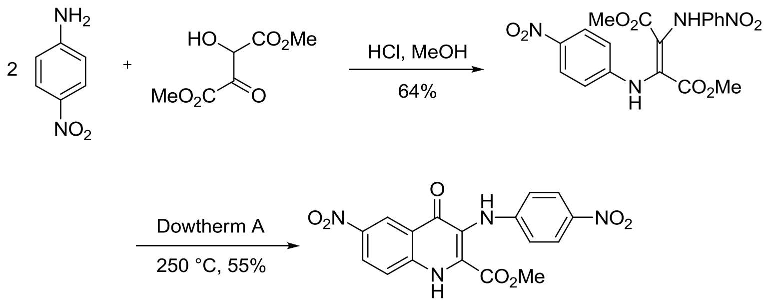
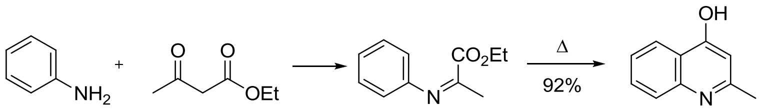
DOI 10.1007/978-3-319-03979-4_66, © Springer International Publishing Switzerland 2014



Example 3[8]



Example 4, Thermal Conrad–Limpach cyclization[11]

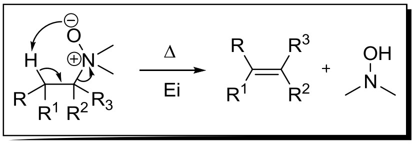


References

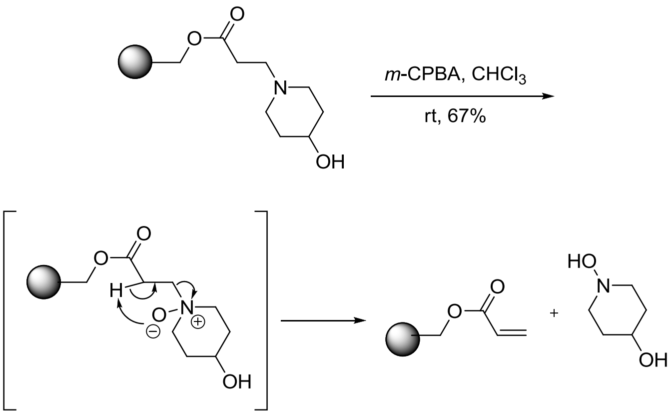
1. Conrad, M.; Limpach, L. *Ber.* **1887,** *20*, 944. Max Conrad (1848–1920), born in Munich, Germany, was a professor of the University of Würzburg, where he collaborated with Leonhard Limpach (1852–1933) on the synthesis of quinoline derivatives.
2. Manske, R. F. *Chem Rev*. **1942,** *30*, 113–114. (Review).
3. Misani, F.; Bogert, M. T. *J. Org. Chem.* **1945,** *10*, 347–365
4. Reitsema, R. H. *Chem. Rev*. **1948,** *43*, 43–68. (Review).
5. Elderfield, R. C. In *Chemistry of Heterocyclic Compounds*, Elderfield, R. C., Wiley & Sons, New York, **1952,** *vol. 4*, 31–36. (Review).
6. Jones, G. In *Heterocyclic Compounds*, Jones, G., ed.; Wiley & Sons, New York, **1977,** Quinolines, Vol 32, 137–151. (Review).
7. Deady, L. W.; Werden, D. M. *Synth. Commun*. **1987,** *17*, 319–328.
8. Kemp, D. S.; Bowen, B. R. *Tetrahedron Lett*. **1988,** *29*, 5077–5080.
9. Curran, T. T. *Conrad–Limpach Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 398–406. (Review).
10. Chan, B. K.; Ciufolini, M. A. *J. Org. Chem.* **2008,** *72*, 8489–8495.
11. Lengyel, L.; Nagy, T. Z.; Sipos, G.; Jones, R.; Dormán, G.; Üerge, L.; Darvas, F. *Tetrahedron Lett*. **2012,** *53*, 738–743.

Cope elimination reaction

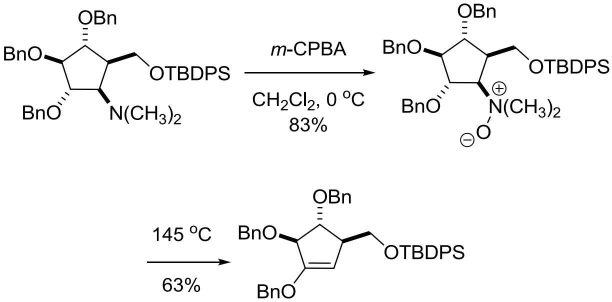
Thermal elimination of *N*-oxides to olefins and *N*-hydroxyl amines.



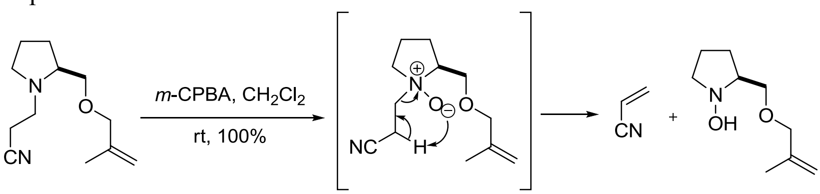
Example 1, Solid-phase Cope elimination[5]



Example 2[6]



Example 3[8]



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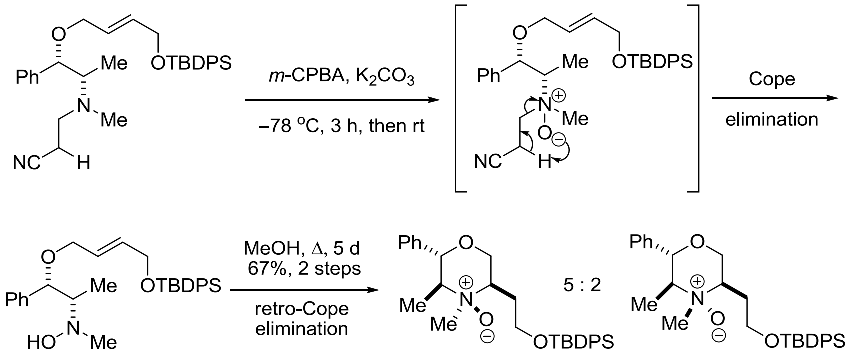
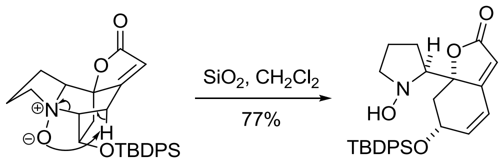
DOI 10.1007/978-3-319-03979-4_67, © Springer International Publishing Switzerland 2014

Example 4, Retro-Cope elimination[9]



Example 5[12]

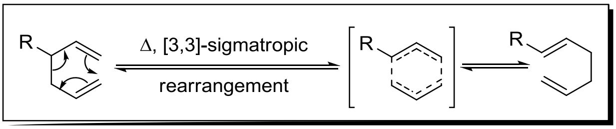


References

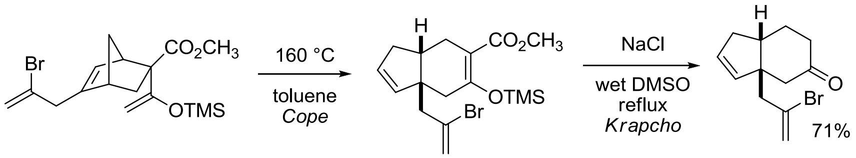
1. Cope, A. C.; Foster, T. T.; Towle, P. H. *J. Am. Chem. Soc.* **1949,** *71*, 3929–3934. Arthur Clay Cope (1909–1966) was born in Dunreith, Indiana. He was a professor and head at MIT where he discovered the Cope elimination reaction after he taught at Bryn Mawr and Columbia where he discovered the Cope rearrangement. The Arthur Cope Award is a prestigious award in organic chemistry administered by the American Chemical Society.
2. Cope, A. C.; Trumbull, E. R. *Org. React.* **1960,** *11*, 317–493. (Review).
3. DePuy, C. H.; King, R. W. *Chem. Rev.* **1960,** *60*, 431–457. (Review).
4. Gallagher, B. M.; Pearson, W. H. *Chemtracts: Org. Chem*. **1996,** *9*, 126–130. (Review).
5. Sammelson, R. E.; Kurth, M. J. *Tetrahedron Lett*. **2001,** *42*, 3419–3422.
6. Vasella, A.; Remen, L. *Helv. Chim. Acta.* **2002,** *85*, 1118–1127.
7. Garcia Martinez, A.; Teso Vilar, E.; Garcia Fraile, A.; de la Moya Cerero, S.; Lora Maroto, B. *Tetrahedron: Asymmetry* **2002,** *13*, 17–19.
8. O'Neil, I. A.; Ramos, V. E.; Ellis, G. L.; Cleator, E.; Chorlton, A. P.; Tapolczay, D. J.; Kalindjian, S. B. *Tetrahedron Lett*. **2004,** *45*, 3659–3661.
9. Henry, N.; O'Meil, I. A. *Tetrahedron Lett*. **2007,** *48*, 1691–1694.
10. Fuchter, M. J. *Cope Elimination Reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 342–353. (Review).
11. Bourgeois, J.; Dion, I.; Cebrowski, P. H.; Loiseau, F.; Bedard, A.-C.; Beauchemin, A. M. *J. Am. Chem. Soc.* **2009,** *131*, 874–875.
12. Miyatake-Ondozabal, H.; Bannwart, L. M.; Gademann, K. *Chem. Commun*. **2013,** *49*, 1921–1923.

Cope rearrangement

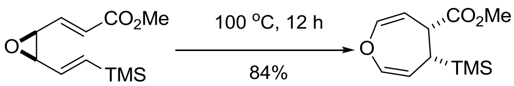
The Cope, aza-Cope, anionic oxy-Cope, and oxy-Cope rearrangements belong to the category of *[3,3]-sigmatropic rearrangements*. Since it is a concerted process, the arrow pushing here is only illustrative. This reaction is an equilibrium process. *Cf.* Claisen rearrangement.



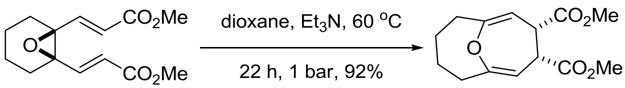
Example 1[4]



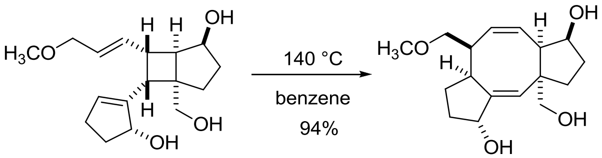
Example 2[6]



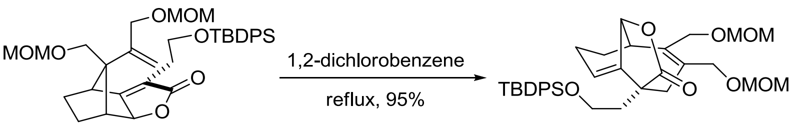
Example 3[9]



Example 4[10]



Example 5[11]



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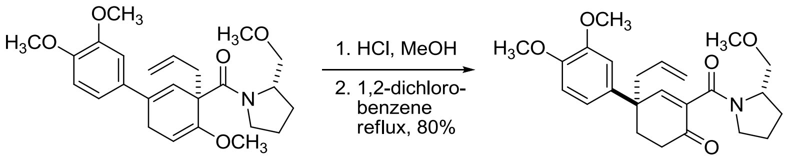
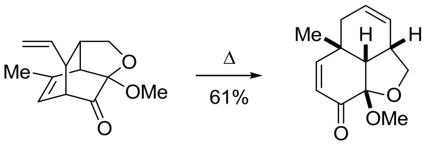
DOI 10.1007/978-3-319-03979-4_68, © Springer International Publishing Switzerland 2014

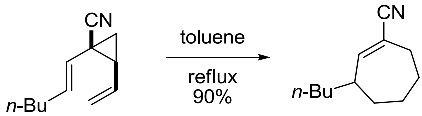
Example 6[12]



Example 7, Cope rearrangement[14]



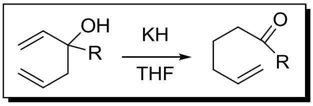
Example 8[15]

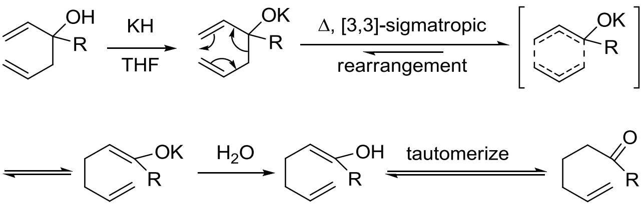


References

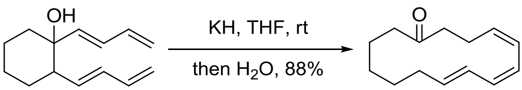
1. Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940,** *62*, 441–444.
2. Frey, H. M.; Walsh, R. *Chem. Rev.* **1969,** *69*, 103–124. (Review).
3. Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975,** *22*, 1–252. (Review).
4. Wender, P. A.; Schaus, J. M. White, A. W. *J. Am. Chem. Soc.* **1980,** *102*, 6159–6161.
5. Hill, R. K. In *Comprehensive Organic Synthesis* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 5*, 785–826. (Review).
6. Chou, W.-N.; White, J. B.; Smith, W. B. *J. Am. Chem. Soc.* **1992,** *114*, 4658–4667.
7. Davies, H. M. L. *Tetrahedron* **1993,** *49*, 5203–5223. (Review).
8. Miyashi, T.; Ikeda, H.; Takahashi, Y. *Acc. Chem. Res.* **1999,** *32*, 815–824. (Review).
9. Von Zezschwitz, P.; Voigt, K.; Lansky, A.; Noltemeyer, M.; De Meijere, A. *J. Org. Chem.* **1999,** *64*, 3806–3812.
10. Lo, P. C.-K.; Snapper, M. L. *Org. Lett.* **2001,** *3*, 2819–2821.
11. Clive, D. L. J.; Ou, L. *Tetrahedron Lett.* **2002,** *43*, 4559–4563.
12. Malachowski, W. P.; Paul, T.; Phounsavath, S. *J. Org. Chem.* **2007,** *72*, 6792–6796.
13. Mullins, R. J.; McCracken, K. W. *Cope and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 88–135. (Review).
14. Ren, H.; Wulff, W. D. *Org. Lett.* **2013,** *15*, 242–245.
15. Yamada, T.; Yoshimura, F.; Tanino, K. *Tetrahedron Lett.* **2013,** *54*, 522–525.

Anionic oxy-Cope rearrangement

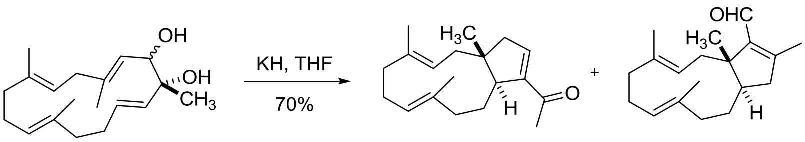




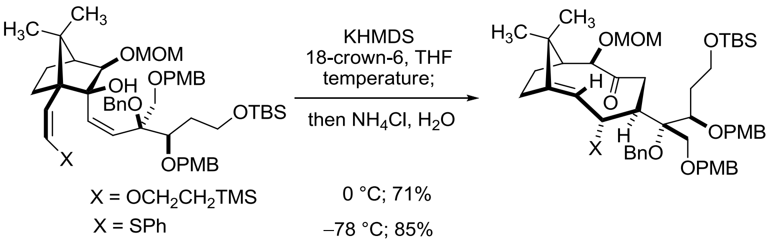
Example 1[1]



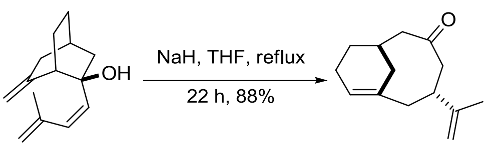
Example 2[4]



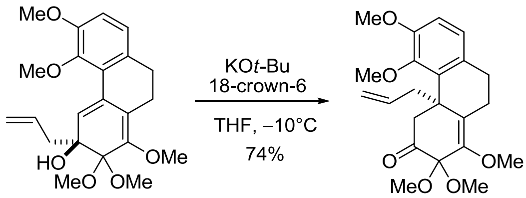
Example 3[5]



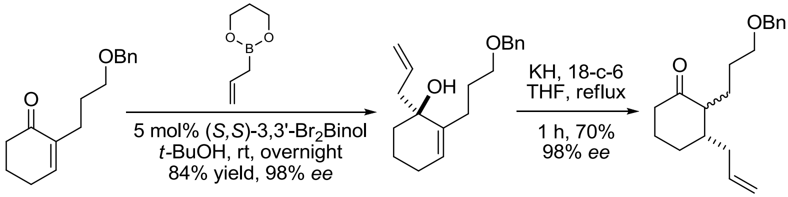
Example 4[8]



Example 5[9]



Example 6[11]

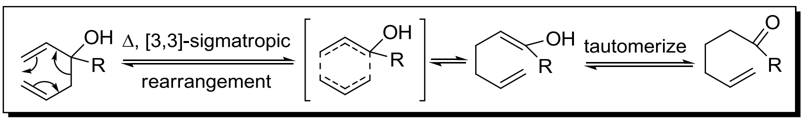


References

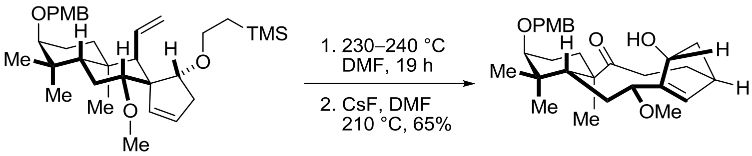
1. Wender, P. A.; Sieburth, S. M.; Petraitis, J. J.; Singh, S. K. *Tetrahedron* **1981,** *37*, 3967–3975.
2. Wender, P. A.; Ternansky, R. J.; Sieburth, S. M. *Tetrahedron Lett*. **1985,** *26*, 4319–4322.
3. Paquette, L. A. *Tetrahedron* **1997,** *53*, 13971−14020. (Review).
4. Corey, E. J.; Kania, R. S. *Tetrahedron Lett.* **1998,** *39*, 741–744.
5. Paquette, L. A.; Reddy, Y. R.; Haeffner, F.; Houk, K. N. *J. Am. Chem. Soc.* **2000,** *122*, 740–741.
6. Voigt, B.; Wartchow, R.; Butenschon, H. *Eur. J. Org. Chem*. **2001,** 2519–2527.
7. Hashimoto, H.; Jin, T.; Karikomi, M.; Seki, K.; Haga, K.; Uyehara, T. *Tetrahedron Lett*. **2002,** *43*, 3633–3636.
8. Gentric, L.; Hanna, I.; Huboux, A.; Zaghdoudi, R. *Org. Lett.* **2003,** *5*, 3631–3634.
9. Jones, S. B.; He, L.; Castle, S. L. *Org. Lett.* **2006,** *8*, 3757–3760.
10. Mullins, R. J.; McCracken, K. W. *Cope and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 88−135. (Review).
11. Taber, D. F.; Gerstenhaber, D. A.; Berry, J. F. *J. Org. Chem*. **2013,** *76*, 7614–7617.

Oxy-Cope rearrangement

While the anionic oxy-Cope rearrangements work at low temperature, the oxy-Cope rearrangements require high temperature but provide a thermodynamic sink.



Example 1[2]



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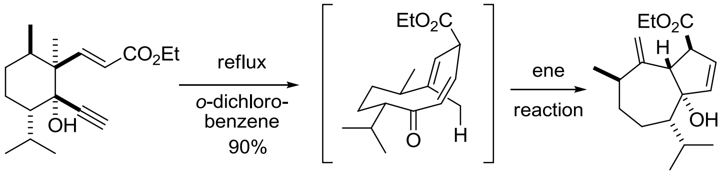
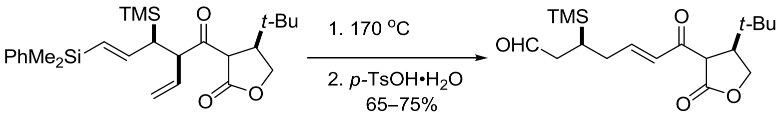
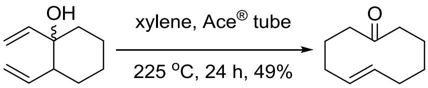


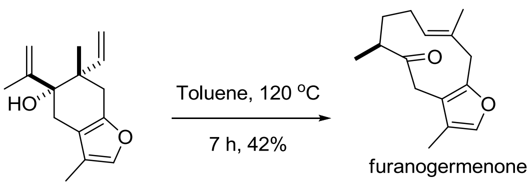
Example 3[4]



Example 4[6]



Example 5[8]



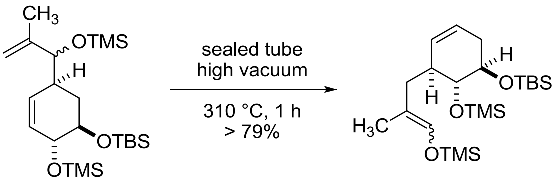
References

1. Paquette, L. A. *Angew. Chem. Int. Ed.* **1990,** *29*, 609–626. (Review).
2. Paquette, L. A.; Backhaus, D.; Braun, R. *J. Am. Chem. Soc.* **1996,** *118*, 11990–11991.
3. Srinivasan, R.; Rajagopalan, K. *Tetrahedron Lett.* **1998,** *39*, 4133–4136.
4. Schneider, C.; Rehfeuter, M. *Chem. Eur. J.* **1999,** *5*, 2850–2858.
5. Schneider, C. *Synlett* **2001,** 1079–1091. (Review on siloxy-Cope rearrangement).
6. DiMartino, G.; Hursthouse, M. B.; Light, M. E.; Percy, J. M.; Spencer, N. S.; Tolley, M. *Org. Biomol. Chem.* **2003,** *1*, 4423–4434.

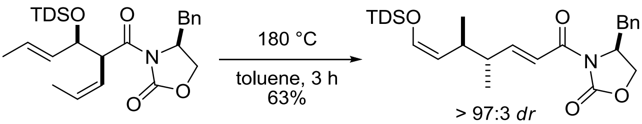
7. Mullins, R. J.; McCracken, K. W. *Cope and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 88–135. (Review).
8. Anagnostaki, E. E.; Zografos, A. L. *Org. Lett*. **2013,** *15*, 152–155.

Siloxy-Cope rearrangement

Example 1[1]

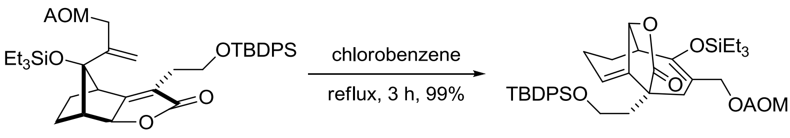


Example 2[2]



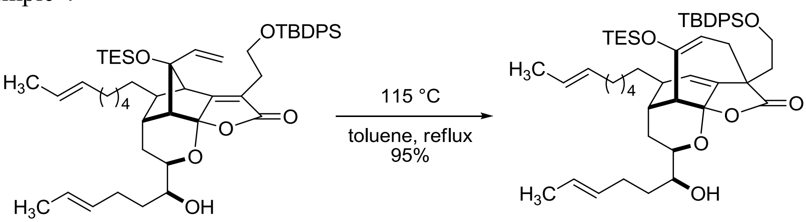
TDS = thexyldimethylsilyl

Example 3[3]

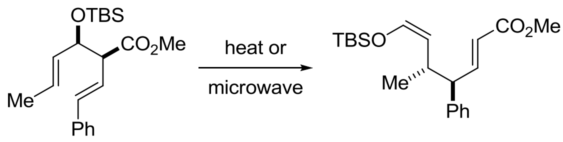


AOM = *p*-Anisyloxymethyl = *p*-$MeOC_6H_4OCH_2$-

Example 4[4]



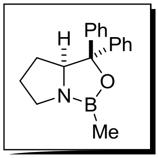
Example 5, Tandem aldol reaction/siloxy-Cope rearrangement[6]



References

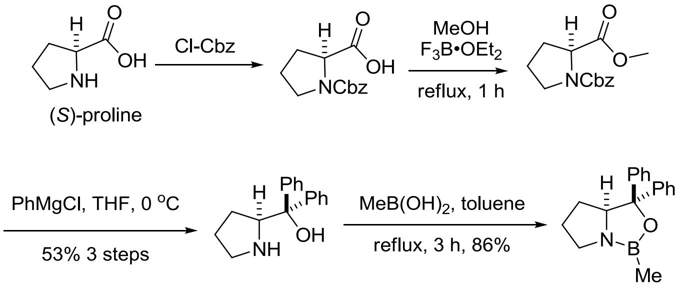
1. Askin, D.; Angst, C.; Danishefsky, D. J. *J. Org. Chem.* **1987,** *52*, 622–635.
2. Schneider, C. *Eur. J. Org. Chem.* **1998,** 1661–1663.
3. Clive, D. L. J.; Sun, S.; Gagliardini, V.; Sano, M. K. *Tetrahedron Lett.* **2000,** *41*, 6259–6263.
4. Bio, M. M.; Leighton, J. L. *J. Org. Chem.* **2003,** *68*, 1693–1700.
5. Mullins, R. J.; McCracken, K. W. *Cope and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 88–135. (Review).
6. Davies, H. M. L.; Lian, Y. *Acc. Chem. Res.* **2013,** *45*, 923–935. (Review).

Corey–Bakshi–Shibata (CBS) reagent

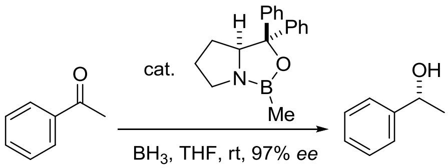


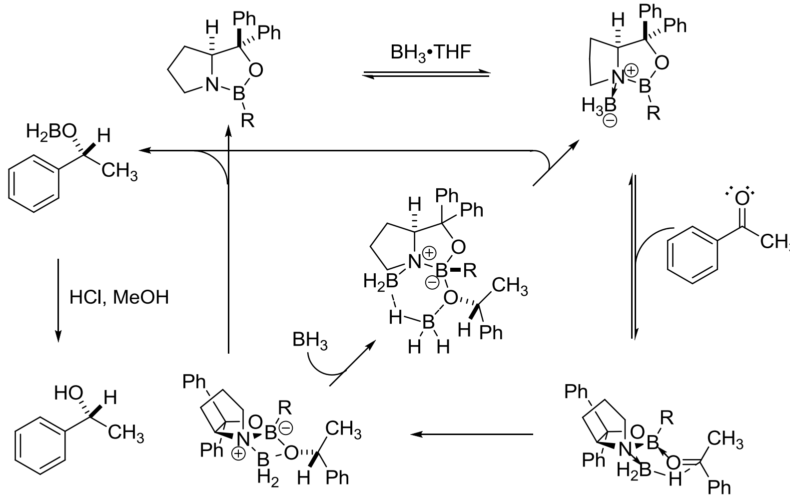
The CBS (Corey–Bakshi–Shibata) reagent is a chiral catalyst derived from proline. Also known as Corey's oxazaborolidine, it is used in enantioselective borane reduction of ketones, asymmetric Diels–Alder reactions and [3 + 2] cycloadditions.

Preparation[1,3]



The mechanism and catalytic cycle:[1,3]





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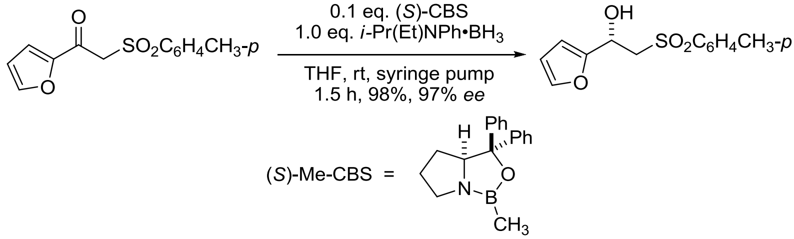
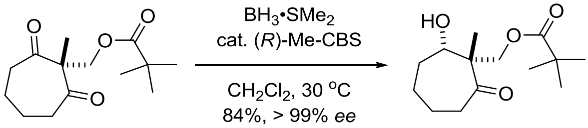
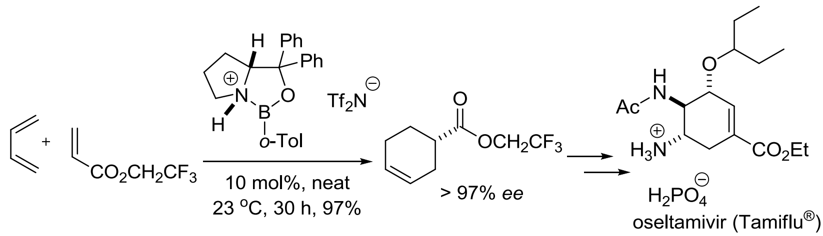
Example 1[6]



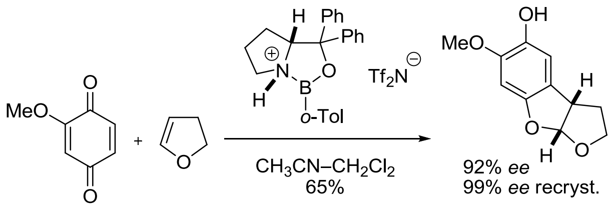
Example 2[9]



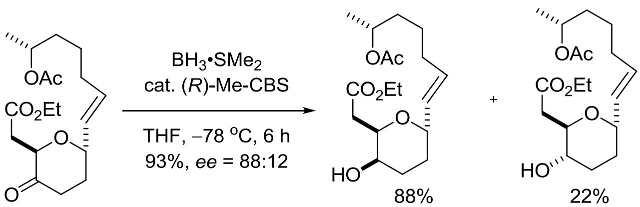
Example 3[11]



Example 4, Asymmetric [3 + 2]-cycloaddition[10]



Example 5[13]

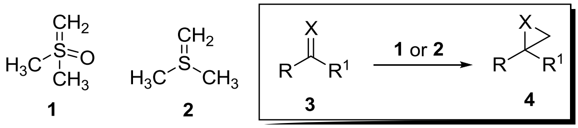


References

1. (a) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987,** *109*, 5551–5553. (b) Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C.-P.; Singh, V. K. *J. Am. Chem. Soc.* **1987,** *109*, 7925–7926. (c) Corey, E. J.; Shibata, S.; Bakshi, R. K. *J. Org. Chem.* **1988,** *53*, 2861–2863.
2. Reviews: (a) Corey, E. J. *Pure Appl. Chem*. **1990,** *62*, 1209–1216. (b) Wallbaum, S.; Martens, J. *Tetrahedron: Asymm*. **1992,** *3*, 1475–1504. (c) Singh, V. K. *Synthesis* **1992,** 605–617. (d) Deloux, L.; Srebnik, M. *Chem. Rev*. **1993,** *93*, 763–784. (e) Taraba, M.; Palecek, J. *Chem. Listy* **1997,** *91*, 9–22. (f) Corey, E. J.; Helal, C. J. *Angew. Chem. Int. Ed*. **1998,** *37*, 1986–2012. g) Corey, E. J. *Angew. Chem. Int. Ed*. **2002,** *41*, 1650–1667. (h) Itsuno, S. *Org. React*. **1998,** *52*, 395–576. (i) Cho, B. T. *Aldrichimica Acta* **2002,** *35*, 3–16. (j) Glushkov, V. A.; Tolstikov, A. G. *Russ. Chem. Rev*. **2004,** *73*, 581–608. (k) Cho, B .T. *Tetrahedron* **2006,** *62*, 7621–7643.
3. (a) Mathre, D. J.; Thompson, A. S.; Douglas, A. W.; Hoogsteen, K.; Carroll, J. D.; Corley, E. G.; Grabowski, E. J. J. *J. Org. Chem.* **1993,** *58*, 2880–2888. (b) Xavier, L. C.; Mohan, J. J.; Mathre, D. J.; Thompson, A. S.; Carroll, J. D.; Corley, E. G.; Desmond, R. *Org. Synth.* **1997,** *74*, 50–71.
4. Corey, E. J.; Helal, C. J. *Tetrahedron Lett.* **1996,** *37*, 4837–4840.
5. Clark, W. M.; Tickner-Eldridge, A. M.; Huang, G. K.; Pridgen, L. N.; Olsen, M. A.; Mills, R. J.; Lantos, I.; Baine, N. H. *J. Am. Chem. Soc.* **1998,** *120*, 4550–4551.
6. Cho, B. T.; Kim, D. J. *Tetrahedron: Asymmetry* **2001,** *12*, 2043–2047.
7. Price, M. D.; Sui, J. K.; Kurth, M. J.; Schore, N. E. *J. Org. Chem.* **2002,** *67*, 8086–8089.
8. Degni, S.; Wilen, C.-E.; Rosling, A. *Tetrahedron: Asymmetry* **2004,** *15*, 1495–1499.
9. Watanabe, H.; Iwamoto, M.; Nakada, M. *J. Org. Chem.* **2005,** *70*, 4652–4658.
10. Zhou, G.; Corey, E. J. *J. Am. Chem. Soc.* **2005,** *127*, 11958–11959.
11. Yeung, Y.-Y.; Hong, S.; Corey, E. J. *J. Am. Chem. Soc*. **2006,** *128*, 6310–6311.
12. Patti, A.; Pedotti, S. *Tetrahedron: Asymmetry* **2008,** *19*, 1891–1897.
13. Sridhar, Y.; Srihari, P. *Eur. J. Org. Chem.* **2013,** 578–587.

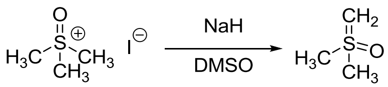
Corey–Chaykovsky reaction

The Corey–Chaykovsky reaction entails the reaction of a sulfur ylide, either dimethylsulfoxonium methylide **1** (Corey's ylide) or dimethylsulfonium methylide **2**, with electrophile **3** such as carbonyl, olefin, imine, or thiocarbonyl, to offer **4** as the corresponding epoxide, cyclopropane, aziridine, or thiirane.

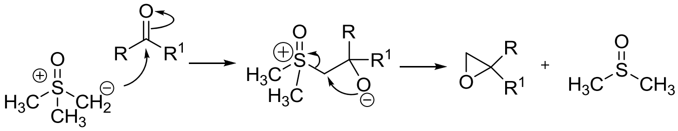


X = O, CH_2, NR^2, S, $CHCOR^3$, $CHCO_2R^3$, $CHCONR_2$, CHCN

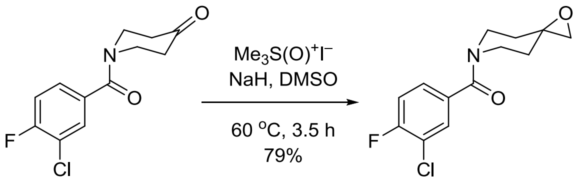
Preparation[1]



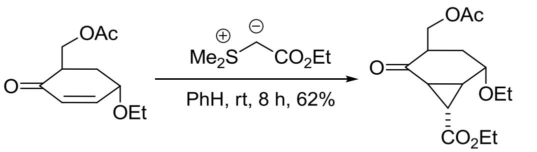
Mechanism[1]



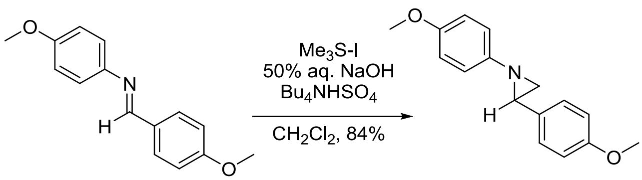
Example 1[11]



Example 2[9]



Example 3[10]



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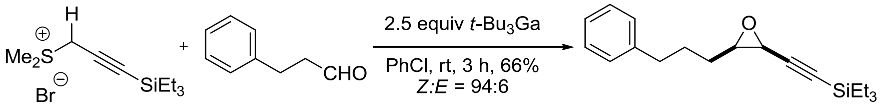
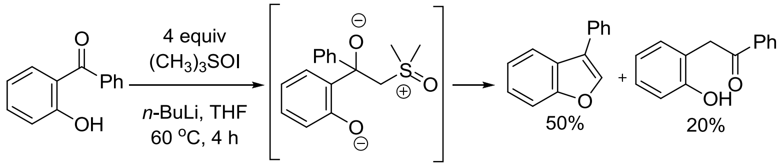
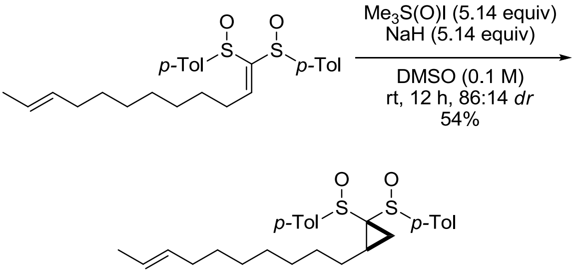
Example 4[14]



Example 5[15]



Example 6[16]



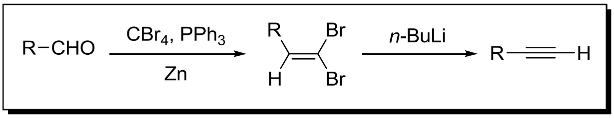
References

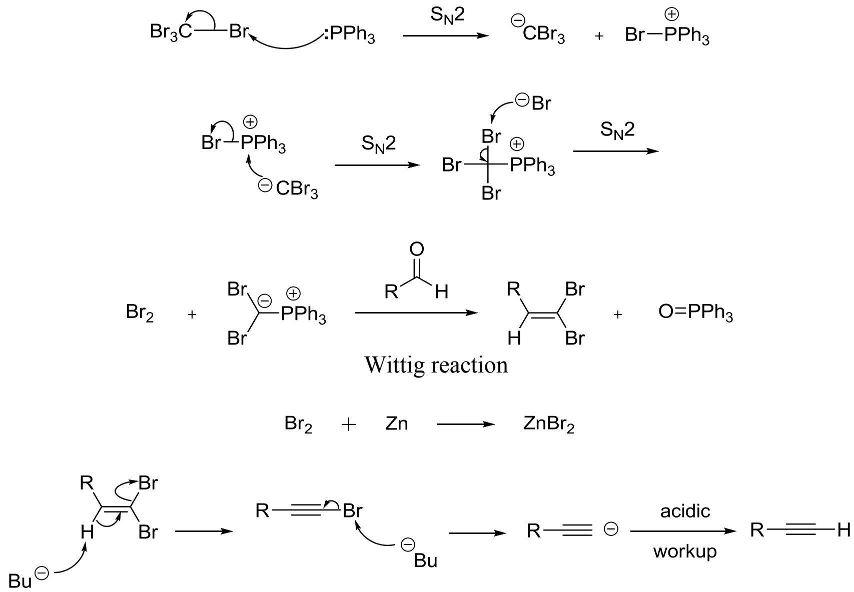
1 (a) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962,** *84*, 867–868. (b) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962,** *84*, 3782. (c) Corey, E. J.; Chaykovsky, M. *Tetrahedron Lett.* **1963,** 169–171. (d) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1964,** *86*, 1639–1640. (e) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965,** *87*, 1353–1364.
2 Okazaki, R.; Tokitoh, N. In *Encyclopedia of Reagents in Organic Synthesis;* Paquette, L. A., Ed.; Wiley: New York, **1995,** pp 2139–2141. (Review).
3 Ng, J. S.; Liu, C. In *Encyclopedia of Reagents in Organic Synthesis;* Paquette, L. A., Ed.; Wiley: New York, **1995,** pp 2159–2165. (Review).
4 Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylides;* Academic Press: New York, **1975**. (Review).
5 Block, E. *Reactions of Organosulfur Compounds* Academic Press: New York, **1978**. (Review).
6 Gololobov, Y. G.; Nesmeyanov, A. N. *Tetrahedron* **1987,** *43*, 2609–2651. (Review).
7 Aubé, J. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Ed.; Pergamon: Oxford, **1991,** *Vol. 1*, pp 820–825. (Review).
8 Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* **1997,** *97*, 2341–2372. (Review).

9 Rosenberger, M.; Jackson, W.; Saucy, G. *Helv. Chim. Acta* **1980,** *63*, 1665−1674.
10 Tewari, R. S.; Awatsthi, A. K.; Awasthi, A. *Synthesis* **1983,** 330−331.
11 Vacher, B.; Bonnaud, B. Funes, P.; Jubault, N.; Koek, W.; Assie, M.-B.; Cosi, C.; Kleven, M. *J. Med. Chem.* **1999,** *42*, 1648−1660.
12 Chandrasekhar, S.; Narasihmulu, Ch.; Jagadeshwar, V.; Reddy, K. V. *Tetrahedron Lett.* **2003,** *44*, 3629−3630.
13 Li, J. J. *Corey–Chaykovsky Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 1−14. (Review).
14 Nishimura, Y.; Shiraishi, T.; Yamaguchi, M. *Tetrahedron Lett.* **2008,** *49*, 3492−3495.
15 Chittimalla, S. K.; Chang, T.-C.; Liu, T.-C.; Hsieh, H.-P.; Liao, C.-C. *Tetrahedron* **2008,** *64*, 2586−2595.
16 Palko, J. W.; Buist, P. H.; Manthorpe, J. M. *Tetrahedron: Asymmetry* **2013,** *24*, 165−168.

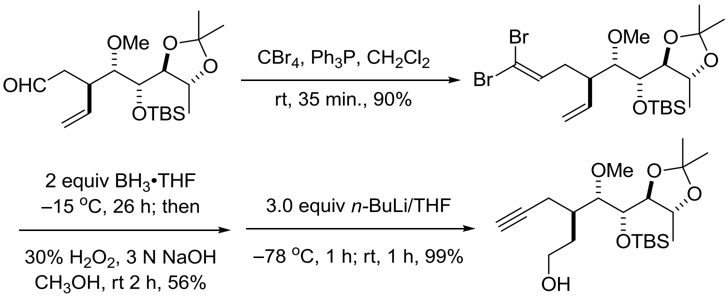
Corey–Fuchs reaction

One-carbon homologation of an aldehyde to dibromoolefin, which is then treated with *n*-BuLi to produce a terminal alkyne.

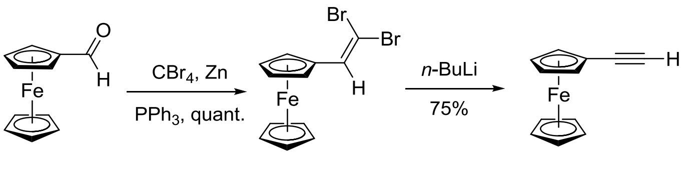




Example 1[3]



Example 2[7]



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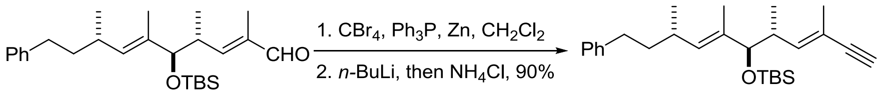
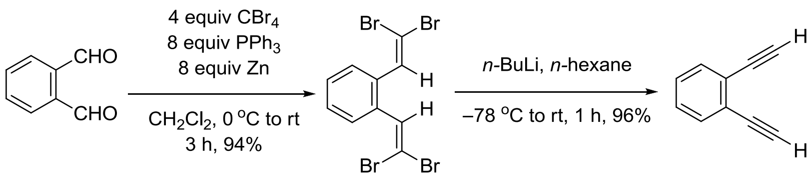
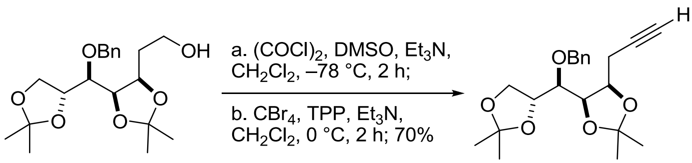
Example 3[8]



Example 4[10]



Example 5[12]



References

1 Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972,** *13,* 3769–3772. Phil Fuchs is a professor at Purdue University.

2 For the synthesis of 1-bromalkynes see Grandjean, D.; Pale, P.; Chuche, J. *Tetrahedron Lett.* **1994,** *35*, 3529–3530.

3 Gilbert, A. M.; Miller, R.; Wulff, W. D. *Tetrahedron* **1999,** *55,* 1607–1630.

4 Muller, T. J. J. *Tetrahedron Lett*. **1999,** *40*, 6563–6566.

5 Serrat, X.; Cabarrocas, G.; Rafel, S.; Ventura, M.; Linden, A.; Villalgordo, J. M. *Tetrahedron: Asymmetry* **1999,** *10*, 3417–3430.

6 Okamura, W. H.; Zhu, G.-D.; Hill, D. K.; Thomas, R. J.; Ringe, K.; Borchardt, D. B.; Norman, A. W.; Mueller, L. J. *J. Org. Chem.* **2002,** *67*, 1637–1650.

7 Tsuboya, N.; Hamasaki, R.; Ito, M.; Mitsuishi, M.; Miyashita, T. Yamamoto, Y. *J. Mater. Chem*. **2003,** *13*, 511–513

8 Zeng, X.; Zeng, F.; Negishi, E.-i. *Org. Lett*. **2004,** *6*, 3245–3248.

9 Quéron, E.; Lett, R. *Tetrahedron Lett*. **2004,** *45*, 4527–4531.

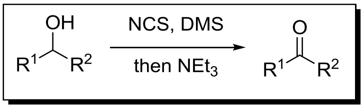
10 Sahu, B.; Muruganantham, R.; Namboothiri, I. N. N. *Eur. J. Org. Chem.* **2007,** 2477–2489.

11 Han, X. *Corey–Fuchs reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 393–403. (Review).

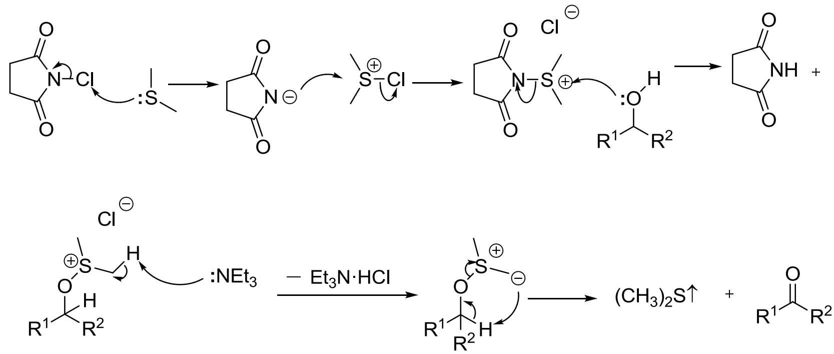
12 Pradhan, T. K.; Lin, C. C.; Mong, K. K. T. *Synlett* **2013,** *24,* 219–222.

Corey–Kim oxidation

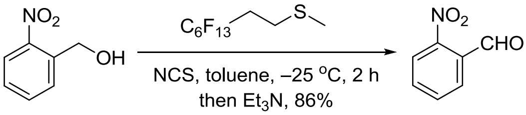
Oxidation of alcohol to the corresponding aldehyde or ketone using NCS/DMS, followed by treatment with a base. *Cf.* Swern oxidation.



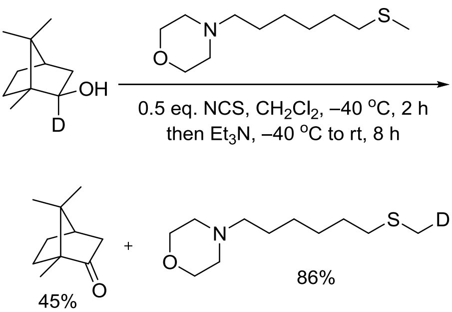
NCS = ***N*****-C**hloro**s**uccinimide; DMS = **Dim**ethyl**s**ulfide.



Example 1, Fluorous Corey–Kim reaction[5]



Example 2, Odorless Corey–Kim reaction[7]



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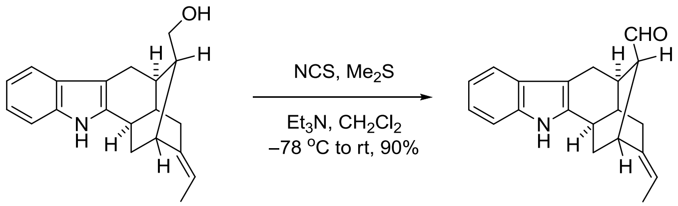
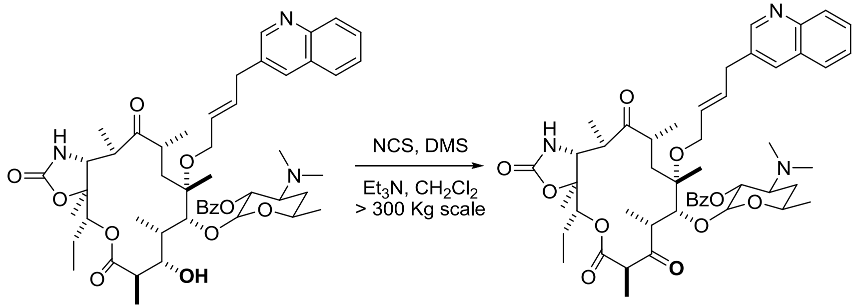
Example 3[9]



Example 4[10]



References

1 Corey, E. J.; Kim, C. U. *J. Am. Chem. Soc.* **1972,** *94*, 7586–7587. Choung U. Kim worked at Gilead Sciences, a company specialized in antiviral drugs in Foster City, California, where he co-discovered oseltamivir (Tamiflu).

2 Katayama, S.; Fukuda, K.; Watanabe, T.; Yamauchi, M. *Synthesis* **1988,** 178–183.

3 Shapiro, G.; Lavi, Y. *Heterocycles* **1990,** *31*, 2099–2102.

4 Pulkkinen, J. T.; Vepsäläinen, J. J. *J. Org. Chem.* **1996,** *61*, 8604–8609.

5 Crich, D.; Neelamkavil, S. *Tetrahedron* **2002,** *58*, 3865–3870.

6 Ohsugi, S.-I.; Nishide, K.; Oono, K.; Okuyama, K.; Fudesaka, M.; Kodama, S.; Node, M. *Tetrahedron* **2003,** *59*, 8393–8398.

7 Nishide, K.; Patra, P. K.; Matoba, M.; Shanmugasundaram, K.; Node, M. *Green Chem.* **2004,** *6*, 142–146.

8 Iula, D. M. *Corey–Kim Oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Corey, E. J. (eds), Wiley: Hoboken, NJ, **2007,** pp 207–217. (Review).

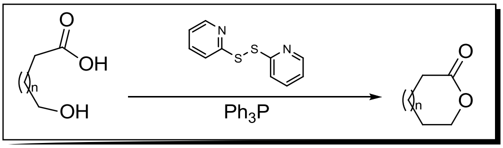
9 Yin, W.; Ma, J.; Rivas, F. M.; Cook, M. *Org. Lett.* **2007,** *9*, 295–298.

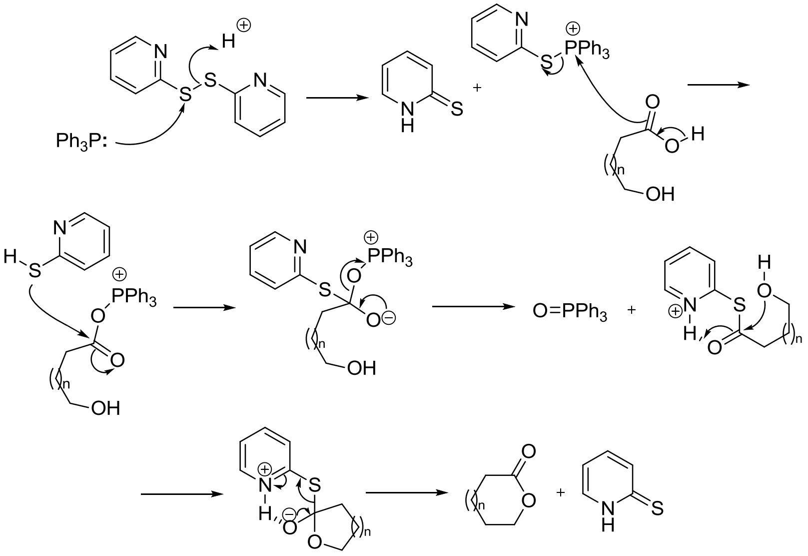
10 Cink, R. D.; Chambournier, G.; Surjono, H.; Xiao, Z.; Richter, S.; Naris, M.; Bhatia, A. V. *Org. Process Res. Dev.* **2007,** *11,* 270–274.

11 Berger, O.; Gavara, L.; Montchamp, J.-L. *Org. Lett.* **2013,** *14*, 3404–3407.

Corey–Nicolaou macrolactonization

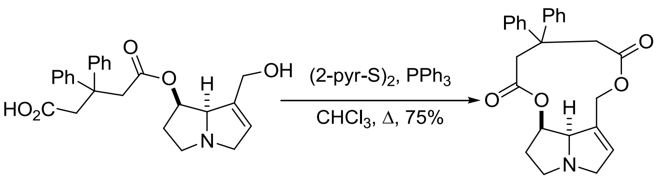
Macrolactonization of ω-hydroxyl-acid using 2,2′-dipyridyl disulfide. Also known as the Corey–Nicolaou double activation method.



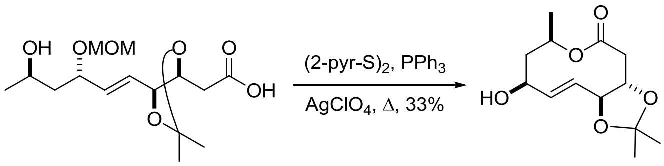


2-pyridinethione

Example 1[3]



Example 2[6]



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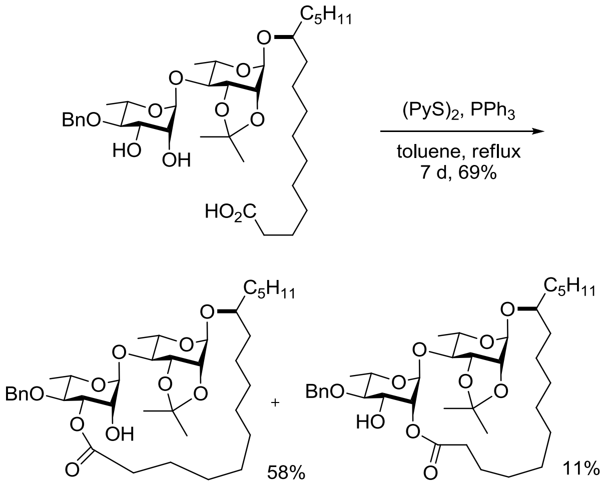
DOI 10.1007/978-3-319-03979-4_73,

Example 3[9]

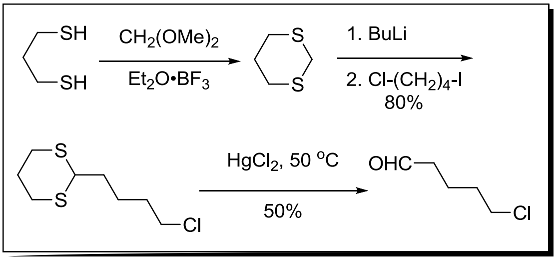


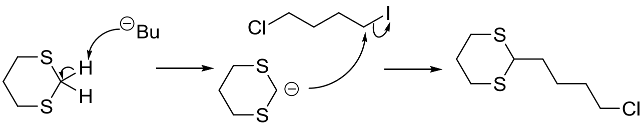
References

1. Corey, E. J.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1974,** *96*, 5614–5616.
2. Nicolaou, K. C. *Tetrahedron* **1977,** *33*, 683–710. (Review).
3. Devlin, J. A.; Robins, D. J.; Sakdarat, S. *J. Chem. Soc., Perkin Trans. 1* **1982,** 1117–1121.
4. Barbour, R. H.; Robins, D. J. *J. Chem. Soc., Perkin Trans. 1* **1985,** 2475–2478.
5. Barbour, R. H.; Robins, D. J. *J. Chem. Soc., Perkin Trans. 1* **1988,** 1169–1172.
6. Andrus, M. B.; Shih, T.-L. *J. Org. Chem.* **1996,** *61*, 8780–8785.
7. Lu, S.-F.; O'yang, Q. Q.; Guo, Z.-W.; Yu, B.; Hui, Y.-Z. *J. Org. Chem.* **1997,** *62*, 8400–8405.
8. Sasaki, T.; Inoue, M.; Hirama, M. *Tetrahedron Lett.* **2001,** *42*, 5299–5303.
9. Zhu, X.-M.; He, L.-L.; Yang, G.-L.; Lei, M.; Chen, S.-S.; Yang, J.-S. *Synlett* **2006,** 3510–3512.
10. Cochrane, J. R.; Yoon, D. H.; McErlean, C. S. P.; Jolliffe, K. A. *Beilstein J. Org. Chem.* **2012,** *8*, 1344–1351.

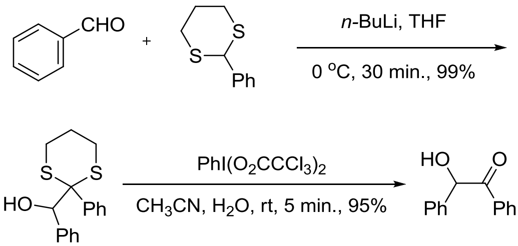
Corey–Seebach reaction

Dithiane as a nucleophile, serving as a masked carbonyl equivalent. This is an example of umpolung.

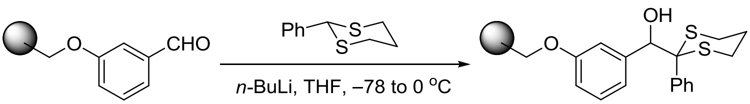




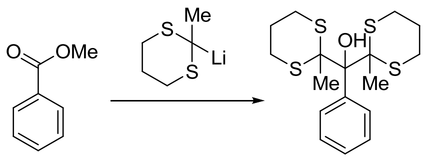
Example 1[2]



Example 2[4]



Example 3, Ethyl is infinitely different from methyl[6]



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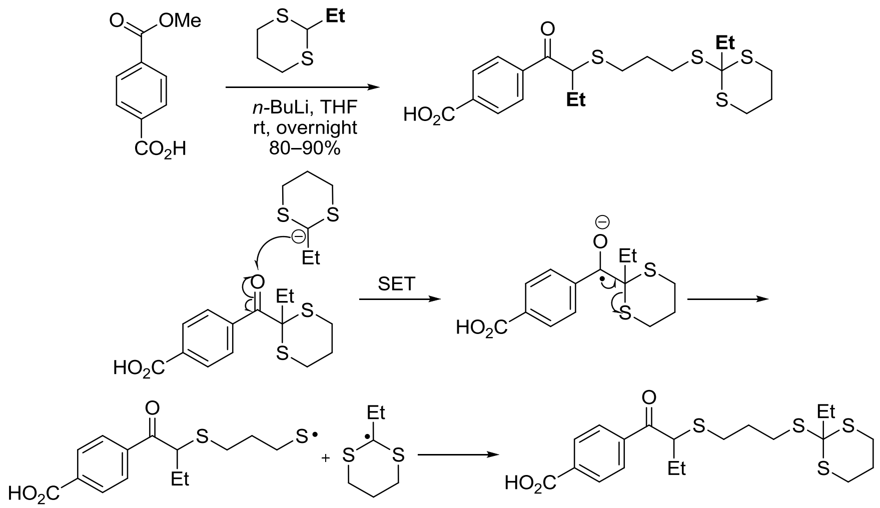
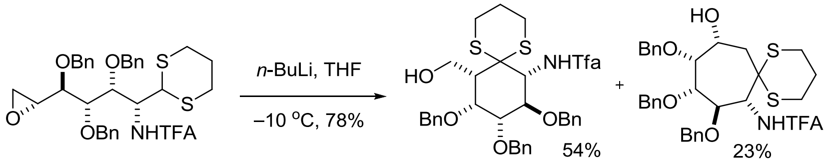
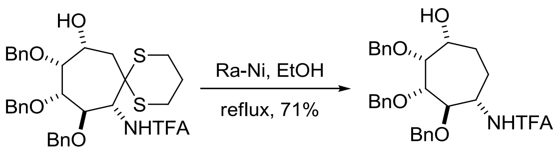
DOI 10.1007/978-3-319-03979-4_74, © Springer International Publishing Switzerland 2014



Example 4[8]



TFA = Trifluoroacetyl

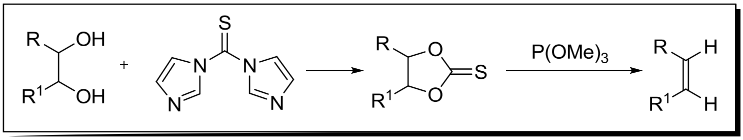


References

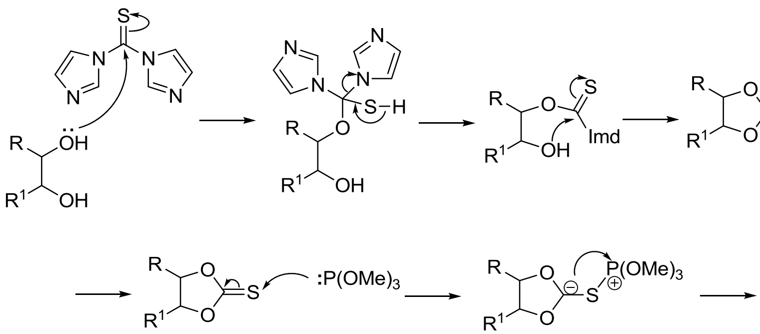
1. (a) Corey, E. J.; Seebach, D. *Angew. Chem. Int. Ed.* **1965,** *4,* 1075–1077. Dieter Seebach is a professor at ETH in Zürich, Switzerland. (b) Corey, E. J.; Seebach, D. *J. Org. Chem*. **1966,** *31*, 4097–4099. (c) Seebach, D.; Jones, N. R.; Corey, E. J. *J. Org. Chem*. **1968,** *33*, 300–305. (d) Seebach, D.; Corey, E. J. *Org. Synth.* **1968,** *50*, 72. (e) Seebach, D.; Corey, E. J. *J. Org. Chem*. **1975,** *40*, 231–237.
2. Stowell, M. H. B.; Rock, R. S.; Rees, D. C.; Chan, S. I. *Tetrahedron Lett*. **1996,** *37*, 307–310.
3. Hassan, H. H. A. M.; Tamm, C. *Helv. Chim. Acta* **1996,** *79*, 518–526.
4. Lee, H. B.; Balasubramanian, S. *J. Org. Chem*. **1999,** *64*, 3454–3460.
5. Bräuer, M.; Weston, J.; Anders, E. *J. Org. Chem*. **2000,** *65*, 1193–1199.
6. Valiulin, R. A.; Kottani, R.; Kutateladze, A. G. *J. Org. Chem*. **2006,** *71*, 5047–5049.
7. Chen, Y.-L.; Leguijt, R.; Redlich, H. *J. Carbohydrate Chem*. **2007,** *26*, 279–303.
8. Chen, Y.-L.; Redlich, H.; Bergander, K.; Froehlich, R. *Org. Biomol. Chem*. **2007,** *5*, 3330–3339.
9. Wright, P. M.; Myers, A. G. *Tetrahedron* **2011,** *67*, 9853–9869.

Corey–Winter olefin synthesis

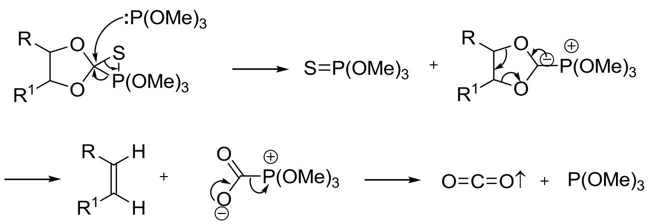
Transformation of diols to the corresponding olefins by sequential treatment with 1,1′-thiocarbonyldiimidazole (TCDI) and trimethylphosphite. Also known as Corey–Winter reductive elimination, or Corey–Winter reductive olefination.



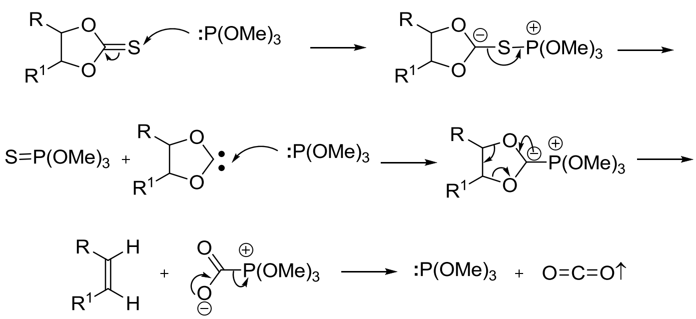
TCDI = Thiocarbonyldiimidazole



1,3-dioxolane-2-thione (cyclic thiocarbonate)



A mechanism involving a carbene intermediate can also be drawn and is supported by pyrolysis studies:



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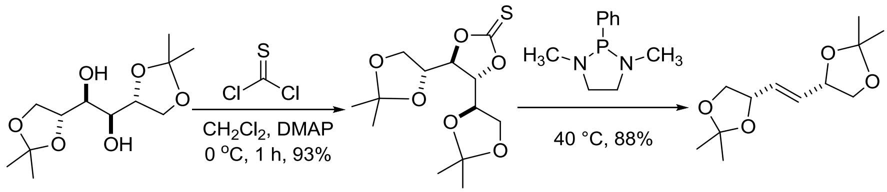
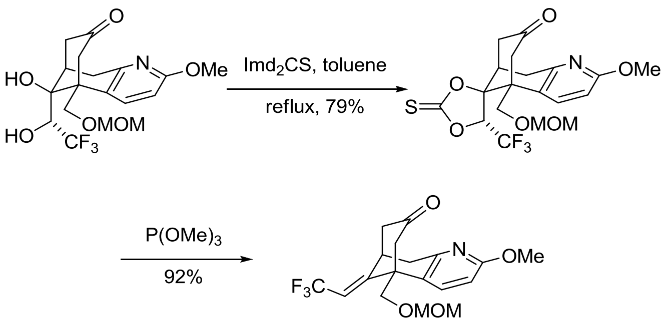
DOI 10.1007/978-3-319-03979-4_75, © Springer International Publishing Switzerland 2014

Example 1[2]

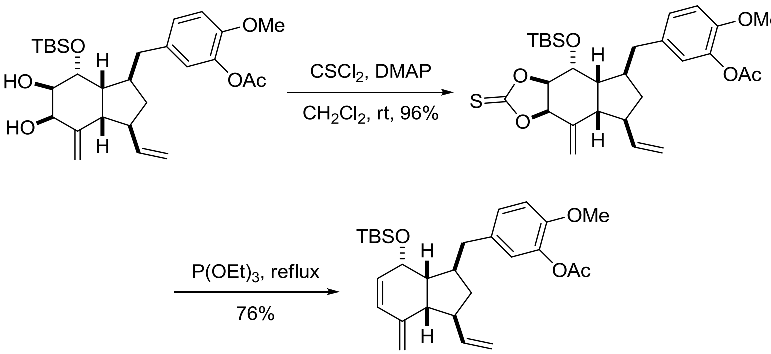


Example 2[4]

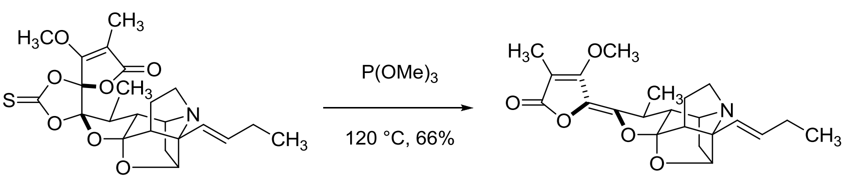


Single olefin isomer

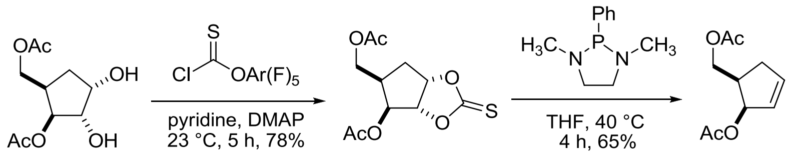
Example 3[8]



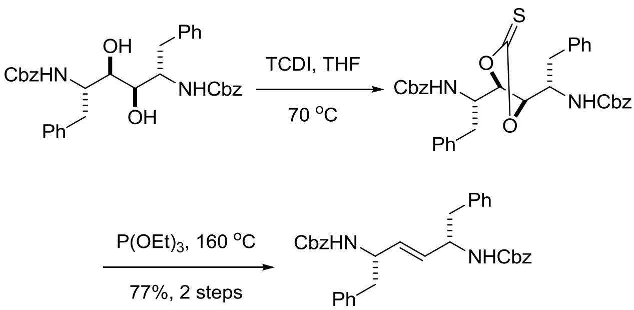
Example 4[9]



Example 5[10]



Example 6[11]

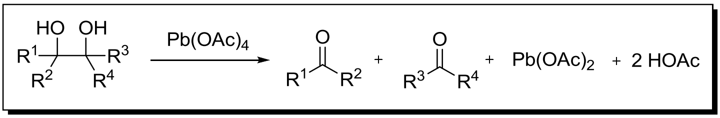


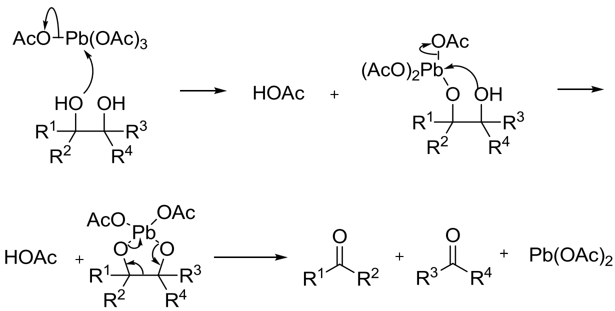
References

1. Corey, E. J.; Winter, R. A. E. *J. Am. Chem. Soc.* **1963,** *85*, 2677–2678. Roland A. E. Winter works at Ciba Specialty Chemicals Corporation, USA.
2. Corey, E. J.; Carey, F. A.; Winter, R. A. E. *J. Am. Chem. Soc.* **1965,** *87*, 934–935.
3. Block, E. *Org. React.* **1984,** *30*, 457–566. (Review).
4. Kaneko, S.; Nakajima, N.; Shikano, M.; Katoh, T.; Terashima, S. *Tetrahedron* **1998,** *54*, 5485–5506.
5. Crich, D.; Pavlovic, A. B.; Wink, D. J. *Synth. Commun.* **1999,** *29*, 359–377.
6. Palomo, C.; Oiarbide, M.; Landa, A.; Esnal, A.; Linden, A. *J. Org. Chem.* **2001,** *66*, 4180–4186.
7. Saito, Y.; Zevaco, T. A.; Agrofoglio, L. A. *Tetrahedron* **2002,** *58*, 9593–9603.
8. Araki, H.; Inoue, M.; Katoh, T. *Synlett* **2003,** 2401–2403.
9. Brüggermann, M.; McDonald, A. I.; Overman, L. E.; Rosen, M. D.; Schwink, L.; Scott, J. P. *J. Am. Chem. Soc.* **2003,** *125*, 15284–15285.
10. Freiría, M.; Whitehead, A. J.; Motherwell, W. B. *Synthesis* **2005,** 3079–3084.
11. Mergott, D. J. *Corey–Winter olefin synthesis*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 354–362. (Review).
12. Xu, L.; Desai, M. C.; Liu, H. *Tetrahedron Lett.* **2009,** *50*, 552–554.
13. Iyoda, M.; Kuwatani, Y.; Nishinaga, T.; Takase, M.; Nishiuchi, T. In *Fragments of Fullerenes and Carbon Nanotube,* Petrukhina, M. A.; Scott, L. T. eds.; Wiley: Hoboken, NJ, 2012; pp 311–342. (Review).

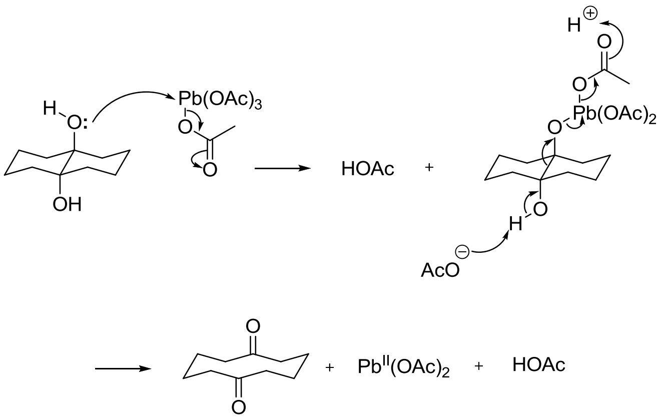
Criegee glycol cleavage

Vicinal diol is oxidized to the two corresponding carbonyl compounds using $Pb(OAc)_4$, (**l**ead **t**etra**a**cetate, LTA).

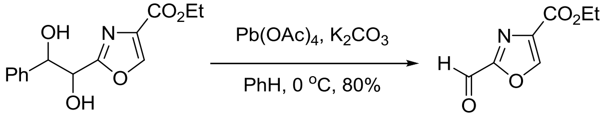




An acyclic mechanism is possible as well. It is much slower than the cyclic mechanism, but is operative when the cyclic intermediate can not form:[3]



Example 1[7]



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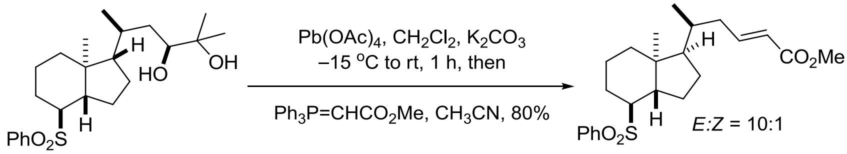
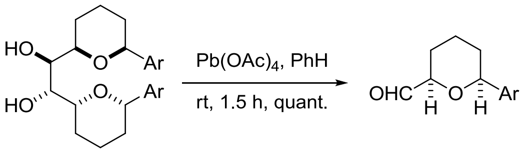
DOI 10.1007/978-3-319-03979-4_76,

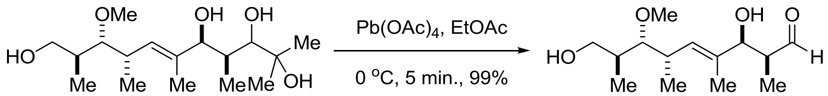
Example 2[9]



Example 3[10]



Example 4[11]



References

1 Criegee, R. *Ber.* **1931,** *64*, 260–266. Rudolf Criegee (1902–1975) was born in Düsseldorf, Germany. He earned his Ph.D. at age 23 under K. Dimroth at Würzburg. Criegee became a professor at Technical Institute at Karlsruhe in 1937, a chair in 1947. He was known for his modesty, mater-of-factness, and his breadth of interests.

2 Mihailovici, M. L.; Cekovik, Z. *Synthesis* **1970,** 209–224. (Review).

3 March, J. *Advanced Organic Chemistry,* 5th ed., Wiley: Hoboken, NJ, **2003**. (Review).

4 Danielmeier, K.; Steckhan, E. *Tetrahedron: Asymmetry* **1995,** *6*, 1181–1190.

5 Masuda, T.; Osako, K.; Shimizu, T.; Nakata, T. *Org. Lett.* **1999,** *1*, 941–944.

6 Lautens, M.; Stammers, T. A. *Synthesis* **2002,** 1993–2012.

7 Hartung, I. V.; Eggert, U.; Haustedt, L. O.; Niess, B.; Schäfer, P. M.; Hoffmann, H. M. R. *Synthesis* **2003,** 1844–1850.

8 Gaul, C.; Njardarson, J. T.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2003,** *125*, 6042–6043.

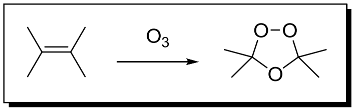
9 Gorobets, E.; Stepanenko, V.; Wicha, J. *Eur. J. Org. Chem.* **2004,** 783–799.

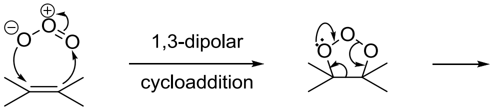
10 Prasad, K. R.; Anbarasan, P. *Tetrahedron* **2006,** *63*, 1089–1092.

11 Prasad, K. R.; Anbarasan, P. *J. Org. Chem.* **2007,** *72,* 3155–3157.

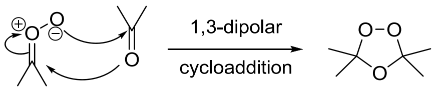
12 Perez, L. J.; Micalizio, G. C. *Synthesis* **2008,** 627–648.

Criegee mechanism of ozonolysis



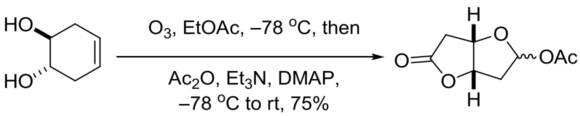


primary ozonide (1,2,3-trioxolane)

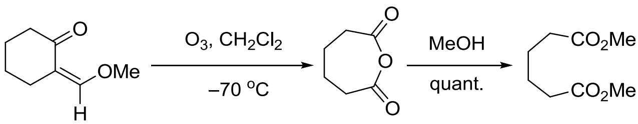


zitterionic peroxide secondary ozonide (1,2,4-trioxolane)
(Criegee zwitterion)
also known as “carbonyl oxide”

Example 1[7]



Example 2[8]



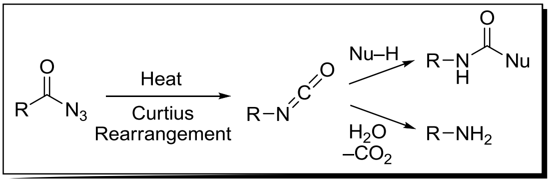
References

1. (a) Criegee, R.; Wenner, G. *Ann.* **1949,** *564*, 9–15. (b) Criegee, R. *Rec. Chem. Prog.* **1957,** *18*, 111–120. (c) Criegee, R. *Angew. Chem.* **1975,** *87*, 765–771.
2. Bunnelle, W. H. *Chem. Rev.* **1991,** *91*, 335–362. (Review).
3. Kuczkowski, R. L. *Chem. Soc. Rev.* **1992,** *21*, 79–83. (Review).
4. Marshall, J. A.; Garofalo, A. W. *J. Org. Chem*. **1993,** *58*, 3675–3680.
5. Ponec, R.; Yuzhakov, G.; Haas, Y.; Samuni, U. *J. Org. Chem*. **1997,** *62*, 2757–2762.
6. Dussault, P. H.; Raible, J. M. *Org. Lett*. **2000,** *2*, 3377–3379.
7. Jiang, L.; Martinelli, J. R.; Burke, S. D. *J. Org. Chem*. **2003,** *68*, 1150–1153.
8. Schank, K.; Beck, H.; Pistorius, S. *Helv. Chim. Acta* **2004,** *87*, 2025–2049.
9. Coleman, B. E.; Ault, B. S. *J. Mol. Struct.* **2013,** *1031*, 138–143.

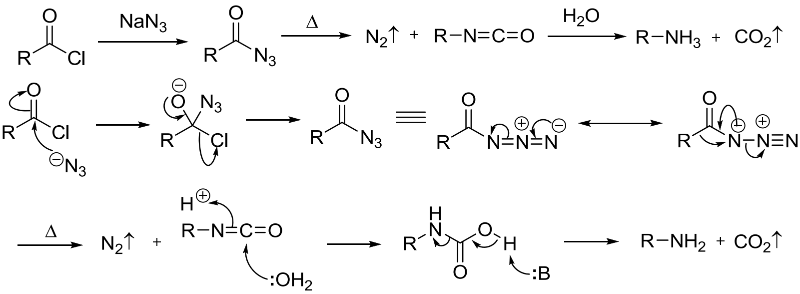
J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_77,

Curtius rearrangement

Alkyl-, vinyl-, and aryl-substituted acyl azides undergo thermal 1,2-carbon-to-nitrogen migration with extrusion of dinitrogen — the Curtius rearrangement — producing isocyantes. Reaction of the isocyanate products with nucleophiles, often *in situ*, provides carbamates, ureas, and other *N*-acyl derivatives. Alternatively, hydrolysis of the isocyanates leads to primary amines.

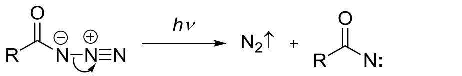


The thermal rearrangement:

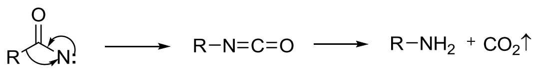


isocyanate intermediate

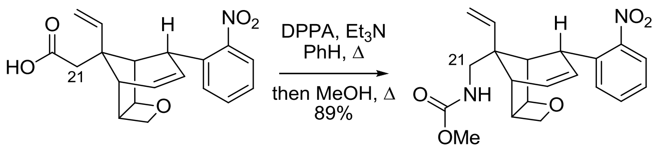
The photochemical rearrangement:



Nitrene

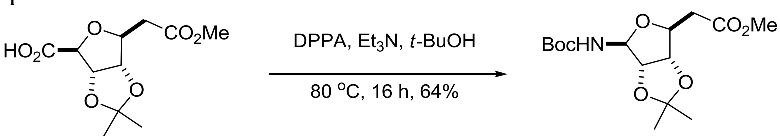


Example 1, The Shioiri–Ninomiya–Yamada modification[2]



DPPA = diphenylphosphoryl azide

Example 2[3]



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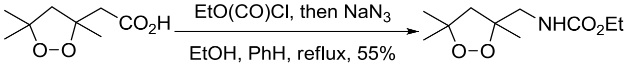
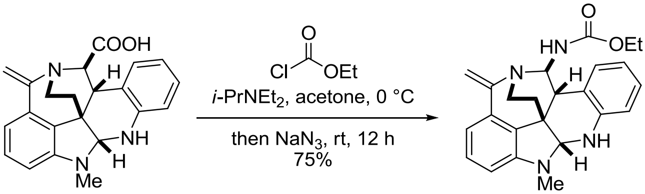
DOI 10.1007/978-3-319-03979-4_78, © Springer International Publishing Switzerland 2014

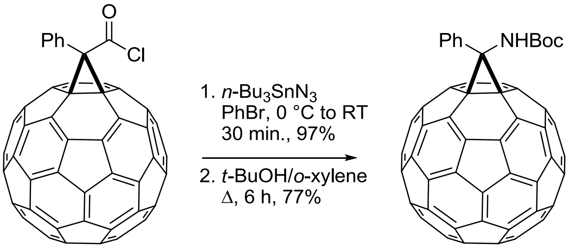
Example 3[4]



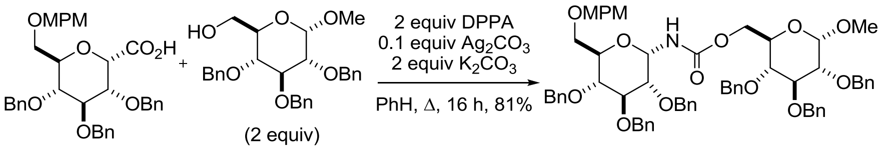
Example 4, The Weinstock variant of the Curtius rearrangement[6]



Example 5[7]



Example 6, The Lebel modification[8]

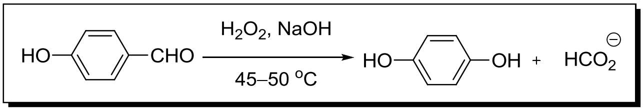


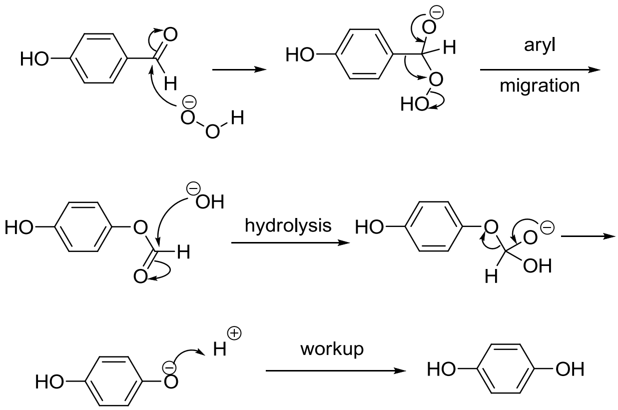
References

1. Curtius, T. *Ber.* **1890,** *23*, 3033–3041. Theodor Curtius (1857–1928) was born in Duisburg, Germany. He studied music before switching to chemistry under Bunsen, Kolbe, and von Baeyer before succeeding Victor Meyer as a Professor of Chemistry at Heidelberg. He discovered diazoacetic ester, hydrazine, pyrazoline derivatives, and many nitrogen-heterocycles. Curtius also sang in concerts and composed music.
2. Ng, F. W.; Lin, H.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2002,** *124*, 9812–9824.
3. van Well, R. M.; Overkleeft, H. S.; van Boom, J. H.; Coop, A.; Wang, J. B.; Wang, H.; van der Marel, G. A.; Overhand, M. *Eur. J. Org. Chem.* **2003,** 1704–1710.
4. Dussault, P. H.; Xu, C. *Tetrahedron Lett*. **2004,** *45*, 7455–7457.
5. Holt, J.; Andreassen, T.; Bakke, J. M.; Fiksdahl, A. *J. Heterocycl. Chem.* **2005,** *42*, 259–264.
6. Crawley, S. L.; Funk, R. L. *Org. Lett.* **2006,** *8*, 3995–3998.
7. Tada, T.; Ishida, Y.; Saigo, K. *Synlett* **2007,** 235–238.
8. Sawada, D.; Sasayama, S.; Takahashi, H.; Ikegami, S. *Eur. J. Org. Chem.* **2007,** 1064–1068.
9. Rojas, C. M. *Curtius Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 136–163. (Review).
10. Koza, G.; Keskin, S.; Özer, M. S.; Cengiz, B.; Şahin, E.; Balci, M. *Tetrahedron* **2013,** *69,* 395–409.

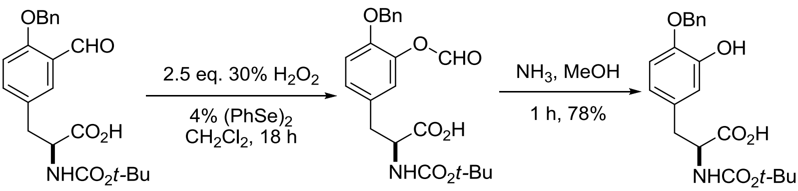
Dakin oxidation

Oxidation of aryl aldehydes or aryl ketones to phenols using basic hydrogen peroxide conditions. *Cf.* A variant of the Baeyer–Villiger oxidation.

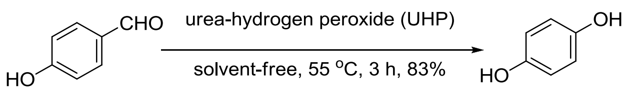




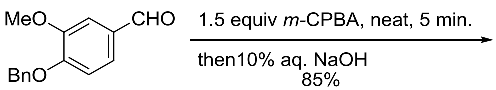
Example 1[6]



Example 2[7]



Example 3, Improved solvent-free Dakin oxidation protocol[9]



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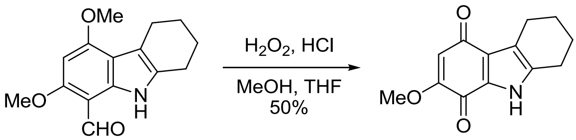
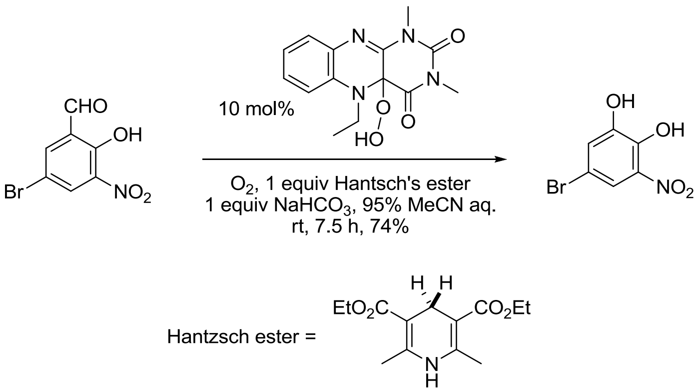
Example 4[10]



Example 5[11]

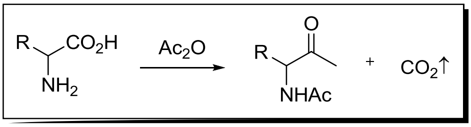


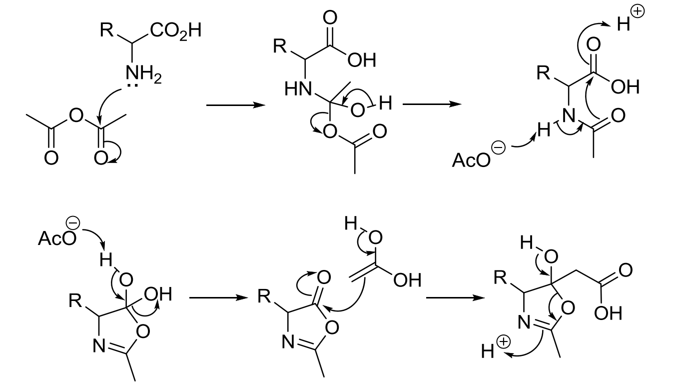
References:

1. Dakin, H. D. *Am. Chem. J.* **1909,** *42*, 477–498. Henry D. Dakin (1880–1952) was born in London, England. During WWI, he invented his hypochlorite solution (Dakin's solution), which became a popular antiseptic for the treatment of wounds. After the Great War, he emmigrated to New York, where he investigated the B vitamins.
2. Hocking, M. B.; Bhandari, K.; Shell, B.; Smyth, T. A. *J. Org. Chem.* **1982,** *47*, 4208–4215.
3. Matsumoto, M.; Kobayashi, H.; Hotta, Y. *J. Org. Chem.* **1984,** *49*, 4740–4741.
4. Zhu, J.; Beugelmans, R.; Bigot, A.; Singh, G. P.; Bois-Choussy, M. *Tetrahedron Lett.* **1993,** *34*, 7401–7404.
5. Guzmán, J. A.; Mendoza, V.; García, E.; Garibay, C. F.; Olivares, L. Z.; Maldonado, L. A. *Synth. Commun*. **1995,** *25*, 2121–2133.
6. Jung, M. E.; Lazarova, T. I. *J. Org. Chem.* **1997,** *62*, 1553–1555.
7. Varma, R. S.; Naicker, K. P. *Org. Lett*. **1999,** *1*, 189–191.
8. Lawrence, N. J.; Rennison, D.; Woo, M.; McGown, A. T.; Hadfield, J. A. *Bioorg. Med. Chem. Lett*. **2001,** *11*, 51–54.
9. Teixeira da Silva, E.; Camara, C. A.; Antunes, O. A. C.; Barreiro, E. J.; Fraga, C. A. M. *Synth. Commun*. **2008,** *38*, 784–788.
10. Alamgir, M.; Mitchell, P. S. R.; Bowyer, P. K.; Kumar, N.; Black, D. St. C. *Tetrahedron* **2008,** *64*, 7136–7142.
11. Chen, S.; Foss, F. W. *Org. Lett*. **2012,** *14*, 5150–5153.

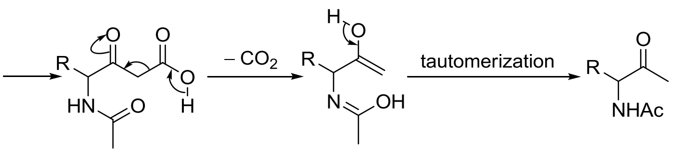
Dakin–West reaction

The direct conversion of an α-amino acid into the corresponding α-acetylamino-alkyl methyl ketone, *via* oxazoline (azalactone) intermediates. The reaction proceeds in the presence of acetic anhydride and a base, such as pyridine, with the evolution of CO_2.

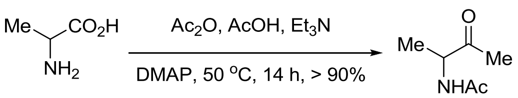




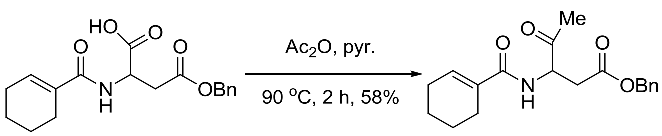
oxazolone (azalactone) intermediate



Example 1[6]



Example 2[7]



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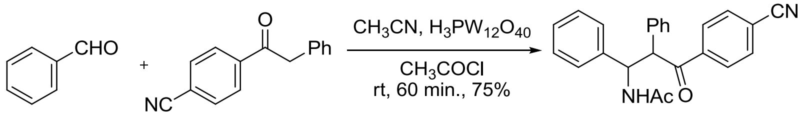
Example 3, A green Dakin–West reaction using the heteropoly acid catalyst, acetonitrile is a reactant[9]

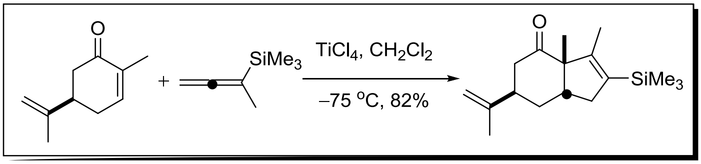


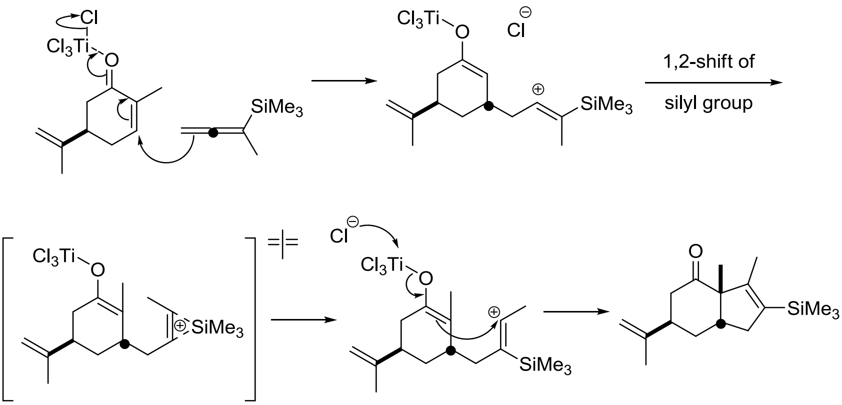
References:

1. Dakin, H. D.; West, R. *J. Biol. Chem.* **1928,** *78,* 91, 745, and 757. In 1928, Henry Dakin and Rudolf West, a clinician, reported on the reaction of α-amino acids with acetic anhydride to give α-acetamido ketones *via* azalactone intermediates. Interestingly, one year before this paper by Dakin and West, Levene and Steiger had observed both tyrosine and α-phenylananine gave "abnormal" products when acetylated under these conditions.[2,3] Unfortunately, they were slow to identify the products and lost an opportunity to be immortalized by a name reaction.
2. Buchanan, G. L. *Chem. Soc. Rev.* **1988,** *17*, 91–109. (Review).
3. Jung, M. E.; Lazarova, T. I. *J. Org. Chem*. **1997,** *62*, 1553–1555.
4. Kawase, M.; Hirabayashi, M.; Koiwai, H.; Yamamoto, K.; Miyamae, H. *Chem. Commun*. **1998,** 641–642.
5. Kawase, M.; Hirabayashi, M.; Saito, S. *Recent Res. Dev. Org. Chem*. **2001,** *4*, 283–293. (Review).
6. Fischer, R. W.; Misun, M. *Org. Proc. Res. Dev*. **2001,** *5*, 581–588.
7. Godfrey, A. G.; Brooks, D. A.; Hay, L. A.; Peters, M.; McCarthy, J. R.; Mitchell, D. *J. Org. Chem*. **2003,** *68*, 2623–2632.
8. Khodaei, M. M.; Khosropour, A. R.; Fattahpour, P. *Tetrahedron Lett*. **2005,** *46*, 2105–2108.
9. Rafiee, E.; Tork, F.; Joshaghani, M. *Bioorg. Med. Chem. Lett*. **2006,** *16*, 1221–1226.
10. Tiwari, A. K.; Kumbhare, R. M.; Agawane, S. B.; Ali, A. Z.; Kumar, K. V. *Bioorg. Med. Chem. Lett*. **2008,** *18*, 4130–4132.
11. Dalla-Vechia, L.; Santos, V. G.; Godoi, M. N.; Cantillo, D.; Kappe, C. O.; Eberlin, M. N.; de Souza, R. O. M. A.; Miranda, L. S. M. *Org. Biomol. Chem*. **2012,** *10*, 9013–9020. (Mechanism).

Danheiser annulation

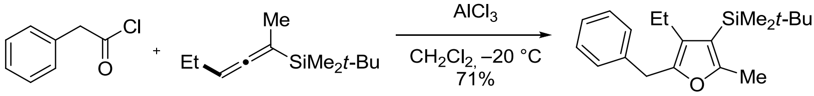
Trimethylsilylcyclopentene annulation from an α,β-unsaturated ketone and trimethylsilylallene in the presence of a Lewis acid.



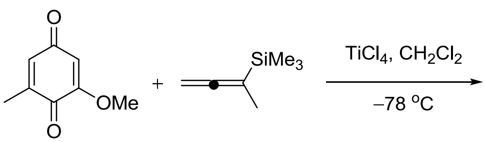


Transition State

Example 1[7]



Example 2[8]



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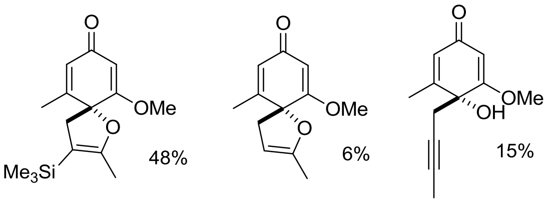
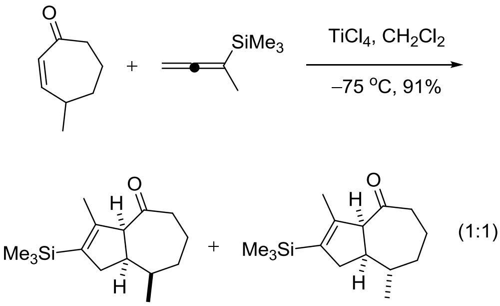
DOI 10.1007/978-3-319-03979-4_81, © Springer International Publishing Switzerland 2014



Example 3[9]

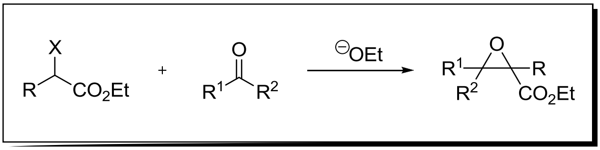


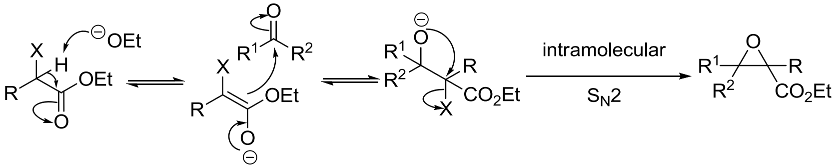
References

1. Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981,** *103*, 1604. Born in 1951, Rick L. Danheiser worked as an undergraduate under the direction of Professor Gilbert Stork and developed a method for the regiospecific alkylation of β-diketone enol ethers (the "Stork-Danheiser Alkylation"). He earned his Ph.D. in 1978 at Harvard under E. J. Corey. He began his independent academic career at MIT and now he is the Arthur C. Cope Professor of Chemistry. In addition to the Danheiser annulation, his another popular methodology is for the synthesis of aromatic and dihydroaromatic compounds based on cycloadditions of highly unsaturated conjugated molecules such as conjugated 1,3-enynes; and formal [2+2+2] cycloadditions based on propargylic ene reaction/Diels-Alder cycloaddition cascades. His group also applied these methodologies and completed the total synthesis of natural products. He is also a superb teacher, a maestro in the classroom, winning many teaching awards at MIT.
2. Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983,** *39*, 935.
3. Danheiser, R. L.; Kwasigroch, C. A.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1985,** *107*, 7233.
4. Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. *J. Org. Chem*. **1986,** *51*, 3870.
5. Danheiser, R. L.; Tsai, Y.-M.; Fink, D. M. *Org. Synth.* **1988,** *66,* 1.
6. Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem*. **1992,** *57*, 6094.
7. Sibi, M. P.; Christensen, J. W.; Kim, S.; Eggen, F.; Stessman, C.; Oien, L. *Tetrahedron Lett*. **1995,** *36*, 6209–6212.
8. Engler, T. A.; Agrios, K.; Reddy, J. P.; Iyengar, R. *Tetrahedron Lett*. **1996,** *37*, 327.
9. Friese, J. C.; Krause, S.; Schäfer, H. J. *Tetrahedron Lett*. **2002,** *43*, 2683.
10. Peese, K. M. *Danheiser Annulation*, In *Name Reactions in Carbocyclic Ring Formations*, Li, J. J., Ed., Wiley: Hoboken, NJ, **2010,** pp 72–92.

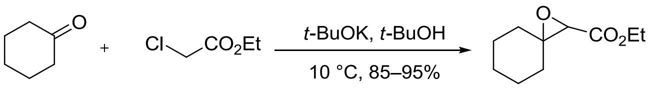
Darzens condensation

α,β-Epoxy esters (glycidic esters) from base-catalyzed condensation of α-haloesters with carbonyl compounds.

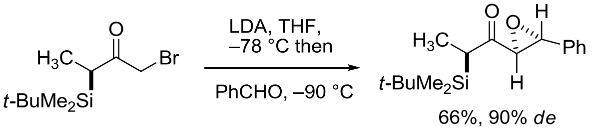




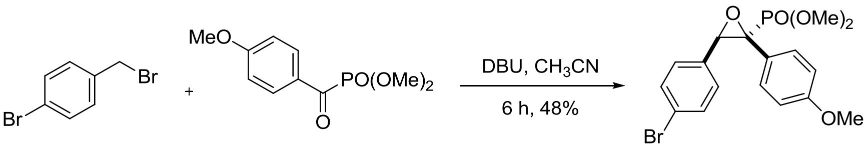
Example 1[4]



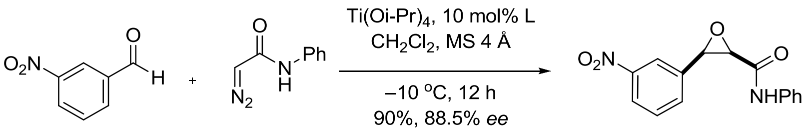
Example 2[6]



Example 3, the phenyl ring substituting for the carbonyl to acidify the protons[10]



Example 4[11]



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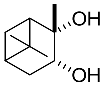
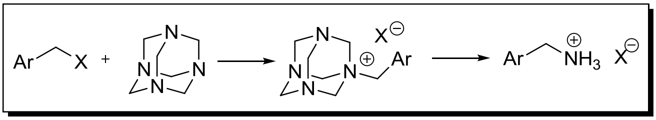
L = 

References

1 Darzens, G. A. *Compt. Rend. Acad. Sci.* **1904,** *139,* 1214–1217. George Auguste Darzens (1867−1954), born in Moscow, Russia, studied at École Polytechnique in Paris and stayed there as a professor.
2 Newman, M. S.; Magerlein, B. J. *Org. React.* **1949,** *5*, 413–441. (Review).
3 Ballester, M. *Chem. Rev.* **1955,** *55*, 283–300. (Review).
4 Hunt, R. H.; Chinn, L. J.; Johnson, W. S. *Org. Syn. Coll. IV*, **1963,** 459.
5 Rosen, T. *Darzens Glycidic Ester Condensation* In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, **1991,** *Vol. 2*, pp 409–439. (Review).
6 Enders, D.; Hett, R. *Synlett* **1998,** 961−962.
7 Davis, F. A.; Wu, Y.; Yan, H.; McCoull, W.; Prasad, K. R. *J. Org. Chem*. **2003,** *68*, 2410−2419.
8 Myers, B. J. *Darzens Glycidic Ester Condensation*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 15−21. (Review).
9 Achard, T. J. R.; Belokon, Y. N.; Ilyin, M.; Moskalenko, M.; North, M.; Pizzato, F. *Tetrahedron Lett*. **2007,** *48*, 2965−2969.
10 Demir, A. S.; Emrullahoglu, M.; Pirkin, E.; Akca, N. *J. Org. Chem*. **2008,** *73*, 8992−8997.
11 Liu, G.; Zhang, D.; Li, J.; Xu, G.; Sun, J. *Org. Biomol. Chem*. **2013,** *11*, 900−904.

Delépine amine synthesis

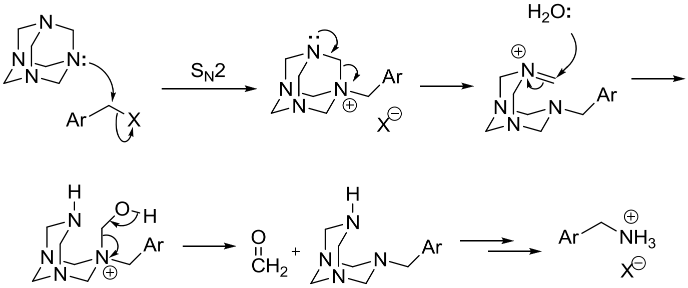
The reaction between alkyl halides and hexamethylenetetramine, followed by cleavage of the resulting salt with ethanolic HCl to yield primary amines.
Cf. Gabriel synthesis, where the product is also an amine and Sommelet reaction, where the product is an aldehyde. The Delépine works well for active halides such as benzyl, allyl halides, and α-halo-ketones.



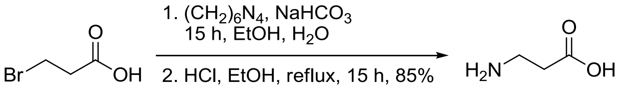
Hexamethylenetetramine

$$[ArCH_2C_6H_{12}N_4]^+X^- \quad + \quad 3\ HCl \quad + 6\ H_2O$$

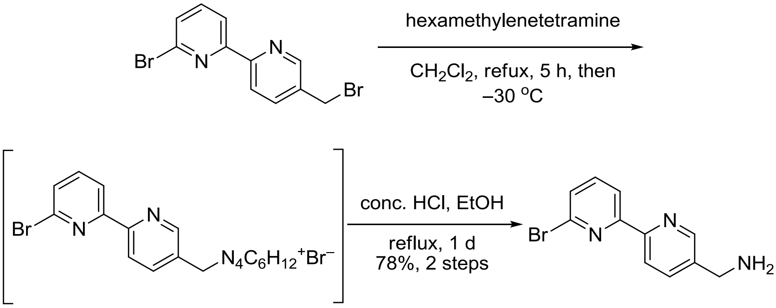
$$\longrightarrow \ ArCH_2NH_2{\bullet}HX \quad + \quad 6\ CH_2O \quad + \quad 3\ NH_4Cl$$



Example 1[3]



Example 2[7]



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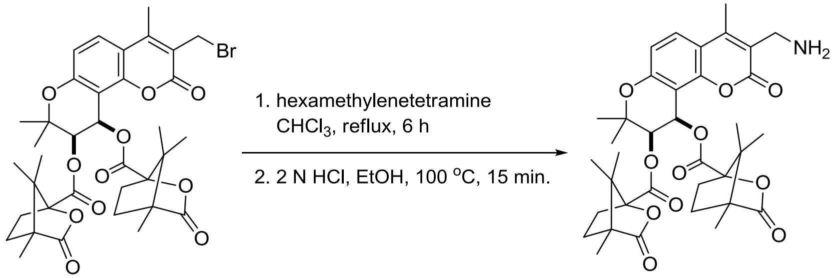
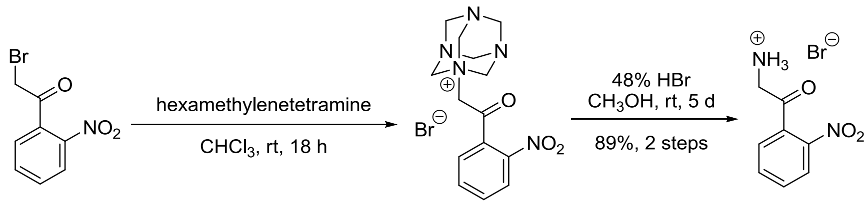
DOI 10.1007/978-3-319-03979-4_83, © Springer International Publishing Switzerland 2014

Example 3[8]



Example 4[9]

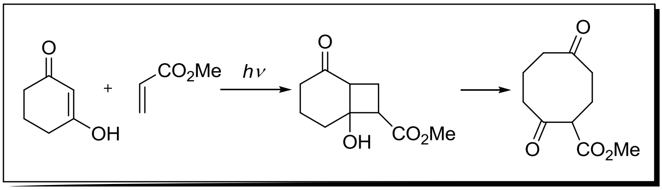


References

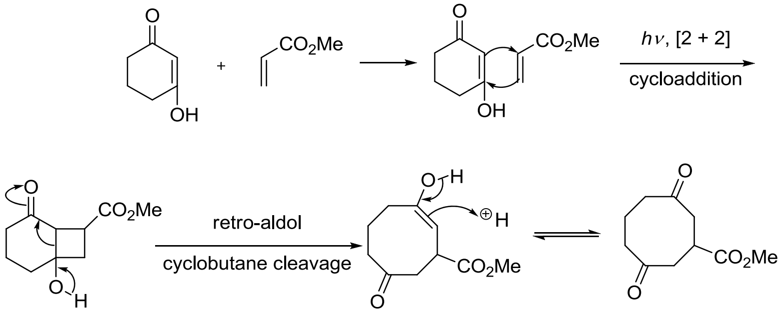
1. (a) Delépine, M. *Bull. Soc. Chim. Paris* **1895,** *13*, 352–355; (b) Delépine, M. *Bull. Soc. Chim. Paris* **1897,** *17*, 292–295. Stephe Marcel Delépine (1871–1965) was born in St. Martin le Gaillard, France. He was a professor at the Collège de France after working for M. Bertholet at that institute. Delépine's long and fruitful career in science encompassed organic chemistry, inorganic chemistry, and pharmacy.
2. Galat, A.; Elion, G. *J. Am. Chem. Soc*. **1939,** *61*, 3585–3586.
3. Wendler, N. L. *J. Am. Chem. Soc*. **1949,** *71*, 375–384.
4. Quessy, S. N.; Williams, L. R.; Baddeley, V. G. *J. Chem. Soc., Perkin Trans. 1* **1979,** 512–516.
5. Blažzević, N.; Kolnah, D.; Belin, B.; Šunjić, V.; Kafjež, F. *Synthesis* **1979,** 161–176. (Review).
6. Henry, R. A.; Hollins, R. A.; Lowe-Ma, C.; Moore, D. W.; Nissan, R. A. *J. Org. Chem*. **1990,** *55*, 1796–1801.
7. Charbonnière, L. J.; Weibel, N.; Ziessel, R. *Synthesis* **2002,** 1101–1109.
8. Xie, L.; Yu, D.; Wild, C.; Allaway, G.; Turpin, J.; Smith, P. C.; Lee, K.-H. *J. Med. Chem*. **2004,** *47*, 756–760.
9. Loughlin, W. A.; Henderson, L. C.; Elson, K. E.; Murphy, M. E. *Synthesis* **2006,** 1975–1980.

de Mayo reaction

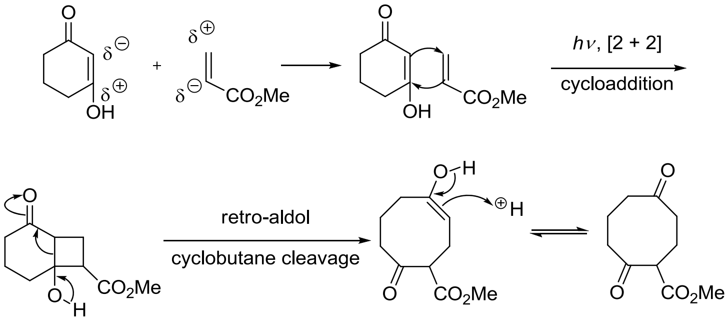
[2 + 2]-Photochemical cyclization of enones with olefins is followed by a retro-aldol reaction to give 1,5-diketones.



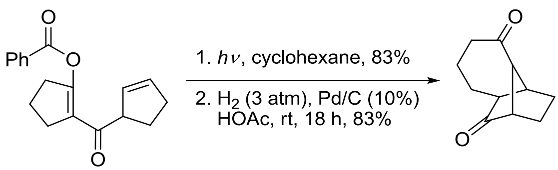
Head-to-tail alignment gives the major product:[1b]



Head-to-head alignment gives the minor regioisomer:



Example 1[3]



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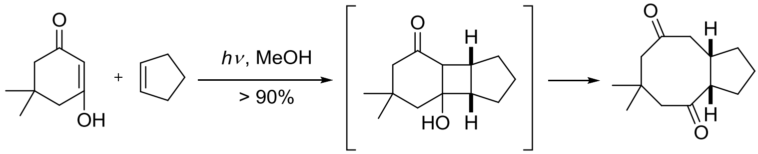
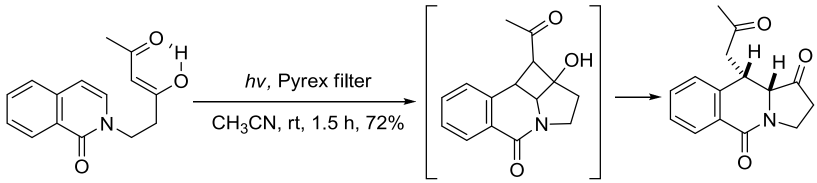
DOI 10.1007/978-3-319-03979-4_84, © Springer International Publishing Switzerland 2014

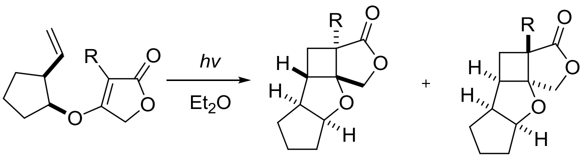
Example 2[6]



Example 3[9]



Example 4[10]



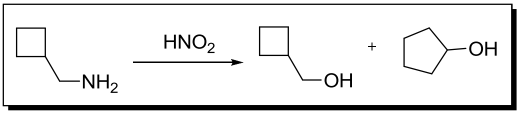
R = H	70%	100	:	0
R = Me	58%	50	:	50
R = *t*-Bu	72%	0	:	100

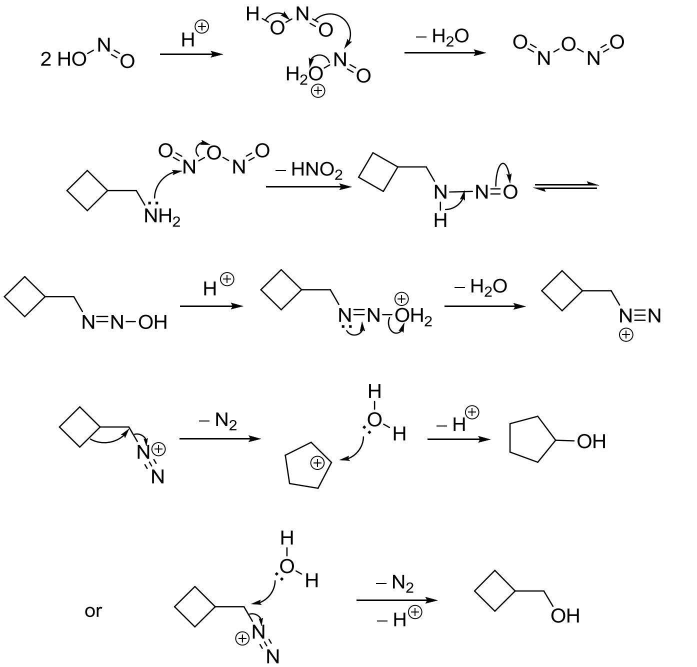
References

1. (a) de Mayo, P.; Takeshita, H.; Sattar, A. B. M. A. *Proc. Chem. Soc., London* **1962,** 119. Paul de Mayo received his doctorate from Sir Derek Barton at Birkbeck College, University of London. He later became a professor at the University of Western Ontario in London, Ontario, Canada, where he discovered the de Mayo reaction. (b) Challand, B. D.; Hikino, H.; Kornis, G.; Lange, G.; de Mayo, P. *J. Org. Chem*. **1969,** *34*, 794–806.
2. de Mayo, P. *Acc. Chem. Res.* **1971,** *4*, 41–48. (Review).
3. Oppolzer, W.; Godel, T. *J. Am. Chem. Soc*. **1978,** *100*, 2583–2584.
4. Oppolzer, W. *Pure Appl. Chem.* **1981,** *53*, 1181–1201. (Review).
5. Kaczmarek, R.; Blechert, S. *Tetrahedron Lett*. **1986,** *27*, 2845–2848.
6. Disanayaka, B. W.; Weedon, A. C. *J. Org. Chem*. **1987,** *52*, 2905–2910.
7. Crimmins, M. T.; Reinhold, T. L. *Org. React.* **1993,** *44*, 297–588. (Review).
8. Quevillon, T. M.; Weedon, A. C. *Tetrahedron Lett*. **1996,** *37*, 3939–3942.
9. Minter, D. E.; Winslow, C. D. *J. Org. Chem*. **2004,** *69*, 1603–1606.
10. Kemmler, M.; Herdtweck, E.; Bach, T. *Eur. J. Org. Chem*. **2004,** 4582–4595.
11. Wu, Y.-J. *Name Reactions in Carbocyclic Ring Formations*, Li, J. J., Ed., Wiley: Hoboken, NJ, 2010; pp 451–488.

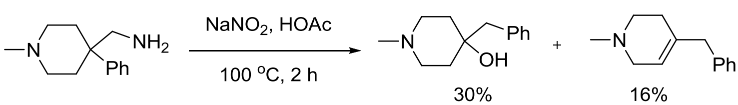
Demjanov rearrangement

Carbocation rearrangement of primary amines *via* diazotization to give alcohols through C–C bond migration.

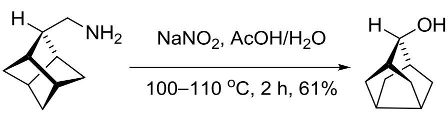




Example 1[3]



Example 2[6]



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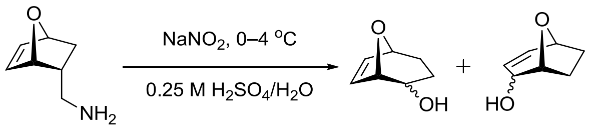
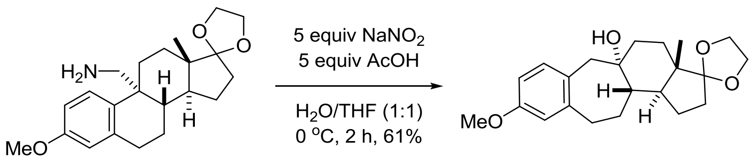
DOI 10.1007/978-3-319-03979-4_85, © Springer International Publishing Switzerland 2014

Example 3[7]



Example 4[8]

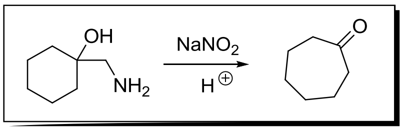


References

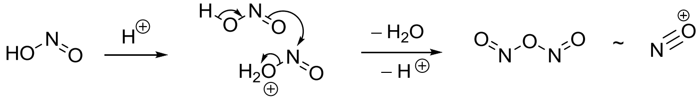
1. Demjanov, N. J.; Lushnikov, M. *J. Russ. Phys. Chem. Soc.* **1903,** *35*, 26–42. Nikolai J. Demjanov (1861–1938) was a Russian chemist.
2. Smith, P. A. S.; Baer, D. R. *Org. React.* **1960,** *11*, 157–188. (Review).
3. Diamond, J.; Bruce, W. F.; Tyson, F. T. *J. Org. Chem*. **1965,** *30*, 1840–184.
4. Kotani, R. *J. Org. Chem*. **1965,** *30*, 350–354.
5. Diamond, J.; Bruce, W. F.; Tyson, F. T. *J. Org. Chem*. **1965,** *30*, 1840–1844.
6. Nakazaki, M.; Naemura, K.; Hashimoto, M. *J. Org. Chem*. **1983,** *48*, 2289–2291.
7. Fattori, D.; Henry, S.; Vogel, P. *Tetrahedron* **1993,** *49*, 1649–1664.
8. Kürti, L.; Czakó, B.; Corey, E. J. *Org. Lett*. **2008,** *10*, 5247–5250.
9. Curran, T. T. *Demjanov and Tiffeneau–Demjanov Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 2–32. (Review).

Tiffeneau–Demjanov rearrangement

Carbocation rearrangement of β-aminoalcohols *via* diazotization to afford carbonyl compounds through C–C bond migration.

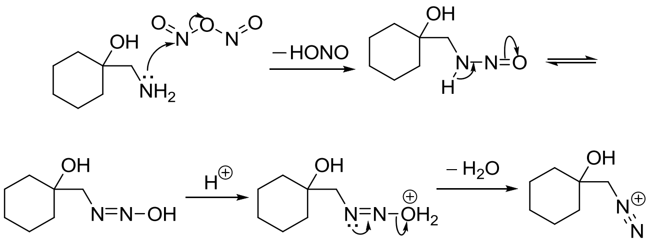


Step 1, Generation of N_2O_3

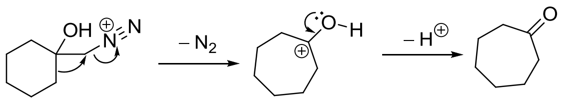


N-nitrosonium ion

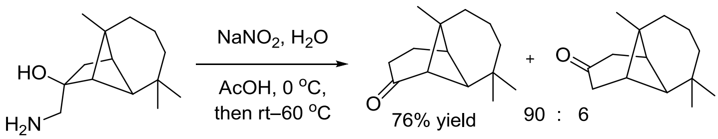
Step 2, Transformation of amine to diazonium salt



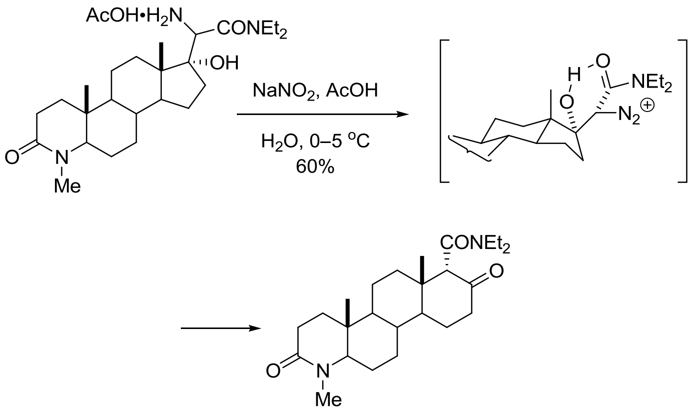
Step 3, Ring-expansion *via* rearrangement



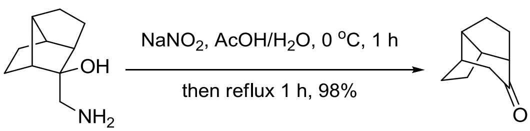
Example 1[5]



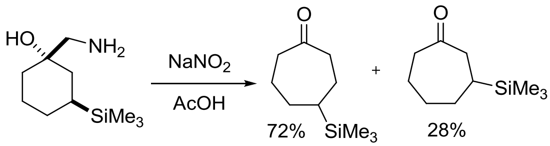
Example 2[6]



Example 3[7]



Example 4[9]

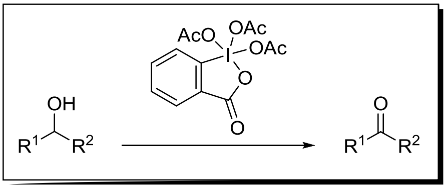


References

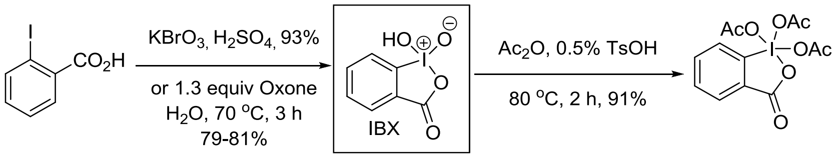
1. Tiffeneau, M.; Weill, P.; Tehoubar, B. *Compt. Rend.* **1937,** *205*, 54–56.
2. Smith, P. A. S.; Baer, D. R. *Org. React.* **1960,** *11*, 157–188. (Review).
3. Parham, W. E.; Roosevelt, C. S. *J. Org. Chem.* **1972,** *37,* 1975–1979.
4. Jones, J. B.; Price, P. *Tetrahedron* **1973,** *29,* 1941–1947.
5. Miyashita, M.; Yoshikoshi, A. *J. Am. Chem Soc*. **1974,** *96*, 1917–1925.
6. Steinberg, N. G.; Rasmusson, G. H.; Reynolds, G. F.; Hirshfield, J. H.; Arison, B. H. *J. Org. Chem*. **1984,** *49*, 4731–4733.
7. Stern, A. G.; Nickon, A. *J. Org. Chem.* **1992,** *57,* 5342–5352.
8. Fattori, D.; Henry, S.; Vogel, P. *Tetrahedron* **1993,** *49*, 1649–1664.
9. Chow, L.; McClure, M.; White, J. *Org. Biomol. Chem*. **2004,** *2*, 648–650.
10. Curran, T. T. *Demjanov and Tiffeneau–Demjanov Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 293–304. (Review).
11. Shi, L.; Meyer, K.; Greaney, M. F. *Angew. Chem. Int. Ed.* **2010,** *49,* 9250–9253,

Dess–Martin periodinane oxidation

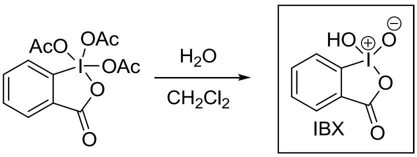
Oxidation of alcohols to the corresponding carbonyl compounds using triacetoxyperiodinane. The Dess–Martin periodinane, 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one, is one of the most useful oxidant for the conversion of primary and secondary alcohols to their corresponding aldehyde or ketone products, respectively.



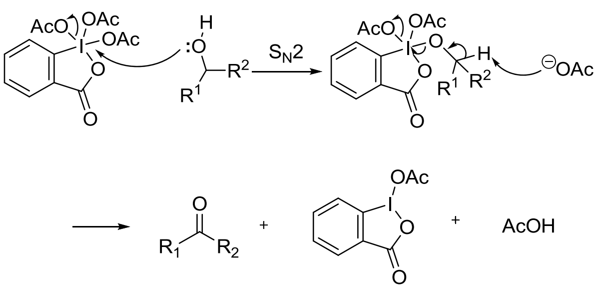
Preparation,[1,2] the oxone preparation is much safer and easier than $KBrO_3$. The IBX intermediate that comes out of it has proven to be far less explosive[12]



However, The Dess–Martin periodinane is hydrolyzed by moisture to *o*-iodoxybenzoic acid (IBX), which is a more powerful oxidizing agent[3]



Mechanism[1]



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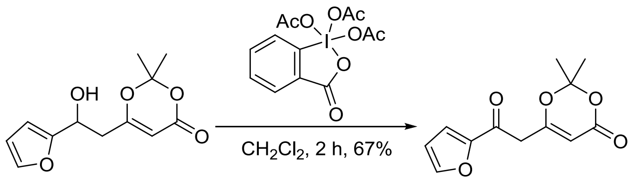
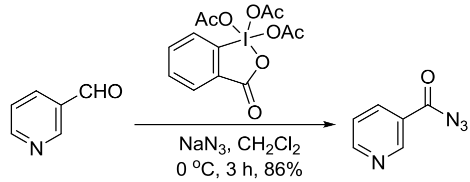
DOI 10.1007/978-3-319-03979-4_86, © Springer International Publishing Switzerland 2014

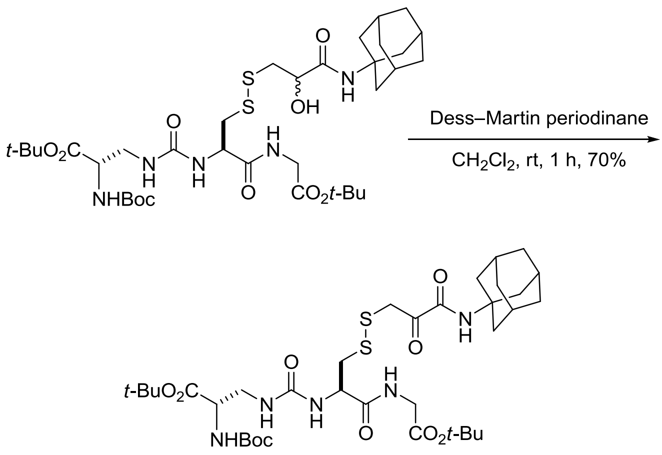
Example 1[6]



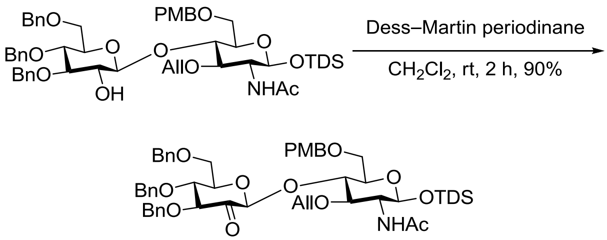
Example 2, An atypical Dess–Martin periodinane reactivity[7]



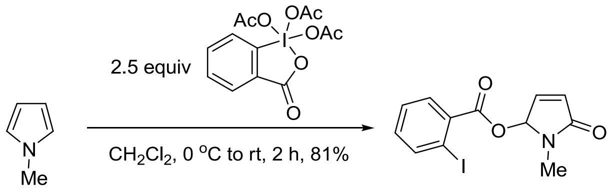
Example 3[10]



Example 4[11]



Example 5[12]

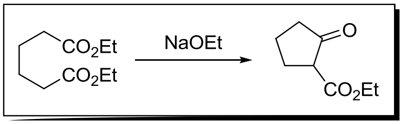


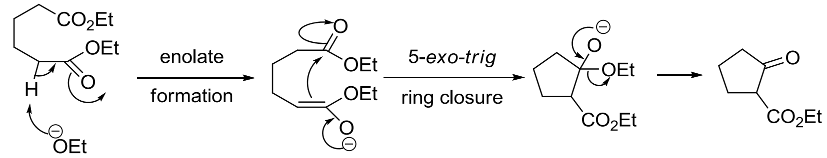
References

1. (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983,** *48*, 4155–4156. James Cullen (J. C.) Martin (1928–1999) had a distinguished career spanning 36 years both at the University of Illinois at Urbana-Champaign and Vanderbilt University. J. C.'s formal training in physical organic chemistry with Don Pearson at Vanderbilt and P. D. Bartlett at Harvard prepared him well for his early studies on carbocations and radicals. However, it was his interest in understanding the limits of chemical bonding that led to his landmark investigations into hypervalent compounds of the main group elements. Over a 20-year period the Martin laboratories successfully prepared unprecedented chemical structures from sulfur, phosphorus, silicon and bromine while the ultimate "Holy Grail" of stable pentacoordinate carbon remained elusive. Although most of these studies were driven by J. C.'s fascination with unusual bonding schemes, they were not without practical value. Two hypervalent compounds, Martin's sulfurane (for dehydration) and the Dess–Martin periodinane have found widespread application in synthetic organic chemistry. J. C. Martin and his student Daniel Dess developed this methodology at the University of Illinois at Urbana. (Martin's biography was kindly supplied by Prof. Scott E. Denmark). (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991,** *113*, 7277–7287.
2. Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993,** *58*, 2899.
3. Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994,** *59*, 7549–7552.
4. Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999,** *64*, 4537–4538.
5. Nicolaou, K. C.; Zhong, Y.-L.; Baran, P. S. *Angew. Chem. Int. Ed.* **2000,** *39,* 622–625.
6. Bach, T.; Kirsch, S. *Synlett* **2001,** 1974–1976.
7. Bose, D. S.; Reddy, A. V. N. *Tetrahedron* **2003,** *44*, 3543–3545.
8. Tohma, H.; Kita, Y. *Adv. Synth. Cat.* **2004,** *346*, 111–124. (Review).
9. Holsworth, D. D. *Dess–Martin oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ; **2007,** pp 218–236. (Review).
10. More, S. S.; Vince, R. *J. Med. Chem.* **2008,** *51*, 4581–4588.
11. Crich, D.; Li, M.; Jayalath, P. *Carbohydrate Res.* **2009,** *344*, 140–144.
12. Howard, J. K.; Hyland, C. J. T.; Just, J.; J. A. *Org. Lett.* **2013,** *15*, 1714–1717.

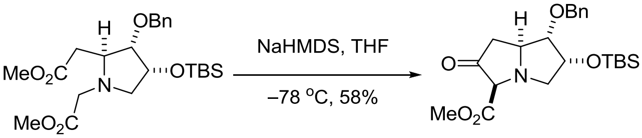
Dieckmann condensation

The Dieckmann condensation is the intramolecular version of the Claisen condensation.

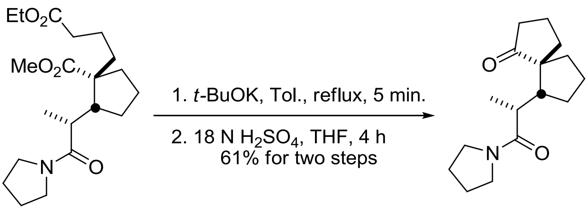




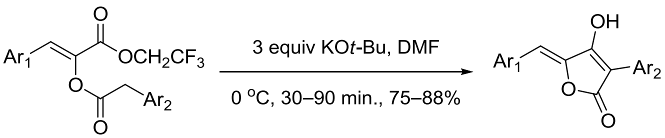
Example 1[4]



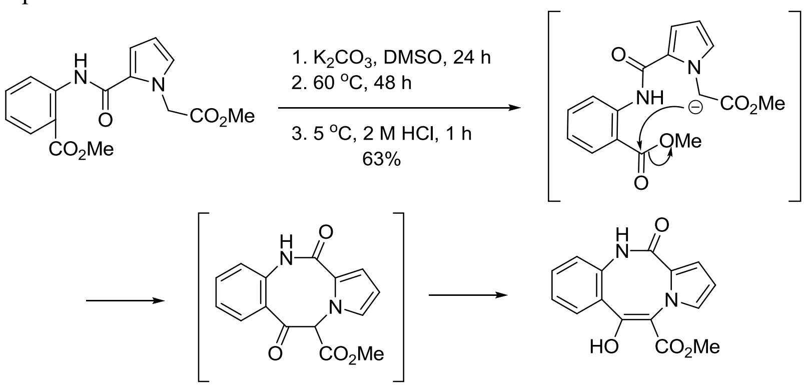
Example 2[6]



Example 3[7]



Example 4[8]



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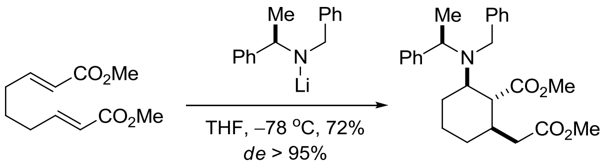
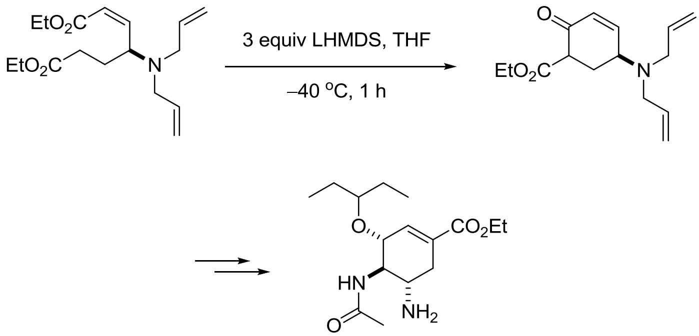
DOI 10.1007/978-3-319-03979-4_87,

Example 5, Michael–Dieckmann condensation[10]



Example 6, Michael–Dieckmann condensation[10]



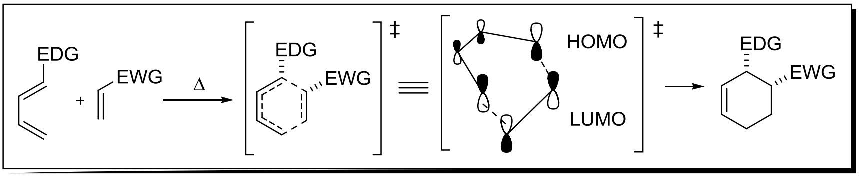
oseltamivir (Tamiflu)

References

1. Dieckmann, W. *Ber.* **1894,** *27*, 102. Walter Dieckman (1869–1925), born in Hamburg, Germany, studied with E. Bamberger at Munich. After serving as an assistant to von Baeyer in his private laboratory, he became a professor at Munich. At age 56, he died while working in his chemical laboratory at the Barvarian Academy of Science.
2. Davis, B. R.; Garratt, P. J. *Comp. Org. Synth.* **1991,** *2*, 795–863. (Review).
3. Shindo, M.; Sato, Y.; Shishido, K. *J. Am. Chem. Soc.* **1999,** *121*, 6507–6508.
4. Rabiczko, J.; Urbańczyk-Lipkowska, Z.; Chmielewski, M. *Tetrahedron* **2002,** *58*, 1433–1441.
5. Ho, J. Z.; Mohareb, R. M.; Ahn, J. H.; Sim, T. B.; Rapoport, H. *J. Org. Chem.* **2003,** *68*, 109–114.
6. de Sousa, A. L.; Pilli, R. A. *Org. Lett.* **2005,** *7*, 1617–1617.
7. Bernier, D.; Brueckner, R. *Synthesis* **2007,** 2249–2272.
8. Koriatopoulou, K.; Karousis, N.; Varvounis, G. *Tetrahedron* **2008,** *64*, 10009–10013.
9. Takao, K.-i.; Kojima, Y.; Miyashita, T.; Yashiro, K.; Yamada, T.; Tadano, K.-i. *Heterocycles* **2009,** *77*, 167–172.
10. Garrido, N. M.; Nieto, C. T.; Diez, D. *Synlett* **2013,** *24*, 169–172.
11. Kaliyamoorthy; A.; Makoto; F.; Kenzo; Y.; Naoya; K.; Takumi; W.; Masakatsu, S. *J. Org. Chem.* **2013,** *78*, 4019–4026.

Diels–Alder reaction

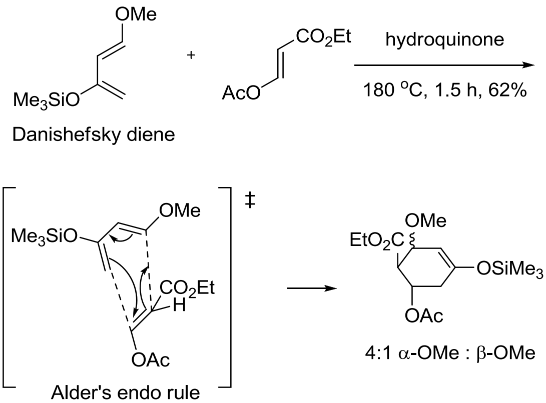
The Diels–Alder reaction, inverse electronic demand Diels–Alder reaction, as well as the hetero-Diels–Alder reaction, belong to the category of *[4+2]-cycloaddition reactions*, which are concerted processes. The arrow pushing here is merely illustrative.



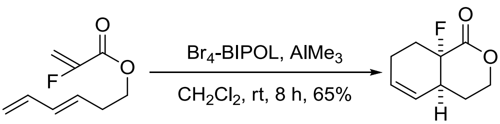
diene dienophile adduct

EDG = electron-donating group; EWG = electron-withdrawing group

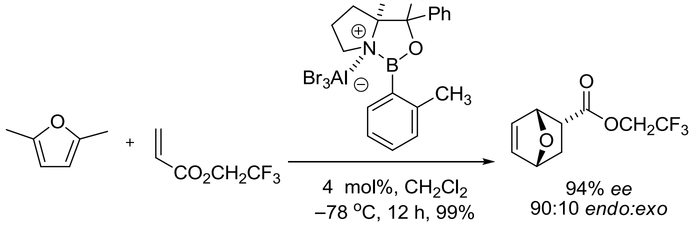
Example 1[6]



Example 2, Intramolecular Diels–Alder reaction[7]



Example 3, Asymmetric Diels–Alder reaction[5,8]



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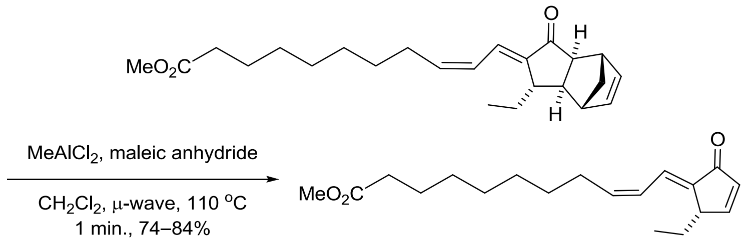
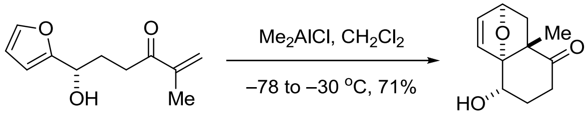
DOI 10.1007/978-3-319-03979-4_88, © Springer International Publishing Switzerland 2014

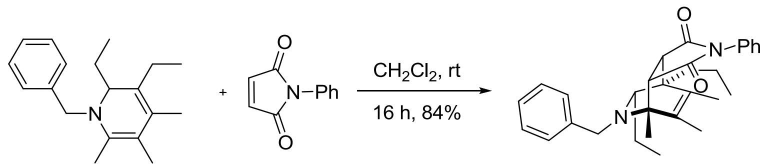
Example 4, Retro-Diels–Alder reaction[4,9]



Example 5, Intramolecular Diels–Alder reaction[11]



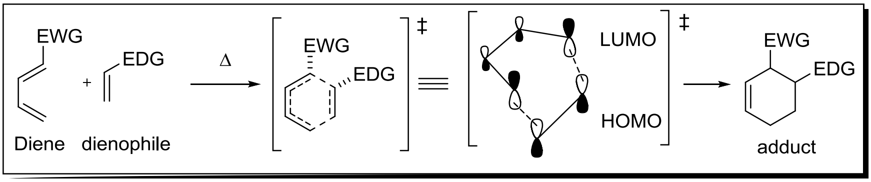
Example 6[11]



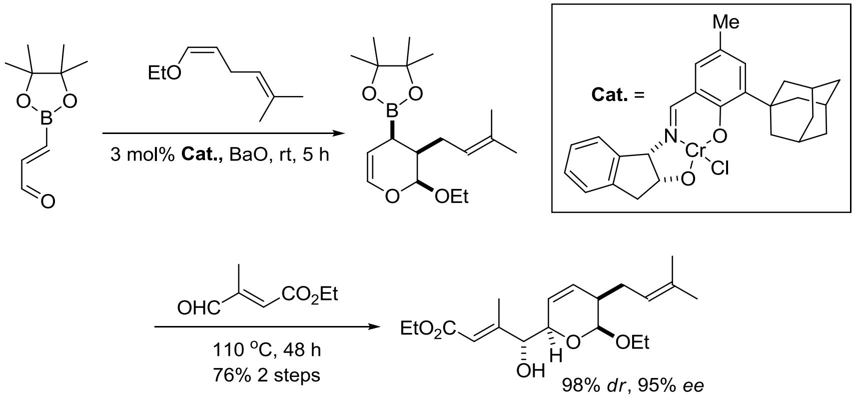
References

1. Diels, O.; Alder, K. *Ann.* **1928,** *460*, 98–122. Otto Diels (Germany, 1876–1954) and his student, Kurt Alder (Germany, 1902–1958), shared the Nobel Prize in Chemistry in 1950 for development of the diene synthesis. In this article they claimed their territory in applying the Diels–Alder reaction in total synthesis: "We explicitly reserve for ourselves the application of the reaction developed by us to the solution of such problems."
2. Oppolzer, W. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 5*, 315–399. (Review).
3. Weinreb, S. M. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 5*, 401–449. (Review).
4. (a) Rickborn, B. The *retro-Diels–Alder reaction. Part I. C–C dienophiles* in *Org. React*. Wiley: Hoboken, NJ, **1998,** *52*. (b) Rickborn, B. *The retro-Diels–Alder reaction. Part II. Dienophiles with one or more heteroatom* in *Org. React*. Wiley: Hoboken, NJ, **1998,** *53*.
5. Corey, E. J. *Angew. Chem. Int. Ed.* **2002,** *41*, 1650–1667. (Review).
6. Wang, J.; Morral, J.; Hendrix, C.; Herdewijn, P. *J. Org. Chem*. **2001,** *66*, 8478–8482.
7. Saito, A.; Yanai, H.; Sakamoto, W.; Takahashi, K.; Taguchi, T. *J. Fluorine Chem.* **2005,** *126*, 709–714.
8. Liu, D.; Canales, E.; Corey, E. J. *J. Am. Chem. Soc*. **2007,** *129*, 1498–1499.
9. Iqbal, M.; Duffy, P.; Evans, P.; Cloughley, G.; Allan, B.; Lledo, A.; Verdaguer, X.; Riera, A. *Org. Biomol. Chem*. **2008,** *6*, 4649–4661.
10. Ibrahim-Ouali, M. *Steroids* **2009,** *74*, 133–162.
11. Gao, S.; Wang, Q.; Chen, C. *J. Am. Chem. Soc*. **2009,** *131*, 1410–1412.
12. Martin, R. M.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2013,** *15*, 444–447.

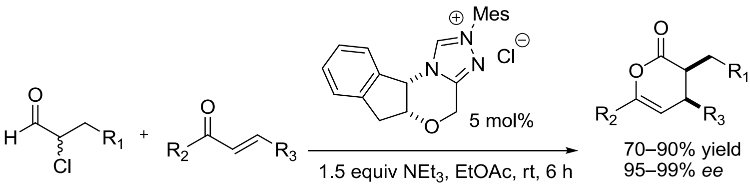
Inverse electronic demand Diels–Alder reaction



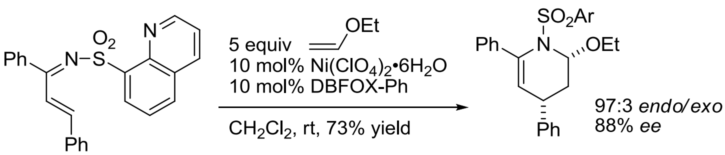
Example 1, Catalytic asymmetric inverse electronic demand Diels–Alder reaction[2]

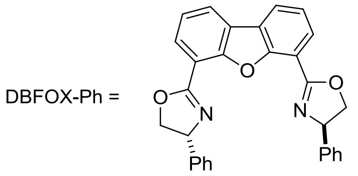


Example 2[3]

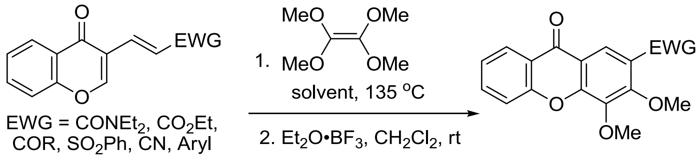


Example 3, Catalytic asymmetric inverse-electron-demand Diels–Alder reaction[4]

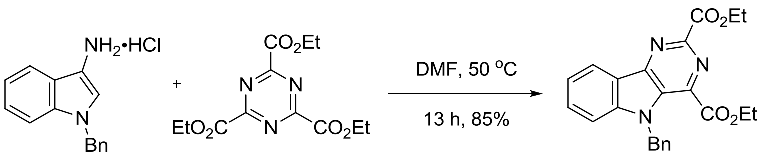




Example 4[5]



Example 5[6]

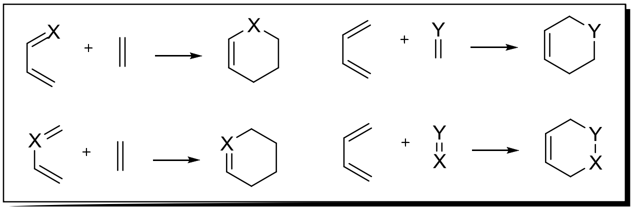


References

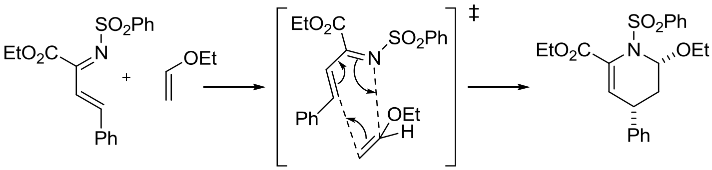
1. Boger, D. L.; Patel, M. *Prog. Heterocycl. Chem*. **1989,** *1*, 30–64. (Review).
2. Gao, X.; Hall, D. G. *J. Am. Chem. Soc*. **2005,** *127*, 1628–1629.
3. He, M.; Uc, G. J.; Bode, J. W. *J. Am. Chem. Soc*. **2006,** *128*, 15088–15089.
4. Esquivias, J.; Gomez Arrayas, R.; Carretero, J. C. *J. Am. Chem. Soc*. **2007,** *129*, 1480–1481.
5. Dang, A.-T.; Miller, D. O.; Dawe, L. N.; Bodwell, G. J. *Org. Lett.* **2008,** *10*, 233–236.
6. Xu, G.; Zheng, L.; Dang, Q.; Bai, X. *Synthesis* **2013,** *45*, 743–752.

Hetero-Diels–Alder reaction

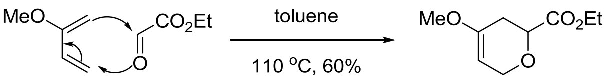
Heterodiene addition to dienophile or heterodienophile addition to diene. Typical hetero-Diels–Alder reactions are aza-Diels–Alder reaction and oxo-Diels–Alder reaction.



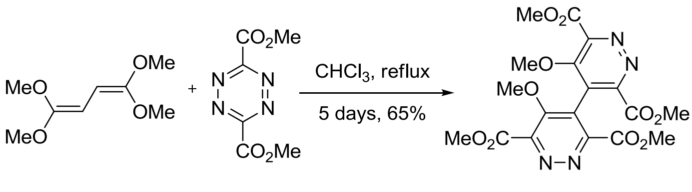
Example 1,



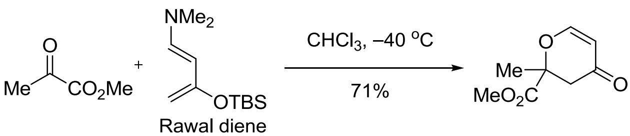
Example 2, Heterodienophile addition to diene[1]



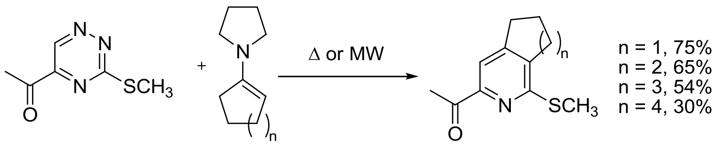
Example 3, Similar to the **Boger pyridine synthesis** (see page 59)[2]



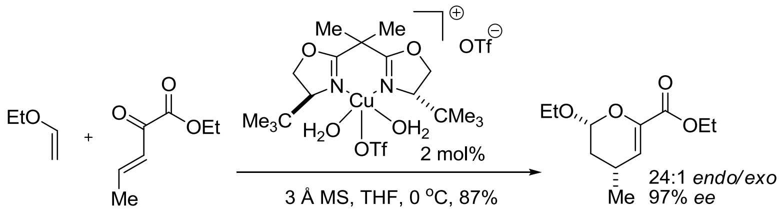
Example 4, Using **the Rawal diene**[4]



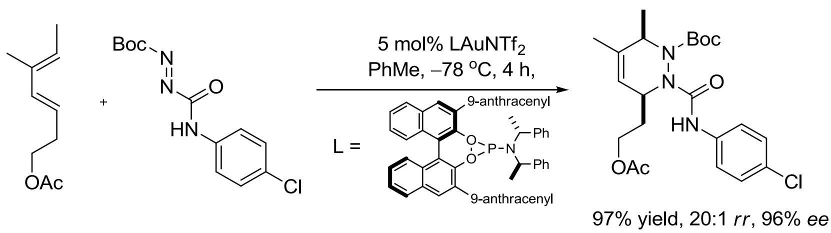
Example 5, Also similar to the Boger pyridine synthesis[6]



Example 6, Asymmetric hetero-Diels–Alder reaction[7]



Example 7, Asymmetric hetero-Diels–Alder reaction[8]

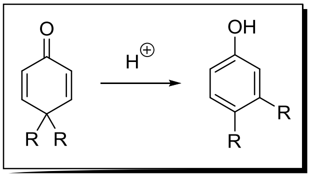


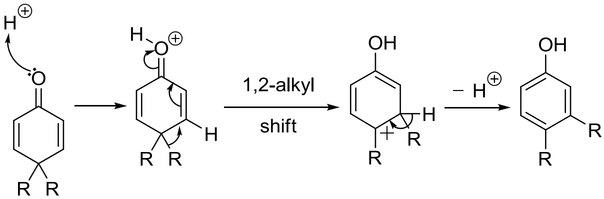
References

1. Wender, P. A.; Keenan, R. M.; Lee, H. Y. *J. Am. Chem. Soc.* **1987,** *109*, 4390–4392.
2. Boger, D. L. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 5*, 451–512. (Review).
3. Boger, D. L.; Baldino, C. M. *J. Am. Chem. Soc.* **1993,** *115*, 11418–11425.
4. Huang, Y.; Rawal, V. H. *Org. Lett.* **2000,** *2*, 3321–3323.
5. Jørgensen, K. A. *Eur. J. Org. Chem.* **2004,** 2093–2102. (Review).
6. Lipińska, T. M. *Tetrahedron* **2006,** *62*, 5736–5747.
7. Evans, D. A.; Kvaerno, L.; Dunn, T. B.; Beauchemin, A.; Raymer, B.; Mulder, J. A.; Olhava, E. J.; Juhl, M.; Kagechika, K.; Favor, D. A. *J. Am. Chem. Soc.* **2008,** *130*, 16295–16309.
8. Liu, B.; Li, K.-N.; Luo, S.-W.; Huang, J.-Z.; Pang, H.; Gong, L.-Z. *J. Am. Chem. Soc.* **2013,** *135*, 3323–3326.

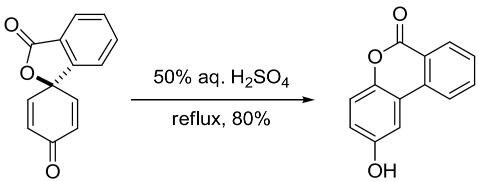
Dienone–phenol rearrangement

Acid-promoted rearrangement of 4,4-disubstituted cyclohexadienones to 3,4-disubstituted phenols.

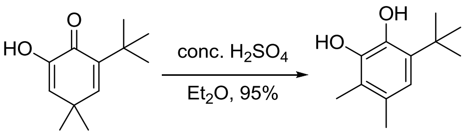




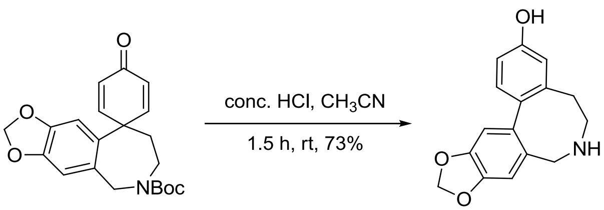
Example 1[4]



Example 2[5]



Example 3[9]



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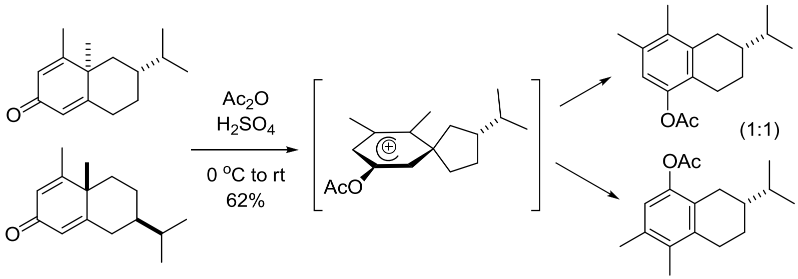
DOI 10.1007/978-3-319-03979-4_89, © Springer International Publishing Switzerland 2014

Example 4[10]

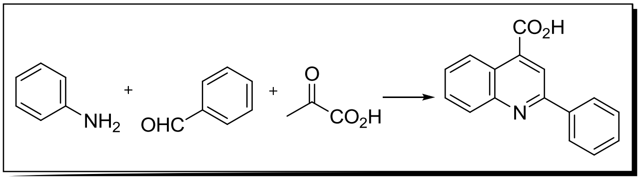


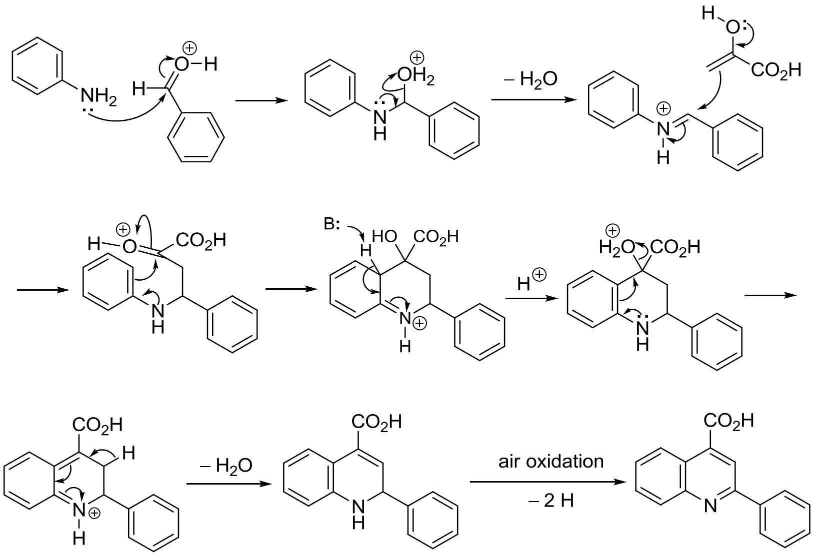
References

1. Shine, H. J. In *Aromatic Rearrangements;* Elsevier: New York, **1967,** pp 55–68. (Review).
2. Schultz, A. G.; Hardinger, S. A. *J. Org. Chem*. **1991,** *56*, 1105–1111.
3. Schultz, A. G.; Green, N. J. *J. Am. Chem. Soc*. **1992,** *114*, 1824–1829.
4. Hart, D. J.; Kim, A.; Krishnamurthy, R.; Merriman, G. H.; Waltos, A.-M. *Tetrahedron* **1992,** *48*, 8179–8188.
5. Frimer, A. A.; Marks, V.; Sprecher, M.; Gilinsky-Sharon, P. *J. Org. Chem.* **1994,** *59*, 1831–1834.
6. Oshima, T.; Nakajima, Y.-i.; Nagai, T. *Heterocycles* **1996,** *43*, 619–624.
7. Draper, R. W.; Puar, M. S.; Vater, E. J.; Mcphail, A. T. *Steroids* **1998,** *63*, 135–140.
8. Kodama, S.; Takita, H.; Kajimoto, T.; Nishide, K.; Node, M. *Tetrahedron* **2004,** *60*, 4901–4907.
9. Bru, C.; Guillou, C. *Tetrahedron* **2006,** *62*, 9043–9048.
10. Sauer, A. M.; Crowe, W. E.; Henderson, G.; Laine, R. A. *Tetrahedron Lett.* **2007,** *48*, 6590–6593.

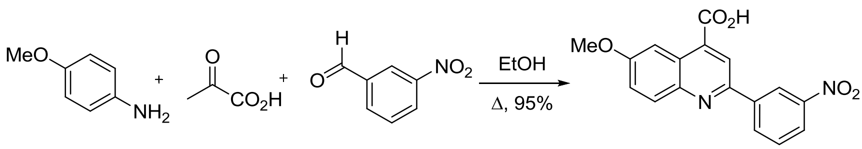
Doebner quinoline synthesis

Three-component coupling of an aniline, pyruvic acid, and an aldehyde to provide a quinoline-4-carboxylic acid.

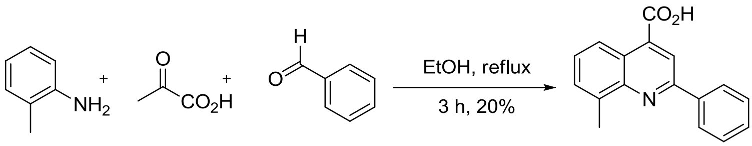




Example 1[2]



Example 2[6]



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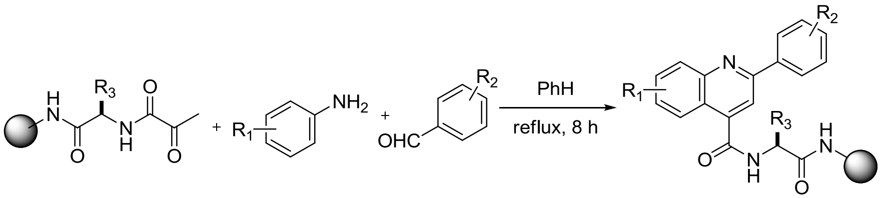
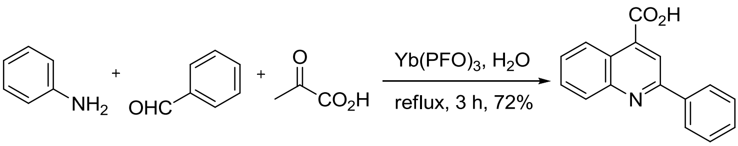
DOI 10.1007/978-3-319-03979-4_90, © Springer International Publishing Switzerland 2014

Example 3, Combinatorial Doebner reaction[7]



Example 4, Ytterbium perfluorooctanoate-catalyzed Doebner reaction in water[9]

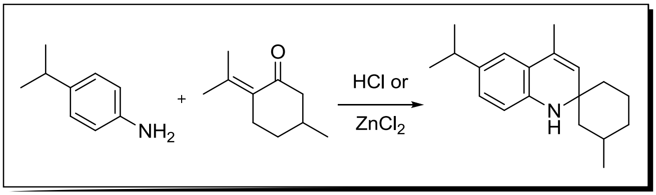


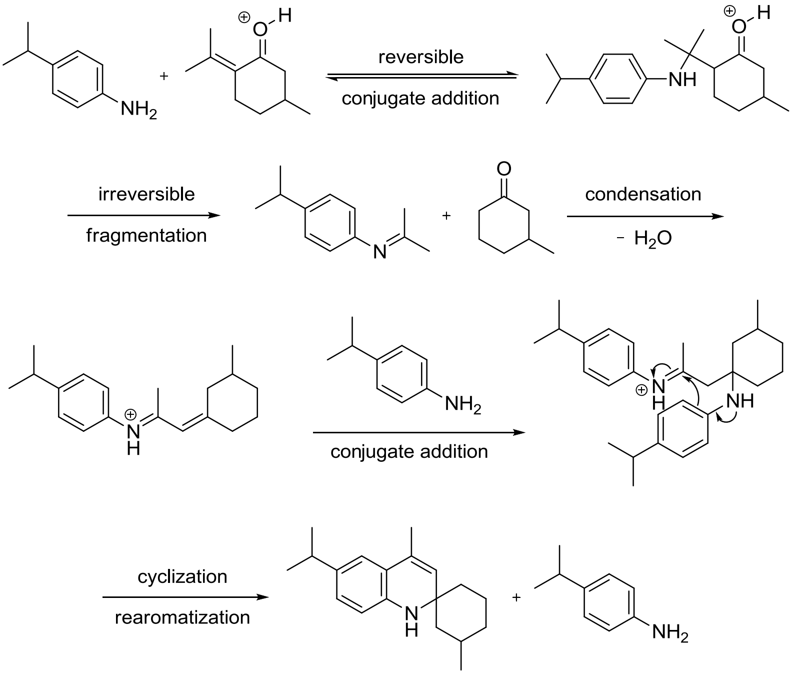
References

1. Doebner, O. G. *Ann.* **1887,** *242*, 265. Oscar Gustav Doebner (1850–1907) was born in Meininggen, Germany. After studying under Liebig, he actively took part in the Franco-Prussian War. He apprenticed with Otto and Hofmann for a few years after the war, then began his independent researches at the University at Halle.
2. Mathur, F. C.; Robinson, R. *J. Chem. Soc.* **1934,** 1520–1523.
3. Elderfield, R. C. *Heterocyclic Compounds*; Elderfield, R. C., Ed.; Wiley: New York, **1952,** *Vol. 4*, *Quinoline, Isoquinoline and Their Benzo Derivatives*, pp. 25–29. (Review).
4. Jones, G. In *Chemistry of Heterocyclic Compounds*, Jones, G., ed.; Wiley: New York, **1977,** *Vol. 32*; Quinolines, pp. 125–131. (Review).
5. Atwell, G. J.; Baguley, B. C.; Denny, W. A. *J. Med. Chem.* **1989,** *32*, 396–401.
6. Herbert, R. B.; Kattah, A. E.; Knagg, E. *Tetrahedron* **1990,** *46*, 7119–7138.
7. Gopalsamy, A.; Pallai, P. V. *Tetrahedron Lett.* **1997,** *38*, 907–910.
8. Pflum, D. A. *Doebner Quinoline Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 407–410. (Review).
9. Wang, L.-M.; Hu, L.; Chen, H.-J.; Sui, Y.-Y.; Shen, W. *J. Fluorine Chem.* **2009,** *130*, 406–409.

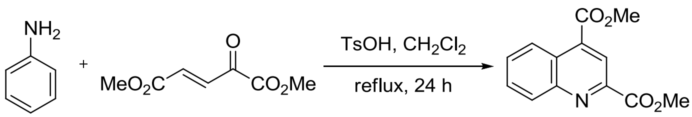
Doebner–von Miller reaction

Doebner–von Miller reaction is a variant of the Skraup quinoline synthesis. Therefore, the mechanism for the Skraup reaction is also operative for the Doebner–von Miller reaction. The following mechanism is favored by Denmark's mechnistic study using ^{13}C-labelled α,β-unsaturated ketones.[9]





Example 1[5]



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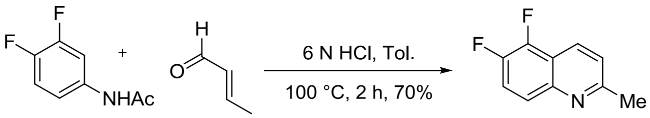
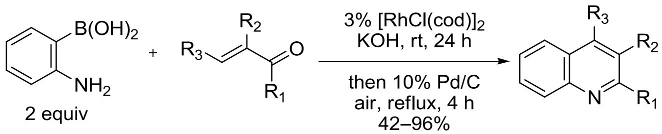
DOI 10.1007/978-3-319-03979-4_91, © Springer International Publishing Switzerland 2014

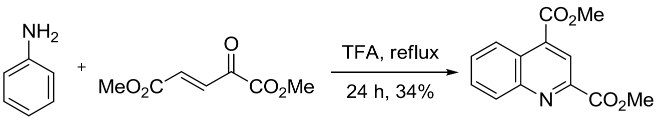
Example 2[6]



Example 3, A novel variant[10]



Example 4, Similar to Example 1[11]

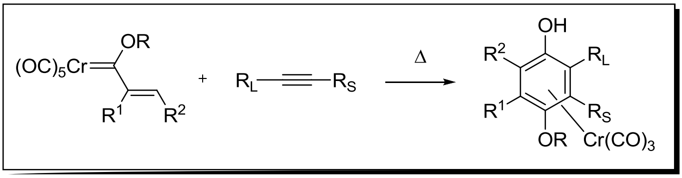


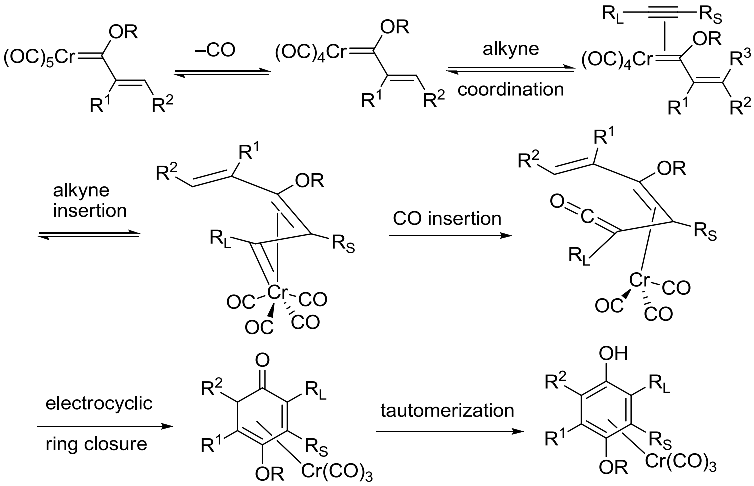
References

1. Doebner, O.; von Miller, W. *Ber.* **1883,** *16*, 2464.
2. Corey, E. J.; Tramontano, A. *J. Am. Chem. Soc.* **1981,** *103*, 5599–5600.
3. Eisch, J. J.; Dluzniewski, T. *J. Org. Chem.* **1989,** *54*, 1269–1274.
4. Zhang, Z. P.; Tillekeratne, L. M. V.; Hudson, R. A. *Tetrahedron Lett.* **1998,** *39*, 5133–5134.
5. Carrigan, C. N.; Esslinger, C. S.; Bartlett, R. D.; Bridges, R. J. *Bioorg. Med. Chem. Lett.* **1999,** *9*, 2607–2712.
6. Sprecher, A.-v.; Gerspacher, M.; Beck, A.; Kimmel, S.; Wiestner, H.; Anderson, G. P.; Niederhauser, U.; Subramanian, N.; Bray, M. A. *Bioorg. Med. Chem. Lett.* **1998,** *8*, 965–970.
7. Fürstner, A.; Thiel, O. R.; Blanda, G. *Org. Lett.* **2000,** *2*, 3731–3734.
8. Moore, A. *Skraup Doebner–von Miller Reaction.* In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 488–494. (Review).
9. Denmark, S. E.; Venkatraman, S. *J. Org. Chem.* **2006,** *71*, 1668–1676. Mechanistic study using ^{13}C-labelled α,β-unsaturated ketones.
10. Horn, J.; Marsden, S. P.; Nelson, A.; House, D.; Weingarten, G. G. *Org. Lett.* **2008,** *10*, 4117–4120.
11. Laras, Y.; Hugues, V.; Chandrasekaran, Y.; Blanchard-Desce, M.; Acher, F. C.; Pietrancosta, N. *J. Org. Chem.* **2012,** *77*, 8294–8302.

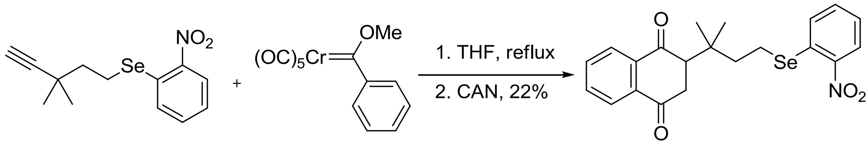
Dötz reaction

Also known as the Dötz benzannulation, the Dötz reaction is the $Cr(CO)_3$-coordinated hydroquinone from vinylic alkoxy pentacarbonyl chromium carbene (Fischer carbene) complex and alkynes.

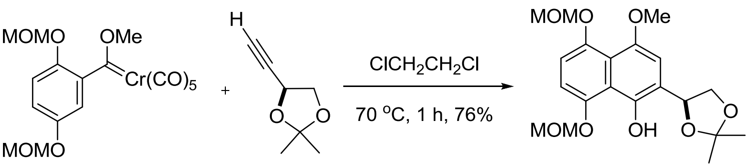




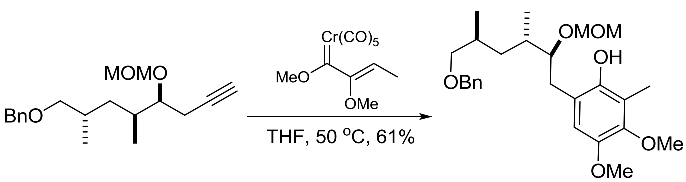
Example 1[5]



Example 3[8]



Example 3[8]



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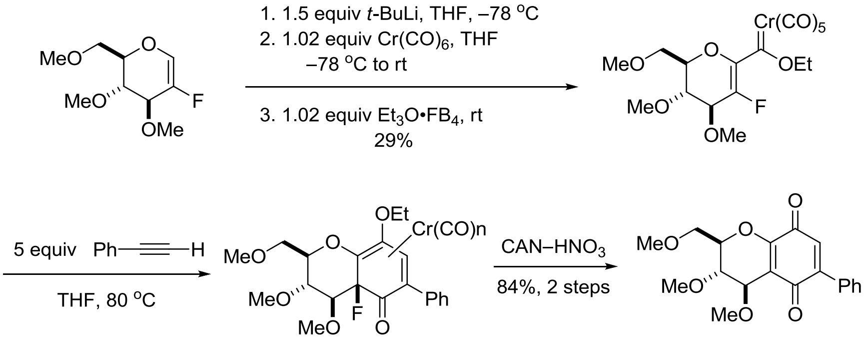
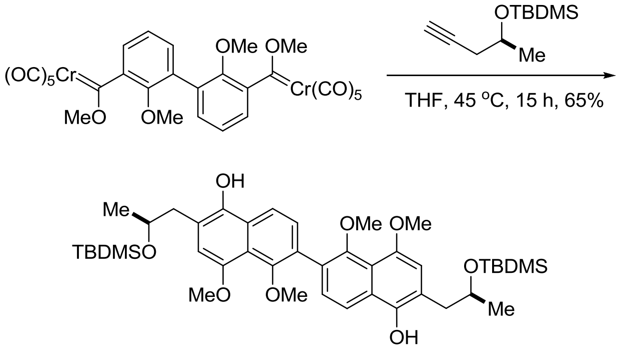
DOI 10.1007/978-3-319-03979-4_92, © Springer International Publishing Switzerland 2014

Example 3[9]



Example 4[10]

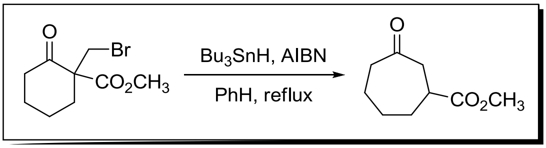


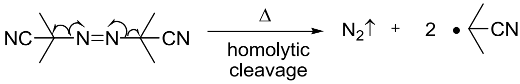
References

1. Dötz, K. H. *Angew. Chem. Int. Ed.* **1975,** *14*, 644–645. Karl H. Dötz (1943–) was a professor at the University of Munich in Germany.
2. Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press, Greenwich, CT; **1989**; *Vol. 1*. (Review).
3. Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, **1995**; *Vol. 12*. (Review).
4. Torrent, M.; Solá, M.; Frenking, G. *Chem. Rev.* **2000,** *100*, 439–494. (Review).
5. Caldwell, J. J.; Colman, R.; Kerr, W. J.; Magennis, E. J. *Synlett* **2001,** 1428–1430.
6. Solá, M.; Duran, M.; Torrent, M. *The Dötz reaction: A chromium Fischer carbene-mediated benzannulation reaction*. In *Computational Modeling of Homogeneous Catalysis* Maseras, F.; Lledós, eds.; Kluwer Academic: Boston; **2002,** 269–287. (Review).
7. Pulley, S. R.; Czakó, B. *Tetrahedron Lett.* **2004,** *45*, 5511–5514.
8. White, J. D.; Smits, H. *Org. Lett.* **2005,** *7*, 235–238.
9. Boyd, E.; Jones, R. V. H.; Quayle, P.; Waring, A. J. *Tetrahedron Lett.* **2005,** *47*, 7983–7986.
10. Fernandes, R. A.; Mulay, S. V. *J. Org. Chem.* **2010,** *75*, 7029–7032.

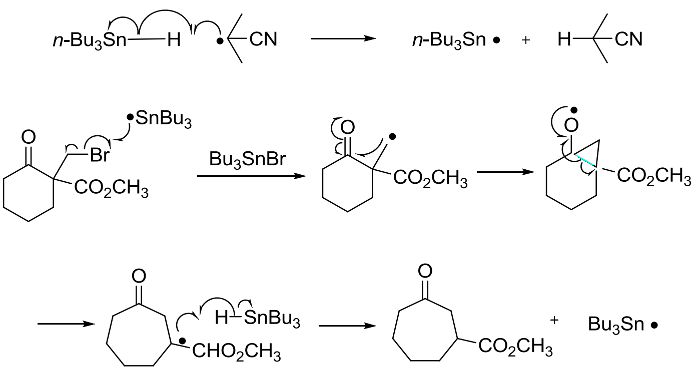
Dowd–Beckwith ring expansion

Radical-mediated ring expansion of 2-halomethyl cycloalkanones.

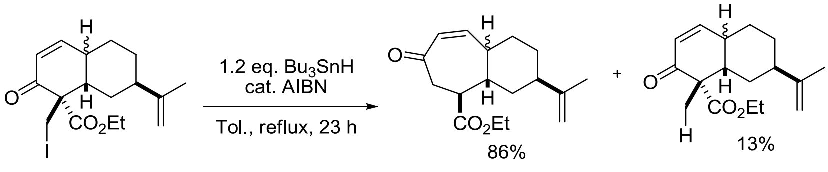




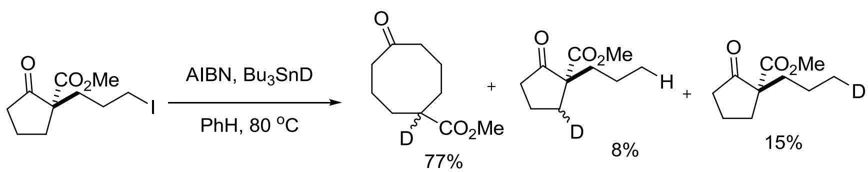
2,2′-azobisisobutyronitrile (AIBN)



Example 1[4]



Example 2[9]



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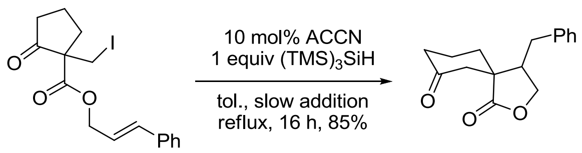
DOI 10.1007/978-3-319-03979-4_93,

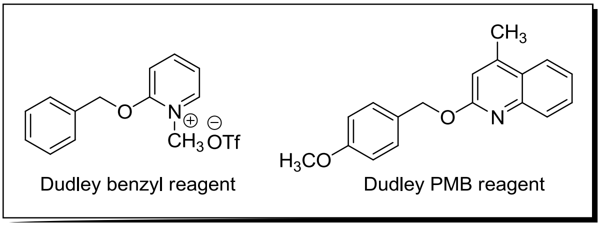
Example 3, Cascade Dowd–Beckwith Ring Expansion/Cyclization[10]



References

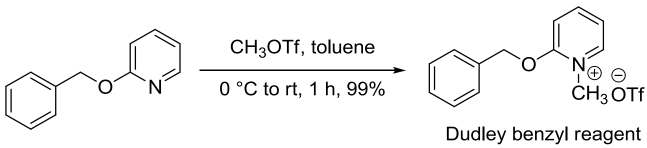
1. Dowd, P.; Choi, S.-C. *J. Am. Chem. Soc.* **1987,** *109*, 3493–3494. Paul Dowd (1936–1996) was a professor at the University of Pittsburgh.
2. (a) Beckwith, A. L. J.; O'Shea, D. M.; Gerba, S.; Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987,** 666–667. Athelstan L. J. Beckwith is a professor at University of Adelaide, Adelaide, Australia. (b) Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988,** *110*, 2565–2575. (c) Dowd, P.; Choi, S.-C. *Tetrahedron* **1989,** *45*, 77–90. (d) Dowd, P.; Choi, S.-C. *Tetrahedron Lett.* **1989,** *30*, 6129–6132. (e) Dowd, P.; Choi, S.-C. *Tetrahedron* **1991,** *47*, 4847–4860.
3. Dowd, P.; Zhang, W. *Chem. Rev.* **1993,** *93*, 2091–2115. (Review).
4. Banwell, M. G.; Cameron, J. M. *Tetrahedron Lett.* **1996,** *37*, 525–526.
5. Studer, A.; Amrein, S. *Angew. Chem. Int. Ed.* **2000,** *39*, 3080–3082.
6. Kantorowski, E. J.; Kurth, M. J. *Tetrahedron* **2000,** *56*, 4317–4353. (Review).
7. Sugi, M.; Togo, H. *Tetrahedron* **2002,** *58*, 3171–3177.
8. Ardura, D.; Sordo, T. L. *Tetrahedron Lett.* **2004,** *45*, 8691–8694.
9. Ardura, D.; Sordo, T. L. *J. Org. Chem.* **2005,** *70*, 9417–9423.
10. Lupton, David W.; Hierold, J. *Org. Lett.* **2013,** *14*, 3412–3415.

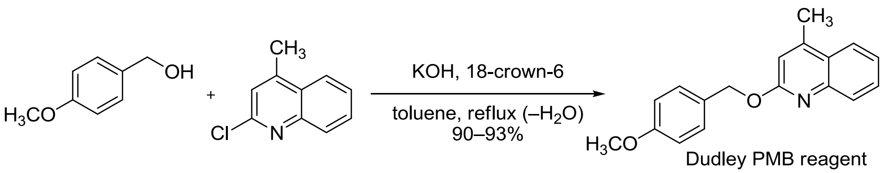
Dudley reagent



The Dudley reagents are employed for the protection of alcohols as benzyl[1] or PMB[2] ethers, respectively, under mild conditions. Carboxylic acids are readily protected as well.[3] Activation of the appropriate Dudley reagent in the presence of an alcohol furnishes the desired arylmethyl ether. The benzyl reagent is activated upon warming to approximately 80–85 °C, whereas activation of the PMB reagent occurs at room temperature upon treatment with methyl triflate (CH_3OTf) or protic acid.[4] Aromatic solvents, most commonly trifluorotoluene, often provide the best results. Magnesium oxide (MgO) is typically included in the reaction mixture as an acid scavenger.[5] For benzylation of carboxylic acids, triethylamine (Et_3N) is used in place of MgO.[3]

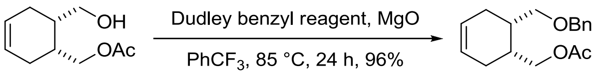
Preparation:[1–3]





The Dudley reagents are conveniently prepared from readily available starting materials and are indefinitely stable to storage and handling under standard laboratory conditions. Alternatively, both reagents are commercially available.

Example 1[6]



Benzylation of a monoacetylated diol is shown in Example 1.[6] The Dudley benzyl reagent was uniquely effective for protection of the free alcohol without loss and/or migration of the labile acetyl group.

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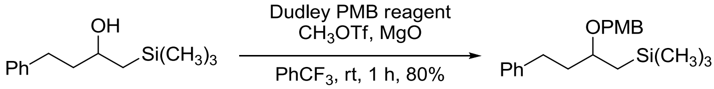
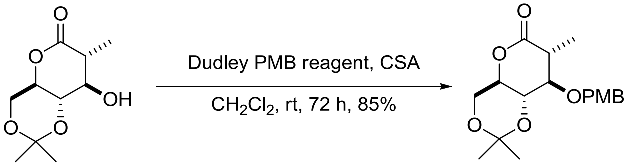
DOI 10.1007/978-3-319-03979-4_94,

Example 2[2]



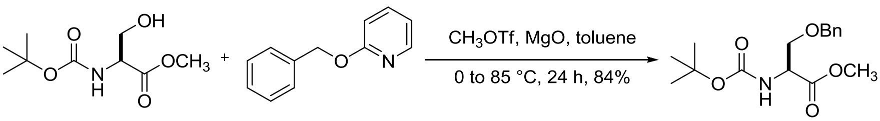
PMB-protection of a β-hydroxysilane can be accomplished without competition from the Peterson elimination (Example 2),[2] which would occur under the basic or acidic conditions required for many other alkylation reactions.

Example 3[4]



The Dudley PMB reagent can also be activated under mildly acidic conditions using catalytic camphorsulfonic acid (CSA) in lieu of CH_3OTf (Example 3).[4]

Example 4, *In situ*-formation of the Dudley benzyl reagent is achieved by treating a mixture of an alcohol and 2-benzyloxypyridine with CH_3OTf[7]

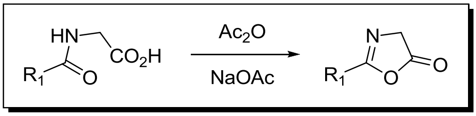


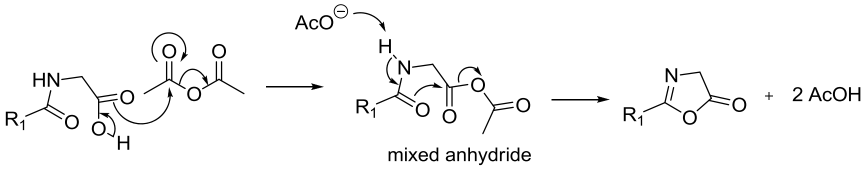
References

1. Poon, K. W. C.; Dudley, G. B. *J. Org. Chem.* **2006,** *71*, 3923–3927.
2. Nwoye, E. O.; Dudley, G. B. *Chem. Commun.* **2007,** 1436–1437.
3. Tummatorn, J.; Albiniak, P. A.; Dudley, G. B. *J. Org. Chem.* **2007,** *72*, 8962–8964.
4. Stewart, C. A.; Peng, X.; Paquette, L. A. *Synthesis* **2008,** 433–437.
5. Poon, K. W. C.; Albiniak, P. A.; Dudley, G. B. *Org. Synth.* **2007,** *84*, 295–305.
6. Schmidt, J. P.; Beltrân-Rodil, S.; Cox, R. J.; McAllister, G. D.; Reid, M.; Taylor, R. J. K. *Org. Lett.* **2007,** *9*, 4041–4044.
7. Lopez, S. S.; Dudley, G. B. *Beilstein J. Org. Chem.* **2008,** *4*, No. 44.
8. Chinigo, G. M.; Breder, A.; Carreira, E. M. *Org. Lett.* **2011,** *13,* 78–81.
9. Taber, D. F.; Nelson, C. G. *J. Org. Chem.* **2011,** *76*, 1874–1882.
10. Tomioka, T.; Yabe, Y.; Takahashi, T.; Simmons, T. K. *J. Org. Chem.* **2011,** *76*, 4669–4674.

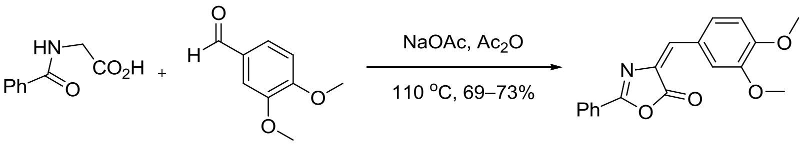
Erlenmeyer–Plöchl azlactone synthesis

Formation of 5-oxazolones (or "azlactones") by intramolecular condensation of acylglycines in the presence of acetic anhydride.

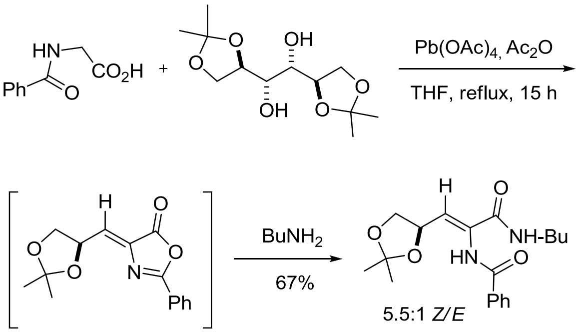




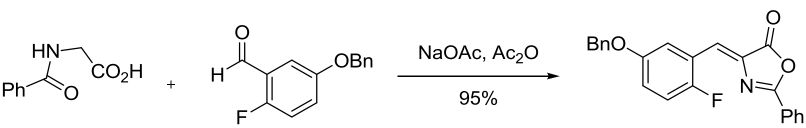
Example 1[2]



Example 2[8]



Example 3[9]



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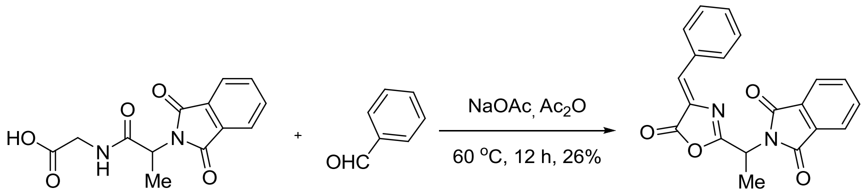
DOI 10.1007/978-3-319-03979-4_95,

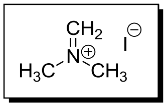
Example 4, The yield suffered for a more complicated substrate:[11]



References

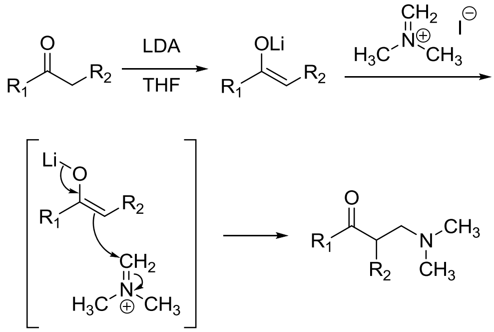
1. (a) Plöchl, J. *Ber.* **1884,** *17*, 1616–1624. (b) Erlenmeyer, E., Jr. *Ann.* **1893,** *275*, 1–3. Emil Erlenmeyer, Jr. (1864–1921) was born in Heidelberg, Germany to Emil Erlenmeyer, Sr. (1825–1909), a famous chemistry professor at the University of Heidelberg. He investigated the Erlenmeyer–Plöchl azlactone synthesis while he was a Professor of Chemistry at Strasburg. The Erlenmeyer flasks "" are ubiquitous in chemistry laboratories.
2. Buck, J. S.; Ide, W.S. *Org. Synth. Coll. II,* **1943,** 55.
3. Carter, H. E. *Org. React.* **1946,** *3*, 198–239. (Review).
4. Baltazzi, E. *Quart. Rev. Chem. Soc.* **1955,** *9*, 150–173. (Review).
5. Filler, R.; Rao, Y. S. *New Development in the Chemistry of Oxazolines*, In *Adv. Heterocyclic Chem*; Katritzky, A. R.; Boulton, A. J., Eds; Academic Press, Inc: New York, **1977**, *Vol. 21*, pp 175–206. (Review).
6. Mukerjee, A. K.; Kumar, P. *Heterocycles* **1981,** *16*, 1995–2034. (Review).
7. Mukerjee, A. K. *Heterocycles* **1987,** *26*, 1077–1097. (Review).
8. Combs, A. P.; Armstrong, R. W. *Tetrahedron Lett.* **1992,** *33*, 6419–6422.
9. Konkel, J. T.; Fan, J.; Jayachandran, B.; Kirk, K. L. *J. Fluorine Chem.* **2002,** *115*, 27–32.
10. Brooks, D. A. *Erlenmeyer–Plöchl Azlactone Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 229–233. (Review).
11. Lee, C.-Y.; Chen, Y.-C.; Lin, H.-C.; Jhong, Y.; Chang, C.-W.; Tsai, C.-H.; Kao, C.-L.; Chien, T.-C. . *Tetrahedron* **2012,** *68*, 5898–5907.

Eschenmoser's salt



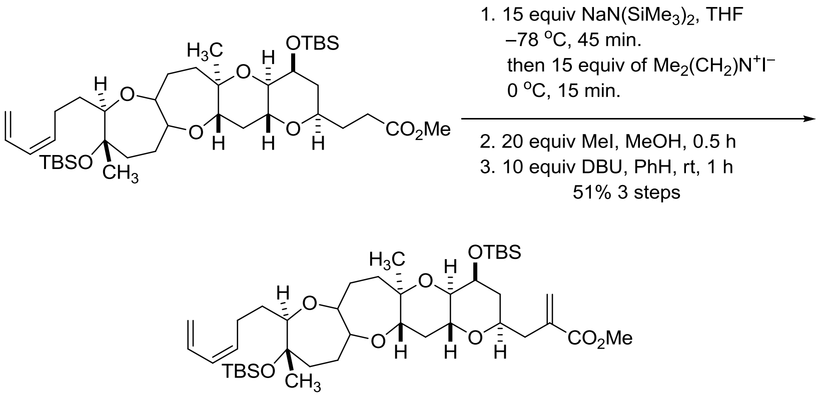
Eschenmoser's salt, dimethylmethylideneammonium iodide, is a strong dimethylaminomethylating agent, used to prepare derivatives of the type $RCH_2N(CH_3)_2$. Enolates, enolsilylethers, and even more acidic ketones undergo efficient dimethylaminomethylation—employed in the Mannich reaction.

Mechanism:



Example 1[3]

Once prepared, the resulting tertiary amines can be further methylated and then subjected to base-induced elimination to afford methylenated carbonyls.



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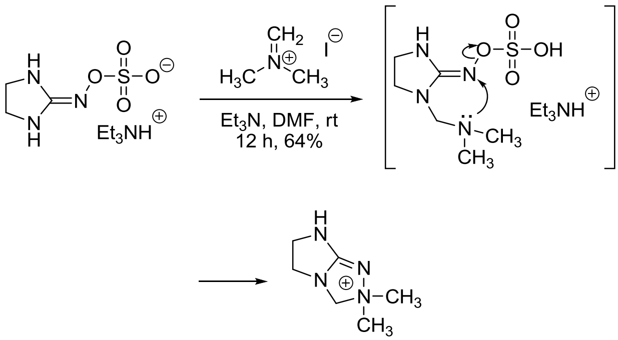
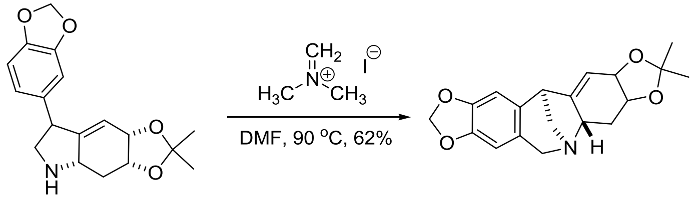
DOI 10.1007/978-3-319-03979-4_96,

Example 2[5]



Example 3[6]

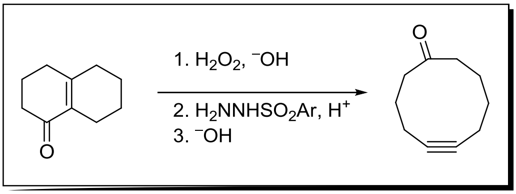


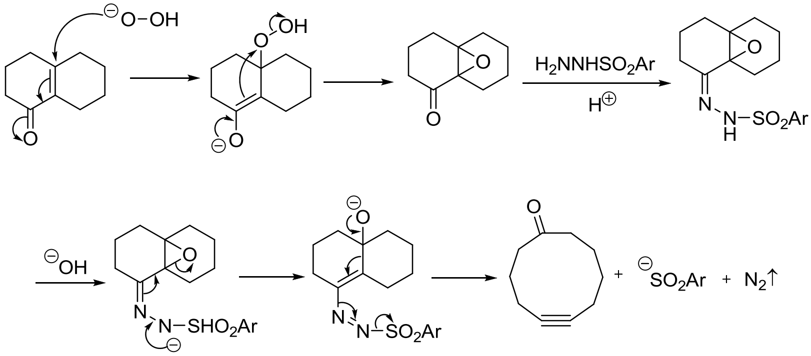
References

1. Schreiber, J.; Maag, H.; Hashimoto, N.; Eschenmoser, A. *Angew. Chem. Int. Ed.* **1971,** *10*, 330–331. Albert Eschenmoser (Switzerland, 1925–) is best known for his work on, among many others, the monumental total synthesis of Vitamin B_{12} with R. B. Woodward in 1973. He now holds joint appointments at ETH Zürich and Scripps Research Institute, La Jolla.
2. Kleinman, E. F. *Dimethylmethyleneammonium Iodide and Chloride.* In *Encyclopedia of Reagents for Organic Synthesis* (Ed: Paquette, L. A.) 2004, WileyNew York. (Review).
3. Nicolaou, K. C.; Reddy, K. R.; Skokotas, G.; Sato, F.; Xiao, X. Y.; Hwang, C. K. *J. Am. Chem. Soc.* **1993,** *115*, 3558–3575.
4. Lidia Kupczyk-Subotkowska, L.; Shine, H. J. *J. Labelled Compd. Radiopharm.* **1993,** *33,* 301–304.
5. Saczewski, J.; Gdaniec, M. *Tetrahedron Lett.* **2007,** *48*, 7624–7627.
6. Hong, A.-W.; Cheng, T.-H.; Raghukumar, V.; Sha, C.-K. *J. Org. Chem.* **2008,** *73*, 7580–7585.
7. Cesario, C.; Miller, M. J. *Org. Lett.* **2009,** *11*, 449–452.
8. Crimmins, M. T.; Zuccarello, J. L.; Ellis, J. M.; McDougall P. J.; Haile, P. A.; Parrish, J. D.; Emmitte, K. A. *Org. Lett.* **2009,** *11*, 489–492.

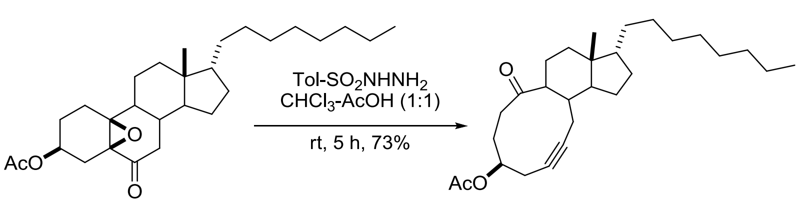
Eschenmoser–Tanabe fragmentation

Fragmentation of α,β-epoxyketones *via* the intermediacy of α,β-epoxy sulfonylhydrazones.





Example 1[4]



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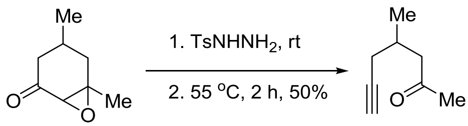

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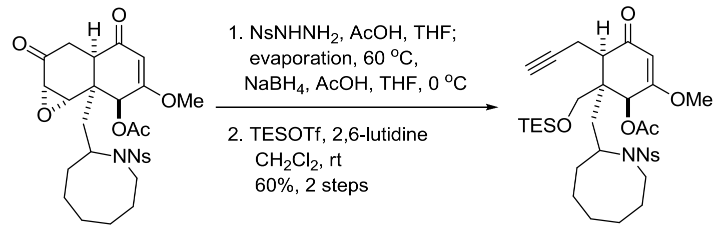
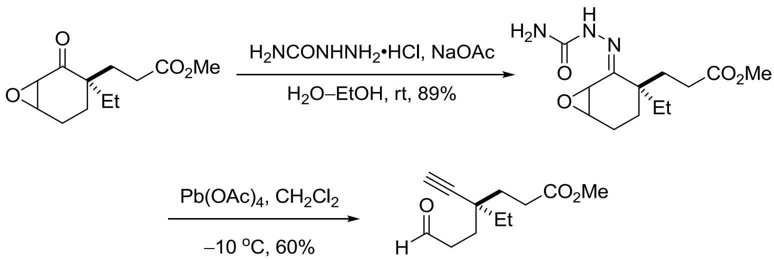
Example 3[9]



Example 4[10]



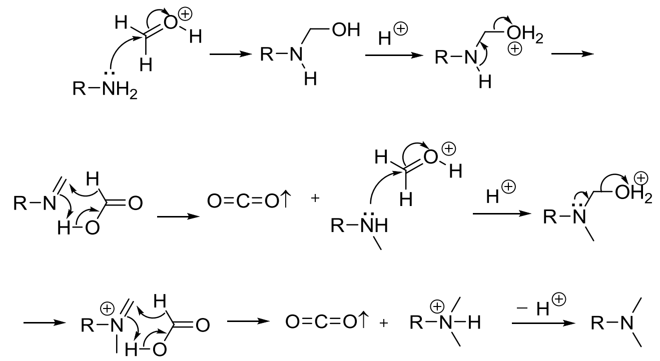
References

1. Eschenmoser, A.; Felix, D.; Ohloff, G. *Helv. Chim. Acta* **1967,** *50*, 708–713.
2. Tanabe, M.; Crowe, D. F.; Dehn, R. L. *Tetrahedron Lett.* **1967,** 3943–3946.
3. Felix, D.; Müller, R. K.; Horn, U.; Joos, R.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1972,** *55*, 1276–1319.
4. Batzold, F. H.; Robinson, C. H. *J. Org. Chem.* **1976,** *41*, 313–317.
5. Covey, D. F.; Parikh, V. D. *J. Org. Chem.* **1982,** *47*, 5315–5318.
6. Chinn, L. J.; Lenz, G. R.; Choudary, J. B.; Nutting, E. F.; Papaioannou, S. E.; Metcalf, L. E.; Yang, P. C.; Federici, C.; Gauthier, M. *Eur. J. Med. Chem.* **1985,** *20*, 235–240.
7. Dai, W.; Katzenellenbogen, J. A. *J. Org. Chem.* **1993,** *58*, 1900–1908.
8. Mück-Lichtenfeld, C. *J. Org. Chem.* **2000,** *65*, 1366–1375.
9. Kita, Y.; Toma, T.; Kan, T.; Fukuyama, T. *Org. Lett.* **2008,** *10*, 3251–3253.
10. Nakajima, R.; Ogino, T.; Yokoshima, S.; Fukuyama, T. *J. Am. Chem. Soc.* **2010,** *132*, 1236–1237.

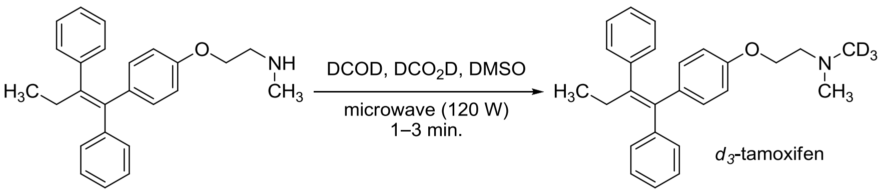
Eschweiler–Clarke reductive alkylation of amines

Reductive methylation of primary or secondary amines using formaldehyde and formic acid. *Cf.* Leuckart–Wallach reaction.

formic acid is the hydride source, serving as a reducing agent



Example 1[7]



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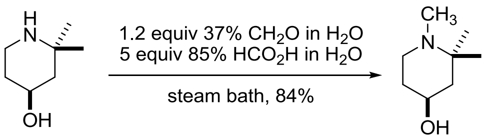
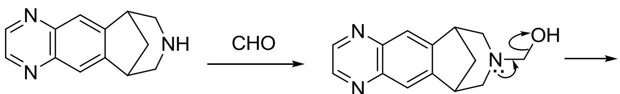


Example 3[10]



varenicline (Chantix)

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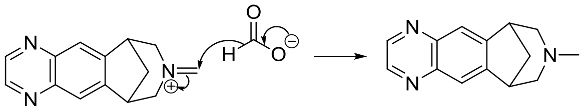
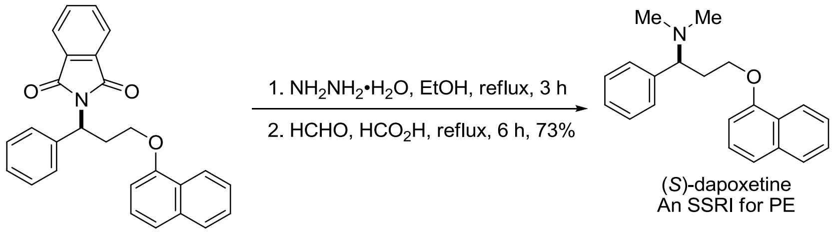


Example 4[11]

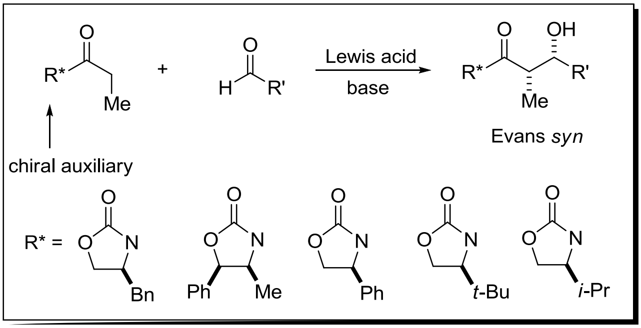


References

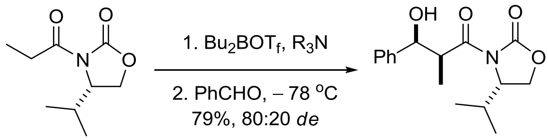
1 (a) Eschweiler, W. *Chem. Ber.* **1905,** *38*, 880–892. Wilhelm Eschweiler (1860–1936) was born in Euskirchen, Germany. (b) Clarke, H. T.; Gillespie, H. B.; Weisshaus, S. Z. *J. Am. Chem. Soc.* **1933,** *55*, 4571–4587. Hans T. Clarke (1887–1927) was born in Harrow, England.
2 Moore, M. L. *Org. React.* **1949,** *5*, 301–330. (Review).
3 Pine, S. H.; Sanchez, B. L. *J. Org. Chem*. **1971,** *36*, 829–832.
4 Bobowski, G. *J. Org. Chem*. **1985,** *50*, 929–931.
5 Alder, R. W.; Colclough, D.; Mowlam, R. W. *Tetrahedron Lett*. **1991,** *32*, 7755–7758.
6 Bulman Page, P. C.; Heaney, H.; Rassias, G. A.; Reignier, S.; Sampler, E. P.; Talib, S. *Synlett* **2000,** 104–106.
7 Harding, J. R.; Jones, J. R.; Lu, S.-Y.; Wood, R. *Tetrahedron Lett*. **2002,** *43*, 9487–9488.
8 Brewer, A. R. E. *Eschweiler–Clarke Reductive Alkylation of Amine*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 86–111. (Review).
9 Weis, R.; Faist, J.; di Vora, U.; Schweiger, K.; Brandner, B.; Kungl, A. J.; Seebacher, W. *Eur. J. Med. Chem*. **2008,** *43*, 872–879.
10 Waterman, K. C.; Arikpo, W. B.; Fergione, M. B.; Graul, T. W.; Johnson, B. A.; Macdonald, B. C.; Roy, M. C.; Timpano, R. J. *J. Pharm. Sci*. **2008,** *97*, 1499–1507.
11 Sasikumar, M.; Nikalje, Milind D. *Synth. Commun*. **2012,** *42*, 3061–3067.

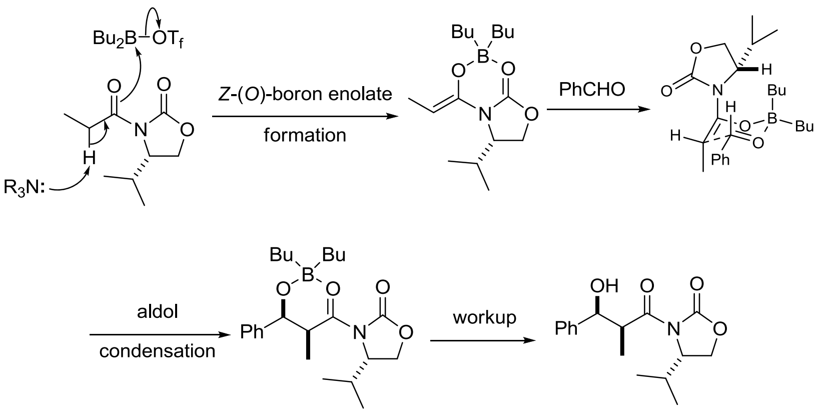
Evans aldol reaction

Asymmetric aldol reaction of aldehyde and chiral acyl oxazolidinone, the Evans chiral auxiliary.

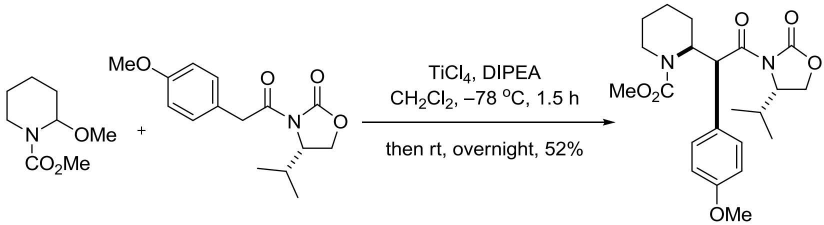


Example 1[2]





Example 2[5]



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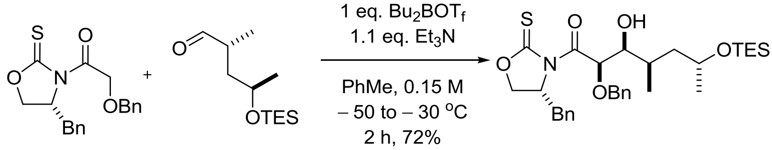
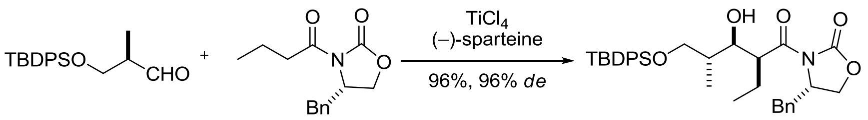
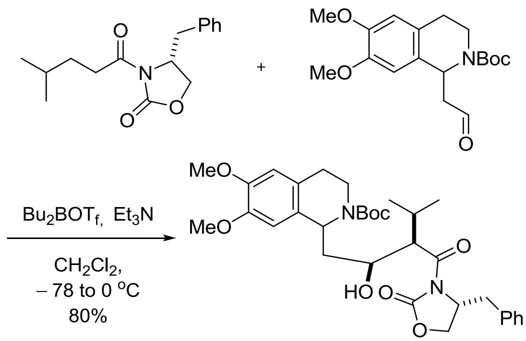
Example 3[9]



Example 4[10]



Example 5[12]

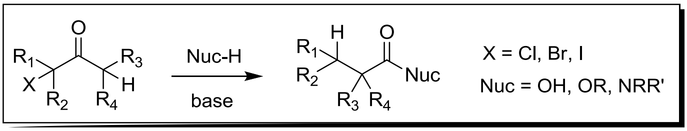


References

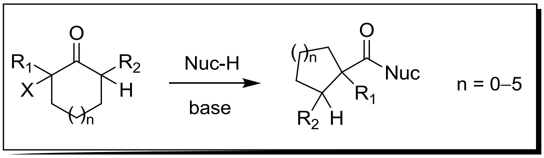
1. (a) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981,** *103*, 2127–2129. David Evans is a professor at Harvard University. (b) Evans, D. A.; McGee, L. R. *J. Am. Chem. Soc.* **1981,** *103*, 2876–2878.
2. Danda, H.; Hansen, M. M.; Heathcock, C. H. *J. Org. Chem.* **1990,** *55*, 173–181.
3. Ager, D. J.; Prakash, I.; Schaad, D. R. *Aldrichimica Acta* **1997,** *30*, 3–12. (Review).
4. Braddock, D. C.; Brown, J. M. *Tetrahedron: Asymmetry* **2000,** *11*, 3591–3607.
5. Matsumura, Y.; Kanda, Y.; Shirai, K.; Onomura, O.; Maki, T. *Tetrahedron* **2000,** *56*, 7411–7422.
6. Williams, D. R.; Patnaik, S.; Clark, M. P. *J. Org. Chem.* **2001,** *66*, 8463–8469.
7. Guerlavais, V.; Carroll, P. J.; Joullié, M. M. *Tetrahedron: Asymmetry* **2002,** *13*, 675–680.
8. Li, G.; Xu, X.; Chen, D.; Timmons, C.; Carducci, M. D.; Headley, A. D. *Org. Lett.* **2003,** *5*, 329–331.
9. Zhang, W.; Carter, R. G.; Yokochi, A. F. T. *J. Org. Chem.* **2004,** *69*, 2569–2572.
10. Ghosh, S.; Kumar, S. U.; Shashidhar, J. *J. Org. Chem.* **2008,** *73*, 1582–1585.
11. Zhang, J. *Evans Aldol Reaction.* In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 532–553. (Review).
12. Siva Senkar Reddy, N.; Srinivas Reddy, A.; Yadav, J. S.; Subba Reddy, B. V. *Tetrahedron Lett.* **2012,** *53*, 6916–6918.

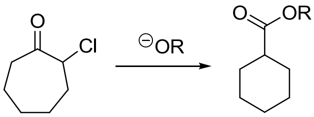
Favorskii rearrangement

Transformation of enolizable α-haloketones to esters, carboxylic acids, or amides *via* alkoxide-, hydroxide-, or amine-catalyzed rearrangements, respectively.

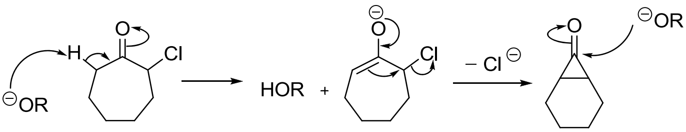


The intramolecular Favorskii Rearrangement:

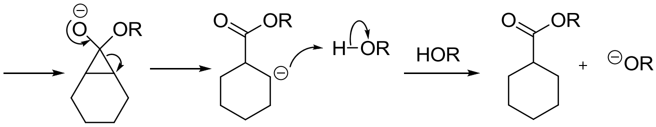




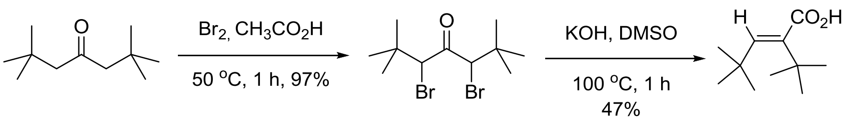
enolizable α-haloketone



cyclopropanone intermediate



Example 1[2]



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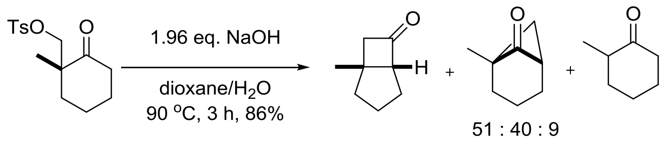
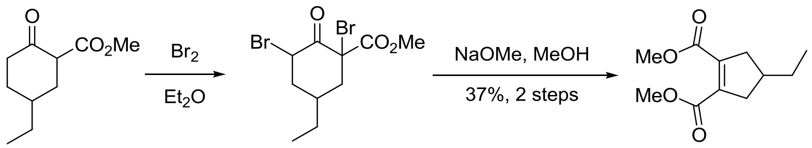
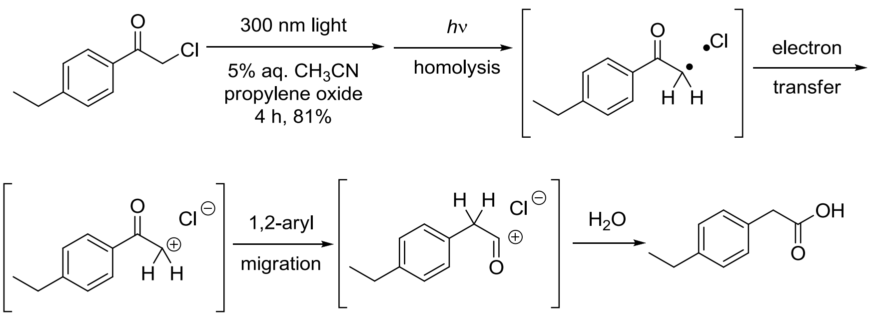
Example 2, Homo-Favorskii rearrangement[3]



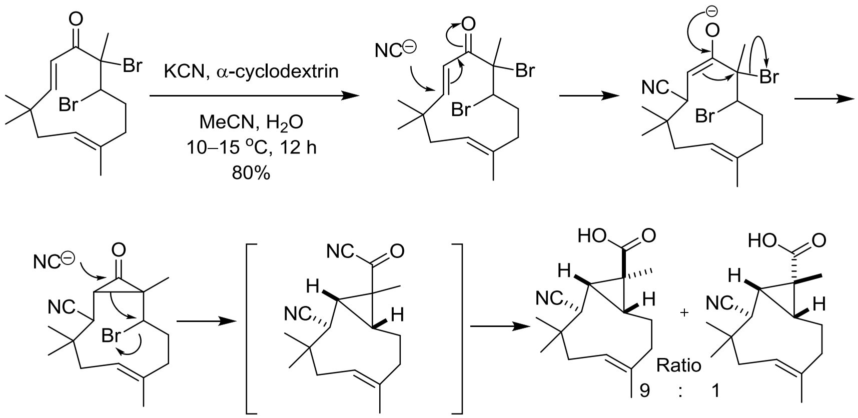
Example 3[6]



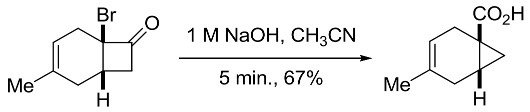
Example 4, Photo-Favorskii Rearrangement[7]



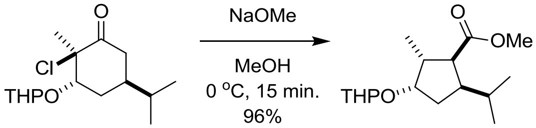
Example 5[8]



Example 6[10]



Example 7[11]

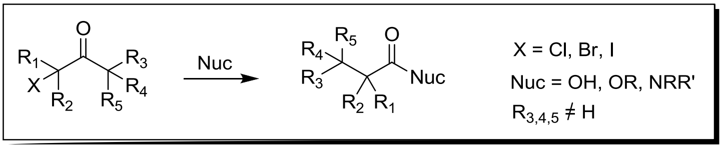


References

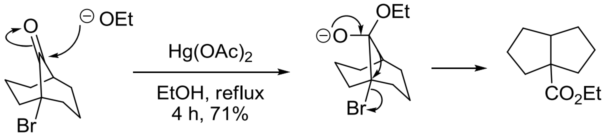
1. (a) Favorskii, A. E. *J. Prakt. Chem.* **1895,** *51*, 533–563. Aleksei E. Favorskii (1860–1945), born in Selo Pavlova, Russia, studied at St. Petersburg State University, where he became a professor since 1900. (b) Favorskii, A. E. *J. Prakt. Chem.* **1913,** *88*, 658.
2. Wagner, R. B.; Moore, J. A. *J. Am. Chem. Soc.* **1950,** *72*, 3655–3658.
3. Wenkert, E.; Bakuzis, P.; Baumgarten, R. J.; Leicht, C. L.; Schenk, H. P. *J. Am. Chem. Soc.* **1971,** *93*, 3208–3216.
4. Chenier, P. J. *J. Chem. Ed.* **1978,** *55*, 286–291. (Review).
5. Barreta, A.; Waegell, B. In *Reactive Intermediates*; Abramovitch, R. A., ed.; Plenum Press: New York, **1982,** *2,* pp 527–585. (Review).
6. White, J. D.; Dillon, M. P.; Butlin, R. J. *J. Am. Chem. Soc.* **1992,** *114*, 9673–9674.
7. Dhavale, D. D.; Mali, V. P.; Sudrik, S. G.; Sonawane, H. R. *Tetrahedron* **1997,** *53*, 16789–16794.
8. Kitayama, T.; Okamoto, T. *J. Org. Chem.* **1999,** *64*, 2667–2672.
9. Mamedov, V. A.; Tsuboi, S.; Mustakimova, L. V.; Hamamoto, H.; Gubaidullin, A. T.; Litvinov, I. A.; Levin, Y. A. *Chem. Heterocyclic Compd.* **2001,** *36*, 911. (Review).
10. Harmata, M.; Wacharasindhu, S. *Org. Lett.* **2005,** *7*, 2563–2565.
11. Pogrebnoi, S.; Saraber, F. C. E.; Jansen, B. J. M.; de Groot, A. *Tetrahedron* **2006,** *62*, 1743–1748.
12. Filipski, K.J.; Pfefferkorn, J. A. *Favorskii Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 238–252. (Review).
13. Kammath, V. B.; Šolomek, T.; Ngoy, B. P.; Heger, D.; Klán, P.; Rubina, M.; Givens, R. S. *J. Org. Chem.* **2013,** *78*, 1718–1729.

Quasi-Favorskii rearrangement

If there are no enolizable hydrogens present, the classical Favorskii rearrangement is not possible. Instead, a semi-benzylic mechanism can lead to a rearrangement referred to as quasi-Favorskii.

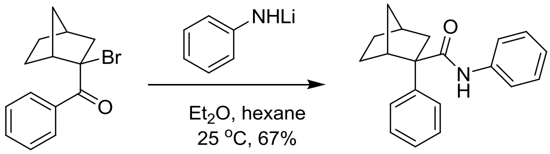


Example 1, Arthur C. Cope's initial discovery[1]

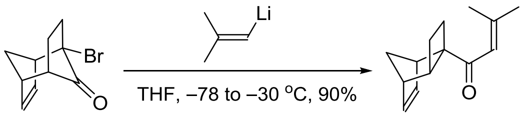


non-enolizable ketone

Example 2[5]



Example 3[9]

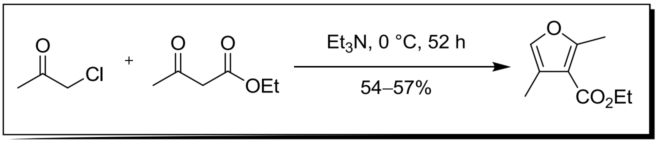


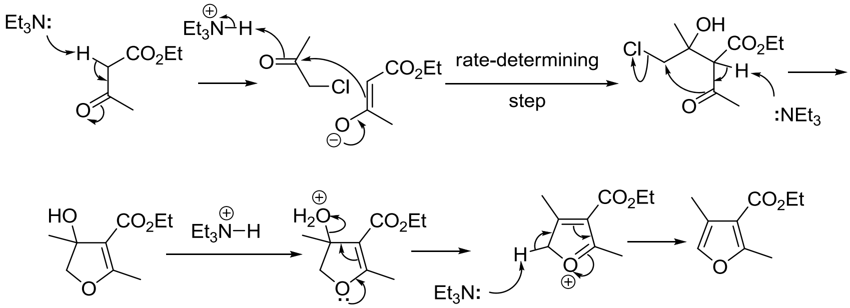
References

1. Cope, A. C.; Graham, E. S. *J. Am. Chem. Soc.* **1951,** *73*, 4702–4706.
2. Smissman, E. E.; Diebold, J. L. *J. Org. Chem.* **1965,** *30*, 4005–4007.
3. Sasaki, T.; Eguchi, S.; Toru, T. *J. Am. Chem. Soc.* **1969,** *91*, 3390–3391.
4. Baudry, D.; Begue, J. P.; Charpentier-Morize, M. *Tetrahedron Lett.* **1970,** 2147–2150.
5. Stevens, C. L.; Pillai, P. M.; Taylor, K. G. *J. Org. Chem*. **1974,** *39*, 3158–3161.
6. Harmata, M.; Wacharasindhu, S. *J. Org. Chem.* **2005,** *70*, 725–728.
7. Filipski, K.J.; Pfefferkorn, J. A. *Favorskii Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 438–452. (Review).
8. Harmata, M.; Wacharasindhu, S. *Synthesis* **2007,** 2365–2369.
9. Ross, A. G.; Townsend, S. D.; Danishefsky, S. J. *J. Org. Chem.* **2013,** *78*, 204–210.

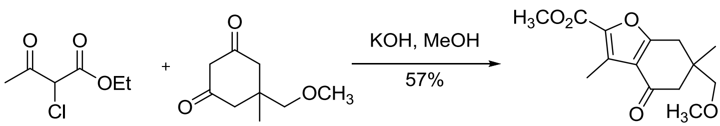
Feist–Bénary furan synthesis

α-Haloketones react with β-ketoesters in the presence of base to fashion furans.

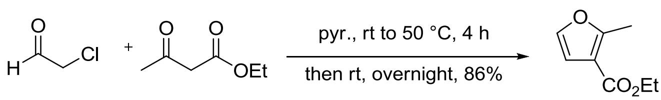




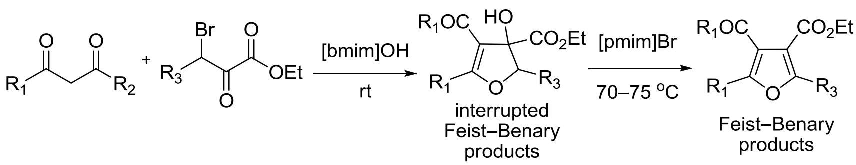
Example 1[2,3]



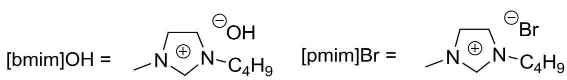
Example 2[4]



Example 3, Ionic liquid-promoted interrupted Feist–Benary reaction[10]



$R_1 = CH_3$, Et, Ph, *n*-Pr, *etc*.
$R_2 = CH_3$, OCH_3, PEt
R_3 = H, *n*-Bu, CO_2Et



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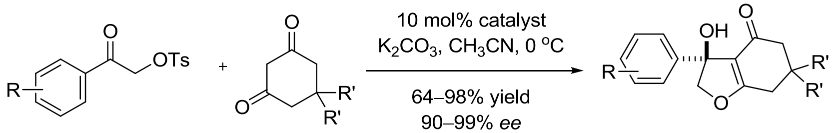
Example 4, interrupted Feist–Benary reaction of α-tosyloxy-acetophenones[10]



Catalyst = bis(cinchona alkaloid)pyrimidines

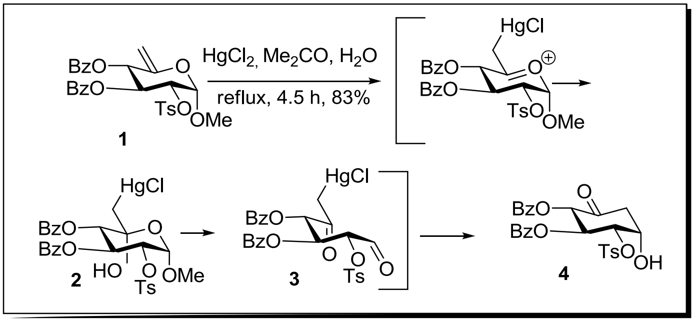
References

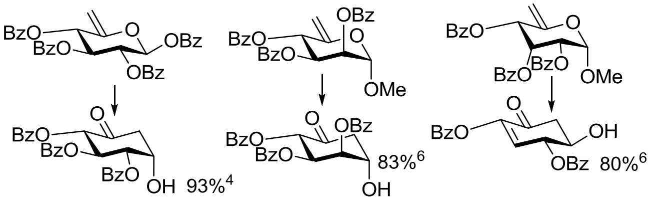
1. (a) Feist, F. *Ber.* **1902,** *35*, 1537–1544. (b) Bénary, E. *Ber.* **1911,** *44*, 489–492.
2. Gopalan, A.; Magnus, P. *J. Am. Chem. Soc.* **1980,** *102*, 1756–1757.
3. Gopalan, A.; Magnus, P. *J. Org. Chem.* **1984,** *49*, 2317–2321.
4. Padwa, A.; Gasdaska, J. R. *Tetrahedron* **1988,** *44*, 4147–4160.
5. Dean, F. M. *Recent Advances in Furan Chemistry. Part I.* In *Advances in Heterocyclic Chemistry*, Katritzky, A. R., Ed.; Academic Press: New York, **1982**; Vol. 30, 167–238. (Review).
6. Cambie, R. C.; Moratti, S. C.; Rutledge, P. S.; Woodgate, P. D. *Synth. Commun*. **1990,** *20*, 1923–1929.
7. Friedrichsen, W. *Furans and Their Benzo Derivatives: Synthesis*. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V.; Bird, C. V. Eds.; Pergamon: New York, **1996**; *Vol. 2*, 351–393. (Review).
8. König, B. *Product Class 9: Furans*. In *Science of Synthesis: Houben–Weyl Methods of Molecular Transformations*; Maas, G., Ed.; Georg Thieme Verlag: New York, **2001**; Cat. 2, Vol. 9, 183–278. (Review).
9. Shea, K. M. *Feist–Bénary Furan Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 160–167. (Review).
10. Ranu, B. C.; Adak, L.; Banerjee, S. *Tetrahedron Lett.* **2008,** *49*, 4613–4617.
11. Calter, M. A.; Korotkov, A. *Org. Lett.* **2013,** *13*, 6328–6330.

Ferrier carbocyclization

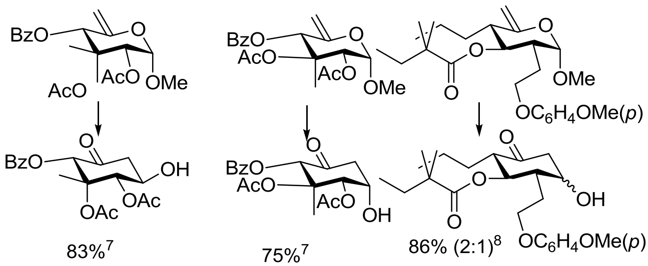
This process (also known as the “Ferrier II Reaction”) has proved to be of considerable value for the efficient, one-step conversion of 5,6-unsaturated hexopyranose derivatives into functionalized cyclohexanones useful for the preparation of such enantiomerically pure compounds as inositols and their amino, deoxy, unsaturated and selectively *O*-substituted derivatives, notably phosphate esters. In addition, the products of the carbocyclization have been incorporated into many complex compounds of interest in biological and medicinal chemistry.[1,2]

General examples:[3]

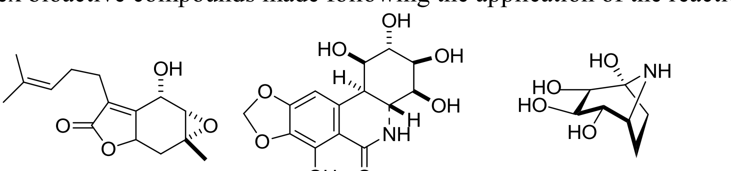




More complex products:



Complex bioactive compounds made following the application of the reaction:



Paniculide A[9] Pancratistatin[10] Calystegine B_2[11]

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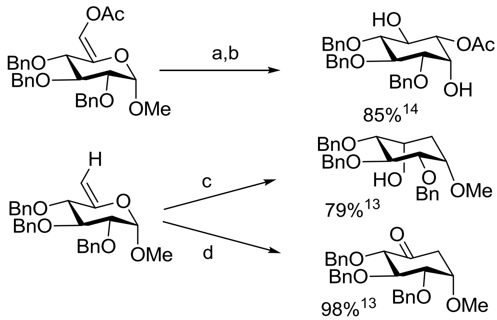
DOI 10.1007/978-3-319-03979-4_102,

Modified hex-5-enopyranosides and reactions



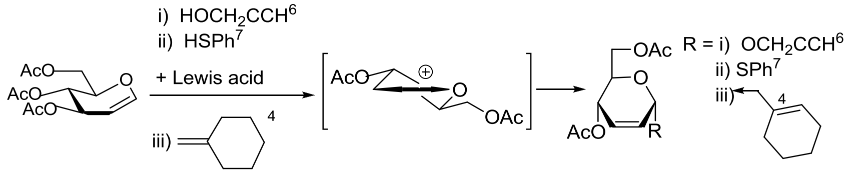
a, $Hg(OCOCF_3)_2$, Me_2CO, H_2O, 0 °C; b, $NaBH(OAc)_3$, AcOH, MeCN, rt; c, *i*-Bu_3Al, PhMe, 40 °C; d, Ti(O*i*-Pr)Cl_3, CH_2Cl_2, –78 °C, 15 min. (Note: The aglycon is retained in the Al- and Ti-induced reactions).

References

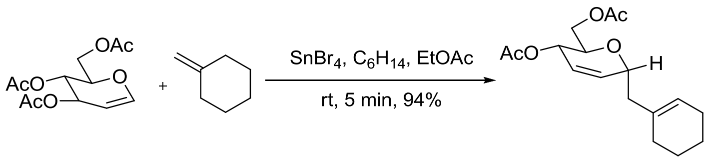
1. Ferrier, R. J.; Middleton, S. *Chem. Rev.* **1993,** *93*, 2779–2831. (Review).
2. Ferrier, R. J. *Top. Curr. Chem.* **2001,** *215*, 277–291 (Review).
3. Ferrier, R. J. *J. Chem. Soc., Perkin Trans. 1* **1979,** 1455–1458. The discovery (1977) was made in the Pharmacology Department, University of Edinburgh, while R. J. Ferrier was on leave from Victoria University of Wellington, New Zealand where he was Professor of Organic Chemistry. He is now a consultant with Industrial Research Ltd., Lower Hutt, New Zealand.
4. Blattner, R.; Ferrier, R. J.; Haines, S. R. *J. Chem. Soc., Perkin Trans. 1*, **1985,** 2413–2416.
5. Chida, N.; Ohtsuka, M.; Ogura, K.; Ogawa, S. *Bull. Chem. Soc. Jpn.* **1991,** *64*, 2118–2121.
6. Machado, A. S.; Olesker, A.; Lukacs, G. *Carbohydr. Res.* **1985,** *135*, 231–239.
7. Sato, K.-i.; Sakuma, S.; Nakamura, Y.; Yoshimura, J.; Hashimoto, H. *Chem. Lett.* **1991,** 17–20.
8. Ermolenko, M. S.; Olesker, A.; Lukacs, G. *Tetrahedron Lett.* **1994,** *35*, 711–714.
9. Amano, S.; Takemura, N.; Ohtsuka, M.; Ogawa, S.; Chida, N. *Tetrahedron* **1999,** *55*, 3855–3870.
10. Park, T. K.; Danishefsky, S. J. *Tetrahedron Lett.* **1995,** *36*, 195–196.
11. Boyer, F.-D.; Lallemand, J.-Y. *Tetrahedron* **1994,** *50*, 10443–10458.
12. Das, S. K.; Mallet, J.-M.; Sinaÿ, P. *Angew. Chem. Int. Ed.* **1997,** *36*, 493–496.
13. Sollogoub, M.; Mallet, J.-M.; Sinaÿ, P. *Tetrahedron Lett.* **1998,** *39*, 3471–3472.
14. Bender, S. L.; Budhu, R. J. *J. Am. Chem. Soc.* **1991,** *113*, 9883–9884.
15. Estevez, V. A.; Prestwich, E. D. *J. Am. Chem. Soc.* **1991,** *113*, 9885–9887.
16. Yadav, J. S.; Reddy, B. V. S.; Narasimha Chary, D.; Madavi, C.; Kunwar, A. C. *Tetrahedron Lett.* **2009,** *50*, 81–84.
17. Chen, P.; Wang, S. *Tetrahedron* **2013,** *69*, 583–588.
18. Chen, P.; Lin, L. *Tetrahedron* **2013,** *69*, 4524–4531.

Ferrier glycal allylic rearrangement

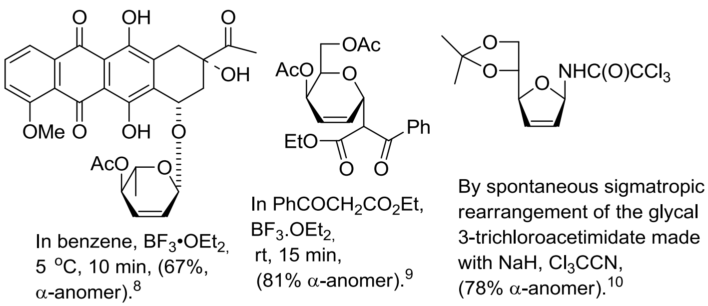
In the presence of Lewis acid catalysts *O*-substituted glycal derivatives can react with *O*-, *S*-, *C*- and, less frequently, *N*-, *P*- and halide nucleophiles to give 2,3-unsaturated glycosyl products.[1,2] This allylic transformation has been termed the "Ferrier Reaction" or, to avoid complications, the "Ferrier I Reaction" or the "Ferrier Rearrangement". However, the reaction was first noted by Emil Fischer when he heated tri-*O*-acetyl-*D*-glucal in water.[3] When carbon nucleophiles are involved, the term "Carbon Ferrier Reaction" has been used,[4] although the only contribution the Ferrier group made in this area was to find that tri-*O*-acetyl-*D*-glucal dimerizes under acid catalysis to give a *C*-glycosidic product.[5] The general reaction is illustrated by the separate conversions of tri-*O*-acetyl-*D*-glucal with *O*-, *S*- and *C*-nucleophiles to the corresponding 2,3-unsaturated glycosyl derivatives. Normally, Lewis acids are used as catalysts, boron trifluoride etherate being the most common. Allyloxycarbenium ions are involved as intermediates, high yields of products are obtained, and glycosidic compounds with quasi-axial bonds (as illustrated) predominate (commonly in the α,β-ratio of about 7:1). The examples illustrated[4,6,7] are typical of a very large number of literature reports.[1]



General examples[4]



More complex products made directly from the corresponding glycols:



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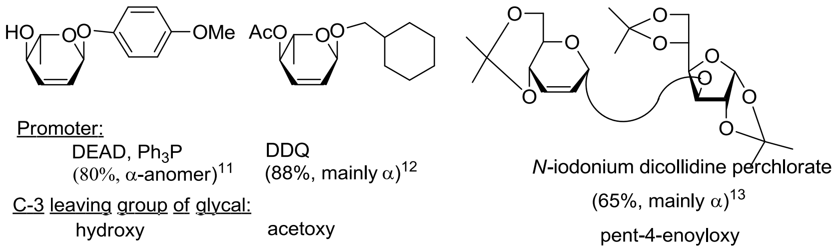
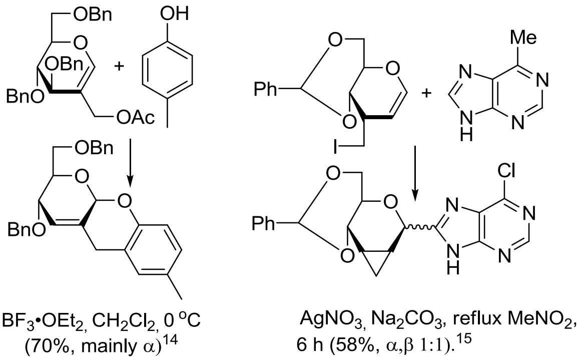
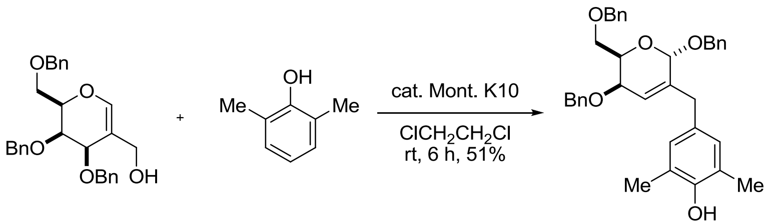
Products formed without acid catalysts:



Modified glycols and their reactions:



A variant using inexpensive Montmorillonite K-10 clay as the catalyst:



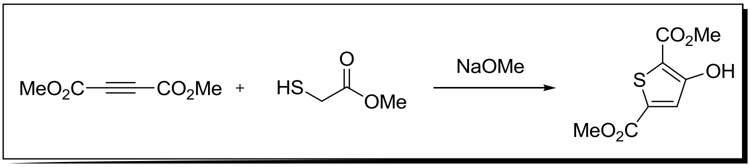
References

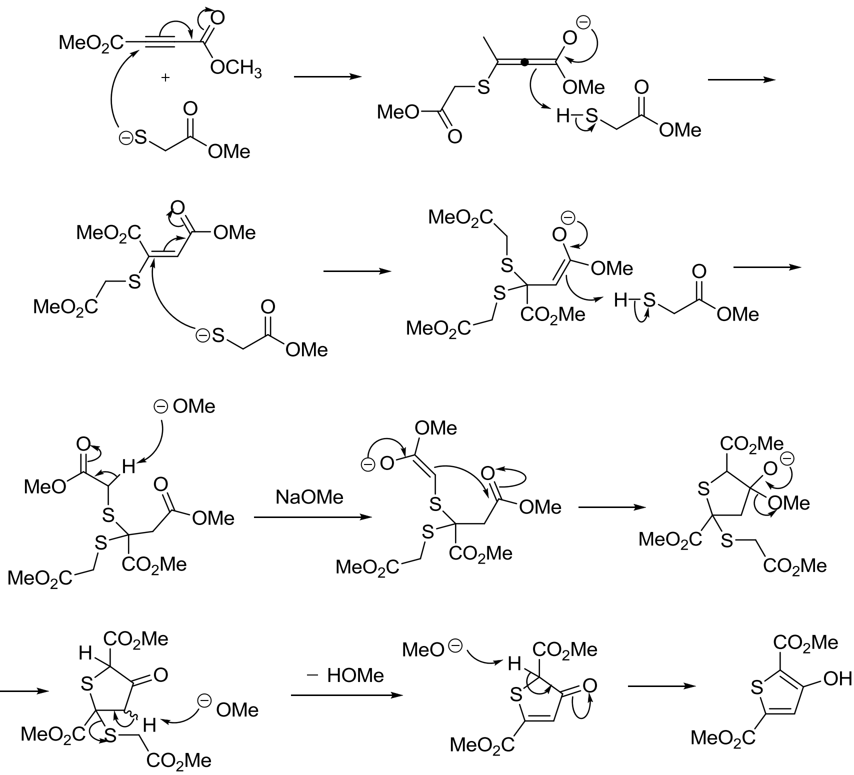
1. Ferrier, R. J.; Zubkov, O. A. Transformation of glycals into 2,3-unsaturated glycosyl derivatives, In *Org. React.* **2003,** *62*, 569–736. (Review). It was almost 50 years after Fischer's seminal finding that water took part in the reaction[3] that Ann Ryan, working in George Overend's Department in Birkbeck College, University of London, found, by chance, that *p*-nitrophenol likewise participates.[16] Robin Ferrier, her immediate supervisor, who suggested her experiment, then found that simple alcohols at high temperatures also take part,[17] and with other students, notably Nagendra Prasad and George Sankey, he explored the reaction extensively. They did not apply it to make the very important *C*-glycosides.

2. Ferrier, R. J. *Top. Curr. Chem*. **2001,** *215*, 153−175. (Review).
3. Fischer, E. *Chem. Ber*. **1914,** *47*, 196–210.
4. Herscovici, J.; Muleka, K.; Boumaïza, L.; Antonakis, K. *J. Chem. Soc., Perkin Trans. 1* **1990,** 1995–2009.
5. Ferrier, R. J.; Prasad, N. *J. Chem. Soc. (C)* **1969,** 581−586.
6. Moufid, N.; Chapleur, Y.; Mayon, P. *J. Chem. Soc., Perkin Trans. 1* **1992,** 999−1007.
7. Whittman, M. D.; Halcomb, R. L.; Danishefsky, S. J.; Golik, J.; Vyas, D. *J. Org. Chem*. **1990,** *55*, 1979−1981.
8. Klaffke, W.; Pudlo, P.; Springer, D.; Thiem, J. *Ann.* **1991,** 509−512.
9. Yougai, S.; Miwa, T. *J. Chem. Soc., Chem. Commun.* **1983,** 68−69.
10. Armstrong, P. L.; Coull, I. C.; Hewson, A. T.; Slater, M. J. *Tetrahedron Lett.* **1995,** *36*, 4311−4314.
11. Sobti, A.; Sulikowski, G. A. *Tetrahedron Lett.* **1994,** *35*, 3661−3664.
12. Toshima, K.; Ishizuka, T.; Matsuo, G.; Nakata, M.; Kinoshita, M. *J. Chem. Soc., Chem. Commun.* **1993,** 704−705.
13. López, J. C.; Gómez, A. M.; Valverde, S.; Fraser-Reid, B. *J. Org. Chem*. **1995,** *60*, 3851−3858.
14. Booma, C.; Balasubramanian, K. K. *Tetrahedron Lett*. **1993,** *34*, 6757−6760.
15. Tam, S. Y.-K.; Fraser-Reid, B. *Can. J. Chem*. **1977,** *55*, 3996–4001.
16. Ferrier, R. J.; Overend, W. G.; Ryan, A. E. *J. Chem. Soc. (C)* **1962,** 3667−3670.
17. Ferrier, R. J. *J. Chem. Soc.* **1964,** 5443−5449.
18. De, K.; Legros, J.; Crousse, B.; Bonnet-Delpon, D. *Tetrahedron* **2008,** *64*, 10497−10500.
19. Kumaran, E.; Santhi, M., Balasubramanian, K. K.; Bhagavathy, S. *Carbohydr Res*. **2011,** *346*, 1654−1661.
20. Okazaki, H.; Hanaya, K.; Shoji, M.; Hada, N.; Sugai, T. *Tetrahedron* **2013,** *69*, 7931−7935.

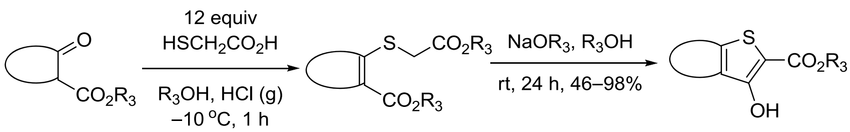
Fiesselmann thiophene synthesis

Condensation reaction of thioglycolic acid derivatives with α,β-acetylenic esters, which upon treatment with base result in the formation of 3-hydroxy-2-thiophenecarboxylic acid derivatives.





Example 1[5]



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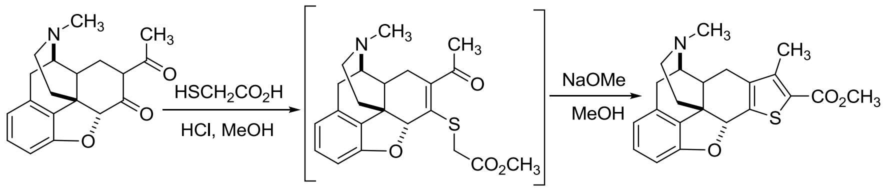
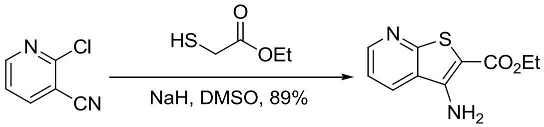
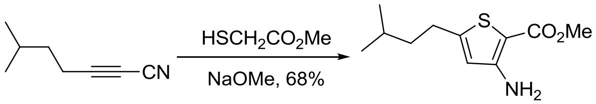
Example 2[6]



Example 3[7]



Example 4[9]

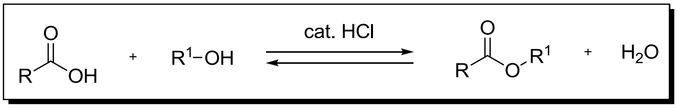


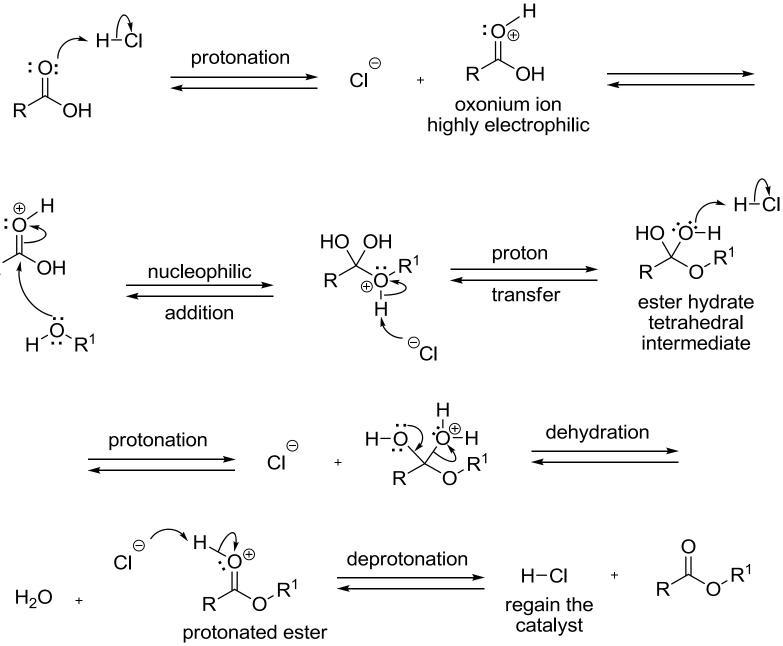
References

1. Fiesselmann, H.; Schipprak, P. *Ber.* **1954,** *87*, 835–841; Fiesselmann, H.; Schipprak, P.; Zeitler, L. *Ber.* **1954,** *87*, 841–848; Fiesselmann, H.; Pfeiffer, G. *Ber.* **1954,** *87*, 848; Fiesselmann, H.; Thoma, F. *Ber.* **1956,** *89*, 1907–1912; Fiesselmann, H.; Schipprak, P. *Ber.* **1956,** *89*, 1897–1902.
2. Gronowitz, S. In *Thiophene and Its Derivatives*, Part 1, Gronowitz, S., Ed.; Wiley: New York, **1985,** 88–125. (Review).
3. Nicolaou, K. C.; Skokotas, G.; Furuya, S.; Suemune, H.; Nicolaou, D. C. *Angew. Chem. Int. Ed.* **1990,** *29*, 1064–1068.
4. Mullican, M. D.; Sorenson, R. J.; Connor, D. T.; Thueson, D. O.; Kennedy, J. A.; Conroy, M. C. *J. Med. Chem.* **1991,** *34*, 2186–2194.
5. Donoso, R.; Jordan de Urries, P.; Lissavetzky, J. *Synthesis* **1992,** 526–528.
6. Ram, V. J.; Goel, A.; Shukla, P. K.; Kapil, A. *Bioorg. Med. Chem. Lett.* **1997,** *7*, 3101–3106.
7. Showalter, H. D. H.; Bridges, A. J.; Zhou, H.; Sercel, A. D.; McMichael, A.; Fry, D. W. *J. Med. Chem.* **1999,** *42*, 5464–5474.
8. Shkinyova, T. K.; Dalinger, I. L.; Molotov, S. I.; Shevelev, S. A. *Tetrahedron Lett.* **2000,** *41*, 4973–4975.
9. Redman, A. M.; Johnson, J. S.; Dally, R.; Swartz, S.; Wild, H.; Paulsen, H.; Caringal, Y.; Gunn, D.; Renick, J.; Osterhout, M. *Bioorg. Med. Chem. Lett.* **2001,** *11*, 9–12.
10. Migianu, E.; Kirsch, G. *Synthesis*, **2002,** 1096.
11. Mullins, R. J.; Williams, D. R. *Fiesselmann Thiophene Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 184–192. (Review).
12. Bezboruah, P.; Gogoi, P.; Junali Gogoi, J.; Boruah, R. C. *Synthesis* **2013,** *45*, 1341–1348.

Fischer–Speier esterification

Esterification by refluxing a carboxylic acid and an alcohol in the presence of an acid catalyst. Often known as simply “Fischer esterification.”





References

1. Fischer, E.; Speier, A. *Ber. Dtsch. Chem. Ges.* **1895,** *28*, 3252–3258.
2. Hardy, J. P.; Kerrin, S. L.; Manatt, S. L. *J. Org. Chem*. **1973,** *38*, 4196–4200.
3. Fujii, T.; Yoshifuji, S. *Chem. Pharm. Bull*. **1978,** *26*, 2253–2257.
4. Pcolinski, M. J.; O’Mathuna, D. P.; Doskotch, R. W. *J. Nat. Prod*. **1995,** *58*, 209–216.
5. Kai, T.; Sun, X.-L.; Tanaka, M.; Takayanagi, H.; Furuhata, K. *Chem. Pharm. Bull*. **1996,** *44*, 208–211.
6. Birney, D. M.; Starnes, S. *J. Chem. Educ*. **1996,** *76*, 1560–1561.
7. Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H., Jr. *J. Am. Chem. Soc.* **2002,** *124*, 5962–5963.
8. Li, J. in *Name Reactions for Functional Group Transformations*, Li, J. J., Ed., Wiley: Hoboken, NJ, 2007. pp 458–461.
9. Saavedra, H. M.; Thompson, C. M.; Hohman, J. N.; Crespi, V. H.; Weiss, P. S. *J. Am. Chem. Soc.* **2009,** *131*, 2252–2259.

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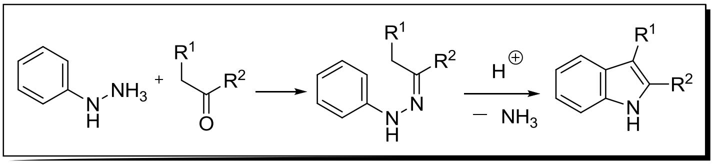
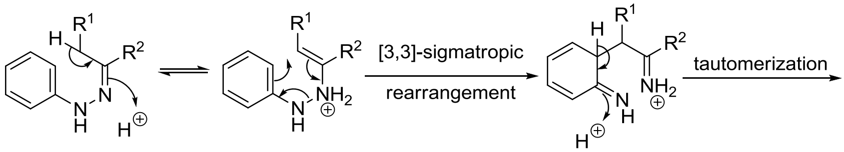
Fischer indole synthesis

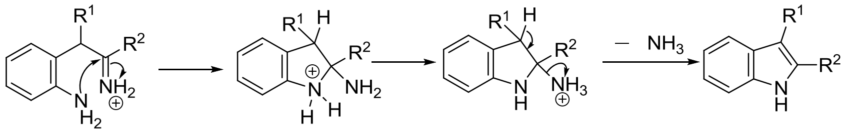
Cyclization of arylhydrazones to indoles.



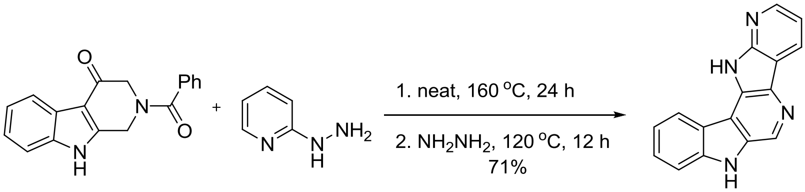
phenylhydrazine phenylhydrazine



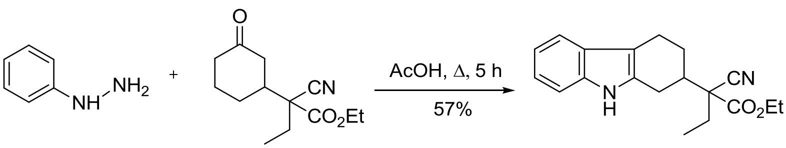
protonation ene-hydrazine double imine



Example 1[3]



Example 2[3]



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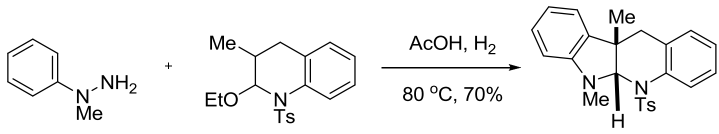
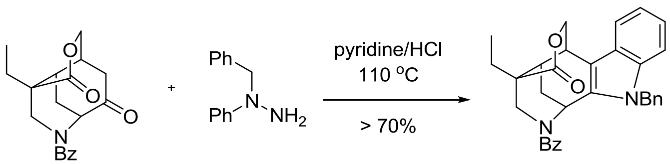
DOI 10.1007/978-3-319-03979-4_106,

Example 3[10]



Example 4[12]

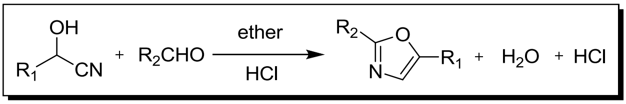


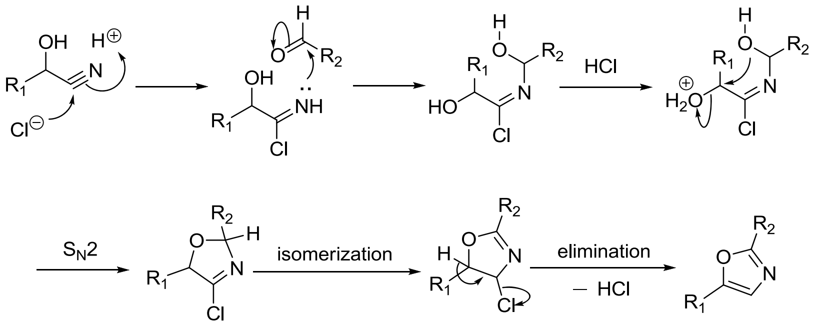
References

1. (a) Fischer, E.; Jourdan, F. *Ber.* **1883,** *16*, 2241–2245. H. Emil Fischer (1852–1919) is arguably the greatest organic chemist ever. He was born in Euskirchen, near Bonn, Germany. When he was a boy, his father, Lorenz, said about him: "The boy is too stupid to go in to business; so in God's name, let him study." Fischer studied at Bonn and then Strassburg under Adolf von Baeyer. Fischer won the Nobel Prize in Chemistry in 1902 (three years ahead of his master, von Baeyer) for his synthetic studies in the area of sugar and purine groups. Sadly, Fischer committed suicide after WWI after his son died during the war and his fortunes completely gone. (b) Fischer, E.; Hess, O. *Ber.* **1884,** *17*, 559.
2. Robinson, B. *The Fisher Indole Synthesis,* Wiley: New York, NY, **1982**. (Book).
3. Martin, M. J.; Trudell, M. L.; Arauzo, H. D.; Allen, M. S.; LaLoggia, A. J.; Deng, L.; Schultz, C. A.; Tan, Y.; Bi, Y.; Narayanan, K.; Dorn, L. J.; Koehler, K. F.; Skolnick, P.; Cook, J. M. *J. Med. Chem.* **1992,** *35*, 4105–4117.
4. Hughes, D. L. *Org. Prep. Proc. Int.* **1993,** *25*, 607–632. (Review).
5. Bosch, J.; Roca, T.; Armengol, M.; Fernández-Forner, D. *Tetrahedron* **2001,** *57*, 1041–1048.
6. Ergün, Y.; Patir, S.; Okay, G. *J. Heterocycl. Chem.* **2002,** *39*, 315–317.
7. Pete, B.; Parlagh, G. *Tetrahedron Lett.* **2003,** *44*, 2537–2539.
8. Li, J.; Cook, J. M. *Fischer Indole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 116–127. (Review).
9. Borregán, M.; Bradshaw, B.; Valls, N.; Bonjoch, J. *Tetrahedron: Asymmetry* **2008,** *19*, 2130–2134.
10. Boal, B. W.; Schammel A. W.; Garg, N. K. *Org. Lett.* **2013,** *11*, 3458–3461.
11. Donald, J. R.; Taylor, R. J. K. *Synlett* **2009,** 59–62.
12. Adams, G. L.; Carroll, P. J.; Smith, A. B. III *J. Am. Chem. Soc.* **2013,** *135*, 519–523.

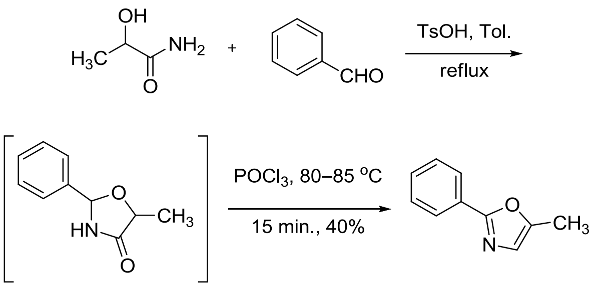
Fischer oxazole synthesis

Oxazoles from the condensation of equimolar amounts of aldehyde cyanohydrins and aromatic aldehydes in dry ether in the presence of dry hydrochloric acid.





Example 1[4]



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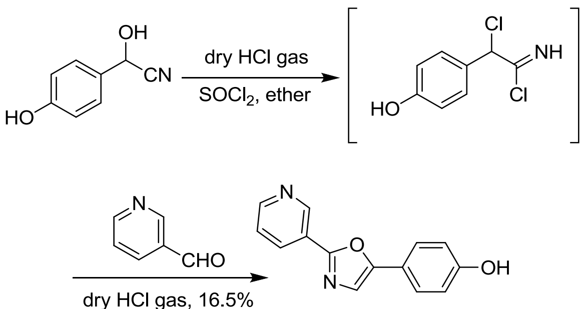

halfordinal

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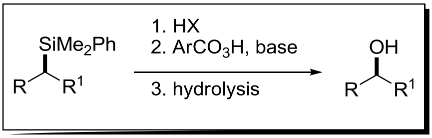
References

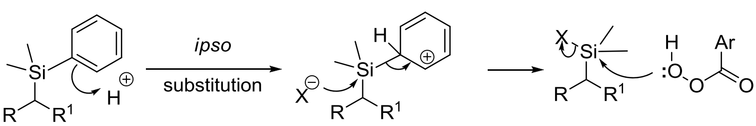
1. Fischer, E. *Ber.* **1896,** *29,* 205.
2. Ladenburg, K.; Folkers, K.; Major, R. T. *J. Am. Chem. Soc.* **1936,** *58*, 1292–1294.
3. Wiley, R. H. *Chem. Rev.* **1945,** *37***,** 401–442. (Review).
4. Cornforth, J. W.; Cornforth, R. H. *J. Chem. Soc.* **1949,** 1028–1030.
5. Cornforth, J. W. In *Heterocyclic Compounds 5*; Elderfield, R. C., Ed.; Wiley: New York, **1957,** *5,* 309–312. (Review).
6. Crow, W. D.; Hodgkin, J. H. *Tetrahedron Lett.* **1963,** *2*, 85–89.
7. Brossi, A.; Wenis, E. *J. Heterocycl. Chem.* **1965,** *2*, 310–312.
8. Onaka, T. *Tetrahedron Lett.* **1971,** 4393–4394.
9. Brooks, D. A. *Fisher Oxazole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 234–236. (Review).

Fleming–Kumada oxidation

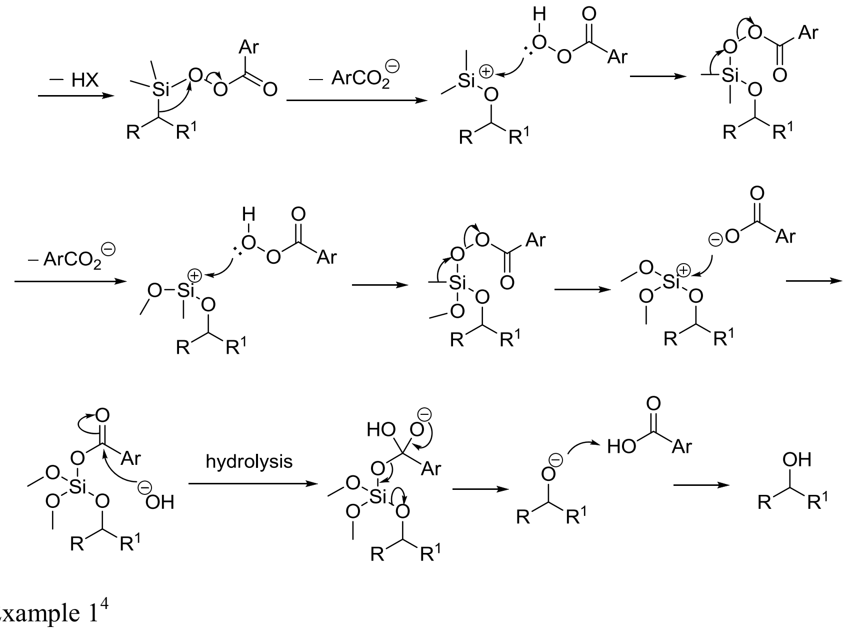
Stereoselective oxidation of alkyl-silanes into the corresponding alkyl-alcohols using peracids.



retention of configuration



the β-carbocation is stabilized by the silicon group



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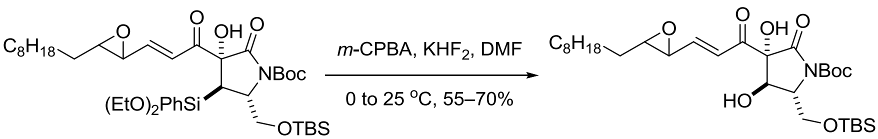

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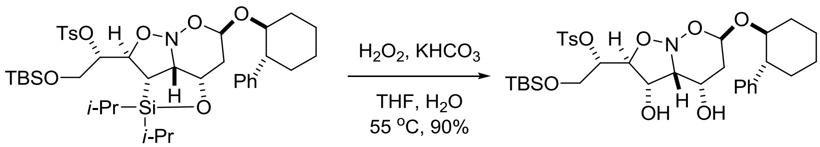
Example 2[5]



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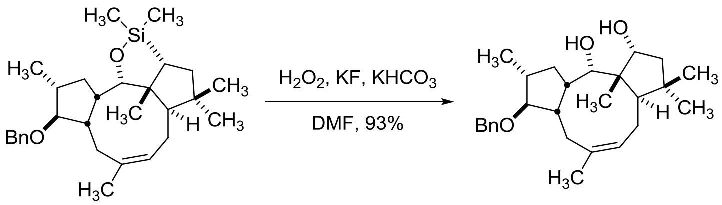

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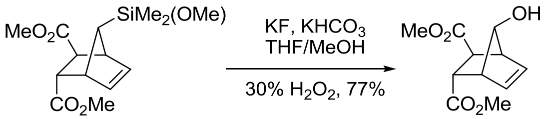
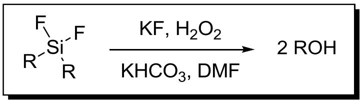


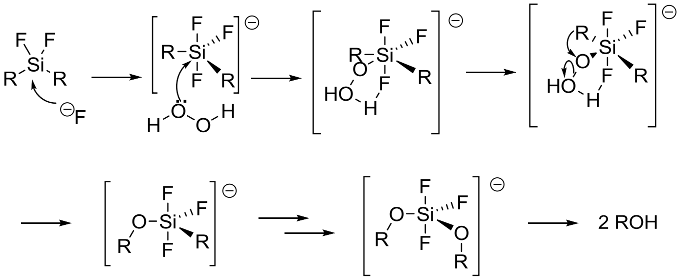
References

1. (a) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984,** 29–31. (b) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987,** *28*, 4229–4232. (c) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989,** *37*, 57–576. (Review).
2. Hunt, J. A.; Roush, W. R. *J. Org. Chem*. **1997,** *62*, 1112–1124.
3. Knölker, H.-J.; Jones, P. G.; Wanzl, G. *Synlett* **1997,** 613–616.
4. Barrett, A. G. M.; Head, J.; Smith, M. L.; Stock, N. S.; White, A. J. P.; Williams, D. J. *J. Org. Chem*. **1999,** *64*, 6005–6018.
5. Denmark, S.; Cottell, J. *J. Org. Chem.* **2001,** *66*, 4276–4284.
6. Lee, T. W.; Corey, E. J. *Org. Lett.* **2001,** *3*, 3337–3339.
7. Jung, M. E.; Piizzi, G. *J. Org. Chem*. **2003,** *68*, 2572–2582.
8. Paquette, L. A.; Yang, J.; Long, Y. O. *J. Am. Chem. Soc.* **2003,** *125*, 1567–1574.
9. Clive, D. L. J.; Cheng, H.; Gangopadhyay, P.; Huang, X.; Prabhudas, B. *Tetrahedron* **2004,** *60*, 4205–4221.
10. Mullins, R. J.; Jolley, S. L.; Knapp, A. R. *Tamao–Kumada–Fleming Oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 237–247. (Review).

Tamao–Kumada oxidation

Oxidation of alkyl fluorosilanes to the corresponding alcohols. A variant of the Fleming–Kumada oxidation.





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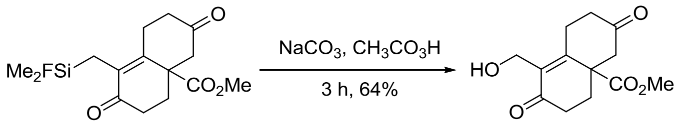
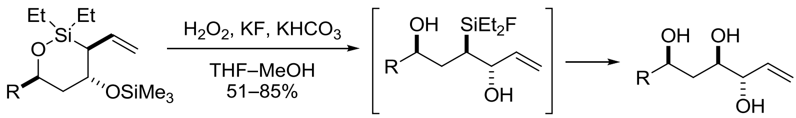


Example 2[4]



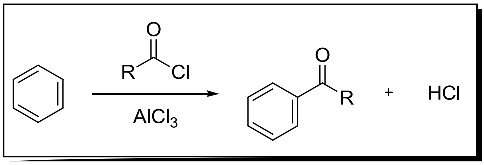
References

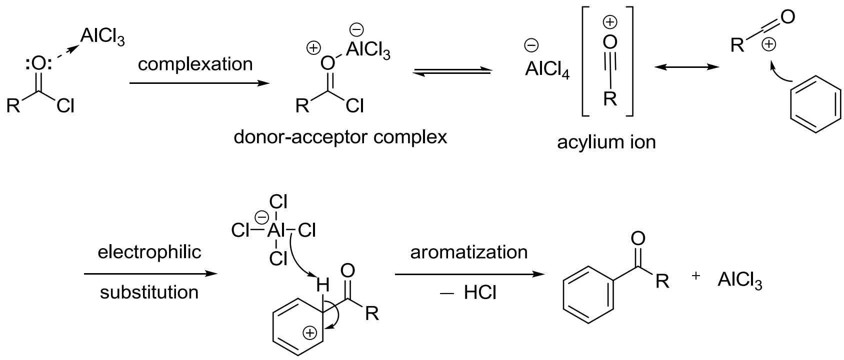
1. Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983,** *48*, 2120–2122.
2. Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989,** *37*, 57–576. (Review).
3. Kim, S.; Emeric, G.; Fuchs, P. L. *J. Org. Chem.* **1992,** *57*, 7362–7364.
4. Mullins, R. J.; Jolley, S. L.; Knapp, A. R. *Tamao–Kumada–Fleming Oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 237–247. (Review).
5. Beignet, J.; Jervis, P. J.; Cox, L. R. *J. Org. Chem.* **2008,** *73*, 5462–5475.
6. Cardona, F.; Parmeggiani, C.; Faggi, E.; Bonaccini, C.; Gratteri, P.; Sim, L.; Gloster, T. M.; Roberts, S.; Davies, G. J.; Rose, D. R.; Goti, A. *Chem. Eur. J.* **2009,** *15*, 1627–1636.
7. Terauchi, T.; Machida, S.; Komba, S. *Tetrahedron Lett.* **2010,** *51*, 1497–1499.

Friedel–Crafts reaction

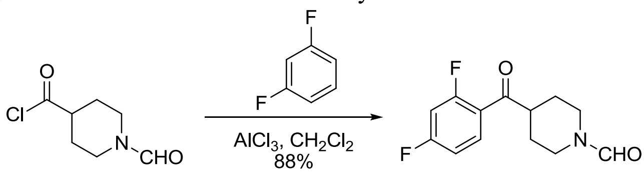
Friedel–Crafts acylation reaction:

Introduction of an acyl group onto an aromatic substrate by treating the substrate with an acyl halide or anhydride in the presence of a Lewis acid.

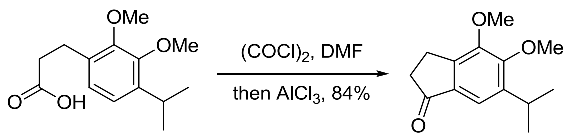




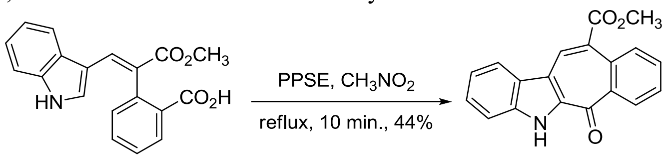
Example 1, Intermolecular Friedel–Crafts acylation[6]



Example 2, Intramolecular Friedel–Crafts acylation[7]



Example 3, Intramolecular Friedel–Crafts acylation[8]



PPSE = Trimethylsilyl polyphosphate

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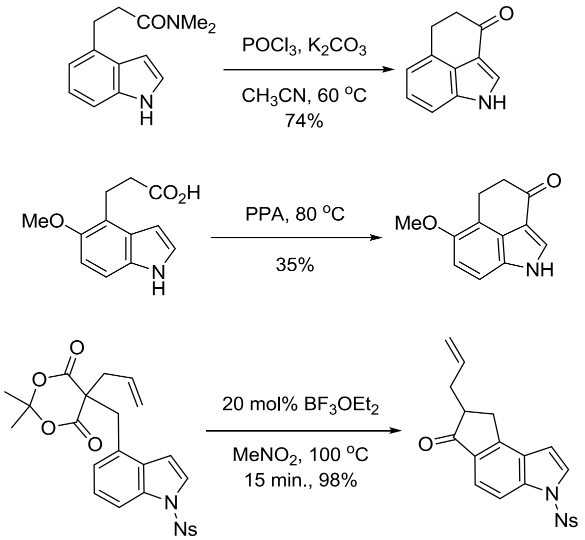
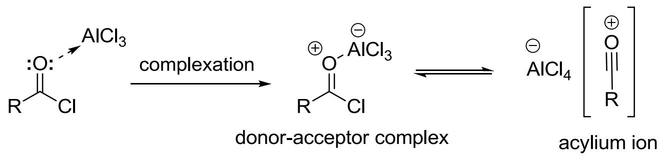
DOI 10.1007/978-3-319-03979-4_109, © Springer International Publishing Switzerland 2014

Example 4, Intramolecular Friedel–Crafts acylation[9]



Example 5, "Kinetic Capture" of Acylium Ion[11]



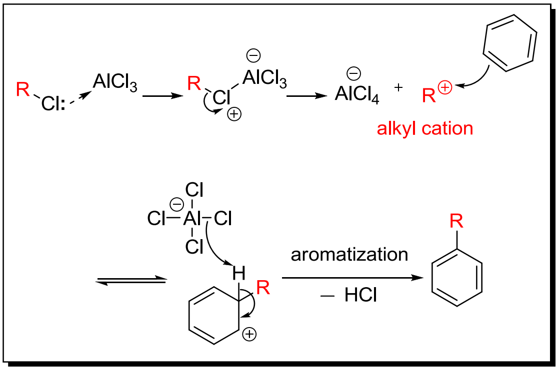
References

1. Friedel, C.; Crafts, J. M. *Compt. Rend.* **1877,** *84*, 1392–1395. Charles Friedel (1832–1899) was born in Strasbourg, France. He earned his Ph.D. In 1869 under Wurtz at Sorbonne and became a professor and later chair (1884) of organic chemistry at Sorbonne. Friedel was one of the founders of the French Chemical Society and served as its president for four terms. James Mason Crafts (1839–1917) was born in Boston, Massachusetts. He studied under Bunsen and Wurtz in his youth and became a professor at Cornell and MIT. From 1874 to 1891, Crafts collaborated with Friedel at École de Mines in Paris, where they discovered the Friedel–Crafts reaction. He returned to MIT in 1892 and later served as its president. The discovery of the Friedel–Crafts reaction was the fruit of serendipity and keen observation. In 1877, both Friedel and Crafts were working in Charles A. Wurtz's laboratory. In order to prepare amyl iodide, they treated amyl chloride with aluminum and iodide using benzene as the solvent. Instead of amyl iodide, they ended up with amylbenzene! Unlike others before them who may have simply discarded the reaction, they thoroughly investigated the Lewis acid-catalyzed alkylations and acylations and published more than 50 papers and patents on the Friedel–Crafts reaction, which has become one of the most useful organic reactions.
2. Pearson, D. E.; Buehler, C. A. *Synthesis* **1972,** 533–542. (Review).

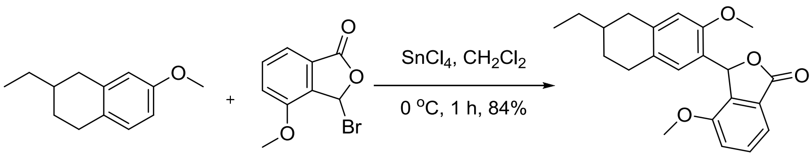
3. Hermecz, I.; Mészáros, Z. *Adv. Heterocyclic Chem.* **1983,** *33*, 241–330. (Review).
4. Metivier, P. *Friedel-Crafts Acylation.* In *Friedel-Crafts Reaction* Sheldon, R. A.; Bekkum, H., eds.; Wiley-VCH: New York. **2001,** pp 161–172. (Review).
5. Basappa; Mantelingu, K.; Sadashira, M. P.; Rangappa, K. S. *Indian J. Chem. B.* **2004,** *43B*, 1954–1957.
6. Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **2006,** *106*, 1077–1104. (Review).
7. Simmons, E.M.; Sarpong, R. *Org. Lett.* **2006,** *8*, 2883–2886.
8. Bourderioux, A.; Routier, S.; Beneteau, V.; Merour, J.-Y. *Tetrahedron* **2007,** *63*, 9465–9475.
9. Fillion, E.; Dumas, A. M. *J. Org. Chem.* **2008,** *73*, 2920–2923.
10. de Noronha, R. G.; Fernandes, A. C.; Romao, C. C. *Tetrahedron Lett.* **2009,** *50*, 1407–1410.
11. Huang, Z.; Jin, L.; Han, H.; Lei, A. *Org. Biomol. Chem.* **2013,** *11*, 1810–1814.

Friedel–Crafts alkylation reaction:

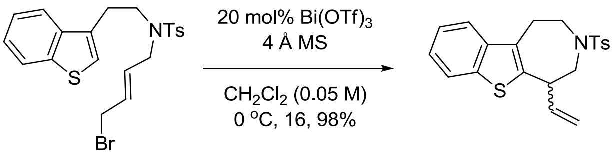
Introduction of an alkyl group onto an aromatic substrate by treating the substrate with an alkylating agent such as alkyl halide, alkene, alkyne and alcohol in the presence of a Lewis acid.



Example 1[1]



Example 2, An intramolecular Friedel–Crafts cyclization[6]

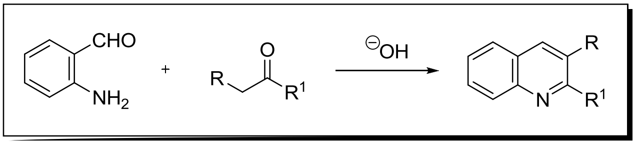


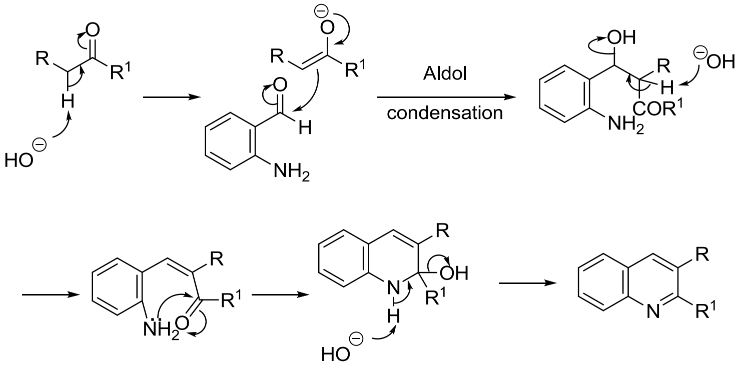
References

1. Patil, M. L.; Borate, H. B.; Ponde, D. E.; Bhawal, B. M.; Deshpande, V. H. *Tetrahedron Lett.* **1999,** *40*, 4437–4438.
2. Meima, G. R.; Lee, G. S.; Garces, J. M. *Friedel-Crafts Alkylation.* In *Friedel–Crafts Reaction* Sheldon, R. A.; Bekkum, H., eds.; Wiley-VCH: New York. **2001,** pp 550–556. (Review).
3. Bandini, M.; Melloni, A.; Umani-Ronchi, A. *Angew. Chem. Int. Ed.* **2004,** *43*, 550–556. (Review).
4. Poulsen, T. B.; Jorgensen, K. A. *Chem. Rev.* **2008,** *108*, 2903–2915. (Review).
5. Silvanus, A. C.; Heffernan, S. J.; Liptrot, D. J.; Kociok-Kohn, G.; Andrews, B. I.; Carbery, D. R. *Org. Lett.* **2009,** *11*, 1175–1178.
6. Kargbo, R. B.; Sajjadi-Hashemi, Z.; Roy, S.; Jin, X.; Herr, R. J. *Tetrahedron Lett.* **2013,** *54*, 2018–2021.

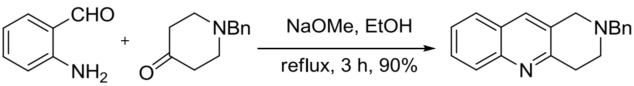
Friedländer quinoline synthesis

Also known as the Friedländer condensation, it combines an α-amino aldehyde or ketone with another aldehyde or ketone with at least one methylene α adjacent to the carbonyl to furnish a substituted quinoline. The reaction can be promoted by either acid, base, or heat.

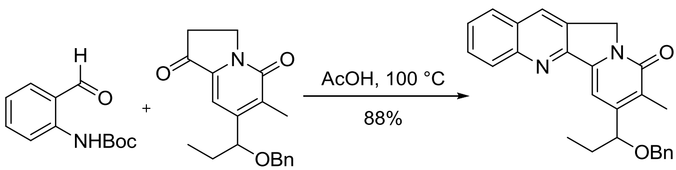




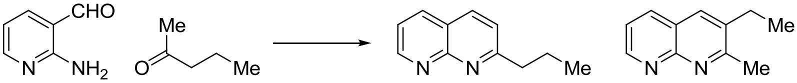
Example 1[5]



Example 2[7]

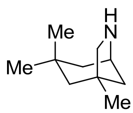


Example 3[8]



Conditions	Conversion	Ratio
NaOH, rt	> 99%	37:63
pyrrolidine, 5% H_2SO_4, rt	97%	86:14
TBAO, 5% H_2SO_4, rt	> 99%	87:13
TBAO, 5% H_2SO_4, slow addition, 65 °C	> 99%	94:6

TBAO = 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane



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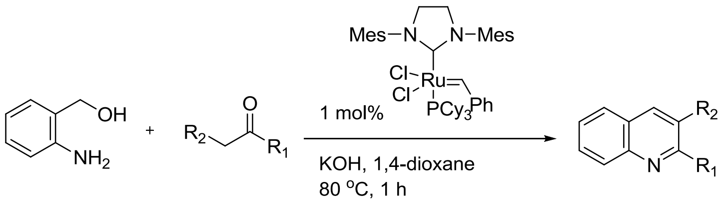
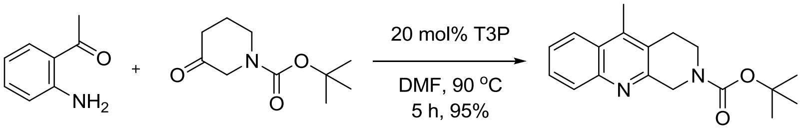
DOI 10.1007/978-3-319-03979-4_110, © Springer International Publishing Switzerland 2014

Example 4[10]



Example 5, Using propylphosphonic anhydride (T3P) as the coupling agent[11]

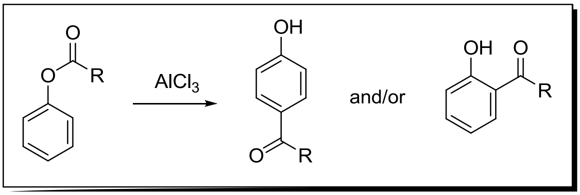


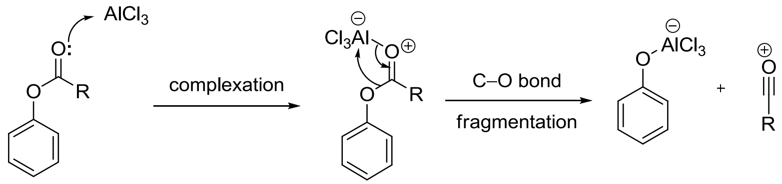
References

1. Friedländer, P. *Ber.* **1882,** *15*, 2572–2575. Paul Friedländer (1857–1923), born in Königsberg, Prussia, apprenticed under Carl Graebe and Adolf von Baeyer. He was interested in music and was an accomplished pianist.
2. Elderfield, R. C. In *Heterocyclic Compounds*, Elderfield, R. C., ed.; Wiley: New York, **1952,** *4*, *Quinoline, Isoquinoline and Their Benzo Derivatives*, 45–47. (Review).
3. Jones, G. In *Heterocyclic Compounds*, Quinolines, vol. 32, **1977**; Wiley: New York, pp 181–191. (Review).
4. Cheng, C.-C.; Yan, S.-J. *Org. React.* **1982,** *28*, 37–201. (Review).
5. Shiozawa, A.; Ichikawa, Y.-I.; Komuro, C.; Kurashige, S.; Miyazaki, H.; Yamanaka, H.; Sakamoto, T. *Chem. Pharm. Bull.* **1984,** *32*, 2522–2529.
6. Gladiali, S.; Chelucci, G.; Mudadu, M. S.; Gastaut, M.-A.; Thummel, R. P. *J. Org. Chem.* **2001,** *66*, 400–405.
7. Henegar, K. E.; Baughman, T. A. *J. Heterocycl. Chem.* **2003,** *40*, 601–605.
8. Dormer, P. G.; Eng, K. K.; Farr, R. N.; Humphrey, G. R.; McWilliams, J. C.; Reider, P. J.; Sager, J. W.; and Volante, R. P. *J. Org. Chem.* **2003,** *68*, 467–477.
9. Pflum, D. A. *Friedländer Quinoline Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 411–415. (Review).
10. Vander Mierde, H.; Van Der Voot, P.; De Vos, D.; Verpoort, F. *Eur. J. Org. Chem.* **2008,** 1625–1631.
11. Augustine, J. K.; Bombrun, A.; Venkatachaliah, S. *Tetrahedron Lett.* **2011,** *52,* 6814–6818.

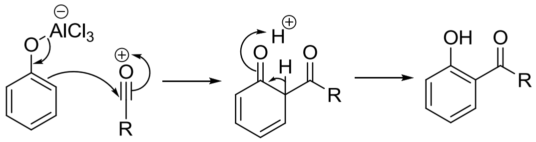
Fries rearrangement

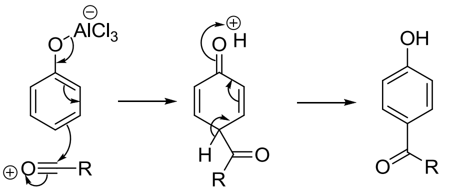
Lewis acid-catalyzed rearrangement of phenol esters and lactams to 2- or 4-ketophenols. Also known as the Fries–Finck rearrangement.



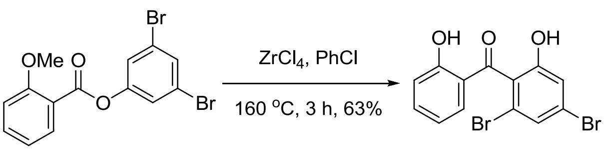


aluminum phenolate, acylium ion

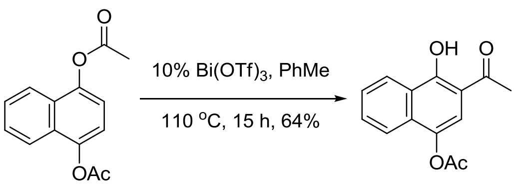




Example 1[5]



Example 2[6]



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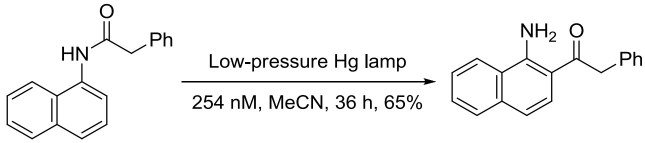
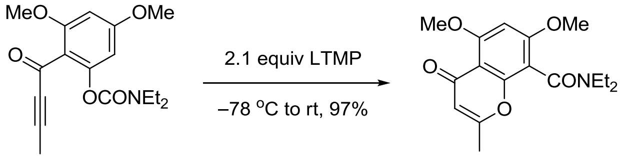
DOI 10.1007/978-3-319-03979-4_111, © Springer International Publishing Switzerland 2014

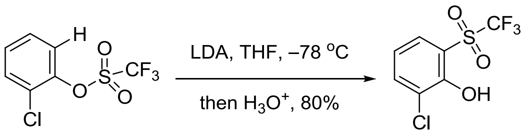
Example 3, Photo-Fries rearrangement[7]



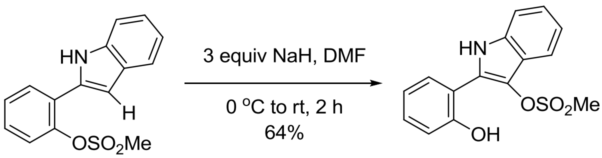
Example 4, *ortho*-Fries rearrangement[8]



Example 5, Thia-Fries rearrangement[9]



Example 6, Remote Anionic Thia-Fries rearrangement[10]

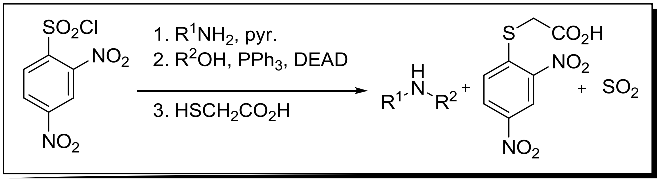


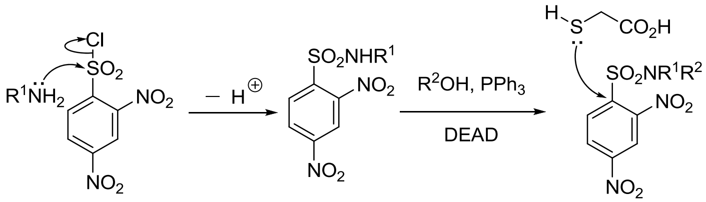
References

1. Fries, K.; Finck, G. *Ber.* **1908,** *41*, 4271–4284. Karl Theophil Fries (1875–1962) was born in Kiedrich near Wiesbaden on the Rhine. He earned his doctorate under Theodor Zincke. Although G. Finck co-discovered the rearrangement of phenolic esters, somehow his name has been forgotten by history. In all fairness, the Fries rearrangement should really be the Fries–Finck rearrangement.
2. Martin, R. *Org. Prep. Proced. Int.* **1992,** *24*, 369–435. (Review).
3. Boyer, J. L.; Krum, J. E.; Myers, M. C.; Fazal, A. N.; Wigal, C. T. *J. Org. Chem.* **2000,** *65,* 4712–4714.
4. Guisnet, M.; Perot, G. *The Fries rearrangement*. In *Fine Chemicals through Heterogeneous Catalysis* **2001,** 211–216. (Review).
5. Tisserand, S.; Baati, R.; Nicolas, M.; Mioskowski, C. *J. Org. Chem.* **2004,** *69,* 8982–8983.
6. Ollevier, T.; Desyroy, V.; Asim, M.; Brochu, M.-C. *Synlett* **2004,** 2794–2796.
7. Ferrini, S.; Ponticelli, F.; Taddei, M. *Org. Lett.* **2007,** *9*, 69–72.
8. Macklin, T. K.; Panteleev, J.; Snieckus, V. *Angew. Chem. Int. Ed.* **2008,** *47*, 2097–2101.
9. Dyke, A. M.; Gill, D. M.; Harvey, J. N.; Hester, A. J.; Lloyd-Jones, G. C.; Munoz, M. P.; Shepperson, I. R. *Angew. Chem. Int. Ed.* **2008,** *47*, 5067–5070.
10. Xu, X.-H.; Taniguchi, M.; Azuma, A.; Liu, G. K.; Tokunaga, E.; Shibata, N. *Org. Lett.* **2013,** *15*, 686–689.

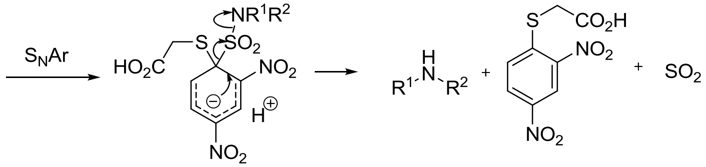
Fukuyama amine synthesis

Transformation of a primary amine to a secondary amine using 2,4-dinitrobenzenesulfonyl chloride and an alcohol. Also known as the Fukuyama–Mitsunobu procedure.



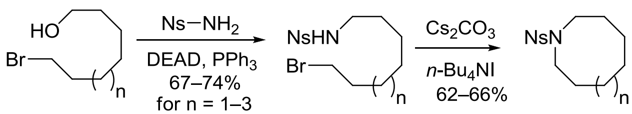


See the Mitsunobu reaction for mechanism.

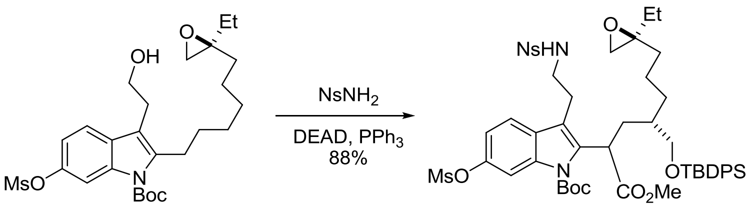


Meisenheimer complex

Example 1[6]



Example 2[7]



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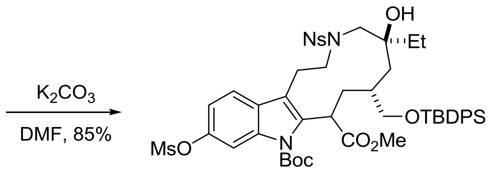
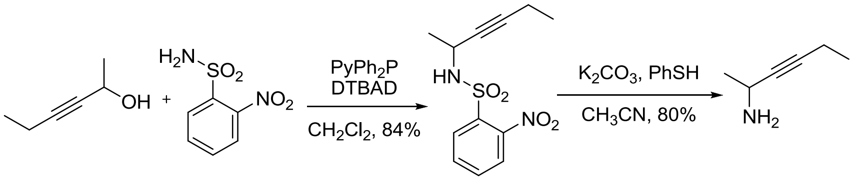
DOI 10.1007/978-3-319-03979-4_112, © Springer International Publishing Switzerland 2014



Example 3[8]



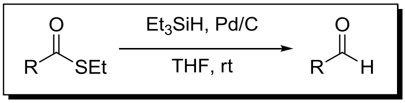
$PyPh_2P$ = diphenyl 2-pyridylphosphine; DTBAD = di-*tert*-butylazodicarbonate

References

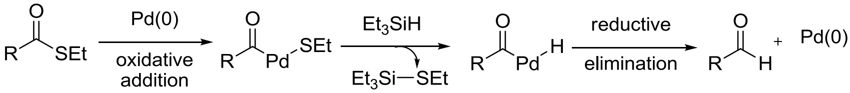
1. (a) Fukuyama, T.; Jow, C.-K.; Cheung, M. *Tetrahedron Lett.* **1995,** *36*, 6373–6374. Tohru Fukuyama earned his Ph.D. at Harvard under the tutelage of Kishi. He started his independent academic career at Rice University but moved to the University of Tokyo from in 1995. (b) Fukuyama, T.; Cheung, M.; Jow, C.-K.; Hidai, Y.; Kan, T. *Tetrahedron Lett.* **1997,** *38*, 5831–5834.
2. Piscopio, A. D.; Miller, J. F.; Koch, K. *Tetrahedron Lett.* **1998,** *39*, 2667–2670.
3. Bolton, G. L.; Hodges, J. C. *J. Comb. Chem*. **1999,** *1*, 130–133.
4. Lin, X.; Dorr, H.; Nuss, J. M. *Tetrahedron Lett*. **2000,** *41*, 3309–3313.
5. Olsen, C. A.; Jørgensen, M. R.; Witt, M.; Mellor, I. R.; Usherwood, P. N. R.; Jaroszewski, J. W.; Franzyk, H. *Eur. J. Org. Chem*. **2003,** 3288-3299.
6. Kan, T.; Fujiwara, A.; Kobayashi, H.; Fukuyama, T. *Tetrahedron* **2002,** *58*, 6267–6276.
7. Yokoshima, S.; Ueda, T.; Kobayashi, S.; Sato, A.; Kuboyama, T.; Tokuyama, H.; Fukuyama, T. *Pure Appl. Chem.* **2003,** *75*, 29–38.
8. Guisado, C.; Waterhouse, J. E.; Price, W. S.; Jørgensen, M. R.; Miller, A. D. *Org. Biomol. Chem*. **2005,** *3*, 1049–1057.
9. Olsen, C. A.; Witt, M.; Hansen, S. H.; Jaroszewski, J. W.; Franzyk, H. *Tetrahedron* **2005,** *61*, 6046–6055.
10. Janey, J. M. *Fukuyama Amine Synthesis*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 424–437. (Review).
11. Hahn, F.; Schepers, U. *Synlett* **2009,** 2755–2760. (Review).

Fukuyama reduction

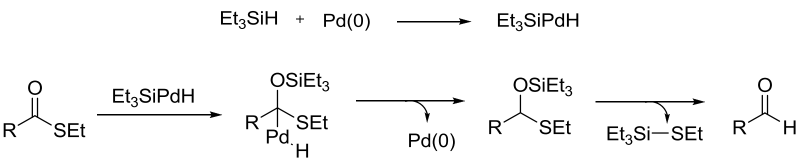
Aldehyde synthesis through reduction of thiol esters with Et_3SiH in the presence of Pd/C catalyst.



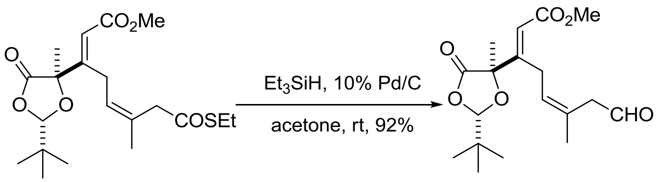
Path A:



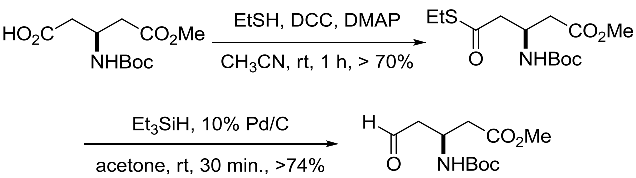
Path B:



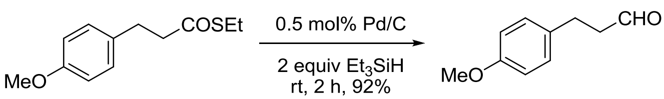
Example 1[1]



Example 2[3]



Example 3[8]



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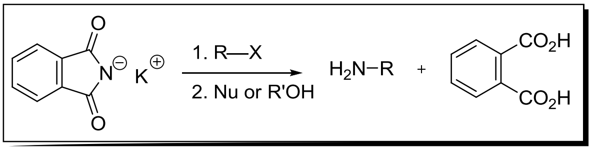
DOI 10.1007/978-3-319-03979-4_113,

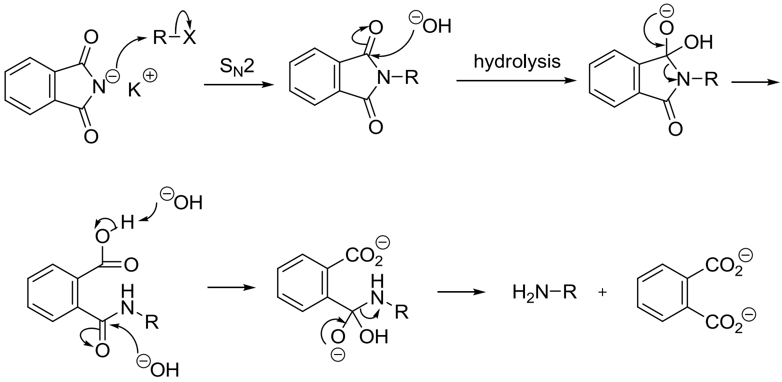
References

1. Fukuyama, T.; Lin, S.-C.; Li, L. *J. Am. Chem. Soc.* **1990,** *112*, 7050–7051.
2. Kanda, Y.; Fukuyama, T. *J. Am. Chem. Soc.* **1993,** *115*, 8451–8452.
3. Fujiwara, A.; Kan, T.; Fukuyama, T. *Synlett* **2000,** 1667–1673.
4. Tokuyama, H.; Yokoshima, S.; Lin, S.-C.; Li, L.; Fukuyama, T. *Synthesis* **2002,** 1121–1123.
5. Evans, D. A.; Rajapakse, H. A.; Stenkamp, D. *Angew. Chem. Int. Ed.* **2002,** *41*, 4569–4573.
6. Shimada, K.; Kaburagi, Y.; Fukuyama, T. *J. Am. Chem. Soc.* **2003,** *125*, 4048–4049.
7. Kimura, M.; Seki, M. *Tetrahedron Lett*. **2004,** *45*, 3219–3223. (Possible mechanisms were proposed in this paper).
8. Miyazaki, T.; Han-ya, Y.; Tokuyama, H.; Fukuyama, T. *Synlett* **2004,** 477–480.
9. Weerasinghe, L. P.; Garner, P. P.; Youngs, W. J.; Wright, B. *Abstracts of Papers, 243rd ACS National Meeting & Exposition*, San Diego, CA, March 25-29, (2012),ORGN-306.

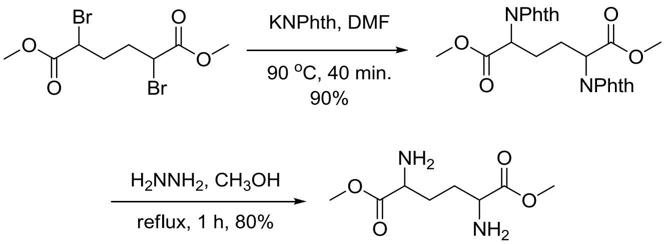
Gabriel synthesis

Synthesis of primary amines using potassium phthalimide and alkyl halides.

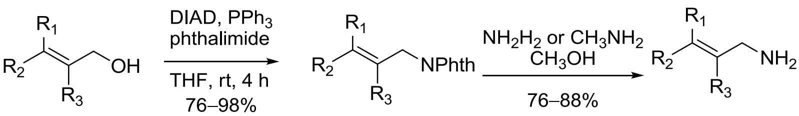




Example 1[2]



Example 2[6]



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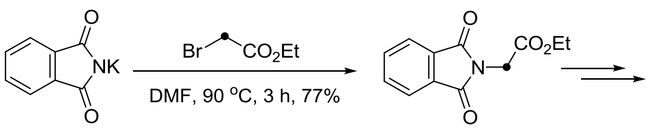

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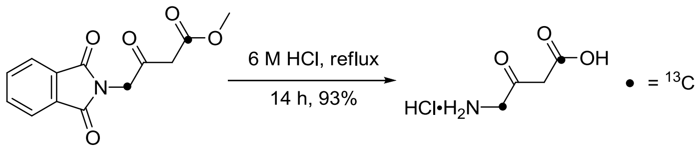
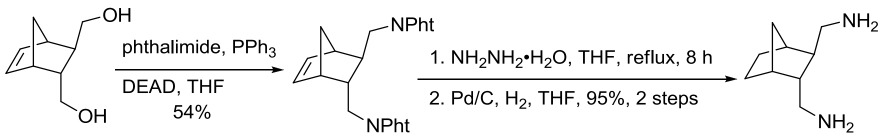


Example 4[9]

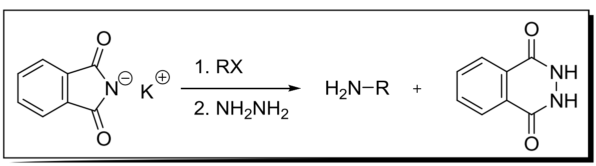


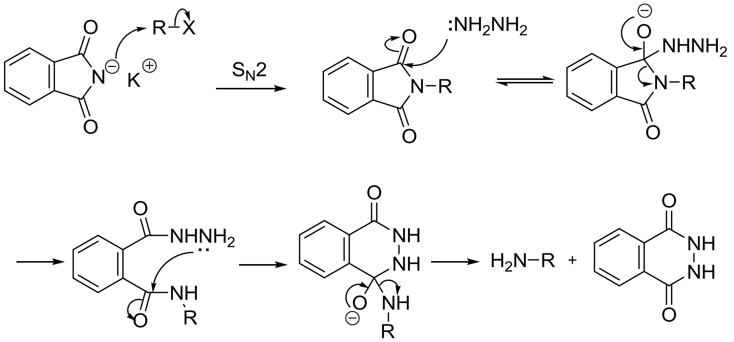
References

1. Gabriel, S. *Ber.* **1887,** *20*, 2224–2226. Siegmund Gabriel (1851–1924), born in Berlin, Germany, studied under Hofmann at Berlin and Bunsen in Heidelberg. He taught at Berlin, where he discovered the Gabriel synthesis of amines. Gabriel, a good friend of Emil Fischer, often substituted for Fischer in his lectures.
2. Sheehan, J. C.; Bolhofer, V. A. *J. Am. Chem. Soc.* **1950,** *72*, 2786–2788.
3. Han, Y.; Hu, H. *Synthesis* **1990,** 122–124.
4. Ragnarsson, U.; Grehn, L. *Acc. Chem. Res.* **1991,** *24*, 285–289. (Review).
5. Toda, F.; Soda, S.; Goldberg, I. *J. Chem. Soc., Perkin Trans. 1* **1993,** 2357–2361.
6. Sen, S. E.; Roach, S. L. *Synthesis*, **1995,** 756–758.
7. Khan, M. N. *J. Org. Chem.* **1996,** *61*, 8063–8068.
8. Iida, K.; Tokiwa, S.; Ishii, T.; Kajiwara, M. *J. Labelled. Compd. Radiopharm.* **2002,** *45*, 569–570.
9. Tanyeli, C.; Özçubukçu, S. *Tetrahedron Asymmetry* **2003,** *14,* 1167–1170.
10. Ahmad, N. M. *Gabriel synthesis*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 438–450. (Review).
11. Al-Mousawi, S. M.; El-Apasery, M. A.; Al-Kanderi, N. H. *ARKIVOC* **2008,** *(16),* 268–278.
12. Richter, J. M. *Name Reactions in Heterocyclic Chemistry-II*, Li, J. J., Ed.; Wiley: Hoboken, NJ, 2011, pp 11–20. (Review).
13. Cytlak, T.; Marciniak, B.; Koroniak, H. In *Efficient Preparations of Fluorine Compounds*; Roesky, H. W., ed.; Wiley: Hoboken, NJ, (2013), pp 375–378. (Review).

Ing–Manske procedure

A variant of Gabriel amine synthesis where hydrazine is used to release the amine from the corresponding phthalimide:





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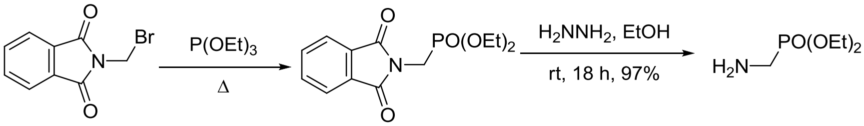
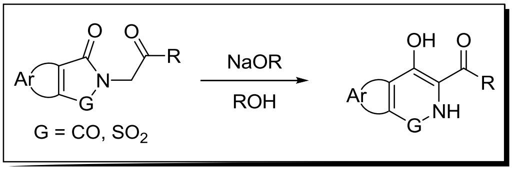


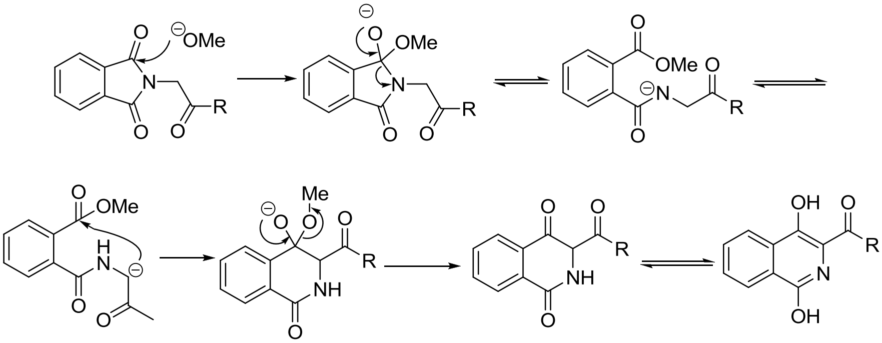
References

1. Ing, H. R.; Manske, R. H. F. *J. Chem. Soc.* **1926,** 2348–2351. H. R. Ing was a professor of pharmacological chemistry at Oxford. R. H. F. Manske, Ing's collaborator at Oxford, was of German origin but trained in Canada before studying at Oxford. Manske left England to return to Canada, eventually to become Director of Research in the Union Rubber Company, Guelph, Ontario, Canada.
2. Ueda, T.; Ishizaki, K. *Chem. Pharm. Bull.* **1967,** *15*, 228–237.
3. Khan, M. N. *J. Org. Chem.* **1995,** *60*, 4536–4541.
4. Hearn, M. J.; Lucas, L. E. *J. Heterocycl. Chem.* **1984,** *21*, 615–622.
5. Khan, M. N. *J. Org. Chem.* **1996,** *61*, 8063–8063.
6. Tanyeli, C.; Özçubukçu, S. *Tetrahedron: Asymmetry* **2003,** *14*, 1167–1170.
7. Ariffin, A.; Khan, M. N.; Lan, L. C.; May, F. Y.; Yun, C. S. *Synth. Commun.* **2004,** *34*, 4439–4445.
8. Ali, M. M.; Woods, M.; Caravan, P.; Opina, A. C. L.; Spiller, M.; Fettinger, J. C.; Sherry, A. D. *Chem. Eur. J.* **2008,** *14*, 7250–7258.
9. Nagarapu, L.; Apuri, S.; Gaddam, C.; Bantu, R. *Org. Prep. Proc. Int.* **2009,** *41*, 243–247.

Gabriel–Colman rearrangement

Reaction of the enolate of a maleimidyl acetate to provide isoquinoline 1,4-diol.





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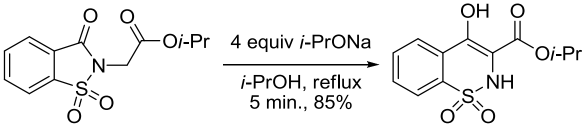
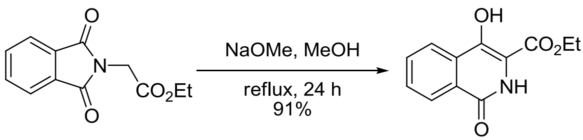


Example 2[9]



References

1. (a) Gabriel, S.; Colman, J. *Ber.* **1900,** *33*, 980–995. (b) Gabriel, S.; Colman, J. *Ber.* **1900,** *33*, 2630–2634. (c) Gabriel, S.; Colman, J. *Ber.* **1902,** *35*, 1358–1368.
2. Allen, C. F. H. *Chem. Rev.* **1950,** *47*, 275–305. (Review).
3. Gensler, W. J. *Heterocyclic Compounds*, Vol. 4, R. C. Elderfield, Ed., Wiley & Sons., New York, N.Y., **1952,** 378. (Review).
4. Hill, J. H. M. *J. Org. Chem.* **1965,** *30*, 620–622. (Mechanism).
5. Lombardino, J. G.; Wiseman, E. H.; McLamore, W. M. *J. Med. Chem.* **1971,** *14*, 1171–1175.
6. Schapira, C. B.; Perillo, I. A.; Lamdan, S. *J. Heterocycl. Chem.* **1980,** *17*, 1281–1288.
7. Lazer, E. S.; Miao, C. K.; Cywin, C. L.; *et al. J. Med. Chem.* **1997,** *40*, 980–989.
8. Pflum, D. A. *Gabriel–Colman Rearrangement*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 416–422. (Review).
9. Kapatsina, E.; Lordon, M.; Baro, A.; Laschat, S. *Synthesis* **2008,** 2551–2560.

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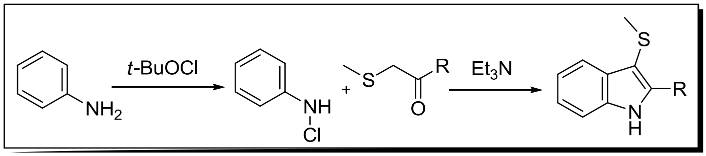
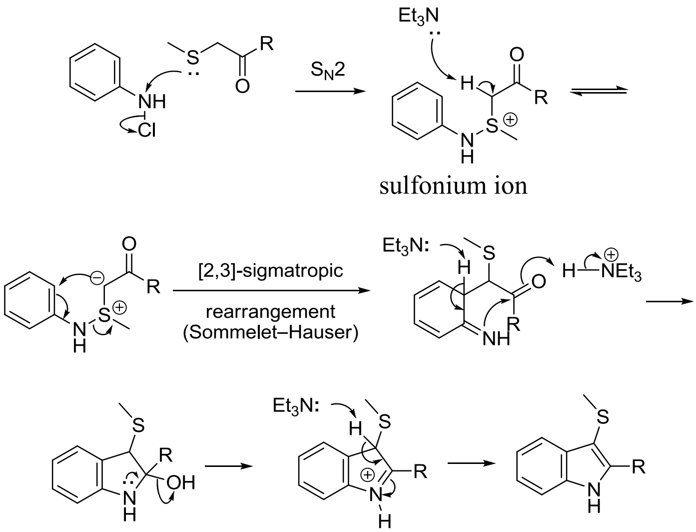
DOI 10.1007/978-3-319-03979-4_115, © Springer International Publishing Switzerland 2014

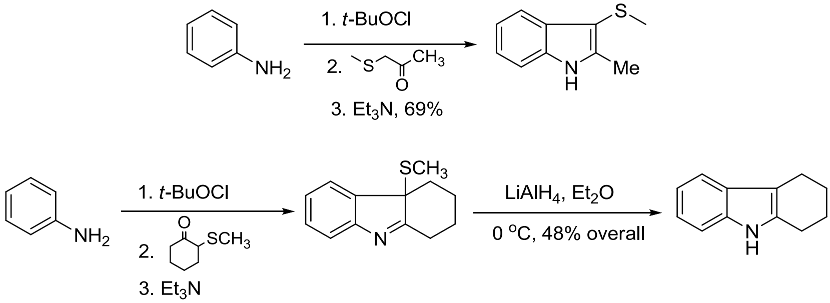
Gassman indole synthesis

The Gassman indole synthesis involves a one-pot process in which a hypohalite, a β-carbonyl sulfide derivative, and a base are added sequentially to an aniline or a substituted aniline to provide 3-thioalkoxyindoles. The mechanism of the Gassman indole synthesis involves a [2,3]-sigmatropic rearrangement (Sommelet–Hauser). The sulfur can be easily removed by hydrogenolysis or Raney nickel.





Example 1[1]



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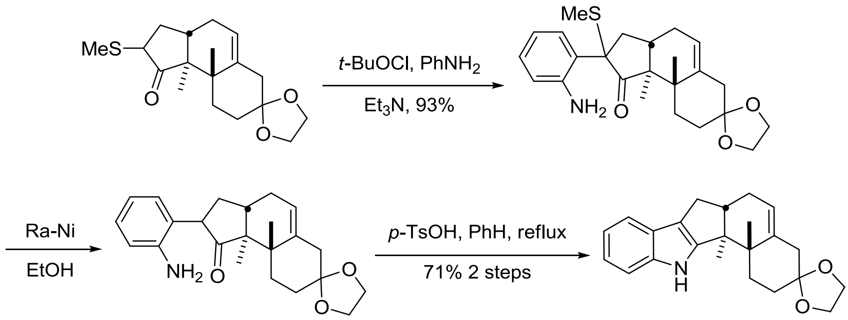
DOI 10.1007/978-3-319-03979-4_116, © Springer International Publishing Switzerland 2014

Example 2[2]

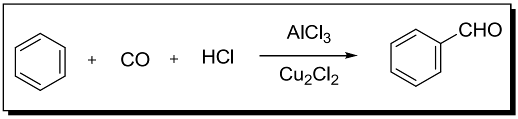


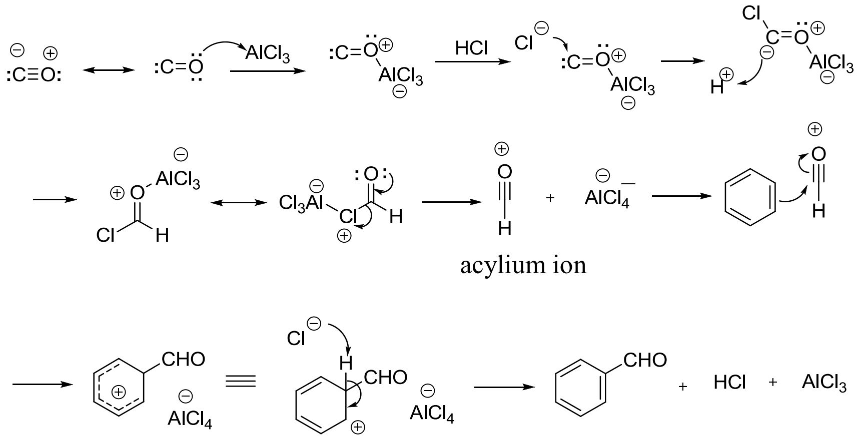
References

1. (a) Gassman, P. G.; van Bergen, T. J.; Gilbert, D. P.; Cue, B. W., Jr. *J. Am. Chem. Soc.* **1974,** *96*, 5495–5508. Paul G. Gassman (1935–1993) was a professor at the University of Minnesota (1974–1993). (b) Gassman, P. G.; van Bergen, T. J. *J. Am. Chem. Soc.* **1974,** *96*, 5508–5512. (c) Gassman, P. G.; Gruetzmacher, G.; van Bergen, T. J. *J. Am. Chem. Soc.* **1974,** *96*, 5512–5517.
2. Wierenga, W. *J. Am. Chem. Soc.* **1981,** *103*, 5621–5623.
3. Ishikawa, H.; Uno, T.; Miyamoto, H.; Ueda, H.; Tamaoka, H.; Tominaga, M.; Nakagawa, K. *Chem. Pharm. Bull.* **1990,** *38*, 2459–2462.
4. Smith, A. B., III; Sunazuka, T.; Leenay, T. L.; Kingery-Wood, J. *J. Am. Chem. Soc.* **1990,** *112*, 8197–8198.
5. Smith, A. B., III; Kingery-Wood, J.; Leenay, T. L.; Nolen, E. G.; Sunazuka, T. *J. Am. Chem. Soc.* **1992,** *114*, 1438–1449.
6. Savall, B. M.; McWhorter, W. W.; Walker, E. A. *J. Org. Chem.* **1996,** *61*, 8696–8697.
7. Li, J.; Cook, J. M. *Gassman Indole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 128–131. (Review).
8. Barluenga, J.; Valdes, C. In *Modern Heterocyclic Chemistry;* Alvarez-Builla, J.; Vaquero, J. J.; Barluenga, J. eds.; Wiley-VCH: Weinheim, Germany; (2011), *1*, 377–531. (Review).

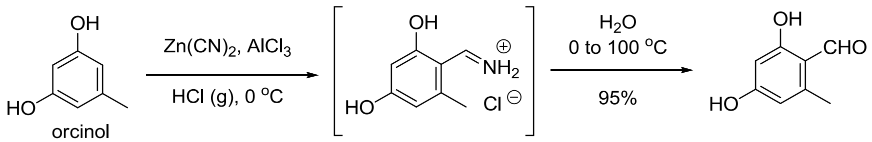
Gattermann–Koch reaction

Formylation of arenes using carbon monoxide and hydrogen chloride in the presence of aluminum chloride under high pressure.





Example 1, A more practical variant[4]



References

1. Gattermann, L.; Koch, J. A. *Ber.* **1897,** *30*, 1622–1624. Ludwig Gattermann (1860–1920) was born in Freiburg, Germany. His textbook, "*Die Praxis de organischen Chemie*" (1894) was well-known all over the world. Some of his peers derided it fondly as "Gattermanns Kochbuch" ("Gattermann's cookbook", his father was a baker).
2. Crounse, N. N. *Org. React.* **1949,** *5,* 290–300. (Review).
3. Truce, W. E. *Org. React.* **1957,** *9,* 37–72. (Review).
4. Solladié, G.; Rubio, A.; et al. *Tetrahedron: Asymmetry* **1990,** *1*, 187–198.
5. (a) Tanaka, M.; Fujiwara, M.; Ando, H. *J. Org. Chem.* **1995,** *60*, 2106–2111. (b) Tanaka, M.; Fujiwara, M.; Ando, H.; Souma, Y. *Chem. Commun.* **1996,** 159–160. (c) Tanaka, M.; Fujiwara, M.; Xu, Q.; Souma, Y.; Ando, H.; Laali, K. K. *J. Am. Chem. Soc.* **1997,** *119*, 5100–5105. (d) Tanaka, M.; Fujiwara, M.; Xu, Q.; Ando, H.; Raeker, T. J. *J. Org. Chem.* **1998,** *63*, 4408–4412.
6. Kantlehner, W.; Vettel, M.; et al. Haas, R. *J. Prakt. Chem.* **2000,** *342*, 297–310.

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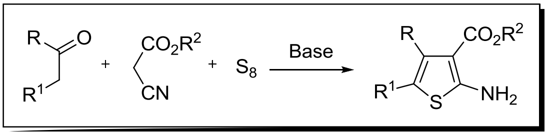
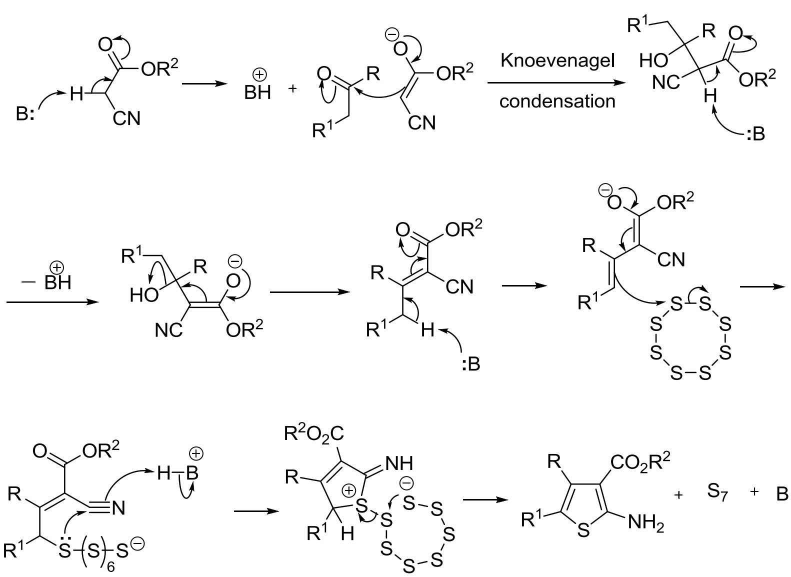
Gewald aminothiophene synthesis

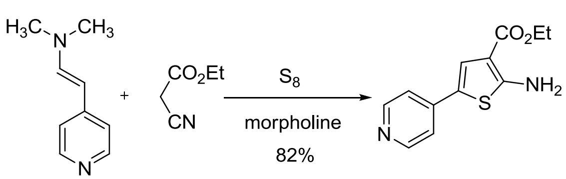
Base-promoted aminothiophene formation from ketone, α-active methylene nitrile and elemental sulfur.



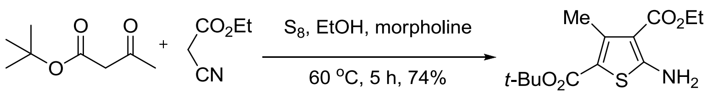


ylidene-sulfur adduct

Example 1[4]



Example 2[7]



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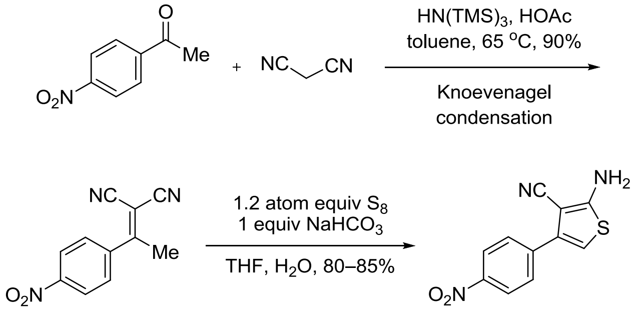
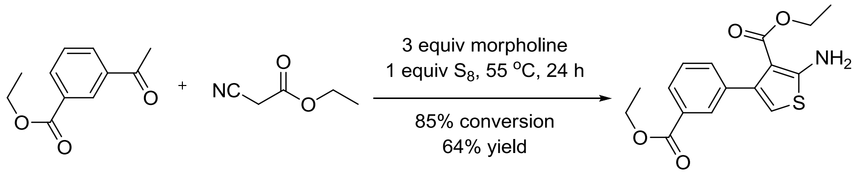
DOI 10.1007/978-3-319-03979-4_118, © Springer International Publishing Switzerland 2014

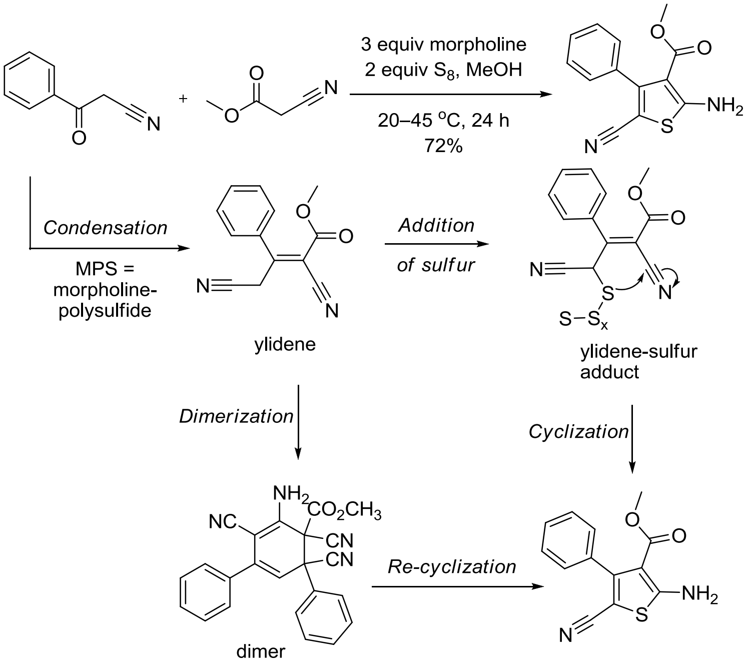
Example 3[9]



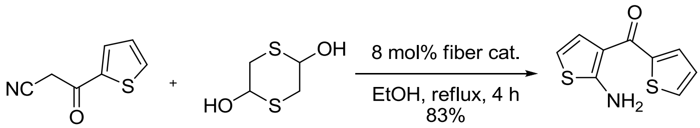
Example 4[10]



Example 5[11]



Example 6, *N*-Methylpiperazine-Functionalized Polyacrylonitrile Fiber Catalyst[12]

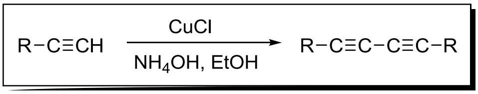


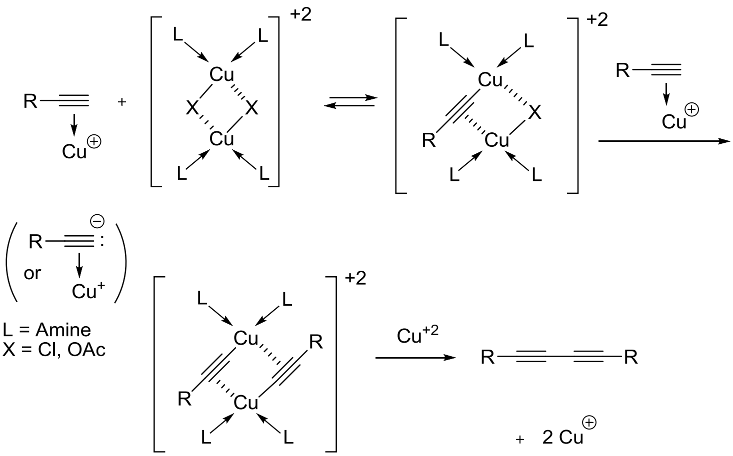
References

1. (a) Gewald, K. *Z. Chem*. **1962,** *2*, 305–306. (b) Gewald, K.; Schinke, E.; Böttcher, H. *Chem. Ber*. **1966,** *99*, 94–100. (c) Gewald, K.; Neumann, G.; Böttcher, H. *Z. Chem*. **1966,** *6*, 261. (d) Gewald, K.; Schinke, E. *Chem. Ber*. **1966,** *99*, 271–275. Karl Gewald(1930–) is a professor at Technical University of Dresden.
2. Mayer, R.; Gewald, K. *Angew. Chem. Int. Ed.* **1967,** *6*, 294–306. (Review).
3. Gewald, K. *Chimia* **1980,** *34*, 101–110. (Review).
4. Bacon, E. R.; Daum, S. J. *J. Heterocycl. Chem*. **1991,** *28*, 1953-1955.
5. Sabnis, R. W. *Sulfur Reports* **1994,** *16*, 1–17. (Review).
6. Sabnis, R. W.; Rangnekar, D. W.; Sonawane, N. D. *J. Heterocycl. Chem*. **1999,** *36*, 333–345. (Review).
7. Gütschow, M.; Kuerschner, L.; Neumann, U.; Pietsch, M.; Löser, R.; Koglin, N.; Eger, K. *J. Med. Chem*. **1999,** *42*, 5437.
8. Tinsley, J. M. *Gewald Aminothiophene Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 193–198. (Review).
9. Barnes, D. M.; Haight, A. R.; Hameury, T.; McLaughlin, M. A.; Mei, J.; Tedrow, J. S.; Dalla Riva Toma, J. *Tetrahedron* **2006,** *62*, 11311–11319.
10. Tormyshev, V. M.; Trukhin, D. V.; Rogozhnikova, O. Yu.; Mikhalina, T. V.; Troitskaya, T. I.; Flinn, A. *Synlett* **2006,** 2559–2564.
11. Puterová, Z.; Andicsová, A.; Végh, D. *Tetrahedron* **2008,** *64*, 11262–11269.
12. Ma, L.; Yuan, L.; Xu, C.; Li, G.; Tao, M.; Zhang, W. *Synthesis* **2013,** *45*, 45–52.

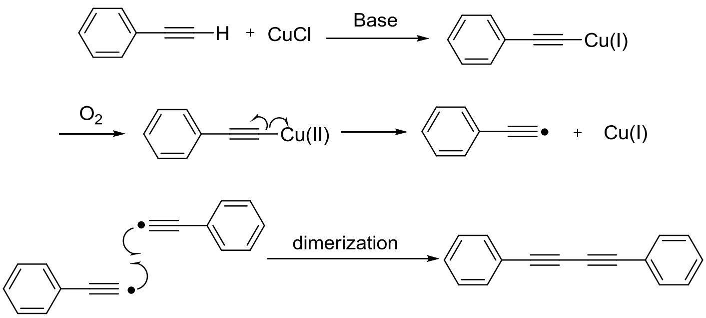
Glaser coupling

Sometimes known as the Glaser–Hay coupling, it is the oxidative homo-coupling of terminal alkynes using copper catalyst in the presence of oxygen.

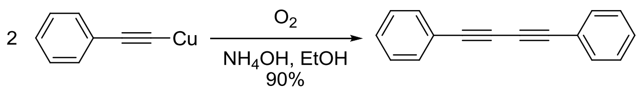




Alternatively, the radical mechanism is also operative:



Example 1[1]



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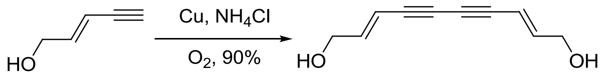
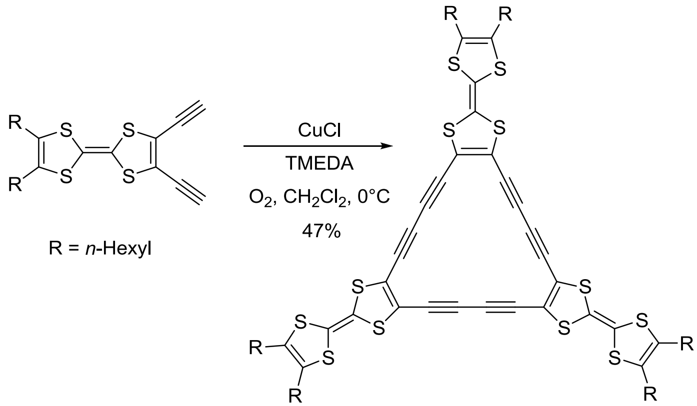
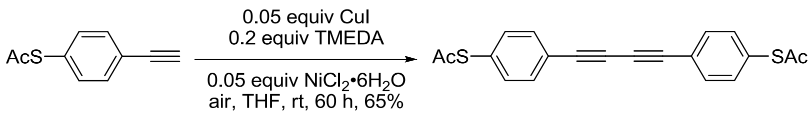
Example 2, Homo-coupling[2]



Example 3[7]



Example 4[9]

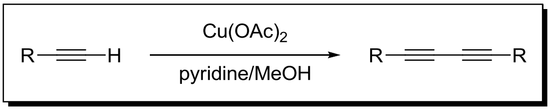


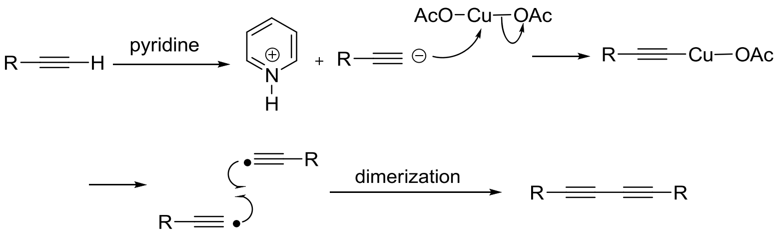
References

1. Glaser, C. *Ber.* **1869,** *2*, 422–424. Carl Andreas Glaser (1841–1935) studied under Justus von Liebig and Adolph Strecker. He became a professor in 1869 when the Glaser coupling was discovered. He became the Chairman of the Board of BASF after WWI.
2. Bowden, K.; Heilbron, I.; Jones, E. R. H.; Sondheimer, F. *J. Chem. Soc.* **1947,** 1583–1590.
3. Hoeger, S.; Meckenstock, A.-D.; Pellen, H. *J. Org. Chem.* **1997,** *62*, 4556–4557.
4. Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000,** *39*, 2632–2657. (Review).
5. Youngblood, W. J.; Gryko, D. T.; Lammi, R. K.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002,** *67*, 2111–2117.
6. Moriarty, R. M.; Pavlovic, D. *J. Org. Chem.* **2004,** *69*, 5501–5504.
7. Andersson, A. S.; Kilsa, K.; Hassenkam, T.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M.; Nielsen, M. B.; Diederich, F. *Chem. Eur. J.* **2006,** *12*, 8451–8459.
8. Gribble, G. W. *Glaser Coupling*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 236–257. (Review).
9. Muesmann, T. W. T.; Wickleder, M. S.; Christoffers, J. *Synthesis* **2011,** 2775–2780.

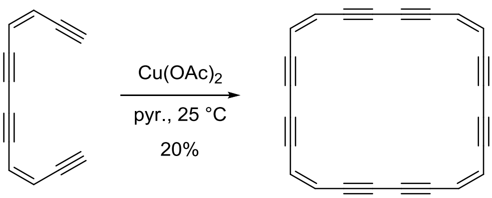
Eglinton coupling

Oxidative homo-coupling of terminal alkynes mediated by stoichiometric (or often excess) $Cu(OAc)_2$. A variant of the Glaser coupling reaction.

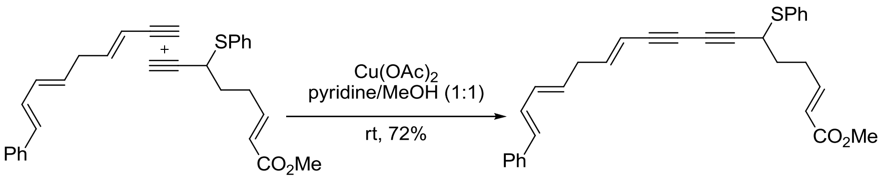




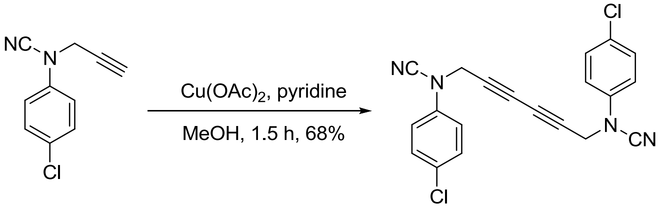
Example 1, Homo-coupling[2]



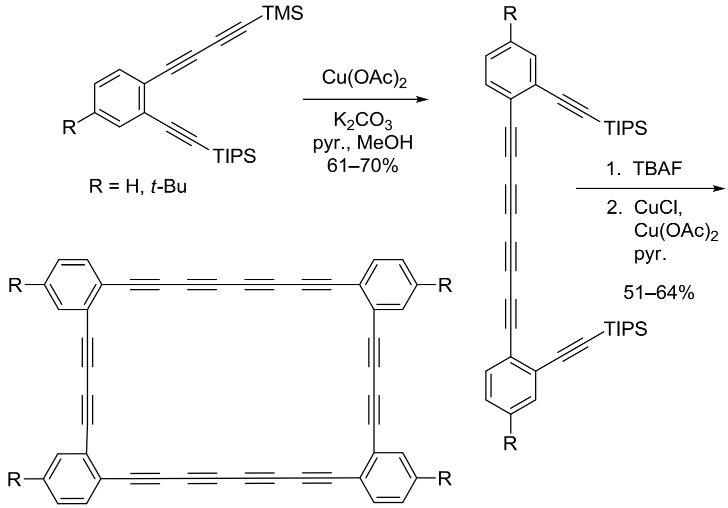
Example 2, Cross-coupling[3]



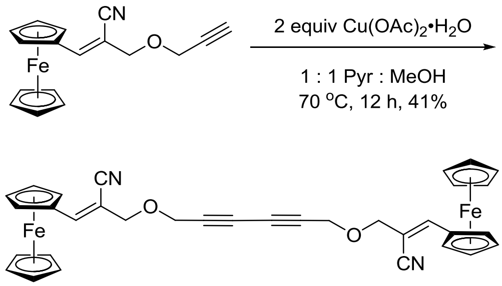
Example 3, Homo-coupling[4]



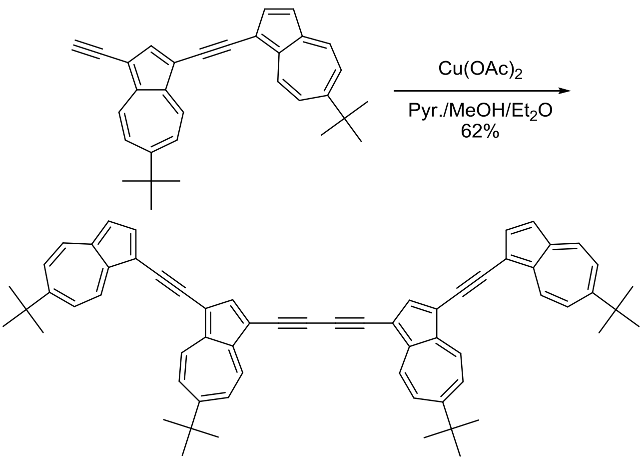
Example 4[5]



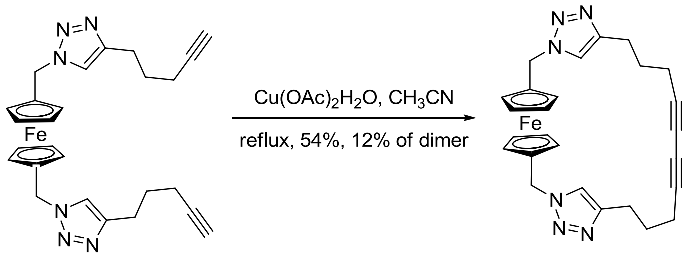
Example 5[11]



Example 6[12]



Example 7[13]

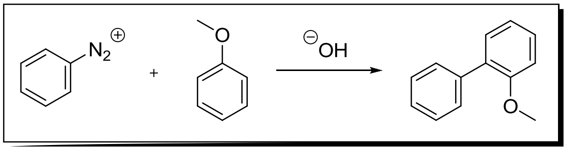


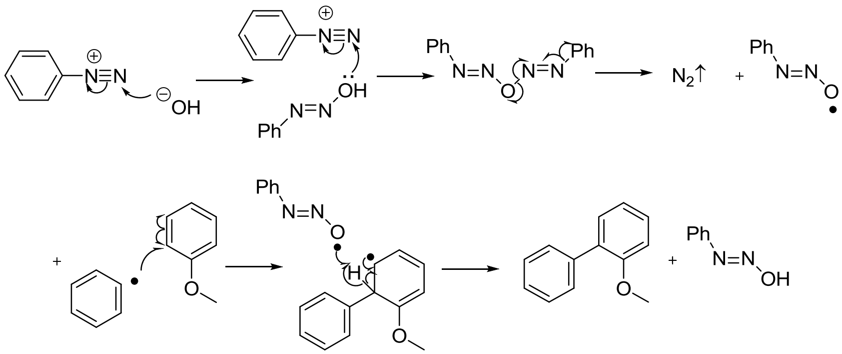
References

1. (a) Eglinton, G.; Galbraith, A. R. *Chem. Ind.* **1956,** 737–738. Geoffrey Eglinton (1927–), born in Cardiff, Wales, is a Professor Emeritus at Bristol University. (b) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960,** 3614–3625. (c) Eglinton, G.; McRae, W. *Adv. Org. Chem.* **1963,** *4*, 225–328. (Review).
2. McQuilkin, R. M.; Garratt, P. J.; Sondheimer, F. *J. Am. Chem. Soc.* **1970,** *92*, 6682–6683.
3. Nicolaou, K. C.; Petasis, N. A.; Zipkin, R. E.; Uenishi, J. *J. Am. Chem. Soc.* **1982,** *104*, 5558–5560.
4. Srinivasan, R.; Devan, B.; Shanmugam, P.; Rajagopalan, K. *Indian J. Chem., Sect. B* **1997,** *36B*, 123–125.
5. Haley, M. M.; Bell, M. L.; Brand, S. C.; Kimball, D. B.; Pak, J. J.; Wan, W. B. *Tetrahedron Lett.* **1997,** *38*, 7483–7486.
6. Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **1998,** *63*, 8632–8633.
7. Kaigtti-Fabian, K. H. H.; Lindner, H.-J.; Nimmerfroh, N.; Hafner, K. *Angew. Chem. Int. Ed.* **2001,** *40*, 3402–3405.
8. Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000,** *39*, 2632–2657. (Review).
9. Inouchi, K.; Kabashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Org. Lett.* **2002,** *4*, 2533–2536.
10. Xu, G.-L.; Zou, G.; Ni, Y.-H.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.* **2003,** *125*, 10057–10065.
11. Shanmugam, P.; Vaithiyananthan, V.; Viswambharan, B.; Madhavan, S. *Tetrahedron Lett.* **2007,** *48*, 9190–9194.
12. Miljanic, O. S.; Dichtel, W. R.; Khan, S. I.; Mortezaei, S.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2007,** *129*, 8236–8246.
13. White, N. G.; Beer, P. D. *Beilstein J. Org. Chem.* **2012,** *8*, 246–252.

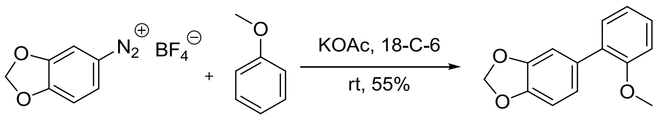
Gomberg–Bachmann reaction

Base-promoted radical coupling between an aryl diazonium salt and an arene to form a diaryl compound.

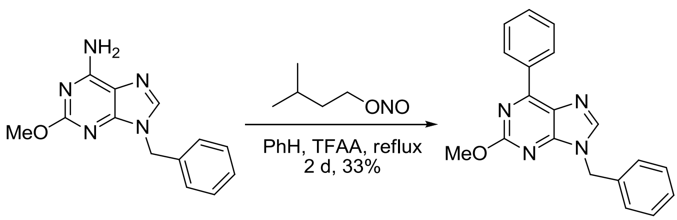




Example 1[5]



Example 2[6]



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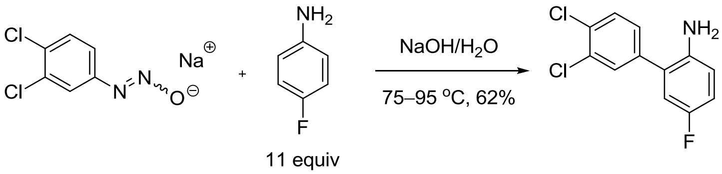
DOI 10.1007/978-3-319-03979-4_120, © Springer International Publishing Switzerland 2014

Example 3, With Diazotate[7]

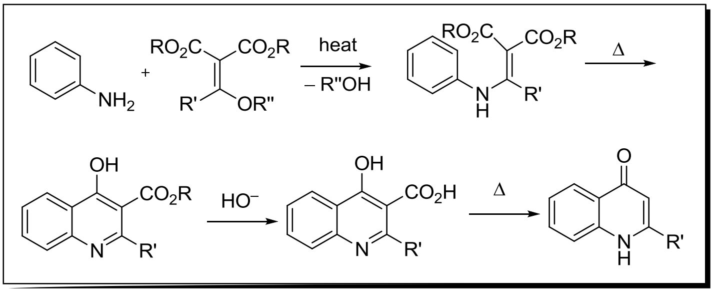


References

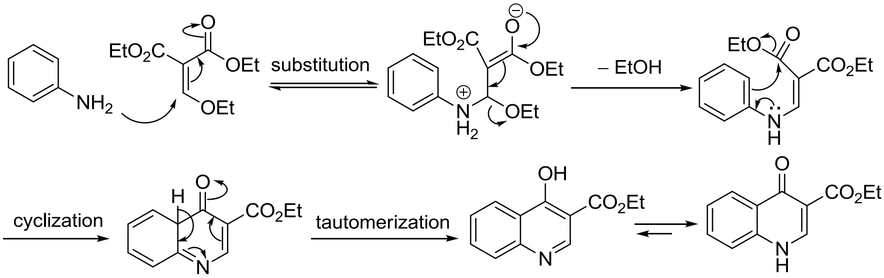
1. Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1924,** *46*, 2339−2343. Moses Gomberg (1866−1947) was born in Elizabetgrad, Russia. He discovered the triphenylmethyl stable radical at the University of Michigan in Ann Arbor, Michigan. In this article, Gomberg declared that he had reserved the field of radical chemistry for himself! Werner Bachmann (1901−1951), Gomberg's Ph.D. student, was born in Detroit, Michigan. After his postdoctoral trainings in Europe Bachmann returned to the University of Michigan, fittingly, as the Moses Gomberg Professor of Chemistry.
2. Dermer, O. C.; Edmison, M. T. *Chem. Rev.* **1957,** *57*, 77–122. (Review).
3. Rüchardt, C.; Merz, E. *Tetrahedron Lett.* **1964,** *5*, 2431–2436. (Mechanism).
4. Beadle, J. R.; Korzeniowski, S. H.; Rosenberg, D. E.; Garcia-Slanga, B. J.; Gokel, G. W. *J. Org. Chem.* **1984,** *49*, 1594−1603.
5. McKenzie, T. C.; Rolfes, S. M. *J. Heterocycl. Chem.* **1987,** *24*, 859−861.
6. Lai, Y.-H.; Jiang, J. *J. Org. Chem.* **1997,** *62*, 4412–4417.
7. Pratsch, G.; Wallaschkowski, T.; Heinrich, M. R. *Chem. Eur. J.* **2012,** *18*, 11555−11559,

Gould–Jacobs reaction

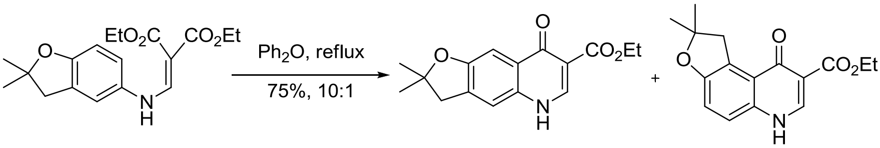
The Gould–Jacobs reaction is a sequence of the following reactions:
a. Substitution of an aniline with either alkoxy methylenemalonic ester or acyl malonic ester providing the anilinomethylenemalonic ester;
b. Cyclization of to the 4-hydroxy-3-carboalkoxyquinoline (4-hydroxyquinolines exist predominantly in 4-oxoform);
c. Saponification to form acid;
d. Decarboxylation to give the 4-hydroxyquinoline. Extension could lead to unsubstituted parent heterocycles with fused pyridine ring of Skraup type.



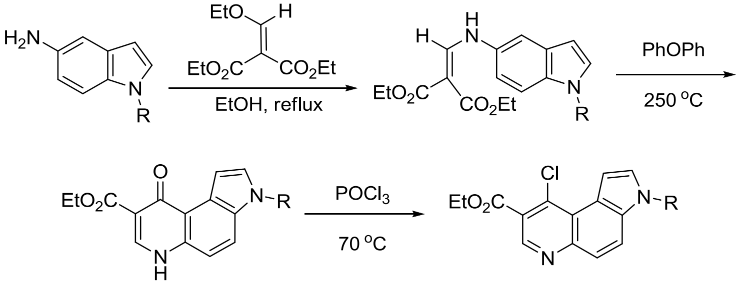
R = alkyl; R' = alkyl, aryl, or H; R" = alkyl or H



Example 1[3]



Example 2[7]



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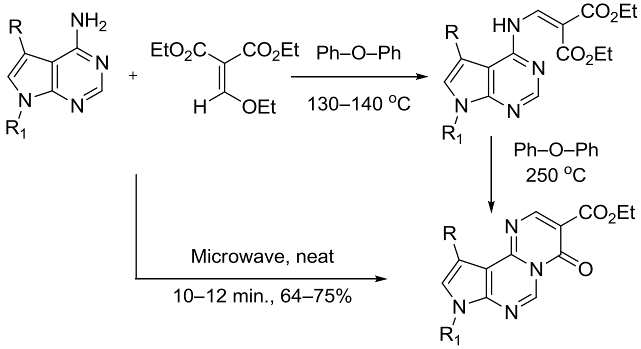
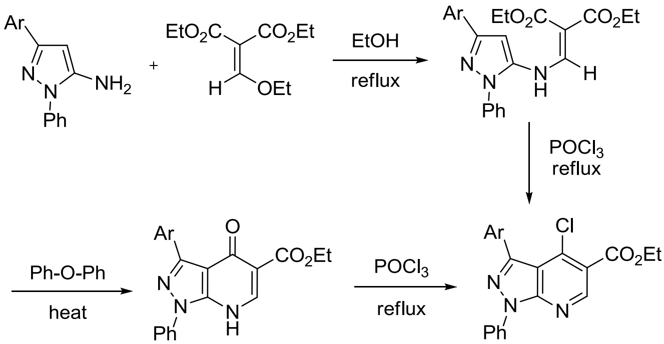
Example 3, Microwave-assisted Gould–Jacobs reaction[8]



Example 4[9]

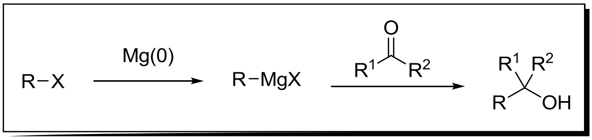


References

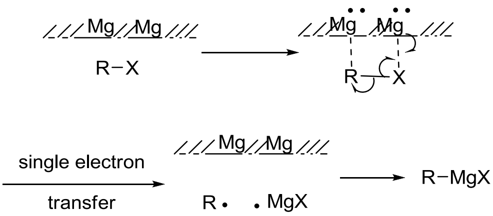
1. Gould, R. G.; Jacobs, W. A. *J. Am. Chem. Soc*. **1939,** *61*, 2890–2895. R. Gordon Gould was born in Chicago in 1909. He earned his Ph.D. at Harvard University in 1933. After serving as an instructor at Harvard and Iowa, Gould worked at Rockefeller Institute for Medical Research where he discovered the Gould–Jacobs reaction with his colleague Walter A. Jacobs.
2. Reitsema, R. H. *Chem. Rev*. **1948,** *53*, 43–68. (Review).
3. Cruickshank, P. A., Lee, F. T., Lupichuk, A. *J. Med. Chem*. **1970,** *13*, 1110–1114.
4. Elguero J., Marzin C., Katritzky A. R., Linda P., *The Tautomerism of Heterocycles*, Academic Press, New York, **1976,** pp 87–102. (Review).
5. Milata, V.; Claramunt, R. M.; Elguero, J.; Zálupský, P. *Targets in Heterocyclic Systems* **2000,** *4*, 167–203. (Review).
6. Curran, T. T. *Gould–Jacobs Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 423–436. (Review).
7. Ferlin, M. G.; Chiarelotto, G.; Dall'Acqua, S.; Maciocco, E.; Mascia, M. P.; Pisu, M. G.; Biggio, G. *Bioorg. Med. Chem*. **2005,** *13*, 3531–3541.
8. Desai, N. D. *J. Heterocycl. Chem*. **2006,** *43*, 1343–1348.
9. Kendre, D. B.; Toche, R. B.; Jachak, M. N. *J. Heterocycl. Chem*. **2008,** *45*, 1281–1286.
10. Lengyel, L.; Nagy, T. Z.; Sipos, G.; Jones, R.; Dormán, G.; Üerge, L.; Darvas, F. *Tetrahedron Lett*. **2012,** *53*, 738–743.

Grignard reaction

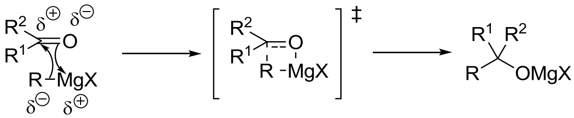
Addition of organomagnesium compounds (Grignard reagents), generated from organohalides and magnesium metal, to electrophiles.



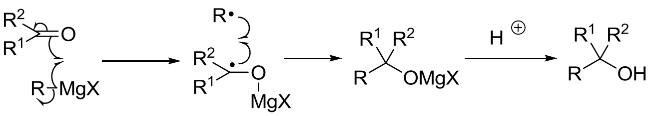
Formation of the Grignard reagent:



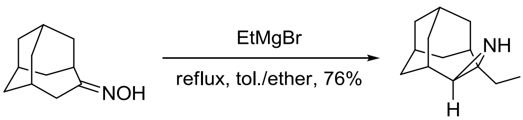
Grignard reaction, ionic mechanism:



Grignard reaction, radical mechanism,



Example 1[4]



This reaction is known as the *Hoch–Campbell aziridine synthesis*, which entails treatment of ketoximes with excess Grignard reagents and subsequent hydrolysis of the organometallic complex to produce aziridines.

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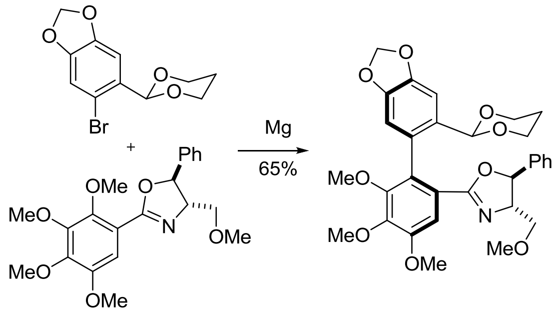
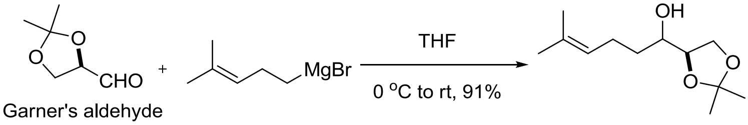
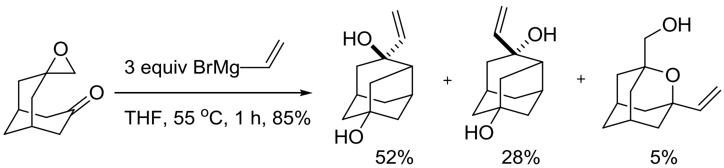
Example 2[5]



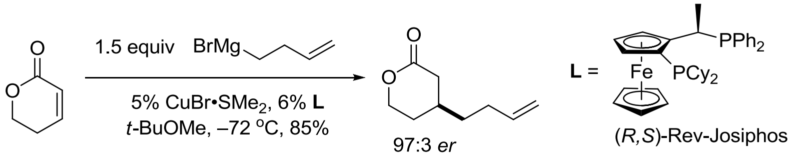
Example 5[10]



Example 6[11]



Example 7, Asymmetric Conjugate Addition[12]

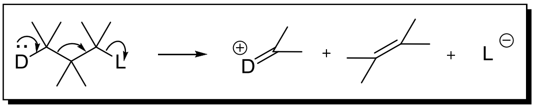


References

1. Grignard, V. *C. R. Acad. Sci.* **1900,** *130*, 1322–1324. Victor Grignard (France, 1871–1935) won the Nobel Prize in Chemistry in 1912 for his discovery of the Grignard reagent.
2. Ashby, E. C.; Laemmle, J. T.; Neumann, H. M. *Acc. Chem. Res.* **1974,** *7*, 272–280. (Review).
3. Ashby, E. C.; Laemmle, J. T. *Chem. Rev.* **1975,** *75*, 521–546. (Review).
4. Sasaki, T.; Eguchi, S.; Hattori, S. *Heterocycles* **1978,** *11*, 235–242.
5. Meyers, A. I.; Flisak, J. R.; Aitken, R. A. *J. Am. Chem. Soc.* **1987,** *109*, 5446–5452.
6. *Grignard Reagents* Richey, H. G., Jr., Ed.; Wiley: New York, **2000**. (Book).
7. Holm, T.; Crossland, I. In *Grignard Reagents* Richey, H. G., Jr., Ed.; Wiley: New York, **2000,** Chapter 1, pp 1–26. (Review).
8. Shinokubo, H.; Oshima, K. *Eur. J. Org. Chem.* **2004,** 2081–2091. (Review).
9. Graden, H.; Kann, N. *Cur. Org. Chem.* **2005,** *9*, 733–763. (Review).
10. Babu, B. N.; Chauhan, K. R. *Tetrahedron Lett.* **2008,** *50*, 66–67.
11. Mlinaric-Majerski, K.; Kragol, G.; Ramljak, T. S. *Synlett* **2008,** 405–409.
12. Mao, B.; Fãnás-Mastral, M.; Feringa, B. L. *Org. Lett.* **2013,** *15*, 286–289.

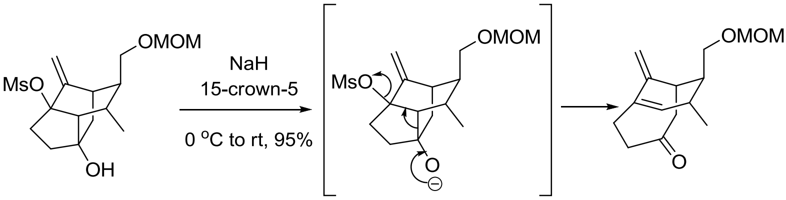
Grob fragmentation

The C–C bond cleavage primarily via a concerted process involving a five atom system.
General scheme:

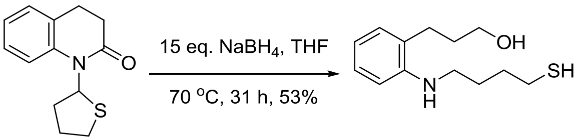


D = O^-, NR_2; L = OH_2^+, OTs, I, Br, Cl

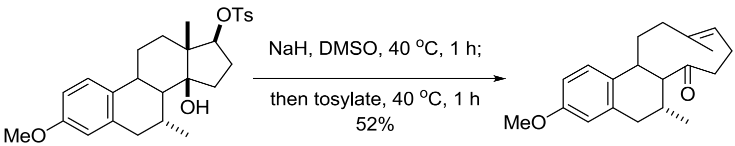
Example 1[2]



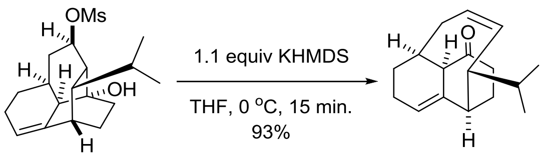
Example 2, Aza-Grob fragmentation[3]



Example 3[7]



Example 4[8]



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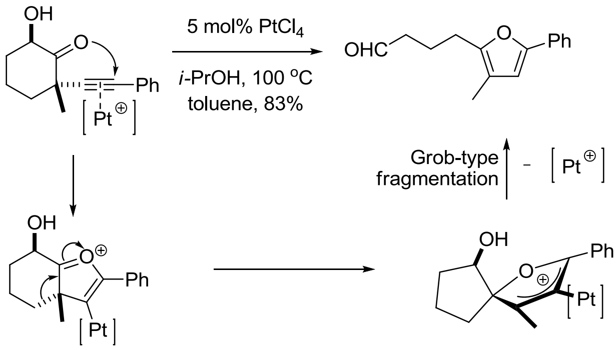
DOI 10.1007/978-3-319-03979-4_123, © Springer International Publishing Switzerland 2014

Example 4[8]

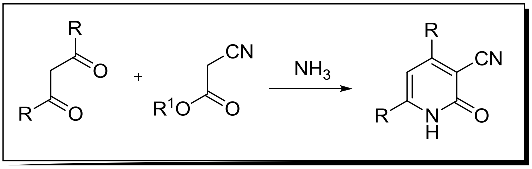


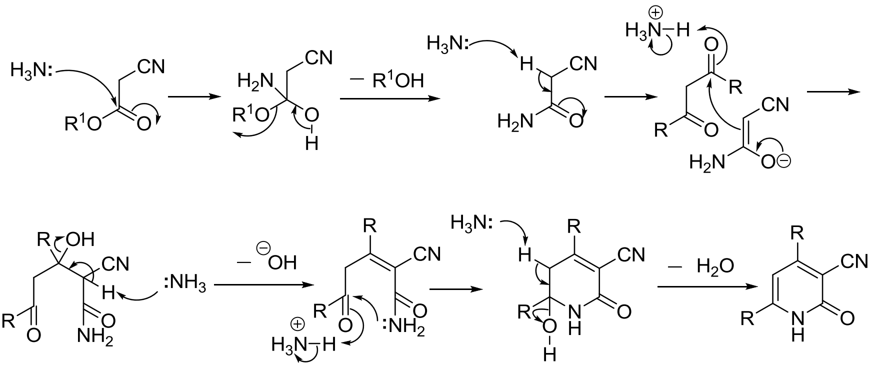
References

1. (a) Grob, C. A.; Baumann, W. *Helv. Chim. Acta* **1955,** *38*, 594–603. (b) Grob, C. A.; Schiess, P. W. *Angew. Chem. Int. Ed.* **1967,** *6,* 1–15. Cyril A. Grob (1917–2003) was born in London (UK) to Swiss parents, studied chemistry at ETH Zürich and completed his PhD in 1943 under the guidance of Leopold Ruzicka (Nobel laureate) on artificial steroidal antigens. He then moved to Basel to work with Taddeus Reichstein (another Nobel laureate) first at the pharmaceutical institute and from 1947 at the organic chemistry institute of the university, where he moved up the academic career ladder to become the director of the institute and holder of the chair there as Reichstein's successor in 1960. An investigation of the reductive elimination of bromine from 1,4-dibromides in the presence of zinc led in 1955 to the recognition of heterolytic fragmentation as a general reaction principle. The heterolytic fragmentation has now entered textbooks under his name. Experimental evidence for vinyl cations as discrete reactive intermediates was also first provided by Grob. Cyril Grob never acted impulsively, but always calmly and deliberately. He never sought attention in public, but fulfilled his social duties efficiently, reliably, and without a fuss. He died in his home in Basel (Switzerland) on December 15, 2003 at the age of 86. (Schiess, P. *Angew. Chem. Int. Ed.* **2004,** *43,* 4392.) A recent review[11] revealed that Grob was not even the first to investigate such reactions!
2. Yoshimitsu, T.; Yanagiya, M.; Nagaoka, H. *Tetrahedron Lett*. **1999,** *40*, 5215–5218.
3. Hu, W.-P.; Wang, J.-J.; Tsai, P.-C. *J. Org. Chem*. **2000,** *65*, 4208–4029.
4. Molander, G. A.; Le Huerou, Y.; Brown, G. A. *J. Org. Chem*. **2001,** *66*, 4511–4516.
5. Paquette, L. A.; Yang, J.; Long, Y. O. *J. Am. Chem. Soc.* **2002,** *124*, 6542–6543.
6. Barluenga, J.; Alvarez-Perez, M.; Wuerth, K.; *et al. Org. Lett*. **2003,** *5*, 905–908.
7. Khripach, V. A.; Zhabinskii, V. N.; Fando, G. P.; *et al. Steroids* **2004,** *69*, 495–499.
8. Maimone, T. J.; Voica, A.-F.; Baran, P. S. *Angew. Chem. Int. Ed.* **2008,** *47*, 3054–3056.
9. Yuan, D.-Y.; Tu, Y.-Q.; Fan, C.-A. *J. Org. Chem*. **2008,** *73*, 7797–7799.
10. Barbe, G.; St-Onge, M.; Charette, A. B. *Org. Lett.* **2008,** *10*, 5497–5499.
11. Mulzer, *Chem. Rev.* **2010,** *110,* 3741–4766.
12. Umland, K.-D.; Palisse, A.; Haug, T. T.; Kirsch, S. F. *Angew. Chem. Int. Ed.* **2011,** *50*, 9965–9968

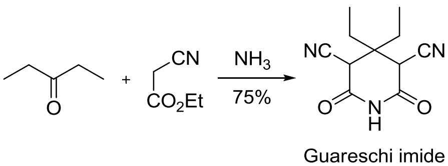
Guareschi–Thorpe condensation

2-Pyridone formation from the condensation of cyanoacetic ester with diketone in the presence of ammonia.

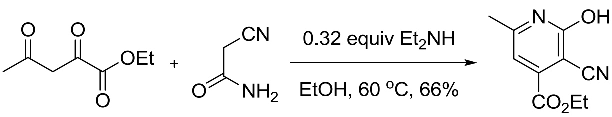




Example 1[6]



Example 2[9]



References

1. (a) Guareschi, I. *Mem. R. Accad. Sci. Torino* **1896,** *II*, 7, 11, 25. (b) Baron, H.; Renfry, F. G. P.; Thorpe, J. F. *J. Chem. Soc*. **1904,** *85*, 1726–1961. Jocelyn F. Thorpe spent two years in Germany where he worked in the laboratory of a dyestuff manufacturer before taking a post as a lecturer at Manchester. Thorpe later became FRS (Fellow of the Royal Society) and professor of organic chemistry at Imperial College.
2. Vogel, A. I. *J. Chem. Soc.* **1934,** 1758–1765.

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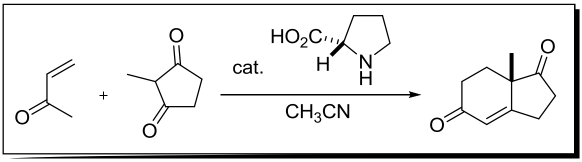
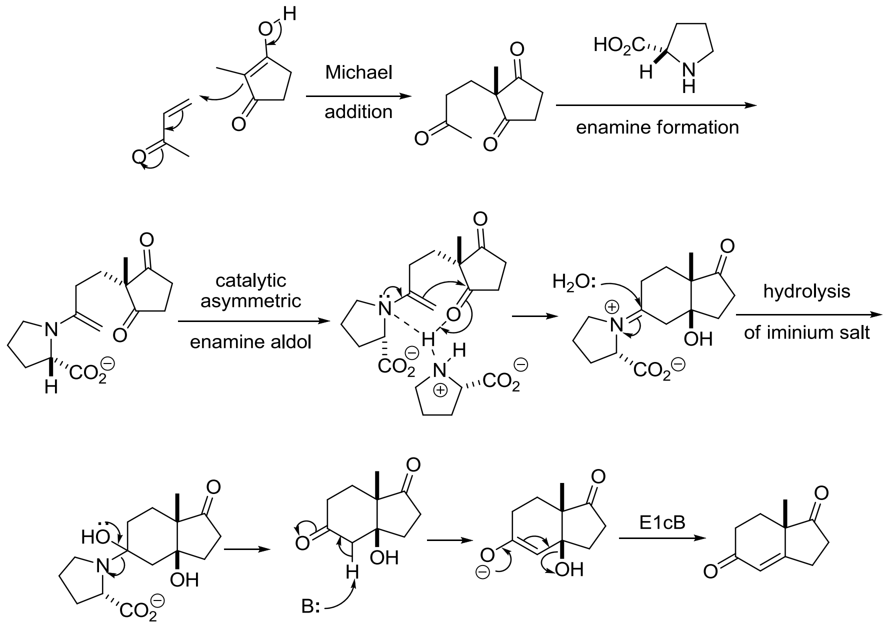
DOI 10.1007/978-3-319-03979-4_124, © Springer International Publishing Switzerland 2014

3. McElvain, S. M.; Lyle, R. E. Jr. *J. Am. Chem. Soc*. **1950,** *72*, 384–389.
4. Brunskill, J. S. A. *J. Chem. Soc. (C)* **1968,** 960–966.
5. Brunskill, J. S. A. *J. Chem. Soc., Perkin Trans. 1* **1972,** 2946–2950.
6. Holder, R. W.; Daub, J. P.; Baker, W. E.; Gilbert, R. H. III; Graf, N. A. *J. Org. Chem.* **1982,** *47*, 1445–1451.
7. Krstic, V.; Misic-Vukovic, M.; Radojkovic-Velickovic, M. *J. Chem. Res. (S)* **1991,** 82.
8. Galatsis, P. *Guareschi–Thorpe Pyridine Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 307–308. (Review).
9. Schmidt, G.; Reber, S.; Bolli, M. H.; Abele, S. *Org. Process Res. Dev.* **2012,** *16*, 595–604.

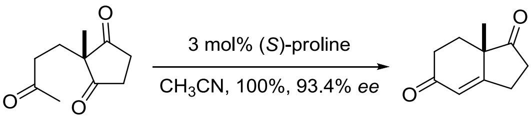
Hajos–Wiechert reaction

Asymmetric Robinson annulation catalyzed by (*S*)-(−)-proline.

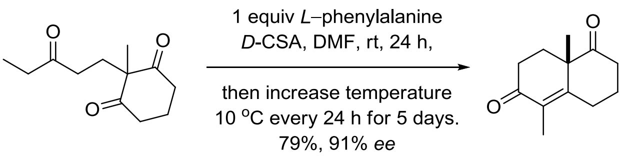




Example 1[1a]



Example 2[3]



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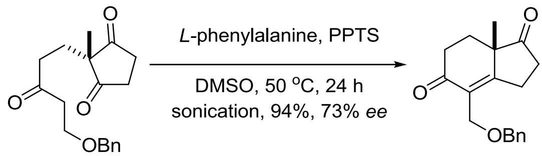
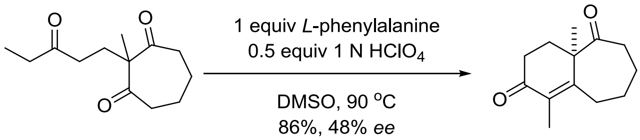
Example 3[8]



Example 4[9]

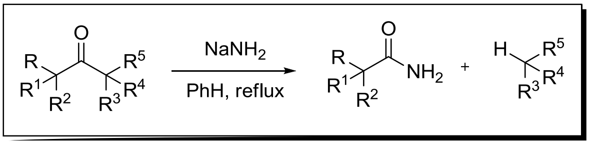


References

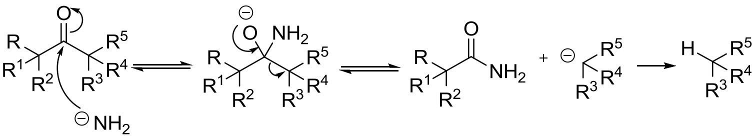
1. (a) Hajos, Z. G.; Parrish, D. R. *J. Org. Chem*. **1974,** *39*, 1615–1621. Hajos and Parrish were chemists at Hoffmann–La Roche. (b) Eder, U.; Sauer, G.; Wiechert, R. *Angew. Chem. Int. Ed.* **1971,** *10*, 496–497.
2. Brown, K. L.; Dann, L.; Duntz, J. D.; Eschenmoser, A.; Hobi, R.; Kratky, C. *Helv. Chim. Acta* **1978,** *61*, 3108–3135.
3. Hagiwara, H.; Uda, H. *J. Org.Chem.* **1998,** *53*, 2308–2311.
4. Nelson, S. G. *Tetrahedron: Asymmetry* **1998,** *9*, 357–389.
5. List, B.; Lerner, R. A.; Barbas, C. F., III. *J. Am. Chem. Soc*. **2000,** *122*, 2395–2396.
6. List, B.; Pojarliev, P.; Castello, C. *Org. Lett*. **2001,** *3*, 573–576.
7. Hoang, L.; Bahmanyar, S.; Houk, K. N.; List, B. *J. Am. Chem. Soc*. **2003,** *125*, 16–17.
8. Shigehisa, H.; Mizutani, T.; Tosaki, S.-y.; Ohshima, T.; Shibasaki, M. *Tetrahedron* **2005,** *61*, 5057–5065.
9. Nagamine, T.; Inomata, K.; Endo, Y.; Paquette, L. A. *J. Org. Chem.* **2007,** *72*, 123–131.
10. Kennedy, J. W. J.; Vietrich, S.; Weinmann, H.; Brittain, D. E. A. *J. Org. Chem*. **2009,** *73*, 5151–5154.
11. Christen, D. P. *Hajos–Wiechert Reaction*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 554–582. (Review).
12. Zhu, H.; Clemente, F. R.; Houk, K. N.; Meyer, M. P. *J. Am. Chem. Soc*. **2009,** *131*, 1632–1633.
13. Bradshaw, B.; Bonjoch, J. *Synlett* **2012,** *23*, 337–356. (Review).

Haller–Bauer reaction

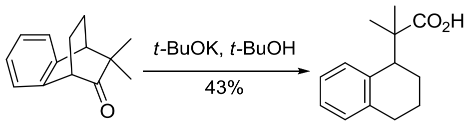
Base-induced cleavage of non-enolizable ketones leading to carboxylic amide or acid derivative and a neutral fragment in which the carbonyl group is replaced by a hydrogen.



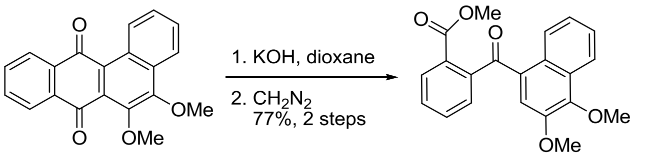
non-enolizable ketone



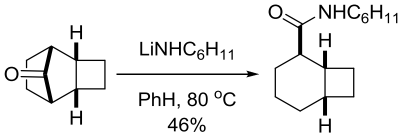
Example 1[4]



Example 2[9]



Example 3, Racemization[10]



References

1. Haller, A.; Bauer, E. *Compt. Rend.* **1908,** *147*, 824–829.
2. Gilday, J. P.; Gallucci, J. C.; Paquette, L. A. *J. Org. Chem.* **1989,** *54*, 1399–1408.
3. Paquette, L. A.; Gilday, J. P.; Maynard, G. D. *J. Org. Chem.* **1989,** *54*, 5044–5053.
4. Paquette, L. A.; Gilday, J. P. *Org. Prep. Proc. Int.* **1990,** *22*, 167–201.
5. Mehta, G.; Praveen, M. *J. Org. Chem.* **1995,** *60*, 279–280.
6. Mehta, G.; Venkateswaran, R. V. *Tetrahedron* **2000,** *56*, 1399–1422. (Review).
7. Arjona, O.; Medel, R.; Plumet, J. *Tetrahedron Lett.* **2001,** *42*, 1287–1288.
8. Ishihara, K.; Yano, T. *Org. Lett.* **2004,** *6*, 1983–1986.
9. Patra, A.; Ghorai, S. K.; De, S. R.; Mal, D. *Synthesis* **2006,** 2556–2562.
10. Braun, I.; Rudroff, F.; Mihovilovic, M. D.; Bach, T. *Synthesis* **2007,** *24*, 3896–3906.
11. Krief, A.; Kremer, A. *Tetrahedron Lett.* **2010,** *51*, 4306–4309.

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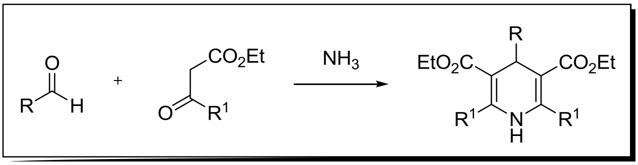
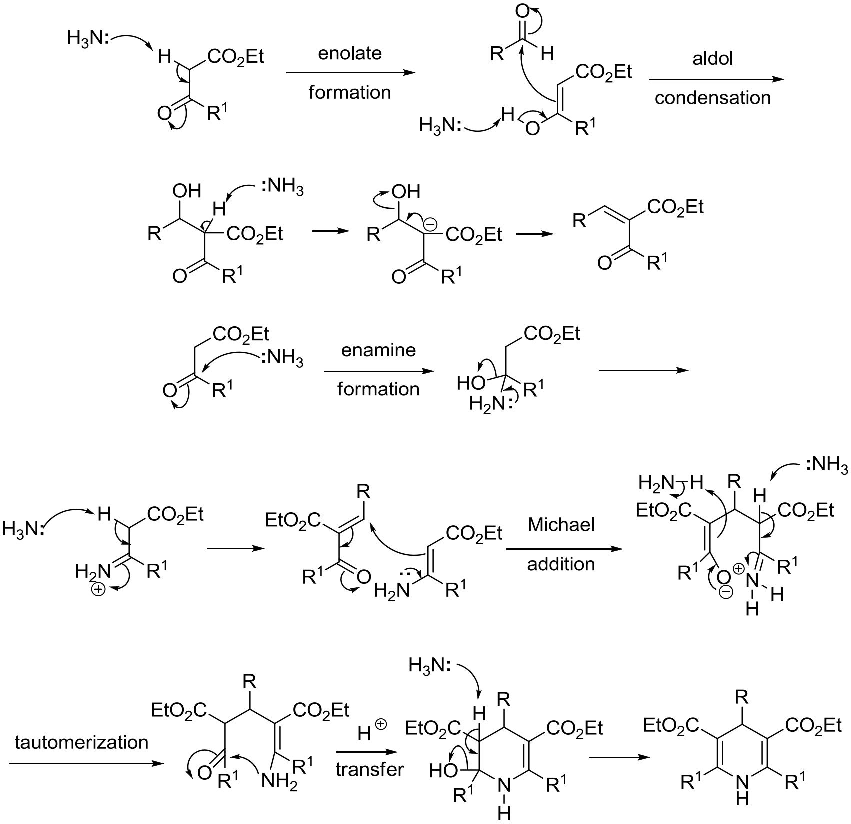
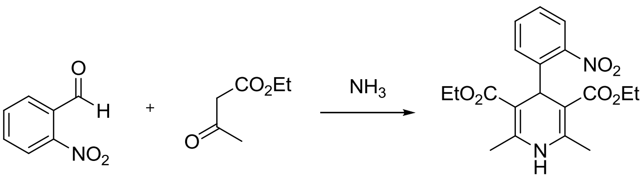
Hantzsch dihydropyridine synthesis

1,4-Dihydropyridine from the condensation of aldehyde, β-ketoester and ammonia. Hantzsch 1,4-dihydropyridines are popular reducing reagents in organo-catalysis.





Example 1[2]



nifedipine

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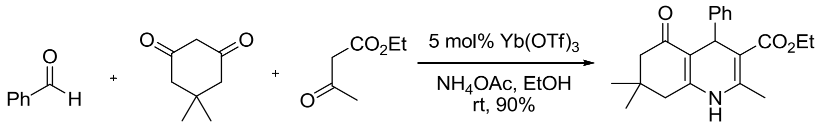
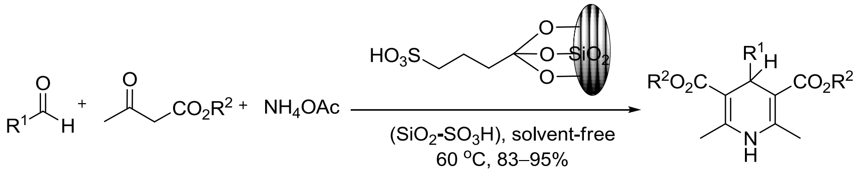
Example 2[10]



Example 3[10]

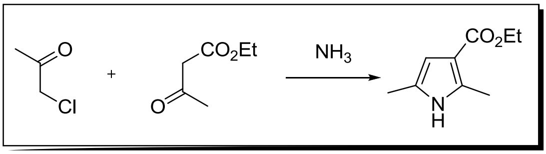


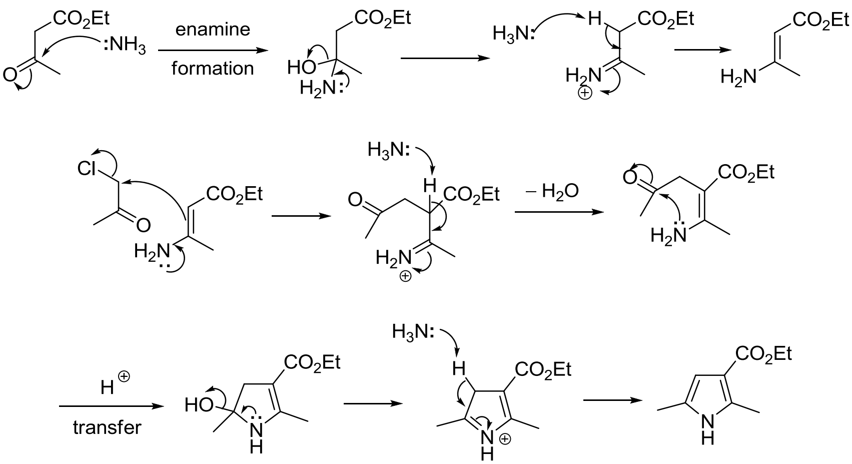
References

1. Hantzsch, A. *Ann.* **1882,** *215*, 1–83.
2. Bossert, F.; Vater, W. *Naturwissenschaften* **1971,** *58*, 578–585.
3. Balogh, M.; Hermecz, I.; Naray-Szabo, G.; Simon, K.; Meszaros, Z. *J. Chem. Soc., Perkin Trans. 1* **1986,** 753–757.
4. Katritzky, A. R.; Ostercamp, D. L.; Yousaf, T. I. *Tetrahedron* **1987,** *43*, 5171–5187.
5. Menconi, I.; Angeles, E.; Martinez, L.; Posada, M. E.; Toscano, R. A.; Martinez, R. *J. Heterocycl. Chem*. **1995,** *32*, 831–833.
6. Raboin, J.-C.; Kirsch, G.; Beley, M. *J. Heterocycl. Chem*. **2000,** *37*, 1077–1080.
7. Sambongi, Y.; Nitta, H.; Ichihashi, K.; Futai, M.; Ueda, I. *J. Org. Chem*. **2002,** *67*, 3499–3501.
8. Wang, L.-M.; Sheng, J.; Zhang, L.; Han, J.-W.; Fan, Z.-Y.; Tian, H.; Qian, C.-T. *Tetrahedron* **2005,** *61*, 1539–1543.
9. Galatsis, P. *Hantzsch Dihydro-Pyridine Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 304–307. (Review).
10. Gupta, R.; Gupta, R.; Paul, S.; Loupy, A. *Synthesis* **2007,** 2835–2838.
11. Snyder, N. L.; Boisvert, C. J. *Hantzsch Synthesis*, in *Name Reactions in Heterocyclic Chemistry II,* Li, J. J., Ed.; Wiley: Hoboken, NJ, **2011,** pp 591–644. (Review).
12. Ghosh, S.; Saikh, F.; Das, J.; Pramanik, A. K. *Tetrahedron Lett.* **2013,** *54*, 58–62.

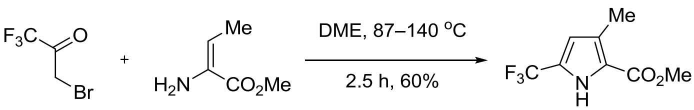
Hantzsch pyrrole synthesis

Reaction of α-chloromethyl ketones with β-ketoesters and ammonia to assemble pyrroles.

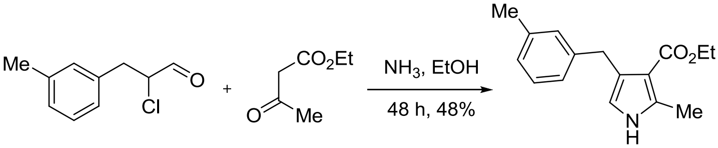




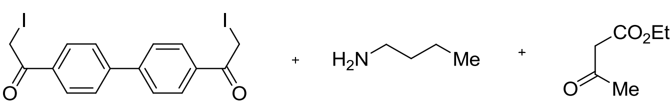
Example 1[4]



Example 2[7]



Example 3[9]



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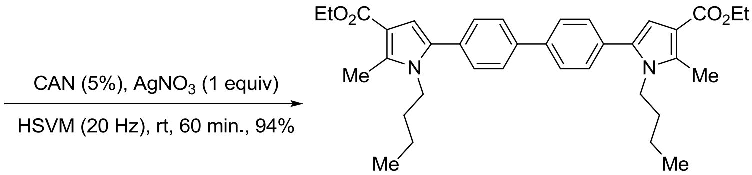
DOI 10.1007/978-3-319-03979-4_128, © Springer International Publishing Switzerland 2014



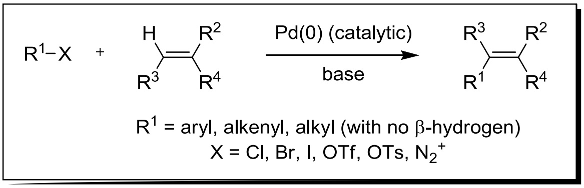
HSVM = high-speed vibration milling

References

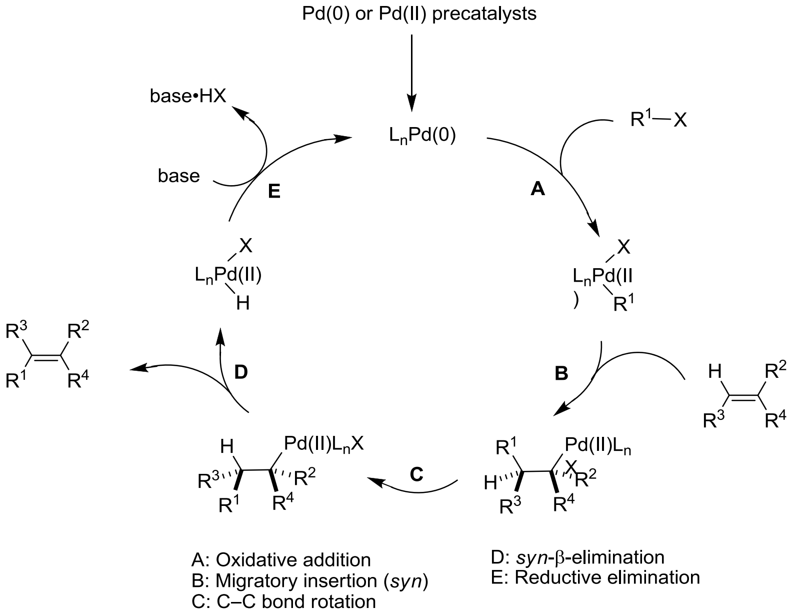
1. Hantzsch, A. *Ber.* **1890,** *23*, 1474–1483.
2. Katritzky, A. R.; Ostercamp, D. L.; Yousaf, T. I. *Tetrahedron* **1987,** *43*, 5171–5186.
3. Kirschke, K.; Costisella, B.; Ramm, M.; Schulz, B. *J. Prakt. Chem.* **1990,** *332*, 143–147.
4. Kameswaran, V.; Jiang, B. *Synthesis* **1997,** 530–532.
5. Trautwein, A. W.; Süβmuth, R. D.; Jung, G. *Bioorg. Med. Chem. Lett.* **1998,** *8*, 2381–2384.
6. Ferreira, V. F.; De Souza, M. C. B. V.; Cunha, A. C.; Pereira, L. O. R.; Ferreira, M. L. G. *Org. Prep. Proced. Int.* **2001,** *33*, 411–454. (Review).
7. Matiychuk, V. S.; Martyak, R. L.; Obushak, N. D.; Ostapiuk, Yu. V.; Pidlypnyi, N. I. *Chem. Heterocycl. Compounds* **2004,** *40*, 1218–1219.
8. Snyder, N. L.; Boisvert, C. J. *Hantzsch Synthesis,* in *Name Reactions in Heterocyclic Chemistry II,* Li, J. J., Ed.; Wiley: Hoboken, NJ, 2011, pp 591–644. (Review).
9. Estevez, Veronica; Villacampa, M.; Menendez, J. C. *Chem. Commun.* **2013,** *49*, 591–593.

Heck reaction

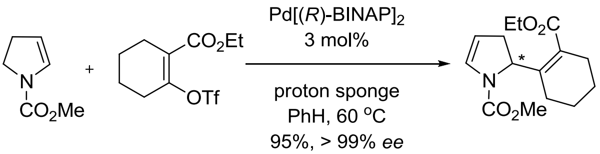
The palladium-catalyzed alkenylation or arylation of olefins.



The catalytic cycle:



Example 1, Asymmetric intermolecular Heck reaction[6]



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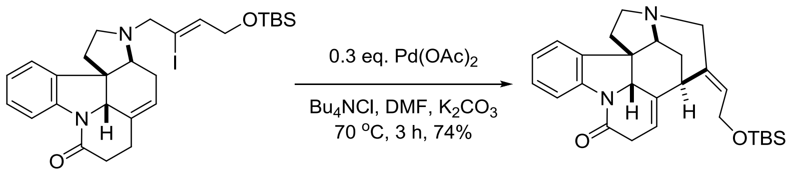
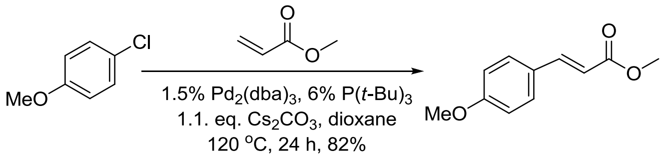
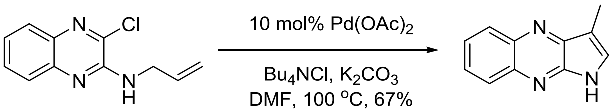
Example 2, Intramolecular Heck[7]



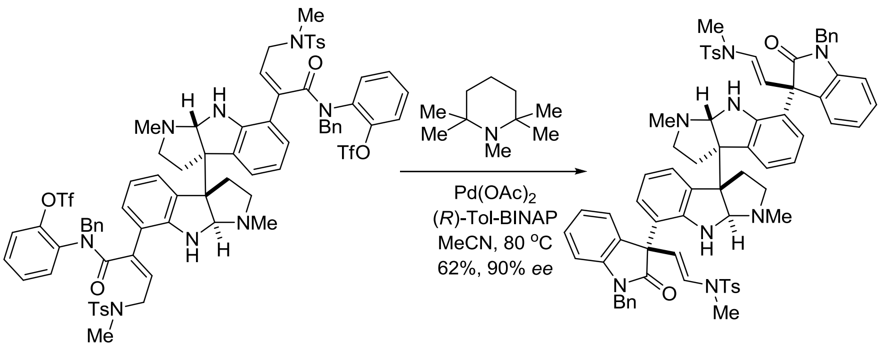
Example 3[8]



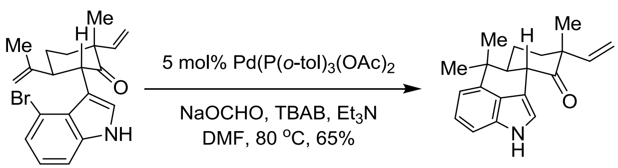
Example 4, Intramolecular Heck[9]



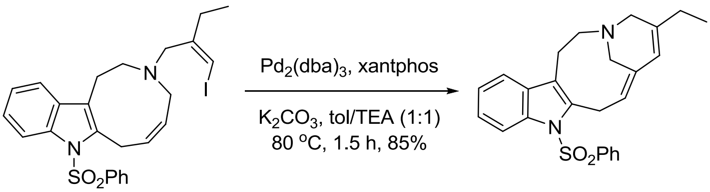
Example 5, Intramolecular Heck[13]



Example 6, Reductive Heck reaction[17]



Example 7, Intramolecular Heck[20]

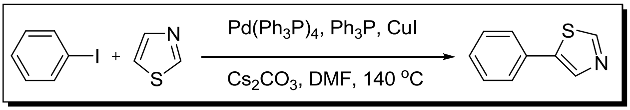


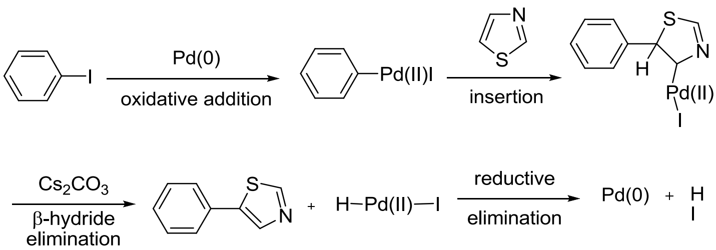
References

1. Heck, R. F.; Nolley, J. P., Jr. *J. Am. Chem. Soc*. **1968,** *90*, 5518–5526. Richard Heck discovered the Heck reaction when he was Hercules Corp. Heck won Nobel Prize in 2010 along with Akira Suzuki and Ei-ichi Negishi "for palladium-catalyzed cross couplings in organic synthesis".
2. Heck, R. F. *Acc. Chem. Res.* **1979,** *12*, 146–151. (Review).
3. Heck, R. F. *Org. React.* **1982,** *27*, 345–390. (Review).
4. Heck, R. F. *Palladium Reagents in Organic Synthesis,* Academic Press, London, **1985**. (Book).
5. Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecule* **1994,** University Science Books: Mill Valley, CA, pp 103–113. (Book).
6. Ozawa, F.; Kobatake, Y.; Hayashi, T. *Tetrahedron Lett.* **1993,** *34*, 2505–2508.
7. Rawal V. H.; Iwasa, H. *J. Org. Chem.* **1994,** *59*, 2685–2686.
8. Littke, A. F.; Fu, G. C. *J. Org. Chem.* **1999,** *64*, 10–11.
9. Li, J. J. *J. Org. Chem.* **1999,** *64*, 8425–8427.
10. Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev*. **2000,** *100*, 3009–3066. (Review).
11. Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000,** *33*, 314–321. (Review).
12. Link, J. T. *Org. React.* **2002,** *60*, 157–534. (Review).
13. Lebsack, A. D.; Link, J. T.; Overman, L. E.; Stearns, B. A. *J. Am. Chem. Soc*. **2002,** *124*, 9008–9009.
14. Dounay, A. B.; Overman, L. E. *Chem. Rev*. **2003,** *103*, 2945–2963. (Review).
15. Beller, M.; Zapf, A.; Riermeier, T. H. *Transition Metals for Organic Synthesis* (2nd edn.) **2004,** *1*, 271–305. (Review).
16. Oestreich, M. *Eur. J. Org. Chem.* **2005,** 783–792. (Review).
17. Baran, P. S.; Maimone, T. J.; Richter, J. M. *Nature* **2007,** *446*, 404–406.
18. Fuchter, M. J. *Heck Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 2–32. (Review).
19. *The Mizoroki–Heck Reaction*; Oestreich, M., Ed.; Wiley: Hoboken, NJ, **2009**.
20. Bennasar, M.-L.; Solé, D.; Zulaica, E.; Alonso, S. *Tetrahedron* **2013,** *69*, 2534–2541.

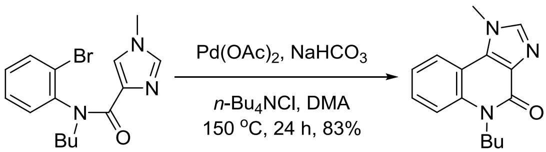
Heteroaryl Heck reaction

Intermolecular or intramolecular Heck reaction that occurs onto a heteroaryl recipient.

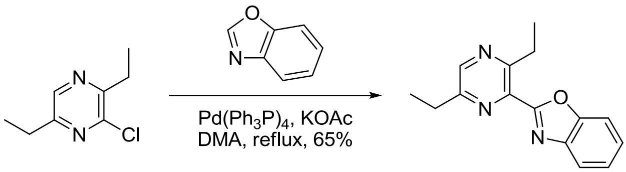




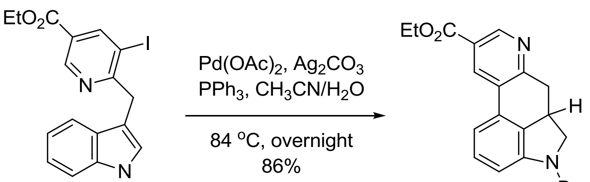
Example 1[2]



Example 2[3]



Example 3[7]

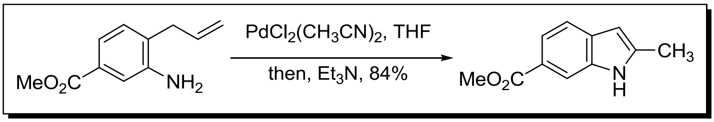


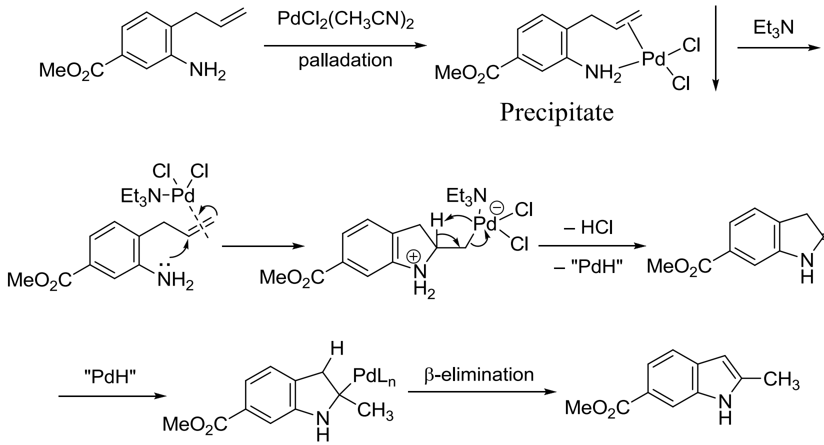
References

1. Ohta, A.; Akita, Y.; Ohkuwa, T.; Chiba, M.; Fukunaka, R.; Miyafuji, A.; Nakata, T.; Tani, N. Aoyagi, Y. *Heterocycles* **1990,** *31*, 1951−1958.
2. Kuroda, T.; Suzuki, F. *Tetrahedron Lett.* **1991,** *32*, 6915−6918.
3. Aoyagi, Y.; Inoue, A.; Koizumi, I.; Hashimoto, R.; Tokunaga, K.; Gohma, K.; Komatsu, J.; Sekine, K.; Miyafuji, A.; Kunoh, J.; Honma, R.; Akita, Y.; Ohta, A. *Heterocycles* **1992,** *33*, 257–272.
4. Proudfoot, J. R.; Patel, U. R.; Kapadia, S. R.; Hargrave, K. D. *J. Med. Chem.* **1995,** *38*, 1406−1410.
5. Pivsa-Art, S.; Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998,** *71*, 467–473.
6. Li, J. J.; Gribble, G. W. In *Palladium in Heterocyclic Chemistry;* 2nd ed.; **2007,** Elsevier: Oxford, UK. (Review).
7. Burley, S. D.; Lam, V. V.; Lakner, F. J.; Bergdahl, B. M.; Parker, M. A. *Org. Lett.* **2013,** *15*, 2598–2600.

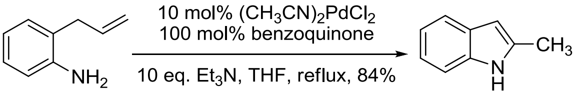
Hegedus indole synthesis

Stoichiometric Pd(II)-mediated oxidative cyclization of alkenyl anilines to indoles. *Cf.* Wacker oxidation.

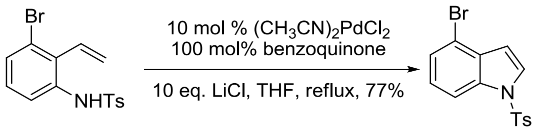




Example 1[1a]



Example 2[1d]



References

1. (a) Hegedus, L. S.; Allen, G. F.; Waterman, E. L. *J. Am. Chem. Soc.* **1976,** *98,* 2674–2676. Lou Hegedus is a professor at Colorado State University. (b) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978,** *100,* 5800–5807. (c) Hegedus, L. S.; Winton, P. M.; Varaprath, S. *J. Org. Chem.* **1981,** *46*, 2215–2221. (d) Harrington, P. J.; Hegedus, L. S. *J. Org. Chem.* **1984,** *49*, 2657–2662. (e) Hegedus, L. S. *Angew. Chem. Int. Ed.* **1988,** *27,* 1113–1126. (Review).
2. Brenner, M.; Mayer, G.; Terpin, A.; Steglich, W. *Chem. Eur. J.* **1997,** *3*, 70–74.
3. Osanai, Y. Y.; Kondo, K.; Murakami, Y. *Chem. Pharm. Bull.* **1999,** *47*, 1587–1590.
4. Kondo, T.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **2002,** *124*, 186–187. A ruthenium variant.
5. Johnston, J. N. *Hegedus Indole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 135–139. (Review).

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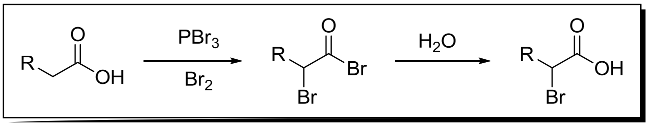
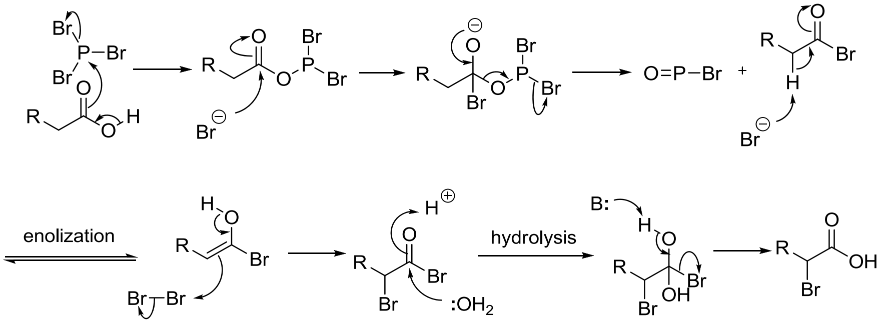
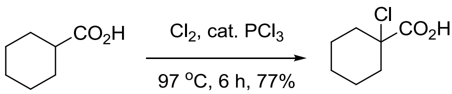
Hell–Volhard–Zelinsky reaction

α-Halogenation of carboxylic acids using X_2/PBr_3.

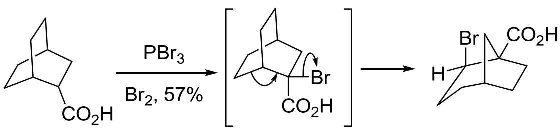




Example 1[5]



Example 2[6]



References

1. (a) Hell, C. *Ber.* **1881,** *14*, 891–893. Carl M. von Hell (1849–1926) was born in Stuttgart, Germany. He studied under Fehling and Erlenmeyer. Hell became a professor at Stuttgart in 1883 where he discovered the Hell–Volhard–Zelinsky reaction. (b) Volhard, J. *Ann.* **1887,** *242*, 141–163. Jacob Volhard (1849–1909) was born in Darmstadt, Germany. He apprenticed under Liebig, Will, Bunsen, Hofmann, Kolbe, and von Baeyer. He improved Hell's original procedure in preparing α-bromo-acid during his research in thiophenes. (c) Zelinsky, N. D. *Ber.* **1887,** *20,* 2026. Nikolay D. Zelinsky (1861–1953) was born in Tiraspol, Russia. He studied in Germany, receiving his degree in 1891. In 1885, Zelinsky was the first to prepare mustard gas unintentionally while exploring polymerization of sulfur dichloride. Zelinsky returned to Rus-

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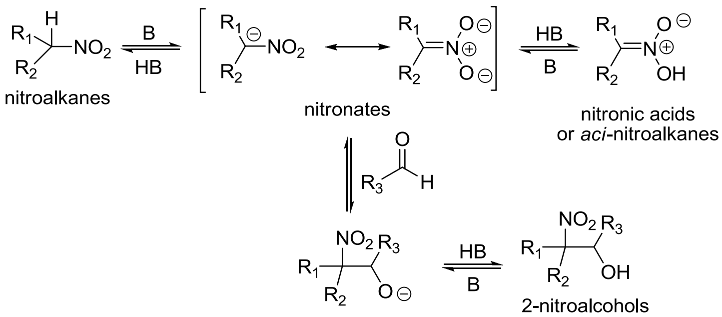
sia and became a professor at the University of Moscow, where he discovered activated charcoal gas mask. He was awarded the Order of Lenin in 1934.

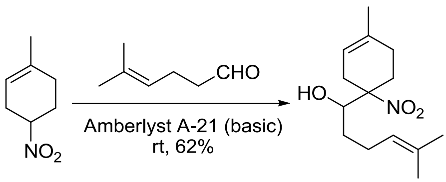
2. Watson, H. B. *Chem. Rev.* **1930,** *7,* 173–201. (Review).
3. Sonntag, N. O. V. *Chem. Rev.* **1953,** *52,* 237–246. (Review).
4. Harwood, H. J. *Chem. Rev.* **1962,** *62,* 99–154. (Review).
5. Jason, E. F.; Fields, E. K. US Patent 3,148,209 (**1964**).
6. Chow, A. W.; Jakas, D. R.; Hoover, J. R. E. *Tetrahedron Lett.* **1966,** *7,* 5427–5431.
7. Liu, H.-J.; Luo, W. *Synth. Commun.* **1991,** *21*, 2097–2102.
8. Zhang, L. H.; Duan, J.; Xu, Y.; Dolbier, W. R., Jr. *Tetrahedron Lett.* **1998,** *39,* 9621–9622.
9. Sharma, A.; Chattopadhyay, S. *J. Org. Chem.* **1999,** *64*, 8059–8062.
10. Stack, D. E.; Hill, A. L.; Diffendaffer, C. B.; Burns, N. M. *Org. Lett.* **2002,** *4*, 4487–4490.
11. Sun, Z.; Peng, X.; Dong, X.; Shi, W. *Asian J. Chem.* **2012,** *24*, 929–930.

Henry nitroaldol reaction

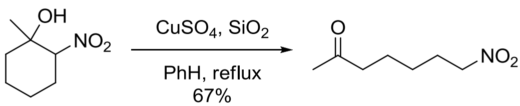
The nitroaldol condensation reaction involving aldehydes and nitronates, derived from deprotonation of nitroalkanes by bases.



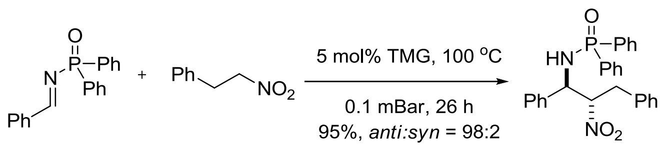
Example 1[4]



Example 2, Retro-Henry reaction[5]



Example 3, Aza-Henry reaction[8]



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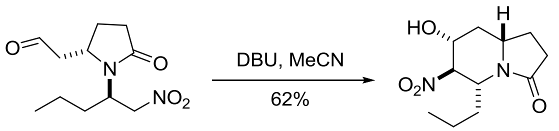
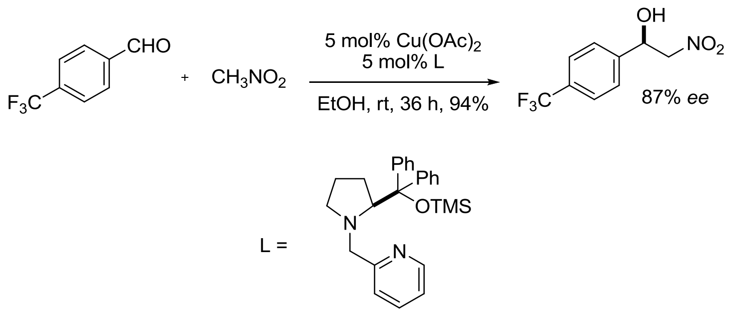
DOI 10.1007/978-3-319-03979-4_132,

Example 4, Intramolecular Henry reaction[10]



Example 4, A highly asymmetric Henry reaction catalyzed by chiral copper(II) complexes[12]

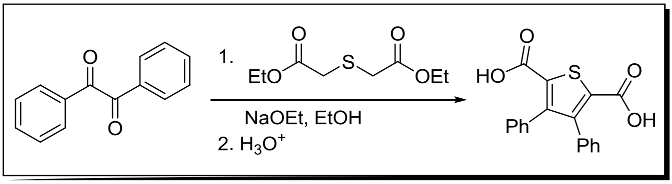


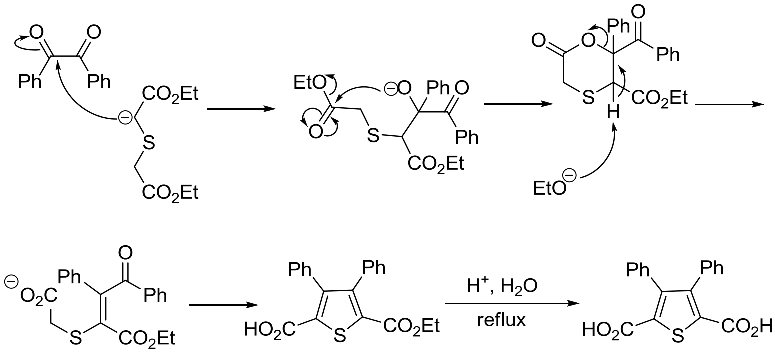
References

1. Henry, L. *Compt. Rend.* **1895,** *120*, 1265–1268.
2. Barrett, A. G. M.; Robyr, C.; Spilling, C. D. *J. Org. Chem.* **1989,** *54*, 1233–1234.
3. Rosini, G. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *2*, 321–340. (Review).
4. Chen, Y.-J.; Lin, W.-Y. *Tetrahedron Lett.* **1992,** *33*, 1749–1750.
5. Saikia, A. K.; Hazarika, M. J.; Barua, N. C.; Bezbarua, M. S.; Sharma, R. P.; Ghosh, A. C. *Synthesis* **1996,** 981–985.
6. Luzzio, F. A. *Tetrahedron* **2001,** *57*, 915–945. (Review).
7. Westermann, B. *Angew. Chem. Int. Ed.* **2003,** *42,* 151–153. (Review on aza-Henry reaction).
8. Bernardi, L.; Bonini, B. F.; Capito, E.; Dessole, G.; Comes-Franchini, M.; Fochi, M.; Ricci, A. *J. Org. Chem.* **2004,** *69*, 8168–8171.
9. Palomo, C.; Oiarbide, M.; Laso, A. *Angew. Chem. Int. Ed.* **2005,** *44*, 3881–3884.
10. Kamimura, A.; Nagata, Y.; Kadowaki, A.; Uchidaa, K.; Uno, H. *Tetrahedron* **2007,** *63*, 11856–11861.
11. Wang, A. X. *Henry Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 404–419. (Review).
12. Ni, B.; He, J. *Tetrahedron Lett.* **2013,** *54*, 462–465.

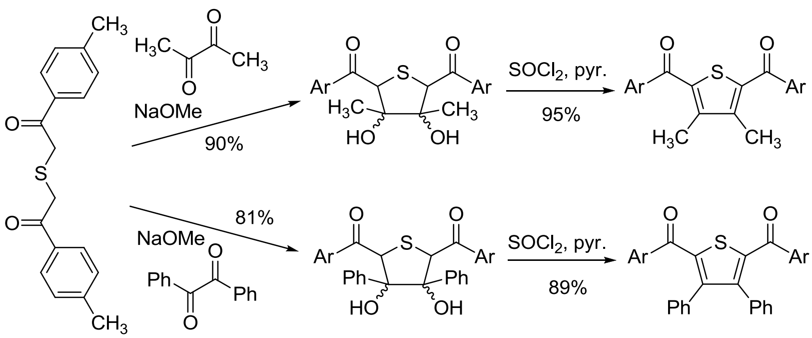
Hinsberg synthesis of thiophenes

Condensation of diethyl thiodiglycolate and α-diketones under basic conditions, which provides 3,4-disubstituted thiophene-2,5-dicarbonyls upon hydrolysis of the crude ester product with aqueous acid.

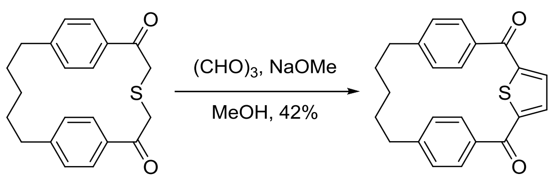




Example 1[2]



Example 2[4]



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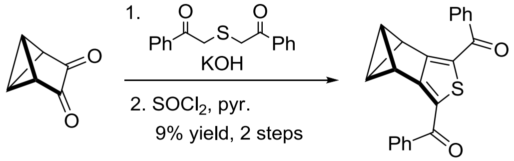
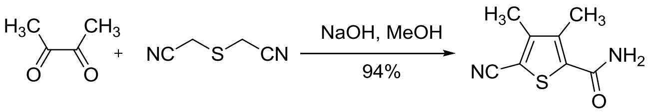
DOI 10.1007/978-3-319-03979-4_133, © Springer International Publishing Switzerland 2014

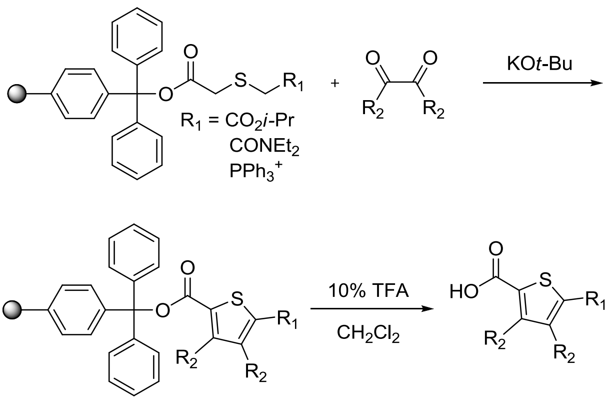
Example 3[5]



Example 4[6]



Example 5, Polymer-support Hinsberg thiophene synthesis[9]

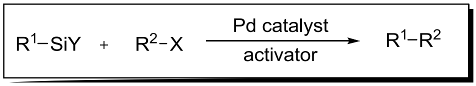


References

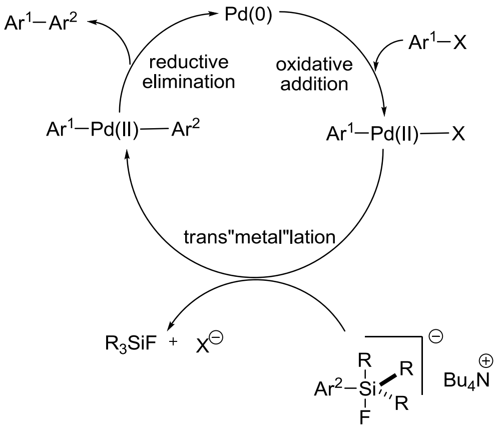
1. Hinsberg, O. *Ber.* **1910,** *43*, 901–906.
2. Miyahara, Y.; Inazu, T.; Yoshino, T. *Bull. Chem. Soc. Jpn.* **1980,** *53*, 1187–1188.
3. Gronowitz, S. In *Thiophene and Its Derivatives*, Part 1, Gronowitz, S., ed.; Wiley-Interscience: New York, **1985,** pp 34–41. (Review).
4. Miyahara, Y.; Inazu, T.; Yoshino, T. *J. Org. Chem.* **1984,** *49*, 1177–1182.
5. Christl, M.; Krimm, S.; Kraft, A. *Angew. Chem. Int. Ed.* **1990,** *29*, 675–677.
6. Beye, N.; Cava, M. P. *J. Org. Chem.* **1994,** *59*, 2223–2226.
7. Vogel, E.; Pohl, M.; Herrmann, A.; Wiss, T.; König, C.; Lex, J.; Gross, M.; Gisselbrecht, J. P. *Angew. Chem. Int. Ed.* **1996,** *35*, 1520–1525.
8. Mullins, R. J.; Williams, D. R. *Hinsberg Synthesis of Thiophene Derivatives*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 199–206. (Review).
9. Traversone, A.; Brill, W. K.-D. *Tetrahedron Lett.* **2007,** *48*, 3535–3538.
10. Jimenez, R. P.; Parvez, M.; Sutherland, T. C.; Viccars, J. *Eur. J. Org. Chem.* **2009,** 5635–5646.

Hiyama cross-coupling reaction

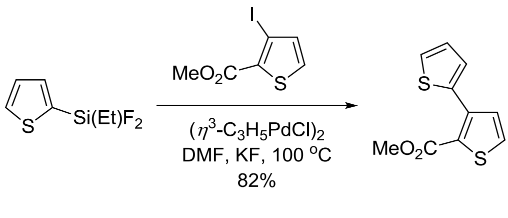
Palladium-catalyzed cross-coupling reaction of organosilicons with organic halides, triflates, *etc*. In the presence of an activating agent such as fluoride or hydroxide (transmetallation is reluctant to occur without the effect of an activating agent). For the catalytic cycle, see the Kumada coupling.



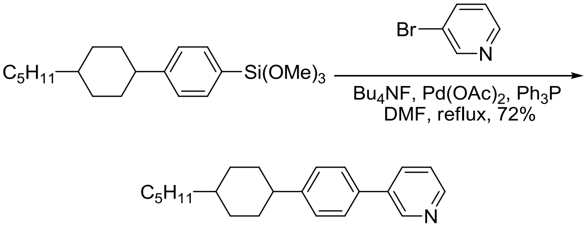
R^1 = alkenyl, aryl, alkynyl, alkyl
R^2 = aryl, alkyl, alkenyl
Y = $(OR)_3$, Me_3, Me_2OH, $Me_{(3-n)}F_{(n+3)}$
X = Cl, Br, I, OTf
activator = TBAF, base



Example 1[1a]



Example 2[2]



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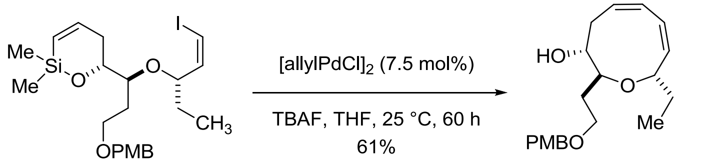
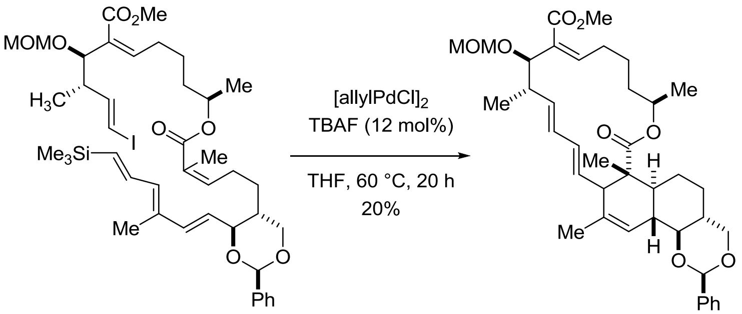
DOI 10.1007/978-3-319-03979-4_134,

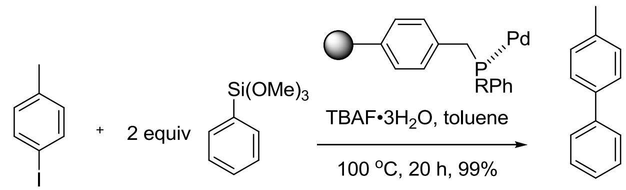
Example 3[7]



Example 4[9]



Example 5, Reusable polystyrene-supported palladium catalyst[11]

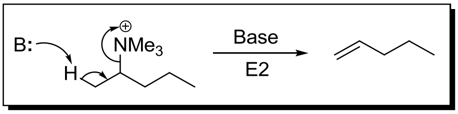


References

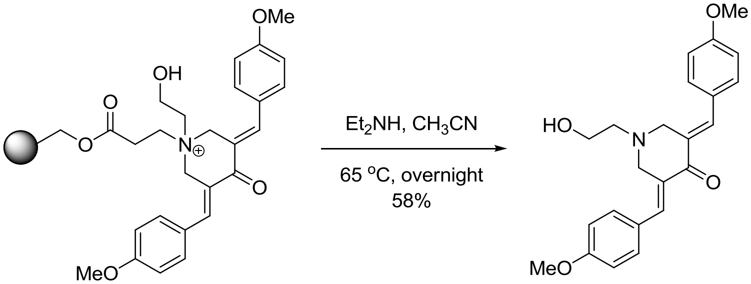
1. (a) Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Heterocycles* **1990,** *30*, 303–306. (b) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994,** *66*, 1471–1478. (c) Matsuhashi, H.; Kuroboshi, M.; Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1994,** *35,* 6507–6510.
2. Shibata, K.; Miyazawa, K.; Goto, Y. *Chem. Commun.* **1997,** 1309–1310.
3. Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions;* **1998,** Diederich, F.; Stang, P. J., Eds.; Wiley–VCH: Weinheim, Germany, pp 421–53. (Review).
4. Denmark, S. E.; Wang, Z. *J. Organomet. Chem*. **2001,** *624*, 372–375.
5. Hiyama, T. *J. Organomet. Chem.* **2002,** *653*, 58–61.
6. Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett*. **2005,** *7*, 697–700.
7. Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2004,** *126*, 12432–12440.
8. Domin, D.; Benito-Garagorri, D.; Mereiter, K.; Froehlich, J.; Kirchner, K. *Organometallics* **2005,** *24*, 3957–3965.
9. Anzo, T.; Suzuki, A.; Sawamura, K.; Motozaki, T.; Hatta, M.; Takao, K.-i.; Tadano, K.-i. *Tetrahedron Lett.* **2007,** *48*, 8442–8448.
10. Yet L. *Hiyama Cross-Coupling Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 33–416. (Review).
11. Diebold, C.; Derible, A.; Becht, J.-M.; Drian, C. L. *Tetrahedron* **2013,** *69*, 264–267.

Hofmann elimination

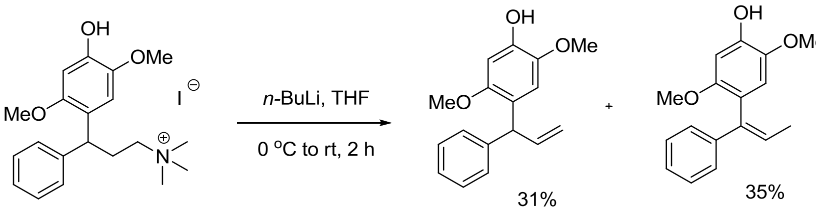
Elimination reaction of alkyl trimethyl amines proceeds with *anti*-stereochemistry, furnishing the least highly substituted olefins.



Example 1, Amine released from the resin by Hofmann elimination[10]



Example 2[11]



References

1. Hofmann, A. W. *Ber.* **1881,** *14*, 659–669.
2. Eubanks, J. R. I.; Sims, L. B.; Fry, A. *J. Am. Chem. Soc.* **1991,** *113*, 8821–8829.
3. Bach, R. D.; Braden, M. L. *J. Org. Chem.* **1991,** *56*, 7194–7195.
4. Lai, Y. H.; Eu, H. L. *J. Chem. Soc., Perkin Trans. 1* **1993,** 233–237.
5. Sepulveda-Arques, J.; Rosende, E. G.; Marmol, D. P.; Garcia, E. Z.; Yruretagoyena, B.; Ezquerra, J. *Monatsh. Chem.* **1993,** *124*, 323–325.
6. Woolhouse, A. D.; Gainsford, G. J.; Crump, D. R. *J. Heterocycl. Chem.* **1993,** *30*, 873–880.
7. Bhonsle, J. B. *Synth. Commun.* **1995,** *25*, 289–300.
8. Berkes, D.; Netchitailo, P.; Morel, J.; Decroix, B. *Synth. Commun.* **1998,** *28*, 949–956.
9. Morphy, J. R.; Rankovic, Z.; York, M. *Tetrahedron Lett.* **2002,** *43*, 6413–6415.
10. Liu, Z.; Medina-Franco, J. L.; Houghten, R. A.; Giulianotti, M. A. *Tetrahedron Lett.* **2010,** *51*, 5003–5004.
11. Arava, V. R.; Malreddy, S.; Thummala, S. R. *Synth. Commun.* **2012,** *42*, 3545–3552.

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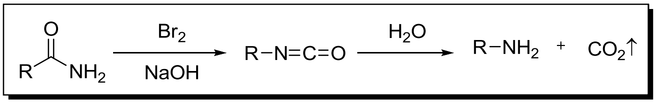
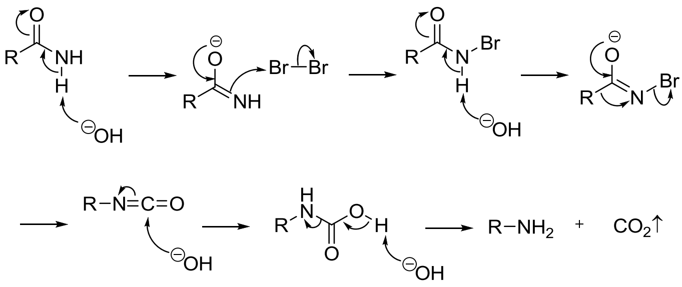
DOI 10.1007/978-3-319-03979-4_135,

Hofmann rearrangement

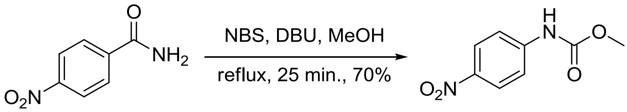
Upon treatment of primary amides with hypohalites, primary amines with one less carbon are obtained *via* the intermediacy of isocyanate. Also know as the Hofmann degradation reaction.



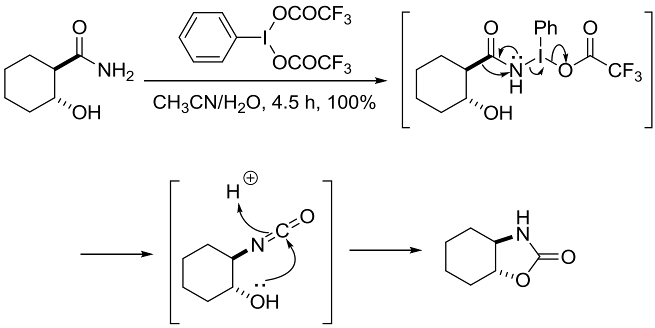


isocyanate intermediate

Example 1, An NBS variant[2]



Example 2, Iodosobenzene diacetate[5]



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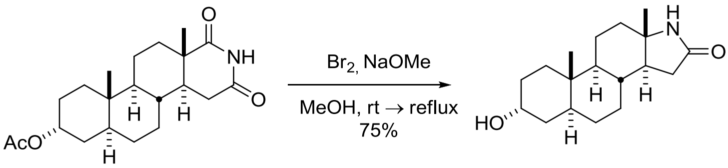
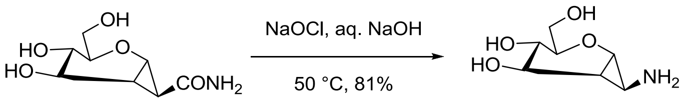
DOI 10.1007/978-3-319-03979-4_136, © Springer International Publishing Switzerland 2014

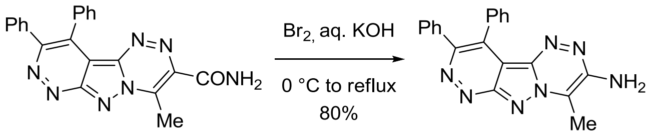
Example 3, Bromine and alkoxide[6]



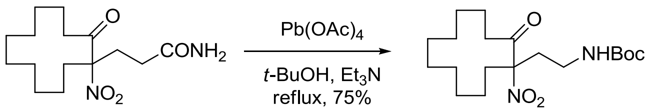
Example 4, Sodium hypochlorite[7]



Example 5, The original conditions, bromine and hydroxide[9]



Example 6, Lead tetraacetate[10]

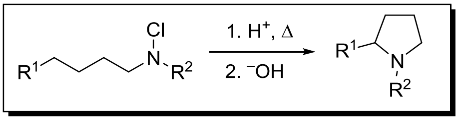


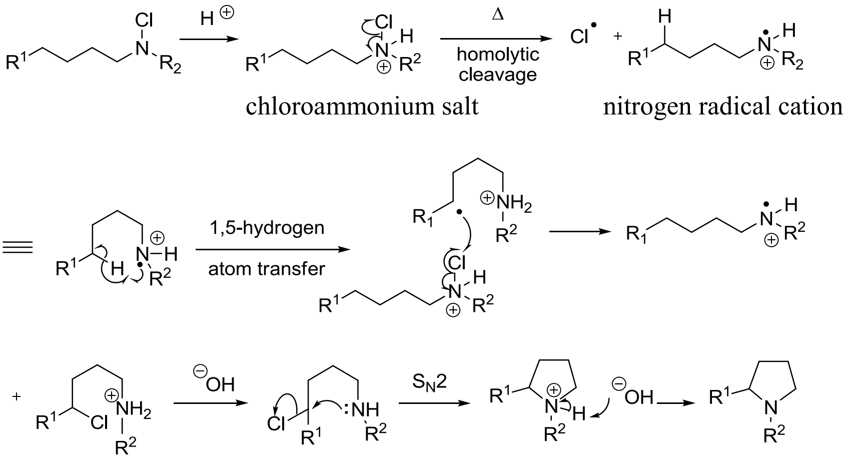
References

1. Hofmann, A. W. *Ber.* **1881,** *14*, 2725–2736.
2. Jew, S.-s.; Kang, M.-h. *Arch. Pharmacol Res*. **1994,** *17*, 490–491.
3. Huang, X.; Seid, M.; Keillor, J. W. *J. Org. Chem*. **1997,** *62*, 7495–7496.
4. Togo, H.; Nabana, T.; Yamaguchi, K. *J. Org. Chem*. **2000,** *65*, 8391–8394.
5. Yu, C.; Jiang, Y.; Liu, B.; Hu, L. *Tetrahedron Lett*. **2001,** *42*, 1449–1452.
6. Jiang, X.; Wang, J.; Hu, J.; Ge, Z.; Hu, Y.; Hu, H.; Covey, D. F. *Steroids* **2001,** *66*, 655–662.
7. Stick, R. V.; Stubbs, K. A. *J. Carbohydr. Chem*. **2005,** *24*, 529–547.
8. Moriarty, R. M. *J. Org. Chem*. **2005,** *70*, 2893–2903. (Review).
9. El-Mariah, F.; Hosney, M.; Deeb, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2006,** *181*, 2505–2517.
10. Jia, Y.-M.; Liang, X.-M.; Chang, L.; Wang, D.-Q. *Synthesis* **2007,** 744–748.
11. Gribble, G. W. *Hofmann rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 164–199. (Review).
12. Yoshimura, A.; Luedtke, M. W.; Zhdankin, V. V. *J. Org. Chem*. **2012,** *77*, 2087–2091.

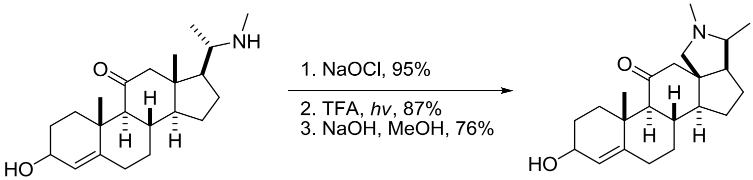
Hofmann–Löffler–Freytag reaction

Formation of pyrrolidines or piperidines by thermal or photochemical decomposition of protonated *N*-haloamines.

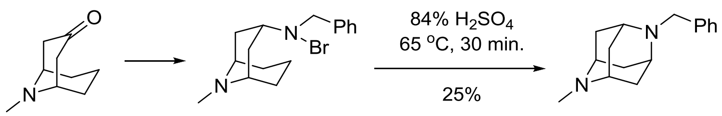




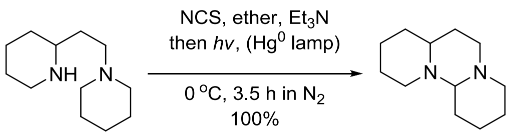
Example 1[2]



Example 2[4]



Example 3[5]



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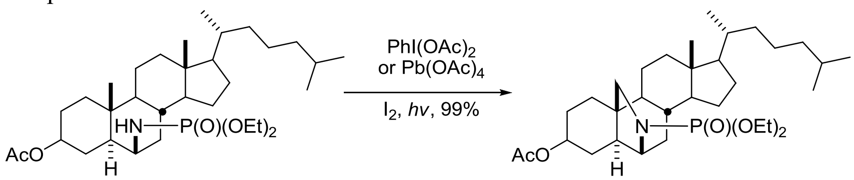
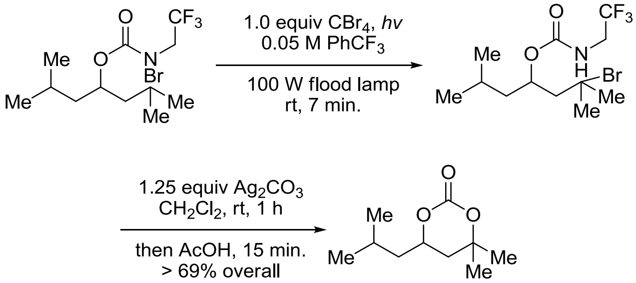
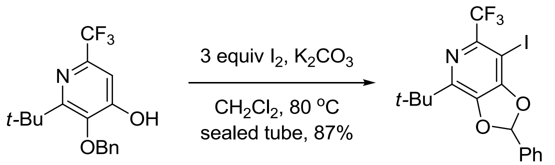
Example 4[7]



Example 5[12]



Example 6[13]

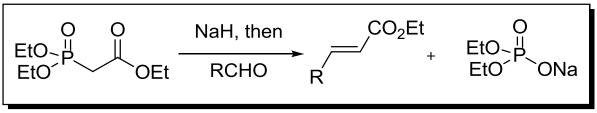


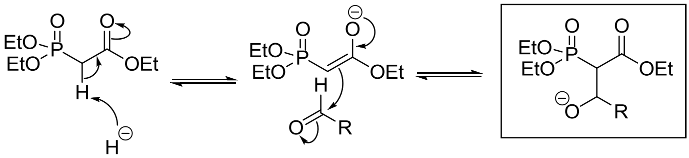
References

1. (a) Hofmann, A. W. *Ber.* **1883,** *16*, 558–560. (b) Löffler, K.; Freytag, C. *Ber.* **1909,** *42*, 3727.
2. Wolff, M. E.; Kerwin, J. F.; Owings, F. F.; Lewis, B. B.; Blank, B.; Magnani, A.; Karash, C.; Georgian, V. *J. Am. Chem. Soc.* **1960,** *82*, 4117–4118.
3. Wolff, M. E. *Chem. Rev.* **1963,** *63,* 55–64. (Review).
4. Dupeyre, R.-M.; Rassat, A. *Tetrahedron Lett.* **1973,** 2699–2701.
5. Kimura, M.; Ban, Y. *Synthesis* **1976,** 201–202.
6. Stella, L. *Angew. Chem. Int. Ed.* **1983,** *22*, 337–422. (Review).
7. Betancor, C.; Concepcion, J. I.; Hernandez, R.; Salazar, J. A.; Suarez, E. *J. Org. Chem.* **1983,** *48*, 4430–4432.
8. Majetich, G.; Wheless, K. *Tetrahedron* **1995,** *51*, 7095–7129. (Review).
9. Togo, H.; Katohgi, M. *Synlett* **2001,** 565–581. (Review).
10. Pellissier, H.; Santelli, M. *Org. Prep. Proced. Int.* **2001,** *33*, 455–476. (Review).
11. Li, J. J. *Hofmann–Löffler–Freytag Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 89–97. (Review).
12. Chen, K.; Richter, J. M.; Baran, P. S. *J. Am. Chem. Soc.* **2008,** *130*, 17247–17249.
13. Lechel, T.; Podolan, G.; Brusilowskij, B.; Schalley, C. A.; Reissig, H.-U. *Eur. J. Org. Chem.* **2012,** 5685–5692.

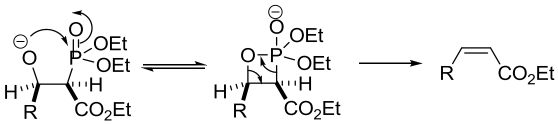
Horner–Wadsworth–Emmons reaction

Olefin formation from aldehydes and phosphonates. Workup is more advantageous than the corresponding Wittig reaction because the phosphate by-product can be washed away with water. Typically gives the *trans*- rather than the *cis*-olefins.

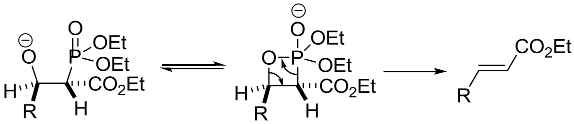




The stereochemical outcome: *erythro* (kinetic) or *threo* (thermodynamic)

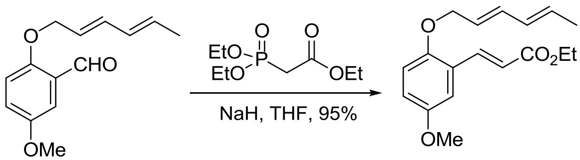


erythro, kinetic adduct

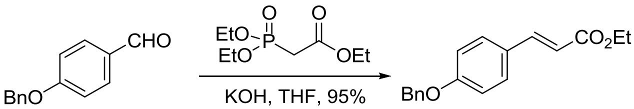


threo, thermodynamic adduct

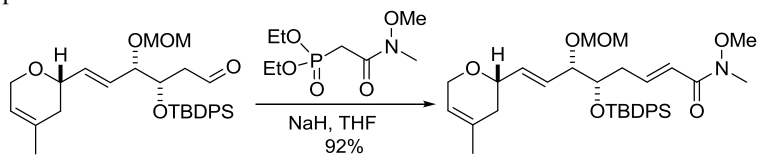
Example 1[3]



Example 2[4]



Example 3[7]



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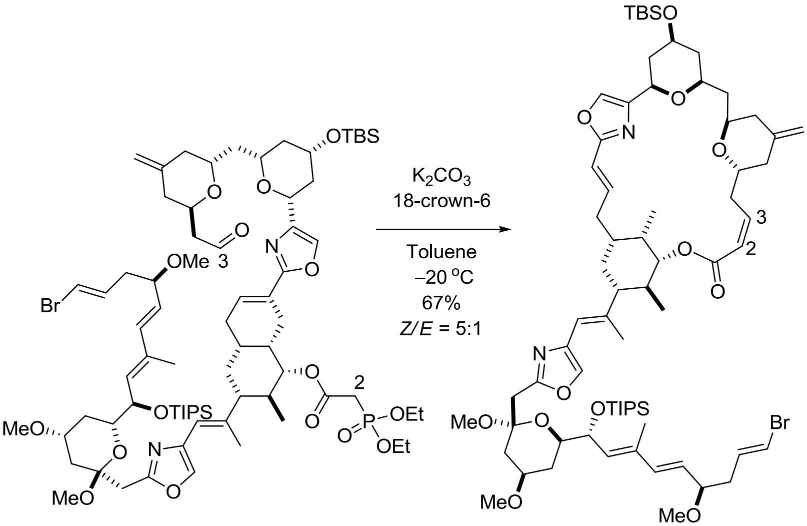
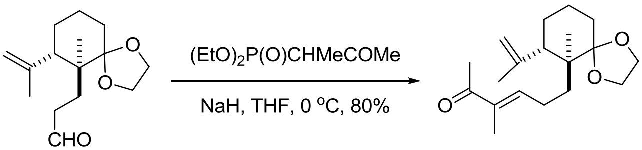
Example 4, Intramolecular Horner–Wadsworth–Emmons[9]



Example 4[11]

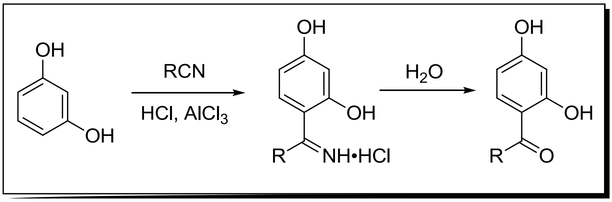


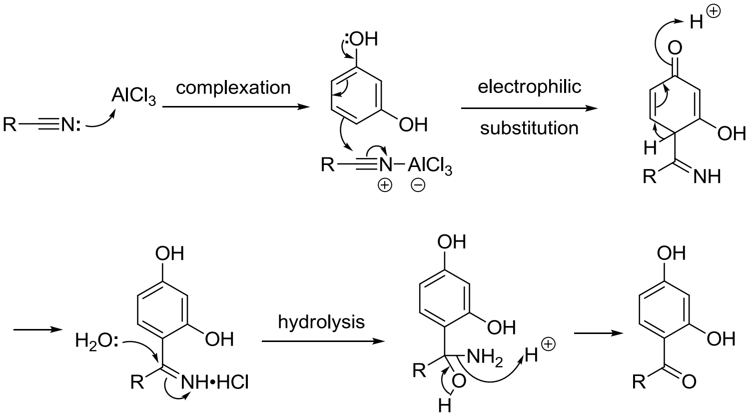
References

1. (a) Horner, L.; Hoffmann, H.; Wippel, H. G.; Klahre, G. *Chem. Ber.* **1959,** *92*, 2499–2505. (b) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961,** *83*, 1733–1738. (c) Wadsworth, D. H.; Schupp, O. E.; Seus, E. J.; Ford, J. A., Jr. *J. Org. Chem.* **1965,** *30*, 680–685.
2. Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989,** *89*, 863–927. (Review).
3. Shair, M. D.; Yoon, T. Y.; Mosny, K. K.; Chou, T. C.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1996,** *118*, 9509–9525.
4. Nicolaou, K. C.; Boddy, C. N. C.; Li, H.; Koumbis, A. E.; Hughes, R. J.; Natarajan, S.; Jain, N. F.; Ramanjulu, J. M.; Bräse, S.; Solomon, M. E. *Chem. Eur. J.* **1999,** *5*, 2602–2621.
5. Comins, D. L.; Ollinger, C. G. *Tetrahedron Lett.* **2001,** *42*, 4115–4118.
6. Lattanzi, A.; Orelli, L. R.; Barone, P.; Massa, A.; Iannece, P.; Scettri, A. *Tetrahedron Lett.* **2003,** *44*, 1333–1337.
7. Ahmed, A.; Hoegenauer. E. K.; Enev, V. S.; Hanbauer, M.; Kaehlig, H.; Öhler, E.; Mulzer, J. *J. Org. Chem.* **2003,** *68*, 3026–3042.
8. Blasdel, L. K.; Myers, A. G. *Org. Lett.* **2005,** *7*, 4281–4283.
9. Li, D.-R.; Zhang, D.-H.; Sun, C.-Y.; Zhang, J.-W.; Yang, L.; Chen, J.; Liu, B.; Su, C.; Zhou, W.-S.; Lin, G.-Q. *Chem. Eur. J.* **2006,** *12*, 1185–1204.
10. Rong, F. *Horner–Wadsworth–Emmons reaction* In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 420–466. (Review).
11. Okamoto, R.; Takeda, K.; Tokuyama, H.; Ihara, M.; Toyota, M. *J. Org. Chem.* **2013,** *78*, 93–103.

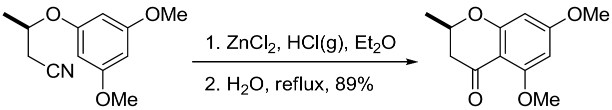
Houben–Hoesch reaction

Acid-catalyzed acylation of phenols as well as phenolic ethers using nitriles.

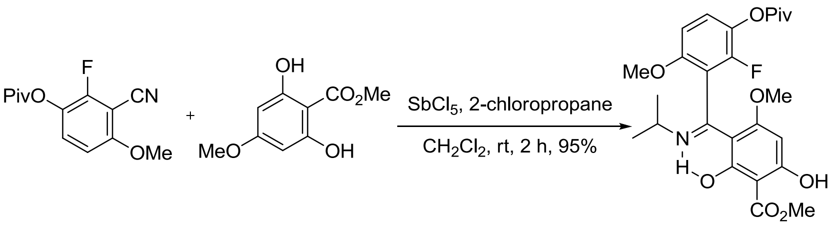




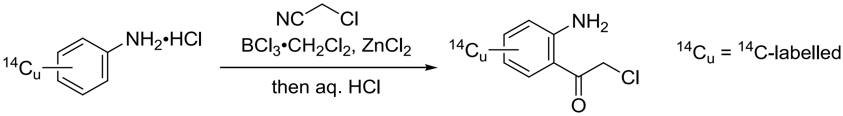
Example 1, Intramolecular Houben–Hoesch reaction[3]



Example 2[6]



Example 3[8]



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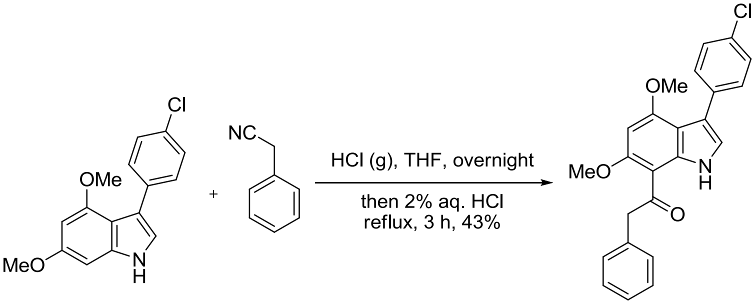
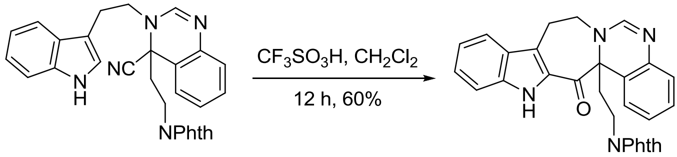
Example 4[9]



Example 5[10]

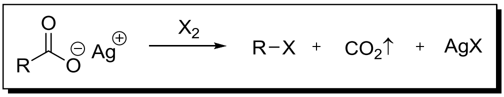


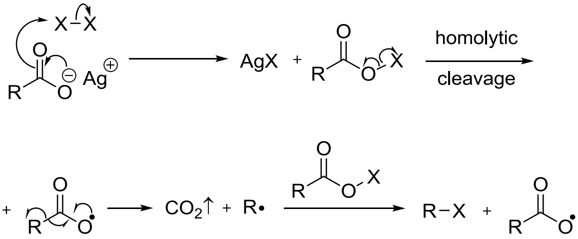
References

1. (a) Hoesch, K. *Ber.* **1915,** *48,* 1122–1133. Kurt Hoesch (1882–1932) was born in Krezau, Germany. He studied at Berlin under Emil Fischer. During WWI, Hoesch was Professor of Chemistry at the University of Istanbul, Turkey. After the war he gave up his scientific activities to devote himself to the management of a family business. (b) Houben, J. *Ber.* **1926,** *59,* 2878–2891.
2. Yato, M.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1991,** *113*, 691–692.
3. Rao, A. V. R.; Gaitonde, A. S.; Prakash, K. R. C.; Rao, S. P. *Tetrahedron Lett.* **1994,** *35*, 6347–6350.
4. Sato, Y.; Yato, M.; Ohwada, T.; Saito, S.; Shudo, K. *J. Am. Chem. Soc.* **1995,** *117*, 3037–3043.
5. Kawecki, R.; Mazurek, A. P.; Kozerski, L.; Maurin, J. K. *Synthesis* **1999,** 751–753.
6. Udwary, D. W.; Casillas, L. K.; Townsend, C. A. *J. Am. Chem. Soc.* **2002,** *124*, 5294–5303.
7. Sanchez-Viesca, F.; Gomez, M. R.; Berros, M. *Org. Prep. Proc. Int.* **2004,** *36*, 135–140.
8. Wager, C. A. B.; Miller, S. A. *J. Labelled Compd. Radiopharm.* **2006,** *49,* 615–622.
9. Black, D. St. C.; Kumar, N.; Wahyuningsih, T. D. *ARKIVOC* **2008,** *(6),* 42–51.
10. Zhao, B.; Hao, X.-Y.; Zhang, J.-X.; Liu, S.; Hao, X.-J. *J. Org. Chem.* **2013,** *15*, 528–530.

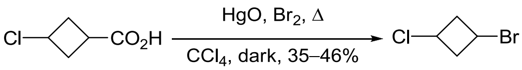
Hunsdiecker–Borodin reaction

Conversion of silver carboxylate to halide by treatment with halogen.

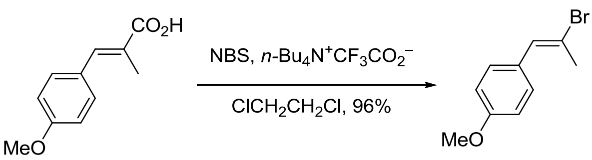




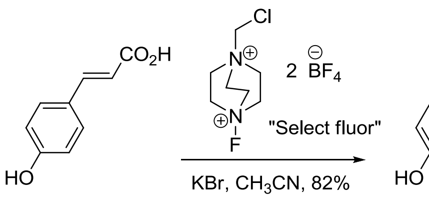
Example 1[5]



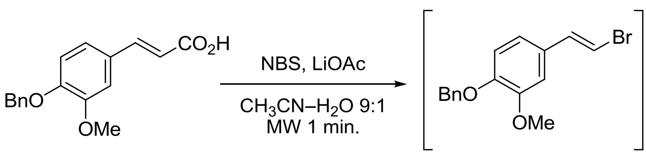
Example 2[6]



Example 3[8]



Example 4, One-pot microwave-Hunsdiecker–Borodin followed by Suzuki[10]



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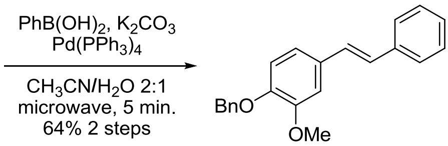
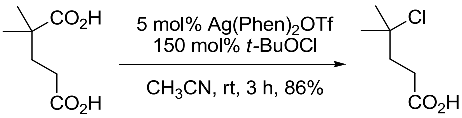


Example 5[11]

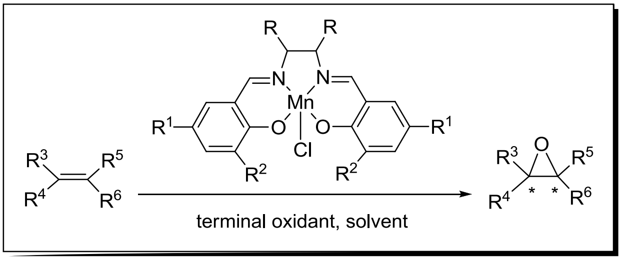


References

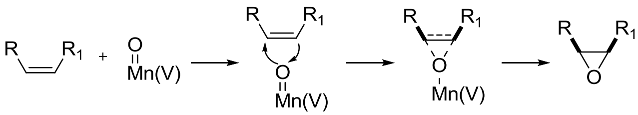
1. (a) Borodin, A. *Ann.* **1861,** *119*, 121–123. Aleksandr Porfirevič Borodin (1833–1887) was born in St Petersburg, the illegitimate son of a prince. He prepared methyl bromide from silver acetate in 1861, but another eighty years elapsed before Heinz and Cläre Hunsdiecker converted Borodin's synthesis into a general method, the Hunsdiecker or Hunsdiecker–Borodin reaction. Borodin was also an accomplished composer and is now best known for his musical masterpiece, opera Prince Igor. He kept a piano outside his laboratory. (b) Hunsdiecker, H.; Hunsdiecker, C. *Ber.* **1942,** *75,* 291–297. Cläre Hunsdiecker was born in 1903 and educated in Cologne. She developed the bromination of silver carboxylate alongside her husband, Heinz.
2. Sheldon, R. A.; Kochi, J. K. *Org. React.* **1972,** *19*, 326–421. (Review).
3. Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron Lett.* **1983,** *24,* 4979–4982.
4. Crich, D. In *Comprehensive Organic Synthesis;* Trost, B. M.; Steven, V. L., Eds.; Pergamon, **1991,** *Vol. 7*, pp 723–734. (Review).
5. Lampman, G. M.; Aumiller, J. C. *Org. Synth.* **1988,** *Coll. Vol. 6*, 179.
6. Naskar, D.; Chowdhury, S.; Roy, S. *Tetrahedron Lett.* **1998,** *39*, 699–702.
7. Das, J. P.; Roy, S. *J. Org. Chem*. **2002,** *67*, 7861–7864.
8. Ye, C.; Shreeve, J. M. *J. Org. Chem.* **2004,** *69*, 8561–8563.
9. Li, J. J. *Hunsdiecker Reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Corey, E. J., Eds., Wiley: Hoboken, NJ, **2007,** pp 623–629. (Review).
10. Bazin, M.-A.; El Kihel, L.; Lancelot, J.-C.; Rault, S. *Tetrahedron Lett.* **2007,** *48*, 4347–4351.
11. Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc*. **2012,** *134*, 4258–4263.

Jacobsen–Katsuki epoxidation

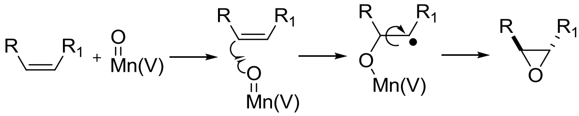
Mn(III)salen-catalyzed asymmetric epoxidation of (*Z*)-olefins.



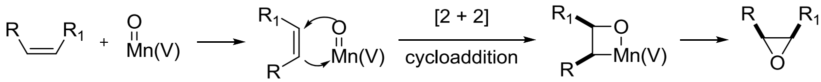
1. Concerted oxygen transfer (*cis*-epoxide):



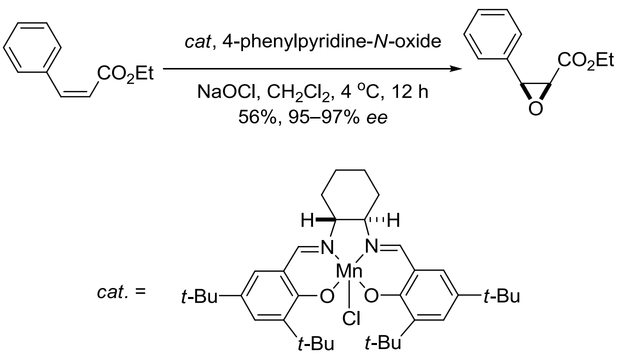
2. Oxygen transfer *via* radical intermediate (*trans*-epoxide):



3. Oxygen transfer *via* manganaoxetane intermediate (*cis*-epoxide):



Example 1[2]



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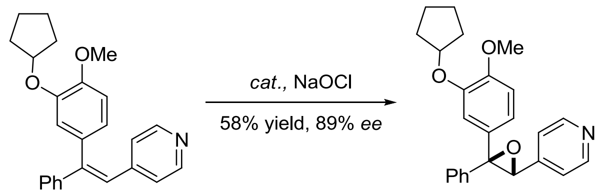
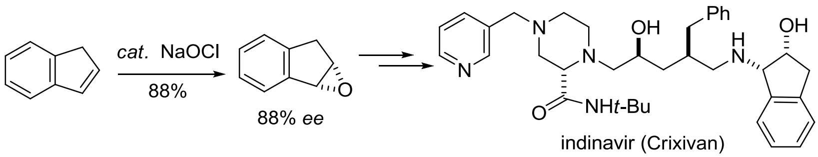
DOI 10.1007/978-3-319-03979-4_141, © Springer International Publishing Switzerland 2014

Example 2[5]



Example 3[6]

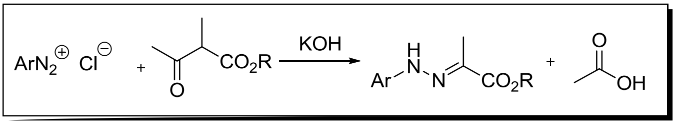


References

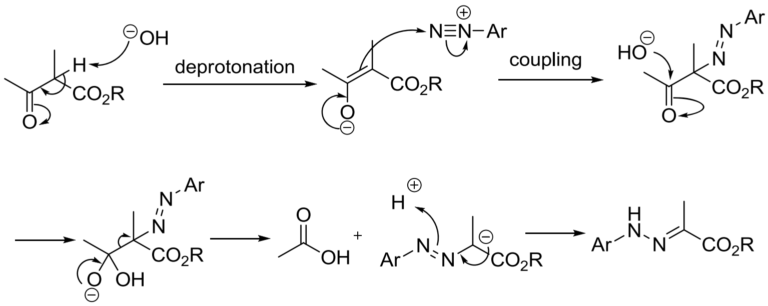
1. (a) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990,** *112,* 2801–2903. (b) Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. *Tetrahedron Lett.* **1990,** *31*, 7345–7348. (c) Irie, R.; Noda, K.; Ito, Y.; Katsuki, T. *Tetrahedron Lett.* **1991,** *32*, 1055–1058. (d) Deng, L.; Jacobsen, E. N. *J. Org. Chem*. **1992,** 57, 4320–4323. (e) Palucki, M.; McCormick, G. J.; Jacobsen, E. N. *Tetrahedron Lett.* **1995,** *36*, 5457–5460.
2. Zhang, W.; Jacobsen, E. N. *J. Org. Chem*. **1991,** *56*, 2296–2298.
3. Jacobsen, E. N. In *Catalytic Asymmetric Synthesis;* Ojima, I., Ed.; VCH: Weinheim, New York, **1993,** Ch. 4.2. (Review).
4. Jacobsen, E. N. In *Comprehensive Organometallic Chemistry II*, Eds. G. W. Wilkinson, G. W.; Stone, F. G. A.; Abel, E. W.; Hegedus, L. S., Pergamon, New York, **1995,** vol 12, Chapter 11.1. (Review).
5. Lynch, J. E.; Choi, W.-B.; Churchill, H. R. O.; Volante, R. P.; Reamer, R. A.; Ball, R. G. *J. Org. Chem.* **1997,** *62*, 9223–9228.
6. Senananyake, C. H. *Aldrichimica Acta* **1998,** *31*, 3–15. (Review).
7. Jacobsen, E. N.; Wu, M. H. In *Comprehensive Asymmetric Catalysis*, Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. Eds.; Springer: New York; 1999, Chapter 18.2. (Review).
8. Katsuki, T. In *Catalytic Asymmetric Synthesis;* 2nd edn.; Ojima, I., Ed.; Wiley-VCH: New York, **2000,** 287. (Review).
9. Katsuki, T. *Synlett* **2003,** 281–297. (Review).
10. Palucki, M. *Jacobsen–Katsuki epoxidation*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 29–43. (Review).
11. Engelhardt, U.; Linker, T. *Chem. Commun*. **2005,** 1152–1154.
12. Fernandez de la Pradilla, R.; Castellanos, A.; Osante, I.; Colomer, I.; Sanchez, M. I. *J. Org. Chem*. **2009,** *74,* 170–181.
13. Olson, J. A.; Shea, K. M. *Acc. Chem. Res*. **2011,** *44*, 311–321. (Review).

Japp–Klingemann hydrazone synthesis

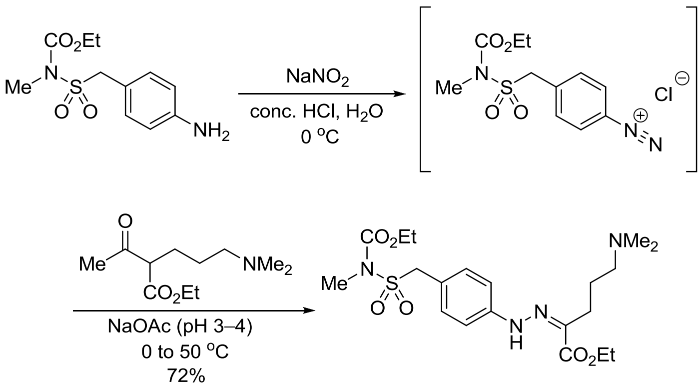
Hydrazones from β-ketoesters and diazonium salts with the acid or base.



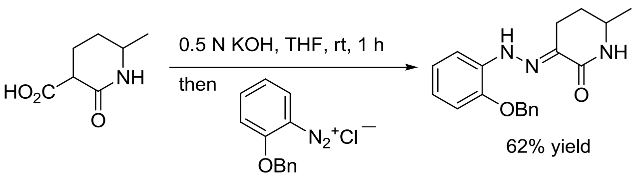
Diazonium salt β-keto-ester hydrazone



Example 1[4]



Example 2[6]



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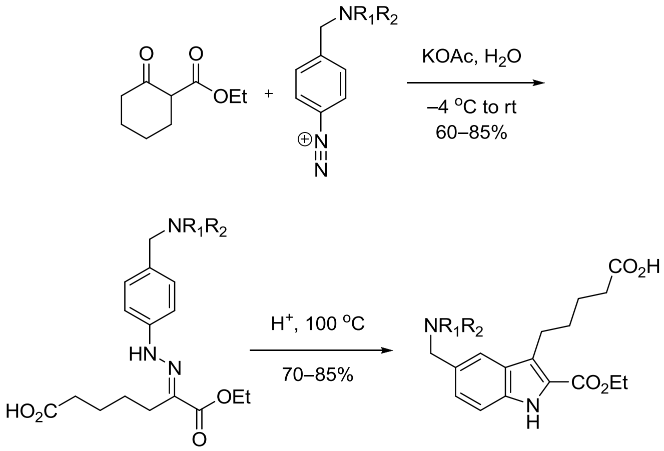
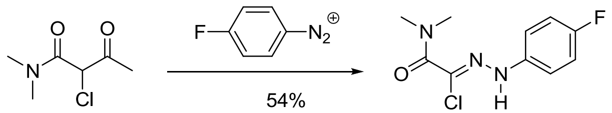
Example 3[10]



Example 4, A Japp–Klingemann cleavage[11]

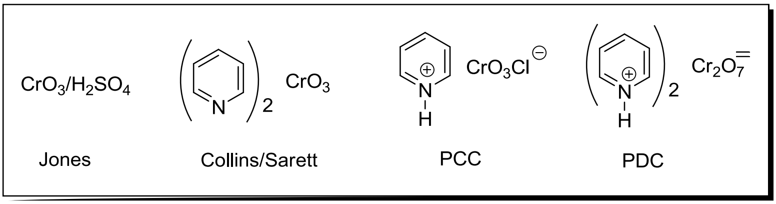


References

1. (a) Japp, F. R.; Klingemann, F. *Ber.* **1887,** *20*, 2942–2944. (b) Japp, F. R.; Klingemann, F. *Ber.* **1887,** *21*, 2934–2936. (c) Japp, F. R.; Klingemann, F. *Ber.* **1887,** *20*, 3398–3401. (d) Japp, F. R.; Klingemann, F. *Ann.* **1888,** *247*, 190–225. (e) Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1888,** *53*, 519–544.
2. Phillips, R. R. *Org. React.* **1959**; *10*, 143–178. (Review).
3. Loubinoux, B.; Sinnes, J.-L.; O'Sullivan, A. C.; Winkler, T. *J. Org. Chem.* **1995,** *60*, 953–959.
4. Pete, B.; Bitter, I.; Harsanyi, K.; Toke, L. *Heterocycles* **2000,** *53*, 665–673.
5. Atlan, V.; Kaim, L. E.; Supiot, C. *Chem. Commun.* **2000,** 1385–1386.
6. Dubash, N. P.; Mangu, N. K.; Satyam, A. *Synth. Commun.* **2004,** *34*, 1791–1799.
7. He, W.; Zhang, B.-L.; Li, Z.-J.; Zhang, S.-Y. *Synth. Commun.* **2005,** *35*, 1359–1368.
8. Li, J. *Japp–Klingemann hydrazone synthesis*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 630–634. (Review).
9. Chen, Y.; Shibata, M.; Rajeswaran, M.; Srikrishnan, T.; Dugar, S.; Pandey, R. K. *Tetrahedron Lett.* **2007,** *48*, 2353–2356.
10. Pete, B. *Tetrahedron Lett.* **2008,** *49*, 2835–2838.
11. Frohberg, P.; Schulze, I.; Donner, C.; Krauth, F. *Tetrahedron Lett.* **2013,** *53*, 4507–4509.

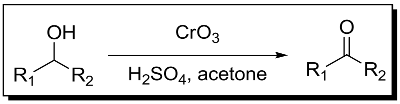
Jones oxidation

The **Collins/Sarett oxidation** (chromium trioxide-pyridine complex), and **Corey´s PCC** (pyridinium chlorochromate) and **PDC** (pyridinium dichromate) **oxidations** follow a similar pathway as the **Jones oxidation** (chromium trioxide and sulfuric acid in acetone). All these oxidants have a chromium (VI), normally orange or yellow, which is reduced to Cr(III), often green.

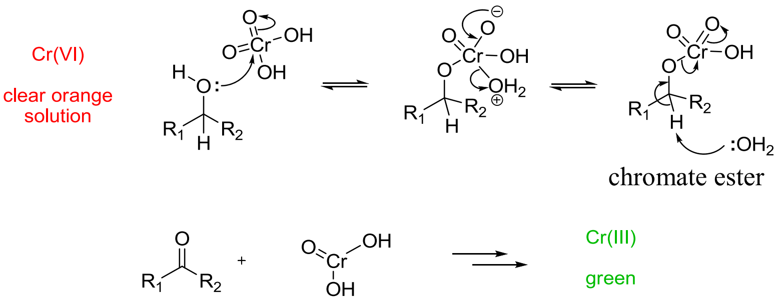


Jones oxidation

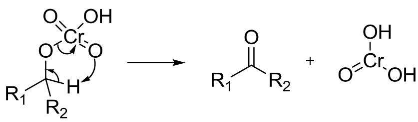
By the Jones oxidation, the primary alcohols are oxidized to the corresponding aldehyde or carboxylic acids, whereas the secondary alcohols are oxidized to the corresponding ketones.



$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$



The intramolecular mechanism is also operative:



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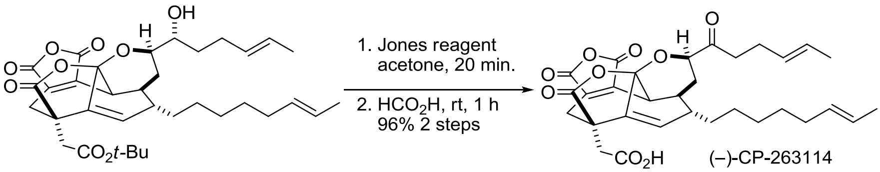
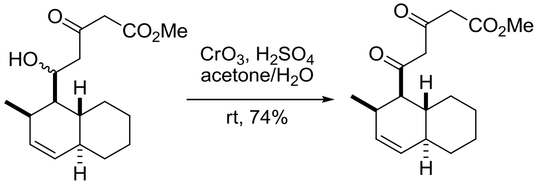
DOI 10.1007/978-3-319-03979-4_143, © Springer International Publishing Switzerland 2014

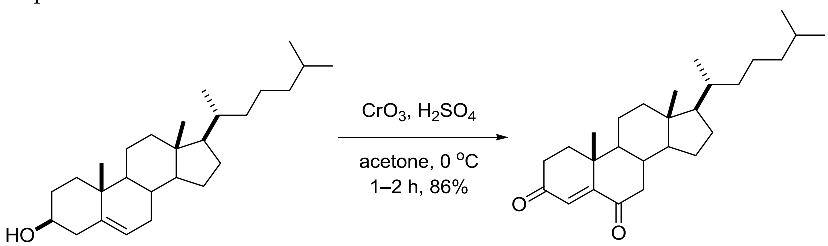
Example 1[6]



Example 2[7]



Example 3[9]



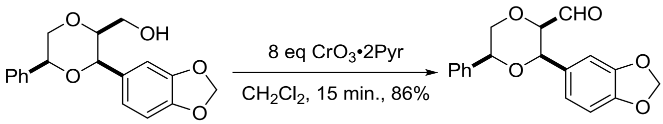
References

1. Bowden, K.; Heilbron, I. M., Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946,** 39–45. Ewart R. H. (Tim) Jones worked with Ian M. Heilbron at Imperial College. Jones later succeeded Robert Robinson to become the prestigious Chair of Organic Chemistry at Manchester. ***The recipe for the Jones reagent: 25 g CrO_3, 25 mL conc. H_2SO_4, and 70 mL H_2O.***
2. Ratcliffe, R. W. *Org. Synth.* **1973,** *53*, 1852.
3. Vanmaele, L.; De Clerq, P.; Vandewalle, M. *Tetrahedron Lett.* **1982,** *23*, 995–998.
4. Luzzio, F. A. *Org. React.* **1998,** *53*, 1–222. (Review).
5. Zhao, M.; Li, J.; Song, Z.; Desmond, R. J.; Tschaen, D. M.; Grabowski, E. J. J.; Reider, P. J. *Tetrahedron Lett.* **1998,** *39*, 5323–5326. (Catalytic CrO_3 oxidation).
6. Waizumi, N.; Itoh, T.; Fukuyama, T. *J. Am. Chem. Soc.* **2000,** *122*, 7825–7826.
7. Hagiwara, H.; Kobayashi, K.; Miya, S.; Hoshi, T.; Suzuki, T.; Ando, M. *Org. Lett.* **2001,** *3*, 251–254.
8. Fernandes, R. A.; Kumar, P. *Tetrahedron Lett.* **2003,** *44*, 1275–1278.
9. Hunter, A. C.; Priest, S.-M. *Steroids* **2006,** *71*, 30–33.
10. Kim, D.-S.; Bolla, K.; Lee, S.; Ham, J. *Tetrahedron* **2013,** *67*, 1062–1070.
10. Marshall, A. J.; Lin, J.-M.; Grey, A.; Reid, I. R; Cornish, J.; Denny, W. A *Bioorg. Med. Chem.* **2013,** *21*, 4112–4119.

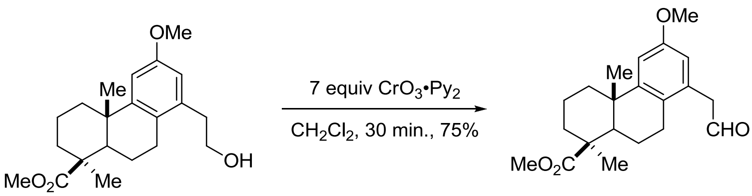
Collins oxidation

Different from the Jones oxidation, the Collins oxidation, also known as the Collins–Sarett oxidation, converts primary alcohols to the corresponding aldehydes. CrO_3•2Pyr is known as the ***Collins reagent***.

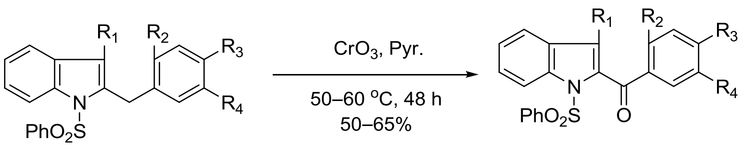
Example 1[5]



Example 2[7]



Example 3[9]



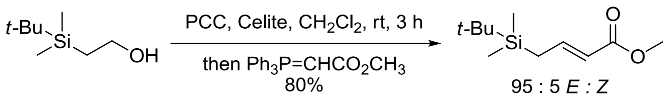
References

1. Poos, G. I.; Arth, G. E.; Beyler, R. E.; Sarett, L. H. *J. Am. Chem. Soc*. **1953,** *75*, 422–429.
2. Collins, J. C; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968,** 3363–3366. J. C. Collins was a chemist at Sterling-Winthrop in Rensselaer, New York.
3. Collins, J. C; Hess, W. W. *Org. Synth.* **1972,** *Coll. Vol. V,* 310.
4. Hill, R. K.; Fracheboud, M. G.; Sawada, S.; Carlson, R. M.; Yan, S.-J. *Tetrahedron Lett.* **1978,** 945–948.
5. Krow, G. R.; Shaw, D. A.; Szczepanski, S.; Ramjit, H. *Synth. Commun.* **1984,** *14*, 429–433.
6. Li, M.; Johnson, M. E. *Synth. Commun*. **1995,** *25*, 533–537.
7. Harris, P. W. R.; Woodgate, P. D. *Tetrahedron* **2000,** *56*, 4001–4015.
8. Nguyen-Trung, N. Q.; Botta, O.; Terenzi, S.; Strazewski, P. *J. Org. Chem.* **2003,** *68*, 2038–2041.
9. Arumugam, N.; Srinivasan, P. C. *Synth. Commun*. **2003,** *33*, 2313–2320.

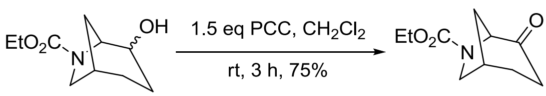
PCC oxidation

Alcohols are oxidized by pyridinium chlorochromate (PCC) to the corresponding aldehydes or ketones. They are not further oxidized to the corresponding carboxylic acids because the reaction was done in organic solvents, not in water. If water existed, the carbonyls would form *aldehyde hydrates* or *ketone hydrates*, which are then oxidized to acids.

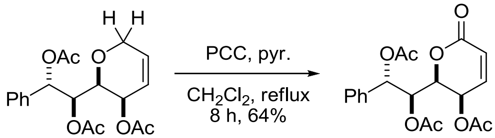
Example 1, One-pot PCC–Wittig reactions[2]



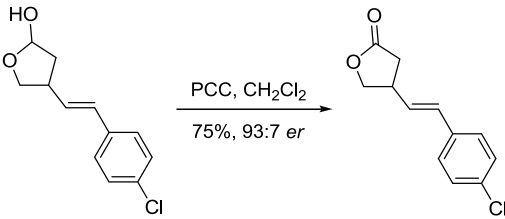
Example 2[3]



Example 3, Allylic oxidation[4]



Example 4, Hemiacetol oxidation[5]



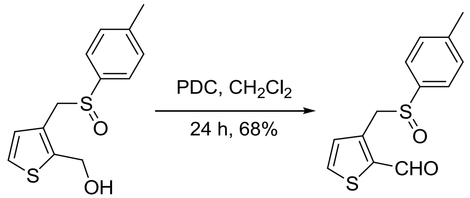
References

1. Corey, E. J.; Suggs, W. *Tetrahedron Lett.* **1975,** *16,* 2647–2650.
2. Bressette, A. R.; Glover, L. C., IV *Synlett* **2004,** 738–740.
3. Breining, S. R.; Bhatti, B. S.; Hawkins, G. D.; Miao, L. WO2005037832 (**2005**).
4. Srikanth, G. S. C.; Krishna, U. M. *Tetrahedron* **2006,** *62*, 11165–11171.
5. Kim, S.-G. *Tetrahedron Lett.* **2008,** *49*, 6148–6151.
6. Mehta, G.; Bera, M. K. *Tetrahedron* **2013,** *69*, 1815–1821.
7. Fowler, K. J.; Ellis, J. L.; Morrow, G. W. *Synth. Commun.* **2013,** *43*, 1676–1682.

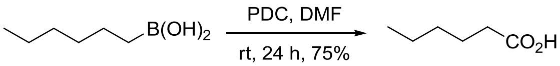
PDC oxidation

Pyridinium dichromate (PDC) may oxidize alcohols all the way to the corresponding carboxylic acids instead of aldehydes and ketones as PCC does.

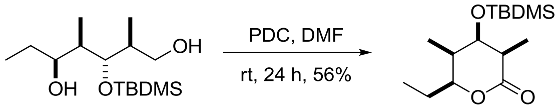
Example 1[2]



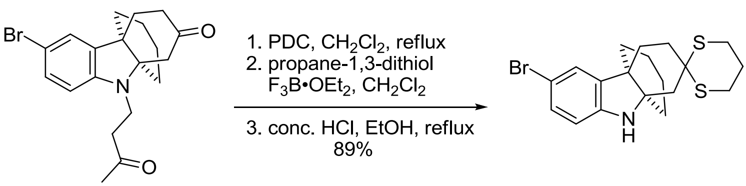
Example 2, Cleavage of primary carbon–boron bond[3]



Example 3, Hemiacetal as an intermediate[5]



Example 4[2]



References

1 Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979,** 399–402.

2 Terpstra, J. W.; Van Leusen, A. M. *J. Org. Chem.* **1986,** *51*, 230–208.

3 Brown, H. C.; Kulkarni, S. V.; Khanna, V. V.; Patil, V. D.; Racherla, U. S. *J. Org. Chem.* **1992,** *57*, 6173–6177.

4 Nakamura, M.; Inoue, J.; Yamada, T. *Bioorg. Med. Chem. Lett*. **2000,** *10*, 2807–2810.

5 Chênevert, R. Courchene, G.; Caron, D. *Tetrahedron: Asymmetry* **2003,** 2567–2571.

6 Jordão, A. K *Synlett* **2006,** 3364–3365. (Review).

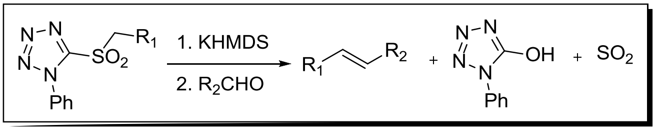
7 Xu, G.; Hou, A.-J.; Wang, R.-R.; Liang, G.-Y.; Zheng, Y.-T.; Liu, Z.-Y.; Li, X.-L.; Zhao, Y.; Huang, S.-X.; Peng, L.-Y.; et al. *Org. Lett*. **2006,** *8*, 4453–4456.

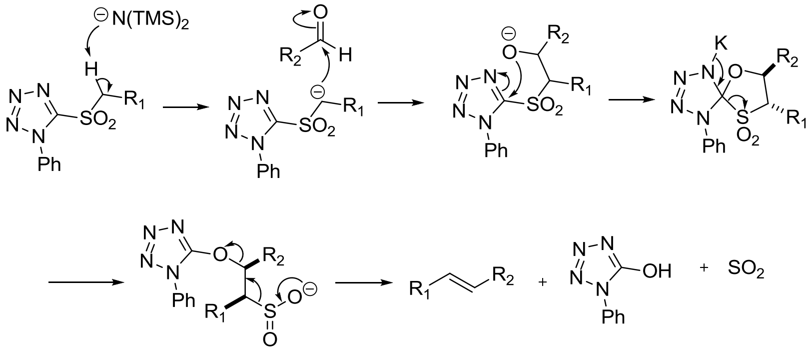
8 Morzycki, J. W; Perez-Diaz, J. O. H; Santillan, R.; Wojtkielewicz, A. *Steroids* **2010,** *75*, 70–76.

9 Cai, Q.; You, S.-L. *Org. Lett*. **2012,** *14*, 3040–3043.

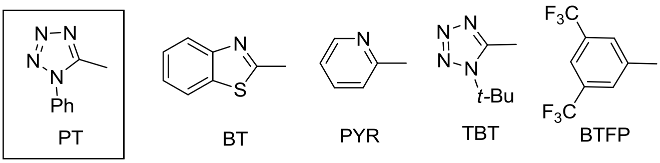
Julia–Kocienski olefination

Modified one-pot Julia olefination to give predominantly (*E*)-olefins from heteroarylsulfones and aldehydes. A sulfone reduction step is *not* required.

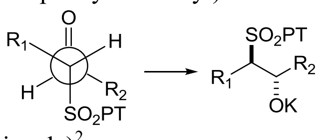




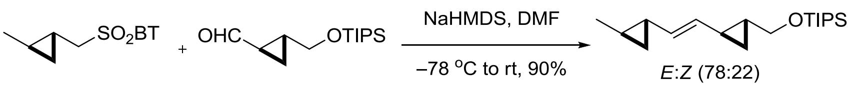
Alternatives to tetrazole:



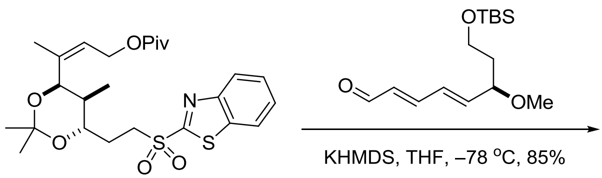
The use of larger counterion (such as K^+) and polar solvents (such as DME) favors an open transition state (PT = phenyltetrazolyl):



Example 1, (BT = benzothiazole)[2]



Example 2[3]



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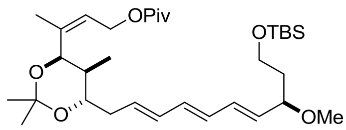
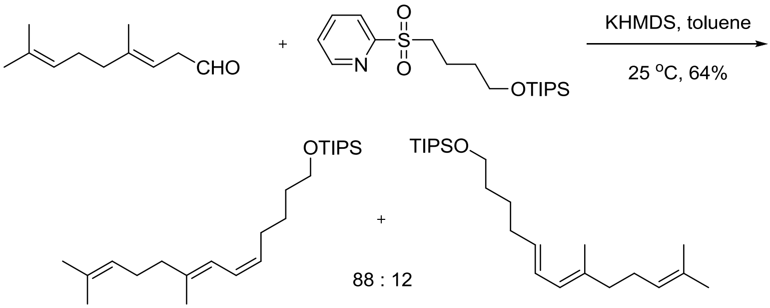
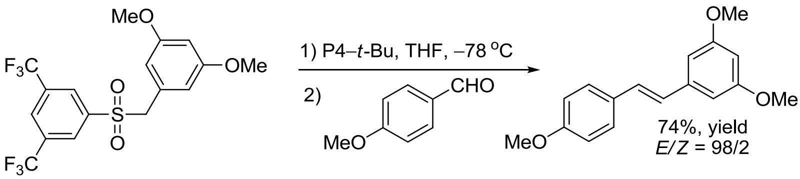
DOI 10.1007/978-3-319-03979-4_144, © Springer International Publishing Switzerland 2014



Example 3[7]



Example 4[8]

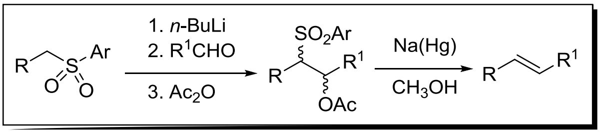


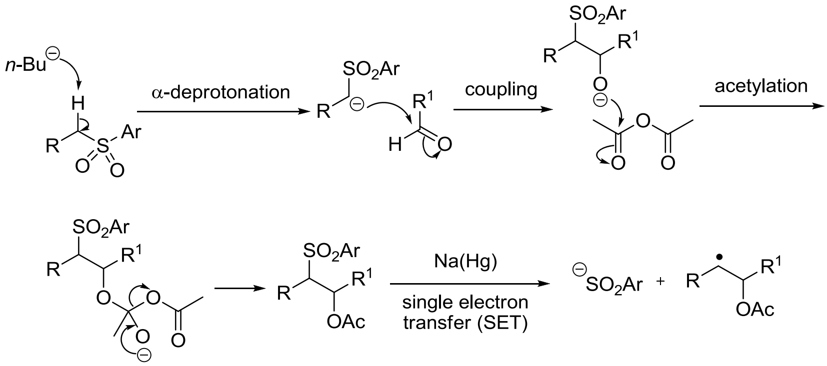
References

1. (a) Baudin, J. B.; Hareau, G.; Julia, S. A.; Ruel, O. *Tetrahedron Lett.* **1991,** *32*, 1175–1178. (b) Baudin, J. B.; Hareau, G.; Julia, S. A.; Ruel, O. *Bull. Soc. Chim. Fr.* **1993,** *130*, 336–357. (c) Baudin, J. B.; Hareau, G.; Julia, S. A.; Loene, R.; Ruel, O. *Bull. Soc. Chim. Fr.* **1993,** *130*, 856–878. (d) Blakemore, P. R.; Cole, W. J.; Kocienski, P. J.; Morely, A. *Synlett* **1998,** 26–28.
2. Charette, A. B.; Lebel, H. *J. Am. Chem. Soc.* **1996,** *118*, 10327–10328.
3. Blakemore, P. R.; Kocienski, P. J.; Morley, A.; Muir, K. *J. Chem. Soc., Perkin Trans. 1* **1999,** 955–968.
4. Williams, D. R.; Brooks, D. A.; Berliner, M. A. *J. Am. Chem. Soc.* **1999,** *121*, 4924–4925.
5. Kocienski, P. J.; Bell, A.; Blakemore, P. R. *Synlett* **2000,** 365–366.
6. Liu, P.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001,** *123*, 10772–10773.
7. Charette, A. B.; Berthelette, C.; St-Martin, D. *Tetrahedron Lett.* **2001,** *42*, 5149–5153.
8. Alonso, D. A.; Najera, C.; Varea, M. *Tetrahedron Lett.* **2004,** *45*, 573–577.
9. Alonso, D. A.; Fuensanta, M.; Najera, C.; Varea, M. *J. Org. Chem.* **2005,** *70*, 6404.
10. Rong, F. *Julia–Lythgoe olefination*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 447–473. (Review).
11. Davies, S. G.; Fletcher, A. M.; Foster, E. M.; Lee, J. A.; Roberts, P. M.; Thomson, J. E. *J. Org. Chem.* **2013,** *78*, 2500–2510.

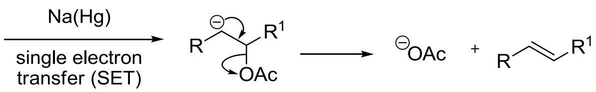
Julia–Lythgoe olefination

(*E*)-Olefins from sulfones and aldehydes.

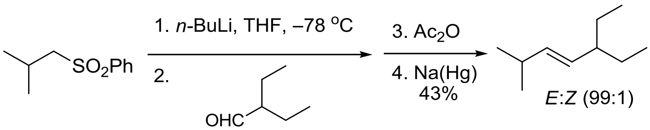




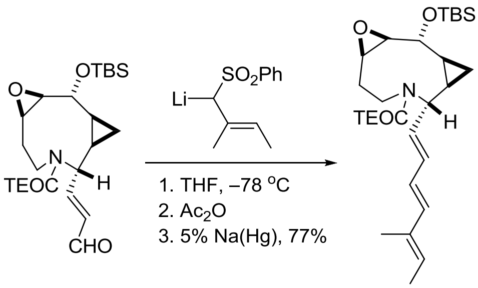
4 possible diastereomers



Example 1[2]



Example 2[3]



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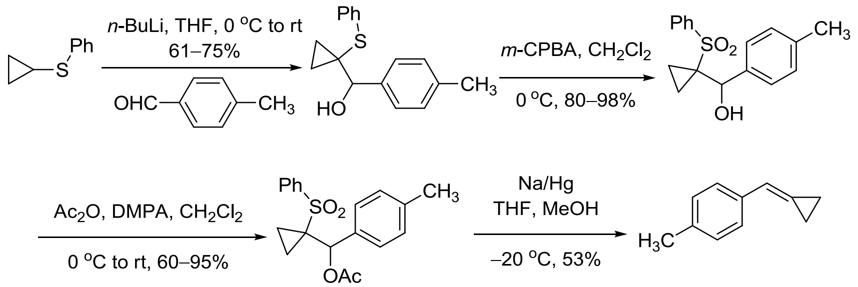
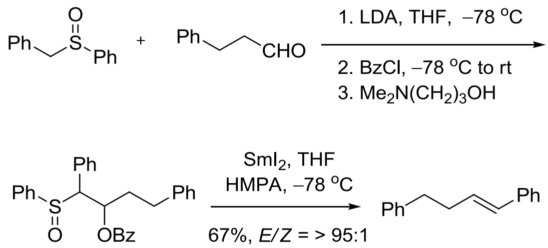
Example 3[7]



Example 4[8]

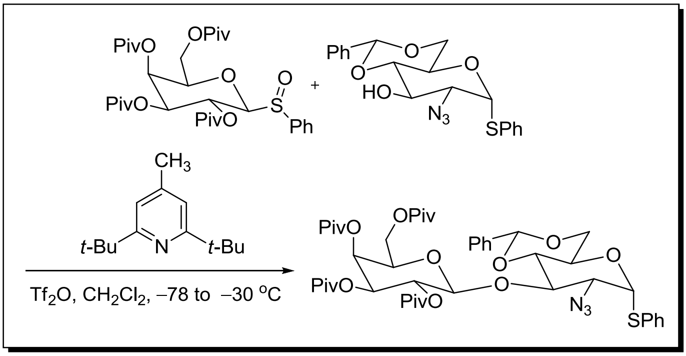


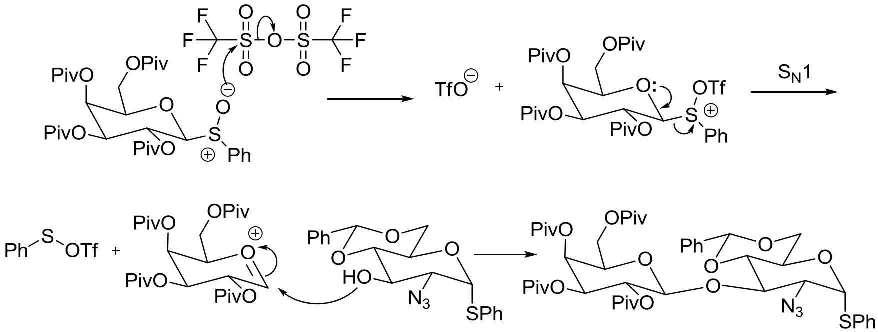
References

1. (a) Julia, M.; Paris, J. M. *Tetrahedron. Lett.* **1973,** 4833–4836. (b) Lythgoe, B. *J. Chem. Soc., Perkin Trans. 1* **1978,** 834–837.
2. Kocienski, P. J.; Lythgoe, B.; Waterhause, I. *J. Chem. Soc., Perkin Trans. 1* **1980,** 1045–1050.
3. Kim, G.; Chu-Moyer, M. Y.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1990,** *112*, 2003–2005.
4. Keck, G. E.; Savin, K. A.; Weglarz, M. A. *J. Org. Chem.* **1995,** *60*, 3194–3204.
5. Breit, B. *Angew. Chem. Int. Ed.* **1998,** 37, 453–456.
6. Marino, J. P.; McClure, M. S.; Holub, D. P.; Comasseto, J. V.; Tucci, F. C. *J. Am. Chem. Soc.* **2002,** *124*, 1664–1668.
7. Bernard, A. M.; Frongia, A.; Piras, P. P.; Secci, F. *Synlett* **2004,** *6*, 1064–1068.
8. Pospíšil, J.; Pospíšil, T, Markó, I. E. *Org. Lett.* **2005,** *7*, 2373–2376.
9. Gollner, A.; Mulzer, J. *Org. Lett.* **2008,** *10*, 4701–4704.
10. Rong, F. *Julia–Lythgoe olefination*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 447–473. (Review).
11. Dams, I.; Chodynski, M.; Krupa, M.; Pietraszek, A.; Zezula, M.; Cmoch, P.; Kosinska, M.; Kutner, A. *Tetrahedron* **2013,** *69*, 1634–1648.

Kahne glycosidation

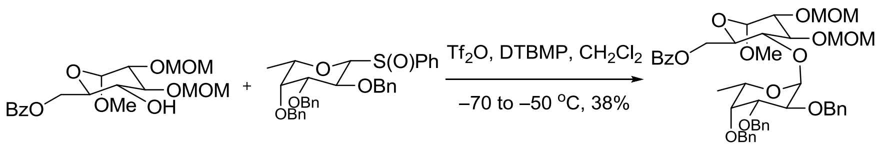
Diastereoselective glycosidation of a sulfoxide at the anomeric center as the glycosyl acceptor. The sulfoxide activation is achieved using Tf_2O.



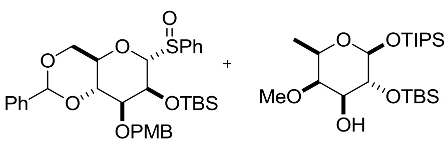


oxonium ion

Example 1[1d]



Example 2[4]



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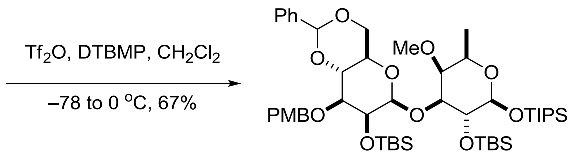
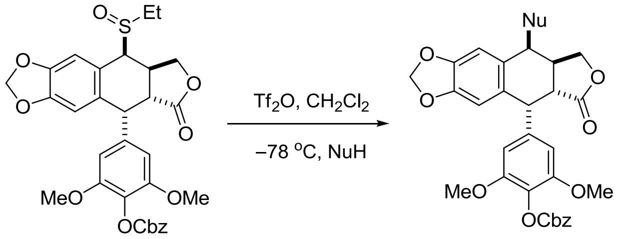
DOI 10.1007/978-3-319-03979-4_146,



Example 3, Reverse Kahne-type glycosylation[6]



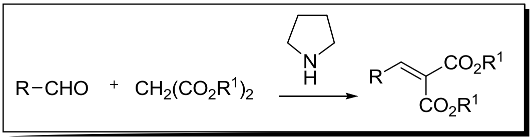
NuH = ROH, ArOH, $ArNH_2$, CH_2=$CHCH_2$TMS

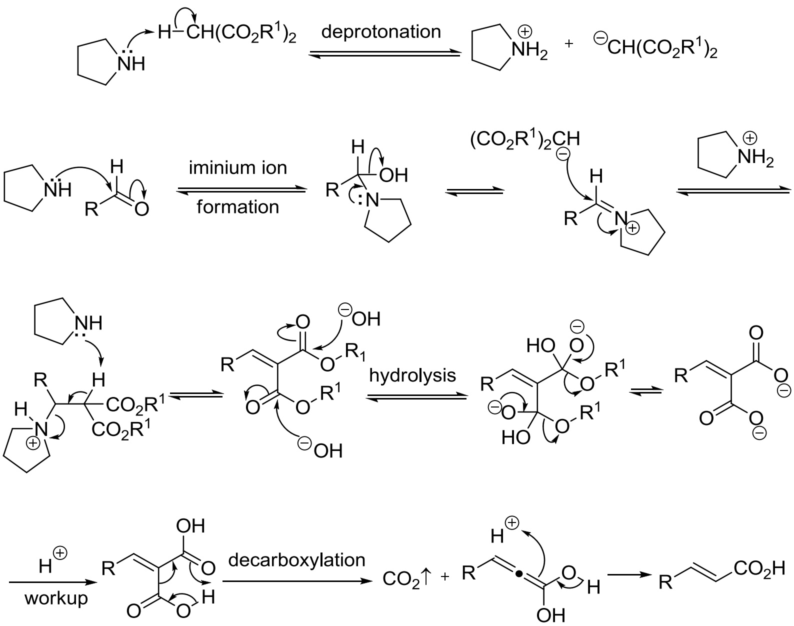
References

1. (a) Kahne, D.; Walker, S.; Cheng, Y.; Van Engen, D. *J. Am. Chem. Soc.* **1989,** *111*, 6881–6882. (b) Yan, L.; Taylor, C. M.; Goodnow, R., Jr.; Kahne, D. *J. Am. Chem. Soc.* **1994,** *116*, 6953–6954. (c) Yan, L.; Kahne, D. *J. Am. Chem. Soc.* **1996,** *118*, 9239–9248. (d) Gildersleeve, J.; Pascal, R. A.; Kahne, D. *J. Am. Chem. Soc.* **1998,** *120*, 5961–5969. Daniel Kahne now teaches at Harvard University.
2. Boeckman, R. K., Jr.; Liu, Y. *J. Org. Chem.* **1996,** *61*, 7984–7985.
3. Crich, D.; Sun, S. *J. Am. Chem. Soc.* **1998,** *120*, 435–436.
4. Crich, D.; Li, H. *J. Org. Chem.* **2000,** *65*, 801–805.
5. Nicolaou, K. C.; Rodríguez, R. M.; Mitchell, H. J.; Suzuki, H.; Fylaktakidou, K. C.; Baudoin, O.; van Delft, F. L. *Chem. Eur. J.* **2000,** *6*, 3095–3115.
6. Berkowitz, D. B.; Choi, S.; Bhuniya, D.; Shoemaker, R. K. *Org. Lett.* **2000,** *2*, 1149–1152.
7. Crich, D.; Li, H.; Yao, Q.; Wink, D. J.; Sommer, R. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2001,** *123*, 5826–5828.
8. Crich, D.; Lim, L. B. L. *Org. React.* **2004,** *64*, 115–251. (Review).
9. Yu, B.; Yang, Z.; Cao, H. *Cur. Org. Chem.* **2005,** *9*, 179–194.

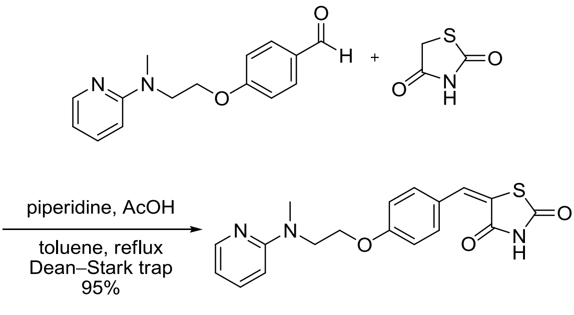
Knoevenagel condensation

Condensation between carbonyl compounds and activated methylene compounds catalyzed by amines.





Example 1[3]



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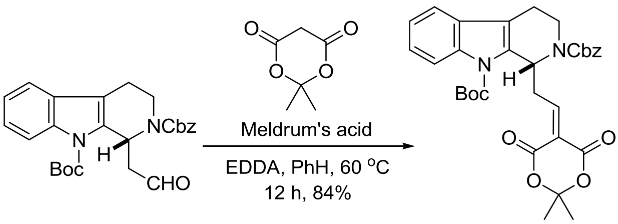
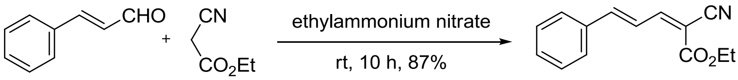
DOI 10.1007/978-3-319-03979-4_147, © Springer International Publishing Switzerland 2014

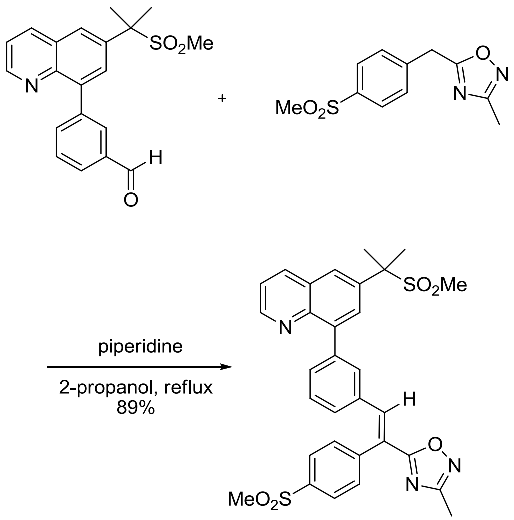
Example 2, EDDA = Ethylenediamine diacetate[5]



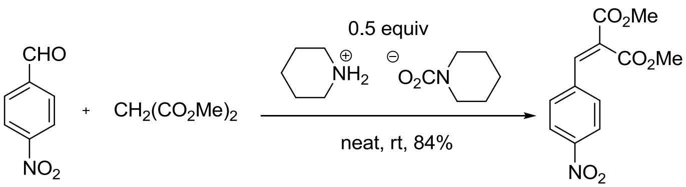
Example 3, Using ionic liquid ethylammonium nitrate (EAN) as solvent[8]



Example 4[9]



Example 5[11]

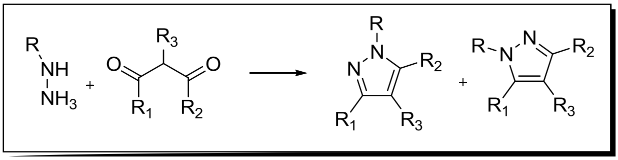


References

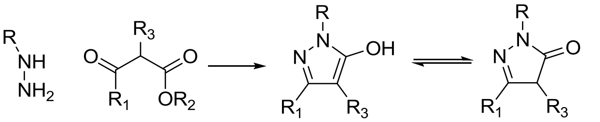
1. Knoevenagel, E. *Ber.* **1898,** *31*, 2596–2619. Emil Knoevenagel (1865–1921) was born in Hannover, Germany. He studied at Göttingen under Victor Meyer and Gattermann, receiving a Ph.D. in 1889. He became a full professor at Heidelberg in 1900. When WWI broke out in 1914, Knoevenagel was one of the first to enlist and rose to the rank of staff officer. After the war, he returned to his academic work until his sudden death during an appendectomy.
2. Jones, G. *Org. React.* **1967,** *15*, 204–599. (Review).
3. Cantello, B. C. C.; Cawthornre, M. A.; Cottam, G. P.; Duff, P. T.; Haigh, D.; Hindley, R. M.; Lister, C. A.; Smith, S. A.; Thurlby, P. L. *J. Med. Chem.* **1994,** *37*, 3977–3985.
4. Paquette, L. A.; Kern, B. E.; Mendez-Andino, J. *Tetrahedron Lett.* **1999,** *40*, 4129–4132.
5. Tietze, L. F.; Zhou, Y. *Angew. Chem. Int. Ed.* **1999,** *38*, 2045–2047.
6. Pearson, A. J.; Mesaros, E. F. *Org. Lett.* **2002,** *4*, 2001–2004.
7. Kourouli, T.; Kefalas, P.; Ragoussis, N.; Ragoussis, V. *J. Org. Chem.* **2002,** *67,* 4615–4618.
8. Hu, Y.; Chen, J.; Le, Z.-G.; Zheng, Q.-G. *Synth. Commun.* **2005,** *35*, 739–744.
9. Conlon, D. A.; Drahus-Paone, A.; Ho, G.-J.; Pipik, B.; Helmy, R.; McNamara, J. M.; Shi, Y.-J.; Williams, J. M.; MacDonald, D. *Org. Process Res. Dev.* **2006,** *10*, 36–45.
10. Rong, F. *Knoevenagel Condensation*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 474–501. (Review).
11. Mase, N.; Horibe, T. *Org. Lett.* **2013,** *15*, 1854–1857.

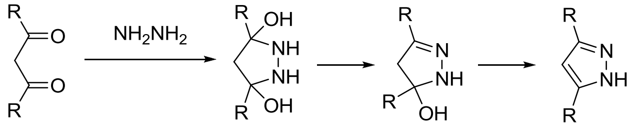
Knorr pyrazole synthesis

Also known as Knorr reaction. Reaction of hydrazine or substituted hydrazine with 1,3-dicarbonyl compounds to provide the pyrazole or pyrazolone ring system. *Cf.* Paal–Knorr pyrrole synthesis.

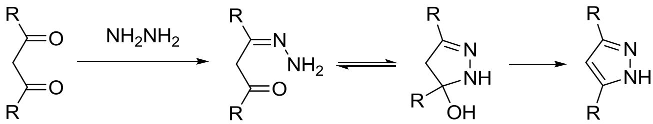


R = H, Alkyl, Aryl, Het-aryl, Acyl, *etc*.





Alternatively,



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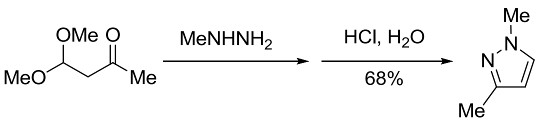
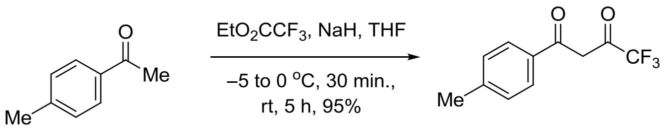


Example 2[8]



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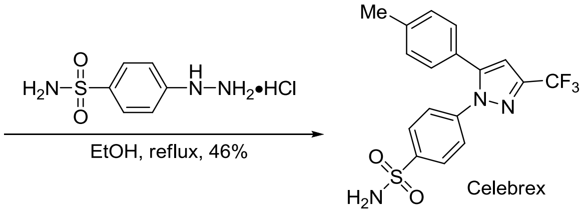
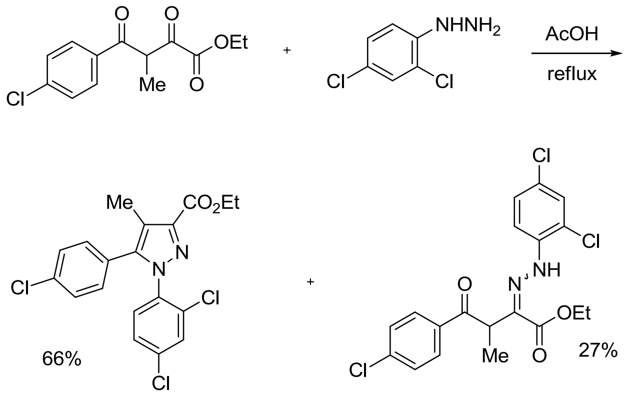
DOI 10.1007/978-3-319-03979-4_148, © Springer International Publishing Switzerland 2014



Example 3[9]



References

1 (a) Knorr, L. *Ber* **1883,** *16*, 2597. Ludwig Knorr (1859−1921) was born near Munich, Germany. After studying under Volhard, Emil Fischer, and Bunsen, he was appointed professor of chemistry at Jena. Knorr made tremendous contributions in the synthesis of heterocycles in addition to discovering the important pyrazolone drug, pyrine. (b) Knorr, L. *Ber* **1884,** *17*, 546, 2032. (c) Knorr, L. *Ber.* **1885,** *18*, 311. (d) Knorr, L. *Ann.* **1887,** *238*, 137.

2 Burness, D. M. *J. Org. Chem.* **1956,** *21*, 97−101.

3 Jacobs, T. L. in *Heterocyclic Compounds*, Elderfield, R. C., Ed.; Wiley: New York, **1957,** *5*, 45. (Review).

4 *Houben−Weyl*, **1967,** *10/2*, 539, 587, 589, 590. (Review).

5 Elguero, J., In *Comprehensive Heterocyclic Chemistry II*, Katrizky, A. R.; Rees, C. W.: Scriven, E. F. V., Eds; Elsevier: Oxford, **1996,** *3*, 1. (Review).

6 Stanovnik, E.; Svete, J. In *Science of Synthesis*, **2002,** *12*, 15; Neier, R., Ed.; Thieme. (Review).

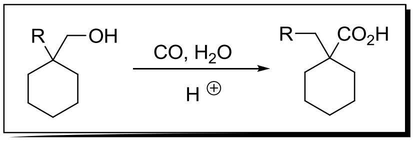
7 Sakya, S. M. *Knorr Pyrazole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Corey, E. J., Eds, Wiley: Hoboken, NJ, **2005,** pp 292−300. (Review).

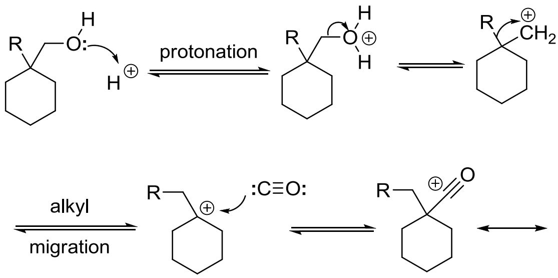
8 Ahlstroem, M. M.; Ridderstroem, M.; Zamora, I.; Luthman, K. *J. Med. Chem.* **2007,** *50*, 4444–4452.

9 Jiang, J. A.; Huang, W. B.; Zhai, J. J.; Liu, H. W.; Cai, Q.; Xu, L. X.; Wang, W.; Ji, Y. F. *Tetrahedron* **2013,** *69*, 627–635.

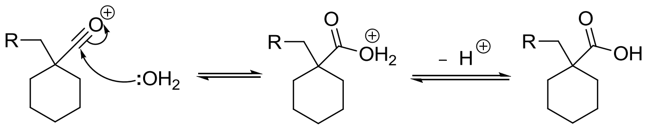
Koch–Haaf carbonylation

Strong acid-catalyzed tertiary carboxylic acid formation from alcohols or olefins and CO.





The tertiary carbocation is thermodynamically favored



acylium ion

References

1. Koch, H.; Haaf, W. *Ann.* **1958,** *618*, 251–266.
2. Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc*. **1977,** *99*, 366–370.
3. Takeuchi, K.; Akiyama, F.; Miyazaki, T.; Kitagawa, I.; Okamoto, K. *Tetrahedron* **1987,** *43*, 701–709.
4. Stepanov, A. G.; Luzgin, M. V.; Romannikov, V. N.; Zamaraev, K. I. *J. Am. Chem. Soc*. **1995,** *117*, 3615–3616.
5. Olah, G. A.; Prakash, G. K. S.; Mathew, T.; Marinez, E. R. *Angew. Chem. Int. Ed.* **2000,** *39*, 2547–2548.
6. Emert, J. I.; Dankworth, D. C.; Gutierrez, A. *Macromol.* **2001,** *34,* 2766–2775.
7. Li, T.; Tsumori, N.; Souma, Y.; Xu, Q. *Chem. Commun.* **2003,** 2070–2071.
8. Davis, M. C.; Liu, S. *Synth. Commun*. **2006,** *36*, 3509–3514.
9. Barton, V.; Ward, S. A.; Chadwick, J.; Hill, A. *J. Med. Chem.* **2010,** *53*, 4555–4559.

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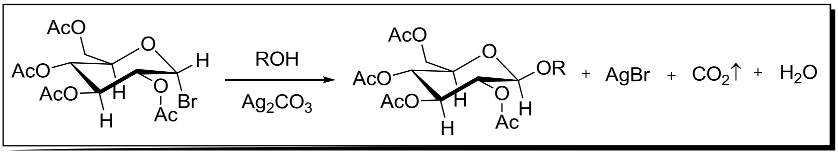
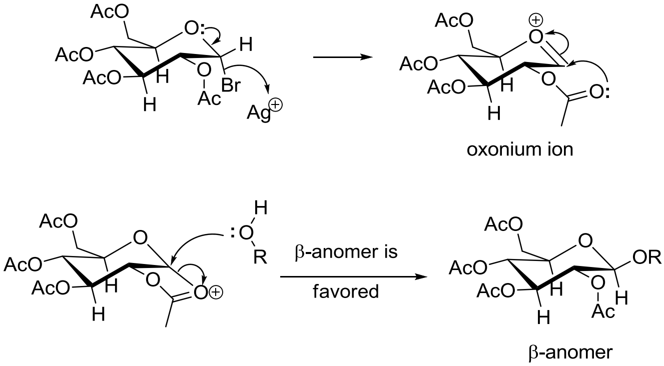
DOI 10.1007/978-3-319-03979-4_149,

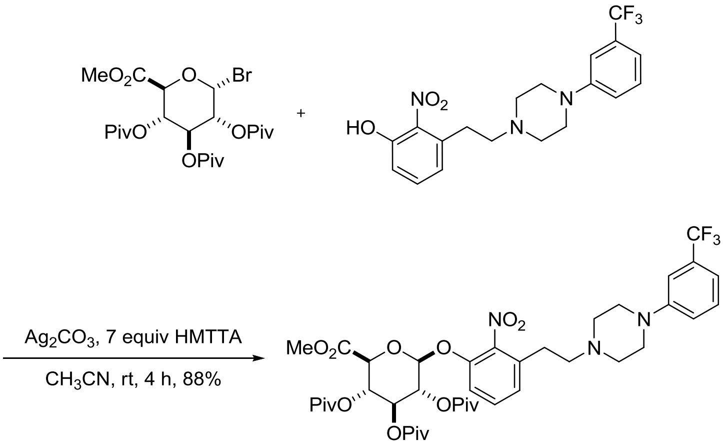
Koenig–Knorr glycosidation

Formation of the β-glycoside from α-halocarbohydrate under the influence of silver salt.





Example 1[7]



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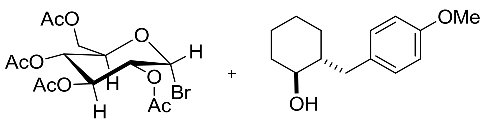

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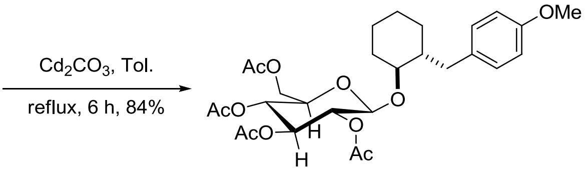
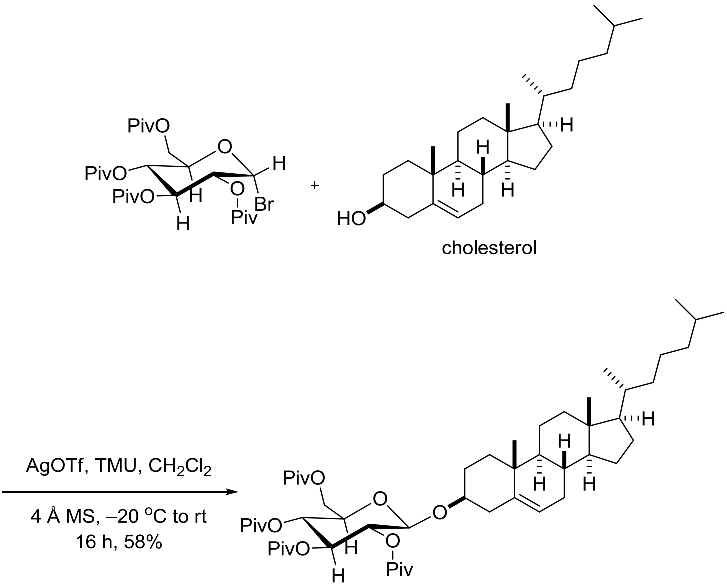
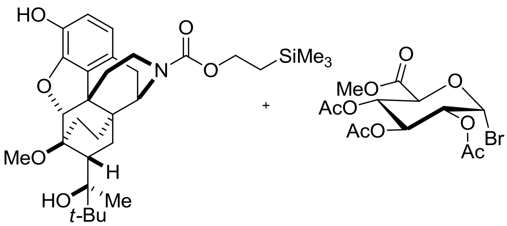
DOI 10.1007/978-3-319-03979-4_150, © Springer International Publishing Switzerland 2014

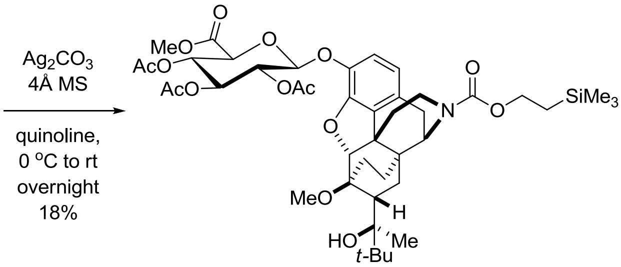


Example 3[9]



Example 4[11]



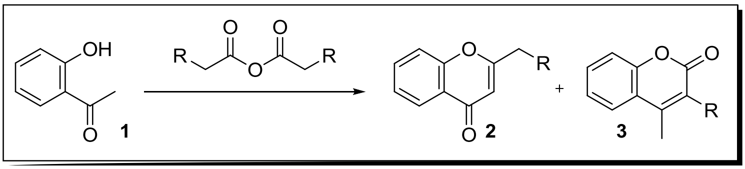


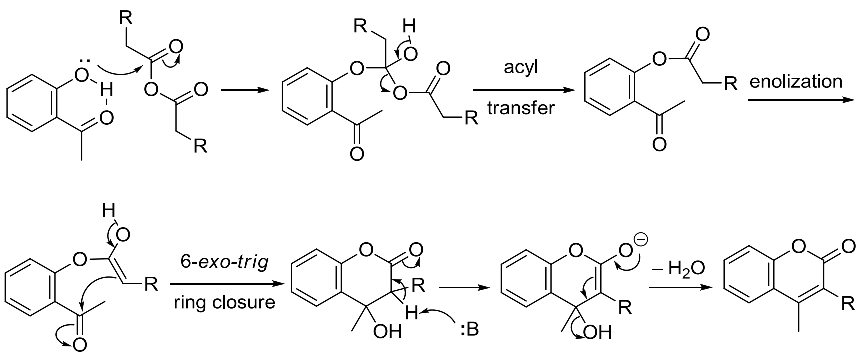
References

1. Koenig, W.; Knorr, E. *Ber.* **1901,** *34*, 957–981.
2. Igarashi, K. *Adv. Carbohydr. Chem. Biochem.* **1977,** *34,* 243–83. (Review).
3. Schmidt, R. R. *Angew. Chem.* **1986,** *98*, 213–236.
4. Smith, A. B., III; Rivero, R. A.; Hale, K. J.; Vaccaro, H. A. *J. Am. Chem. Soc*. **1991,** *113*, 2092–2112.
5. Fürstner, A.; Radkowski, K.; Grabowski, J.; Wirtz, C.; Mynott, R. *J. Org. Chem*. **2000,** *65*, 8758–8762.
6. Yashunsky, D. V.; Tsvetkov, Y. E.; Ferguson, M. A. J.; Nikolaev, A. V. *J. Chem. Soc., Perkin Trans. 1* **2002,** 242–256.
7. Stazi, F.; Palmisano, G.; Turconi, M.; Clini, S.; Santagostino, M. *J. Org. Chem.* **2004,** *69*, 1097–1103.
8. Wimmer, Z.; Pechova, L.; Saman, D. *Molecules* **2004,** *9*, 902–912.
9. Presser, A.; Kunert, O.; Pötschger, I. *Monat. Chem*. **2006,** *137*, 365–374.
10. Schoettner, E.; Simon, K.; Friedel, M.; Jones, P. G.; Lindel, T. *Tetrahedron Lett*. **2008,** *49*, 5580–5582.
11. Fan, J.; Brown, S. M.; Tu, Z.; Kharasch, E. D. *Bioconjugate Chem*. **2011,** *22*, 752–758.

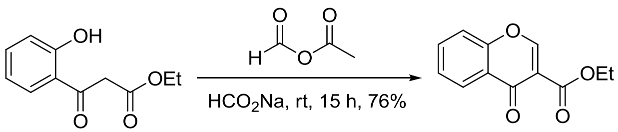
Kostanecki reaction

Also known as **Kostanecki–Robinson reaction**. Transformation **1→2** represents an **Allan–Robinson reaction**, whereas **1→3** is a **Kostanecki (acylation) reaction**:

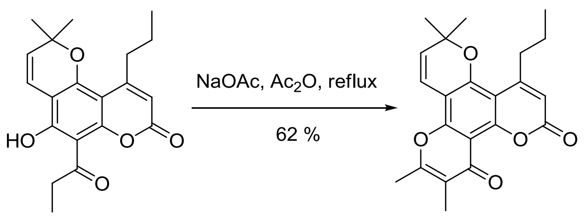




Example 1[2]



Example 2[3]



References

1. von Kostanecki, S.; Rozycki, A. *Ber.* **1901,** *34*, 102–109.
2. Pardanani, N. H.; Trivedi, K. N. *J. Indian Chem. Soc*. **1972,** *49*, 599–604.
3. Flavin, M. T.; Rizzo, J. D.; Khilevich, A.; *et al. J. Med. Chem*. **1996,** *39*, 1303–1313.
4. Mamedov, V. A.; et al. *Chemistry of Heterocyclic Compounds* **2003,** *39*, 96–100.
5. Limberakis, C. *Kostanecki–Robinson Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 521–535. (Review).
6. Hwang, I.-T.; Lee, S.-A.; Hwang, J.-S.; Lee, K.-I. *Mol.* **2011,** *16*, 6313–6321.

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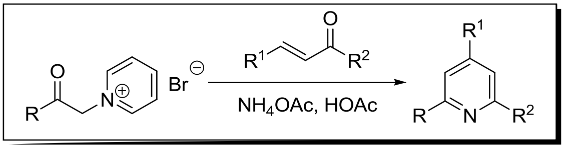
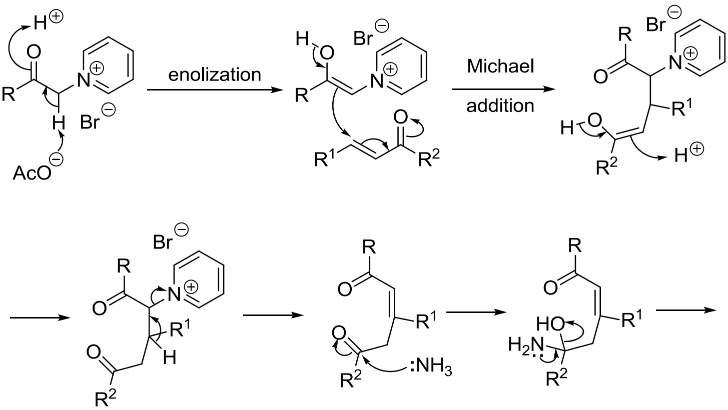
DOI 10.1007/978-3-319-03979-4_151,

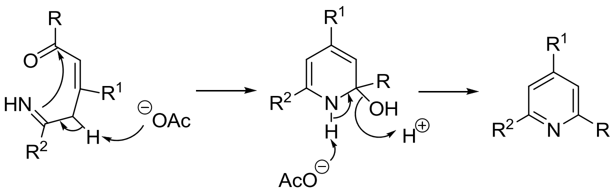
Kröhnke pyridine synthesis

Pyridines from α-pyridinium methyl ketone salts and α,β-unsaturated ketones.

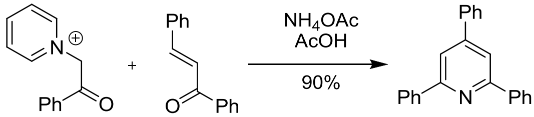




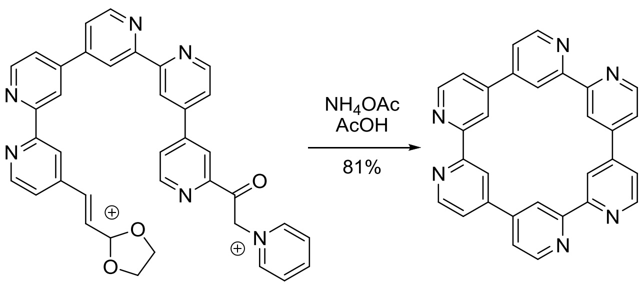
The ketone is more reactive than the enone



Example 1[1b]



Example 2[4]



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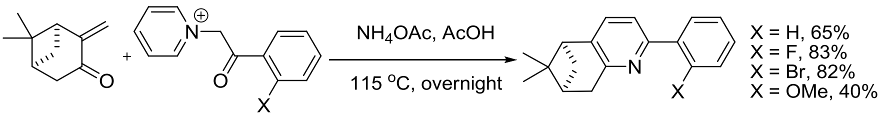
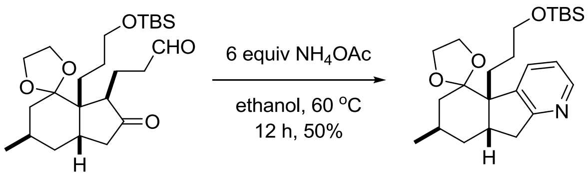
DOI 10.1007/978-3-319-03979-4_152, © Springer International Publishing Switzerland 2014

Example 3[6]



Example 3[6]

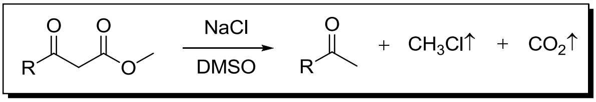


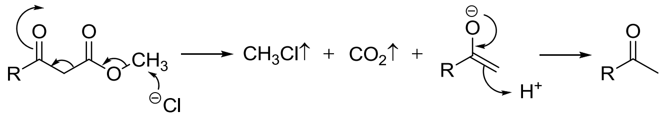
References

1. (a) Zecher, W.; Kröhnke, F. *Ber.* **1961,** *94*, 690–697. (b) Kröhnke, F.; Zecher, W. *Angew. Chem.* **1962,** *74*, 811–817. (c) Kröhnke, F. *Synthesis* **1976,** 1–24. (Review).
2. Potts, K. T.; Cipullo, M. J.; Ralli, P.; Theodoridis, G. *J. Am. Chem. Soc.* **1981,** *103*, 3584–3585, 3585–3586.
3. Newkome, G. R.; Hager, D. C.; Kiefer, G. E. *J. Org. Chem.* **1986,** *51*, 850–853.
4. Kelly, T. R.; Lee, Y.-J.; Mears, R. J. *J. Org. Chem.* **1997,** *62*, 2774–2781.
5. Bark, T.; Von Zelewsky, A. *Chimia* **2000,** *54*, 589–592.
6. Malkov, A. V.; Bella, M.; Stara, I. G.; Kocovsky, P. *Tetrahedron Lett.* **2001,** *42*, 3045–3048.
7. Cave, G. W. V.; Raston, C. L. *J. Chem. Soc., Perkin Trans. 1* **2001,** 3258–3264.
8. Malkov, A. V.; Bell, M.; Vassieu, M.; Bugatti, V.; Kocovsky, P. *J. Mol. Cat. A: Chem.* **2003,** *196*, 179–186.
9. Galatsis, P. *Kröhnke Pyridine Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 311–313. (Review).
10. Yan, C.-G.; Wang, Q.-F.; Cai, X.-M.; Sun, J. *Central Eur. J. Chem.* **2008,** *6*, 188–198.
11. Xu, T.; Luo, X.-L.; Yang, Y.-R. *Tetrahedron Lett.* **2013,** *54*, 2858–2860.

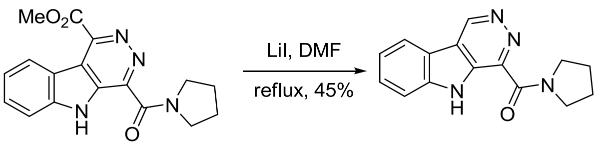
Krapcho reaction

Nucleophilic decarboxylation of β-ketoesters, malonate esters, α-cyanoesters, or α-sulfonylesters.

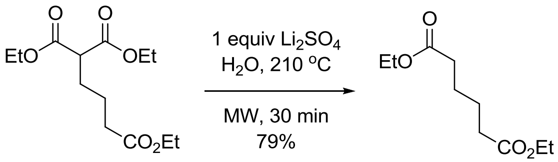




Example 1[5]



Example 2[10]



References

1. Krapcho, A. P.; Glynn, G. A.; Grenon, B. J. *Tetrahedron Lett.* **1967,** 215–217. A. Paul Krapcho is a professor at the University of Vermont.
2. Duval, O.; Gomes, L. M. *Tetrahedron* **1989,** *45*, 4471–4476.
3. Flynn, D. L.; Becker, D. P.; Nosal, R.; Zabrowski, D. L. *Tetrahedron Lett.* **1992,** *33*, 7283–7286.
4. Martin, C. J.; Rawson, D. J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1998,** *9*, 3723–3730.
5. Gonzalez-Gomez, J. C.; Uriarte, E. *Synlett* **2002,** 2095–2097.
6. Bridges, N. J.; Hines, C. C.; Smiglak, M.; Rogers, R. D. *Chem. Eur. J.* **2007,** *13*, 207–5212.
7. Poon, P. S.; Banerjee, A. K.; Laya, M. S. *J. Chem. Res.* **2011,** *35*, 67–73. (Review).
8. Farran, D.; Bertrand, P. *Synth. Commun.* **2012,** *42*, 989–1001.
9. Adepu, R.; Rambabu, D.; Prasad, B.; Meda, C. L. T.; Kandale, A.; Rama Krishna, G.; Malla Reddy, C.; Chennuru, L. N. *Org. Biomol. Chem.* **2012,** *10*, 5554–5569.
10. Mason, J. D.; Murphree, S. S. *Synlett* **2013,** *24*, 1391–1394.

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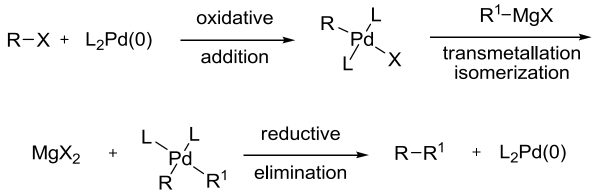
DOI 10.1007/978-3-319-03979-4_153, © Springer International Publishing Switzerland 2014

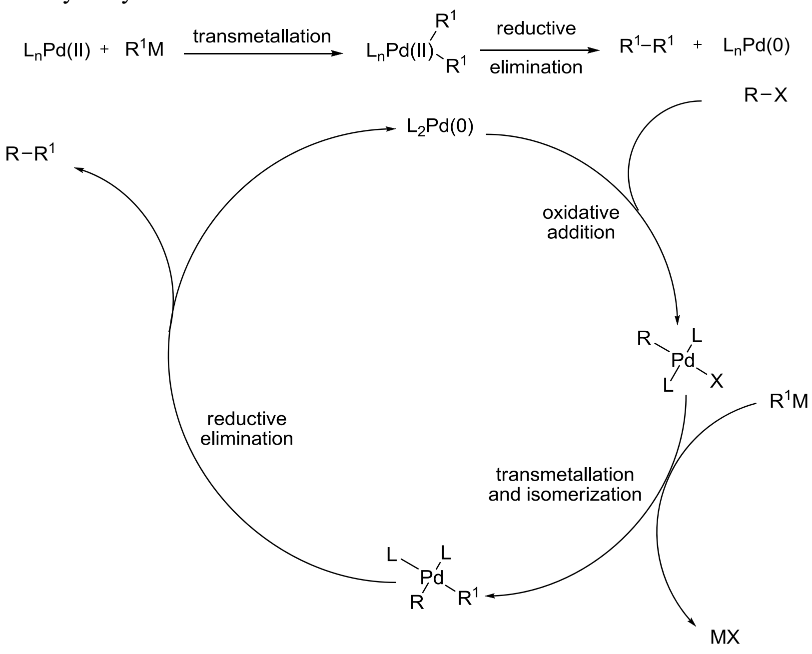
Kumada cross-coupling reaction

The Kumada cross-coupling reaction (also known as Kumada-Tamao-Corriu coupling, also occasionally known as the Kharasch cross-coupling reaction) was originally reported as the nickel-catalyzed cross-coupling of Grignard reagents with aryl- or alkenyl halides. It has subsequently been developed to encompass the coupling of organolithium or organomagnesium compounds with aryl-, alkenyl or alkyl halides, catalyzed by nickel or palladium. The Kumada cross-coupling reaction, as well as the Negishi, Stille, Hiyama, and Suzuki cross-coupling reactions, belong to the same category of Pd-catalyzed cross-coupling reactions of organic halides, triflates and other electrophiles with organometallic reagents. These reactions follow a general mechanistic catalytic cycle as shown below. There are slight variations for the Hiyama and Suzuki reactions, for which an additional activation step is required for the transmetallation to occur.

$$R{-}X + R^1{-}MgX \xrightarrow{Pd(0)} R{-}R^1 + MgX_2$$



The catalytic cycle:



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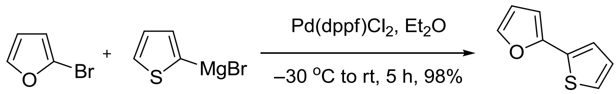
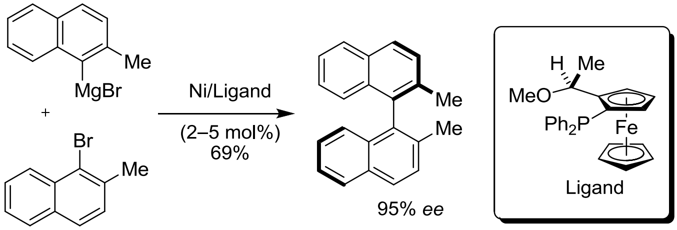
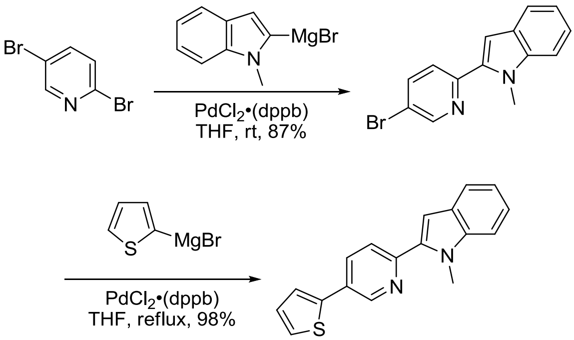
Example 1[2]



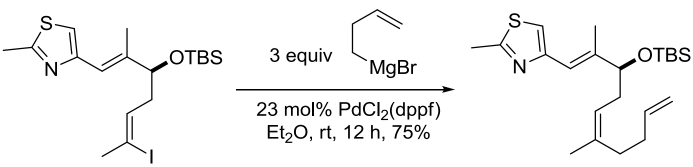
Example 2[3]



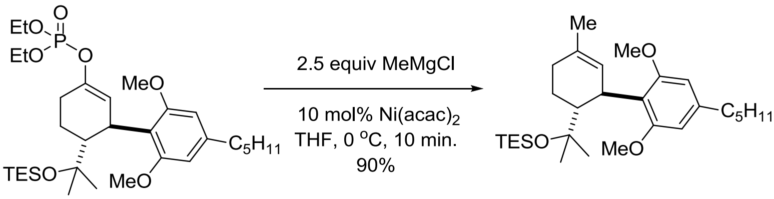
Example 3[5]



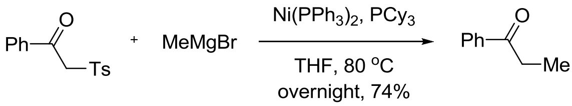
Example 4[8]



Example 5[9]



Example 6, Nickel-catalyzed Kumada reaction of tosylalkanes[11]

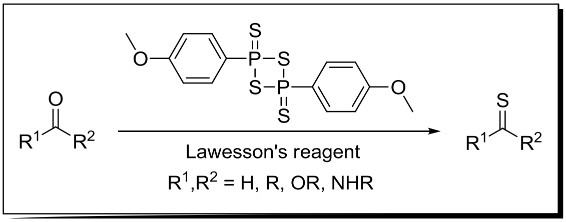


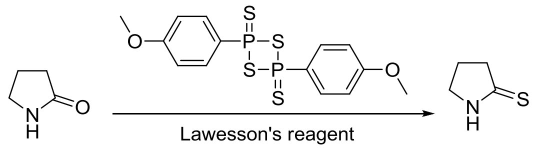
References

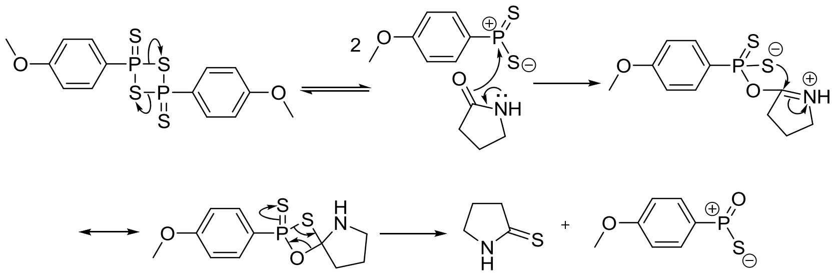
1. Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodma, S.-i.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976,** *49*, 1958–1969.
2. Carpita, A.; Rossi, R.; Veracini, C. A. *Tetrahedron* **1985,** *41*, 1919–1929.
3. Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988,** *110*, 8153–8156.
4. Kalinin, V. N. *Synthesis* **1992,** 413–432. (Review).
5. Meth-Cohn, O.; Jiang, H. *J. Chem. Soc., Perkin Trans. 1* **1998,** 3737–3746.
6. Stanforth, S. P. *Tetrahedron* **1998,** *54,* 263–303. (Review).
7. Huang, J.; Nolan, S. P. *J. Am. Chem. Soc*. **1999,** *121*, 9889–9890.
8. Rivkin, A.; Njardarson, J. T.; Biswas, K.; Chou, T.-C.; Danishefsky, S. J. *J. Org. Chem.* **2002,** *67*, 7737–7740.
9. William, A. D.; Kobayashi, Y. *J. Org. Chem.* **2002,** *67*, 8771–8782.
10. Fuchter, M. J. *Kumada Cross-Coupling Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 47–69. (Review).
11. Wu, J.-C.; Gong, L.-B.; Xia, Y.; Song, R.-J.; Xie, Y.-X.; Li, J.-H. *Angew. Chem. Int. Ed.* **2012,** *51*, 9909–9913.
12. Handa, S.; Arachchige, Y. L. N. M.; Slaughter, L. M. *J. Org. Chem.* **2013,** *78*, 5694–5699.

Lawesson's reagent

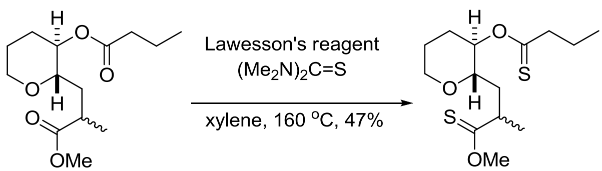
2,4-Bis(4-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide transforms the carbonyl groups of aldehydes, ketones, amides, lactams, esters and lactones into the corresponding thiocarbonyl compounds. *Cf.* Knorr thiophene synthesis.



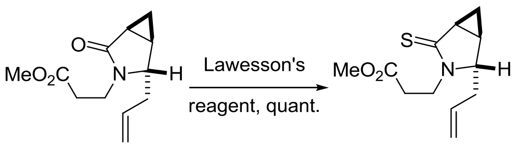




Example 1[4]



Example 2[5]



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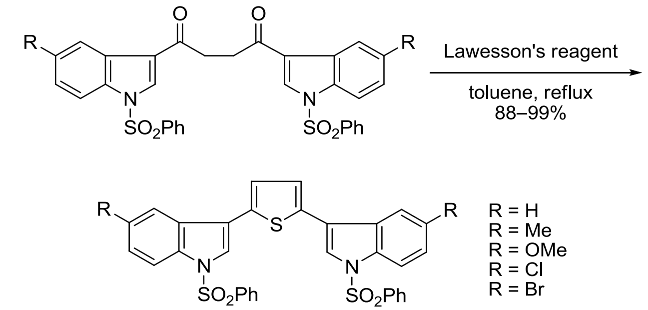
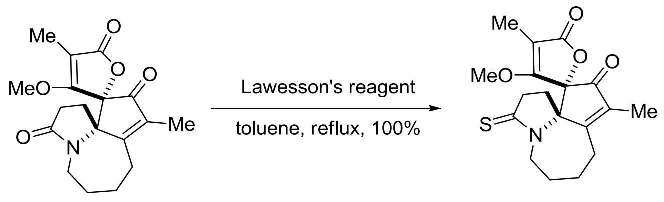
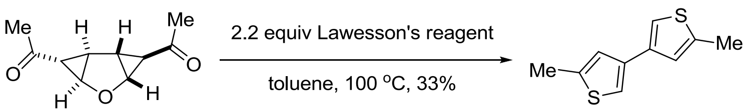
Example 3, Thiophene from dione[8]



Example 4[10]



Example 5[11]

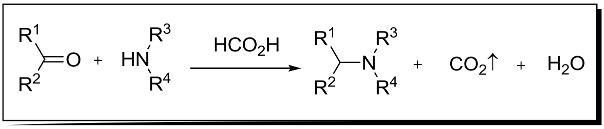


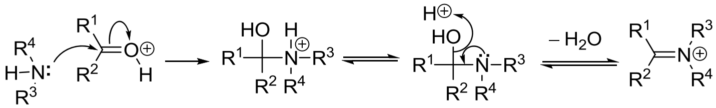
References

1. Scheibye, S.; Shabana, R.; Lawesson, S. O.; Rømming, C. *Tetrahedron* **1982,** *38*, 993–1001.
2. Navech, J.; Majoral, J. P.; Kraemer, R. *Tetrahedron Lett.* **1983,** *24*, 5885–5886.
3. Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985,** *41*, 5061–5087. (Review).
4. Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Nugiel, D. A.; Abe, Y.; Bal Reddy, K.; DeFrees, S. A.; Reddy, D. R.; Awartani, R. A.; Conley, S. R.; Rutjes, F. P. J. T.; Theodorakis, E. A. *J. Am. Chem. Soc.* **1995,** *117*, 10227–10238.
5. Kim, G.; Chu-Moyer, M. Y.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1990,** *112*, 2003–2005.
6. Luheshi, A.-B. N.; Smalley, R. K.; Kennewell, P. D.; Westwood, R. *Tetrahedron Lett.* **1990,** *31*, 123–127.
7. Ishii, A.; Yamashita, R.; Saito, M.; Nakayama, J. *J. Org. Chem.* **2003,** *68*, 1555–1558.
8. Diana, P.; Carbone, A.; Barraja, P.; Montalbano, A.; Martorana, A.; Dattolo, G.; Gia, O.; Dalla Via, L.; Cirrincione, G. *Bioorg. Med. Chem. Lett.* **2007,** *17*, 2342–2346.
9. Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2007,** *107*, 5210–5278. (Review).
10. Taniguchi, T.; Ishibashi, H. *Tetrahedron* **2008,** *64*, 8773–8779.
11. de Moreira, D. R. M. *Synlett* **2008,** 463–464. (Review).
12. Kaschel, J.; Schmidt, C. D.; Mumby, M.; Kratzert, D.; Stalke, D.; Werz, D. B. *Chem. Commun.* **2013,** *49,* 4403-4405.

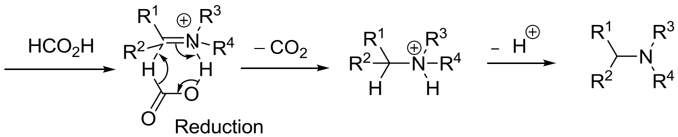
Leuckart–Wallach reaction

Amine synthesis from reductive amination of a ketone and an amine in the presence of excess formic acid, which serves as the reducing reagent by delivering a hydride. When the ketone is replaced by formaldehyde, it becomes the Eschweiler–Clarke reductive alkylation of amines.

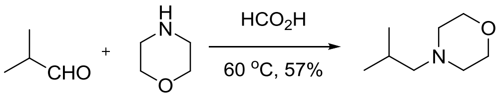




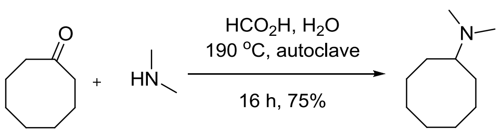
gem-aminoalcohol; iminium ion intermediate



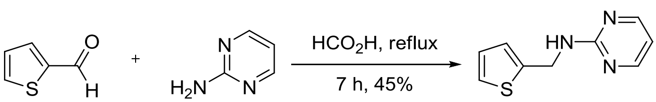
Example 1[4]



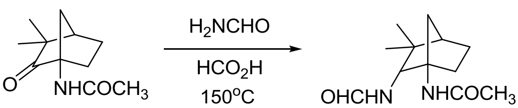
Example 2[6]



Example 3[7]



Example 4[8]



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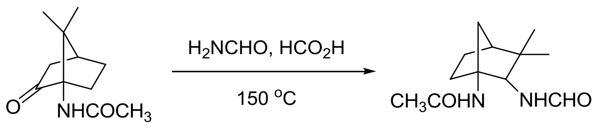
DOI 10.1007/978-3-319-03979-4_156, © Springer International Publishing Switzerland 2014

An unexpected intramolecular transamidation *via* a Wagner–Meerwein shift after the Leuckart–Wallach reaction

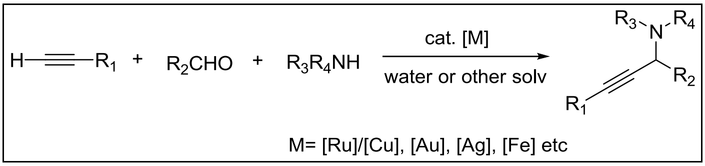


References

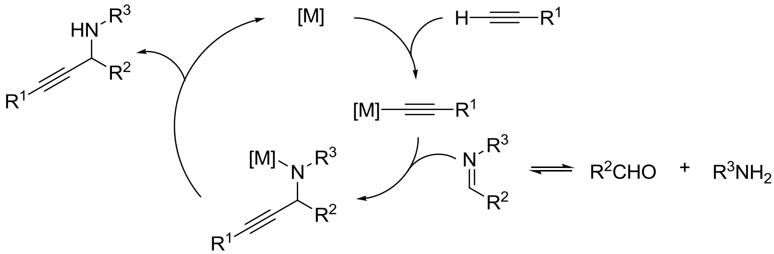
1. Leuckart, R. *Ber.* **1885,** *18*, 2341–2344. Carl L. R. A. Leuckart (1854–1889) was born in Giessen, Germany. After studying under Bunsen, Kolbe, and von Baeyer, he became an assistant professor at Göttingen. Unfortunately, chemistry lost a brilliant contributor by his sudden death at age 35 as a result of a fall in his parent's house.
2. Wallach, O. *Ann.* **1892,** *272*, 99. Otto Wallach (1847–1931), born in Königsberg, Prussia, studied under Wöhler and Hofmann. He was the director of the Chemical Institute at Göttingen from 1889 to 1915. His book "Terpene und Kampfer" served as the foundation for future work in terpene chemistry. Wallach was awarded the Nobel Prize in Chemistry in 1910 for his work on alicyclic compounds.
3. Moore, M. L. *Org. React.* **1949,** *5*, 301–330. (Review).
4. DeBenneville, P. L.; Macartney, J. H. *J. Am. Chem. Soc.* **1950,** *72,* 3073–3075.
5. Lukasiewicz, A. *Tetrahedron* **1963,** *19,* 1789–1799. (Mechanism).
6. Bach, R. D. *J. Org. Chem.* **1968,** *33,* 1647–1649.
7. Musumarra, G.; Sergi, C. *Heterocycles* **1994,** *37*, 1033–1039.
8. Martínez, A. G.; Vilar, E. T.; Fraile, A. G.; Ruiz, P. M.; San Antonio, R. M.; Alcazar, M. P. M. *Tetrahedron: Asymmetry* **1999,** *10*, 1499–1505.
9. Kitamura, M.; Lee, D.; Hayashi, S.; Tanaka, S.; Yoshimura, M. *J. Org. Chem.* **2002,** *67,* 8685–8687.
10. Brewer, A. R. E. *Leuckart–Wallach reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 451–455. (Review).
11. Muzalevskiy, V. M.; Nenajdenko, V. G.; Shastin, A. V.; Balenkova, E. S.; Haufe, G. *J. Fluorine Chem.* **2008,** *129,* 1052–1055.

Li A^3 reaction

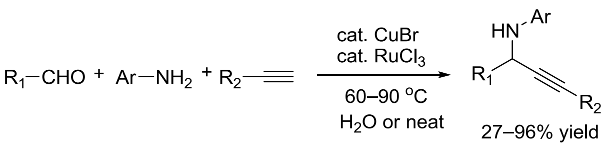
The Li A^3-reaction is the direct dehydrative condensation reaction of aldehyde-alkyne-amine catalyzed by various transition-metals to generate propargyl amines, often in water.[1–4] Many catalyztic systems such as [Ru]/[Cu],[5] [Au],[6] [Ag],[7] and iron[8,9] were effective for such reactions. The catalytic cycle of the reaction involves the in situ generation an alkynylmetal intermediate as well as an imine (or iminium) intermediate, which react together to give the propargylamine products. Carbohydrates[10–11] can be used directly to generate the propagyl amine products. Multi A^3-reactions are also successful,[12] which allows for the site-specific functionalization of amino acids and peptides under physiological conditions.[13] Highly efficient asymmetric A^3-reactions involving both primary amines[14,15] and secondary amines[16] have also been succeeded. The reaction is also amenable for flow chemistry.[17]



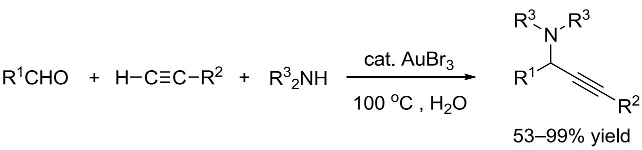
Catalytic cycle of the Li A^3 reaction



Example 1[5]



Example 2[6]



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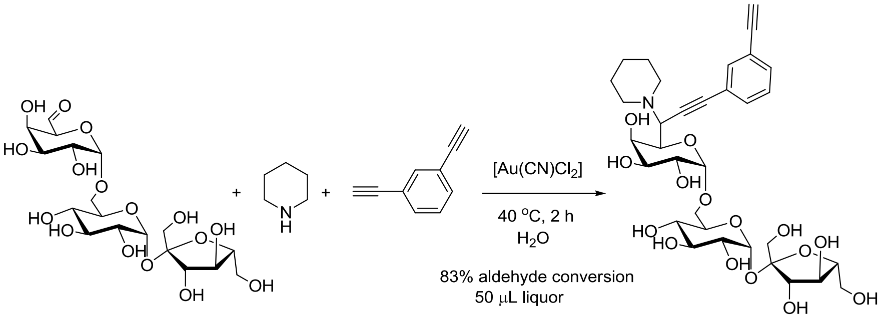
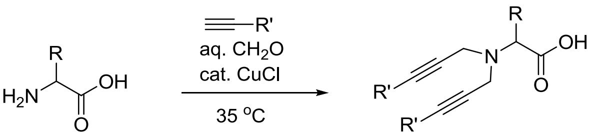
Example 3[11]

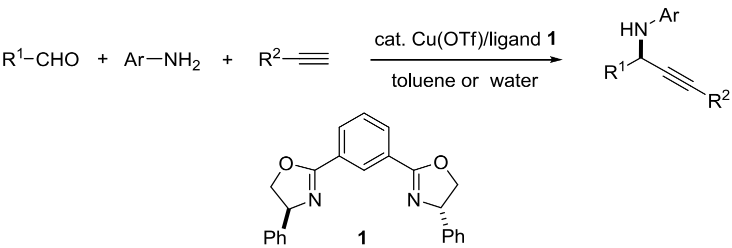


Example 4[13]



R= quanidine, disulfide, thioether, phenol, alcohol
R= aryl, alkyl, TMS

Example 5[14]



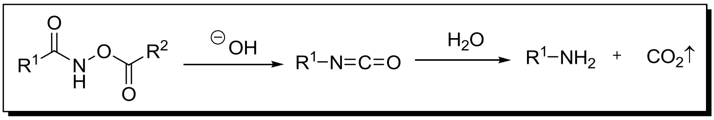
References

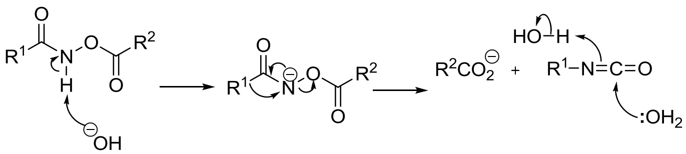
1. Yoo, W.-J.; Zhao, L.; Li, C.-J. *Aldrichimica Acta*, **2011,** *44*, 43–51. (Review).
2. Wei, C.; Li, Z.; Li, C.-J. *Synlett* **2004,** 1472.
3. Zani, L.; Bolm, C. *Chem. Commun.* **2006,** 4263.
4. Peshkov, V. A.; Pereshivko, O. P.; Van der Eycken, E. V. *Chem. Soc. Rev.* **2012,** *41*, 3702 (Review).
5. Li, C. J.; Wei, C. M. *Chem. Commun*. **2002,** 268–269.
6. Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2003,** *125*, 9584.
7. Wei, C. M.; Li, Z. G.; Li, C. J. *Org. Lett*. **2003,** *5*, 4473–4475.
8. Chen, W.-W.; Nguyen, R. V.; Li, C.-J. *Tetrahedron Lett.* **2009,** *50*, 2895.
9. Li, P.; Zhang, Y.; Wang, L. *Chem. Eur. J.* **2009,** *15*, 2045.
10. Roy, B.; Raj, R.; Mukhopadhya, B. *Tetrahedron Lett.* **2009,** *50*, 5838–5841.
11. Kung, K. K. Y.; Li, G. L.; Zou, L.; Chong, H. C.; Leung, Y. C.; Wong, K. H.; Lo, V. K. Y.; Che, C.-M.; Wong, M.-K. *Org. Biomol. Chem.,* **2012,** *10*, 925–930.
12. Bonfield, E. R.; Li, C.-J. *Org. Biomol. Chem.* **2007,** *5*, 435.

13. Uhlig, N.; Li, C.-J. *Org. Lett.* **2012,** *14*, 3000–3003.
14. Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2002,** *124*, 5638.
15. Wei, C.; Mague, J. T.; Li, C.-J. *Proc. Natl. Acad. Sci. U.S.A.* **2004,** *101*, 5749.
16. Gommermann, N.; Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2003,** *42*, 5763.
17. Shore, G.; Yoo, W.-J.; Li, C.-J.; Organ, M. G. *Chem. Eur. J.* **2010,** 16, 126–133.

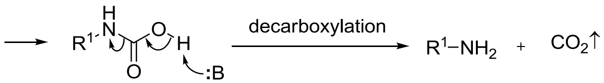
Lossen rearrangement

The Lossen rearrangement involves the generation of an isocyanate via thermal or base-mediated rearrangement of an activated hydroxamate which can be generated from the corresponding hydroxamic acid. Activation of the hydroxamic acid can be achieved through *O*-acylation, *O*-arylation, chlorination, or *O*-sulfonylation. Such hydroxamic acids can also be activated using polyphosphoric acid, carbodiimide, Mitsunobu conditions, or silyation. The product of the Lossen rearrangement, an isocyanate can be subsequently converted to a urea or an amine resulting in the net loss of one carbon atom relative to the starting hydroxamic acid.

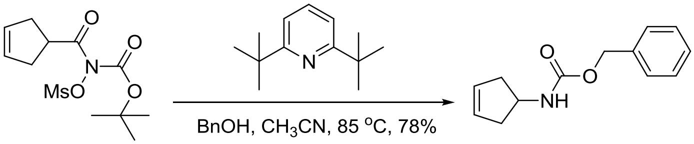




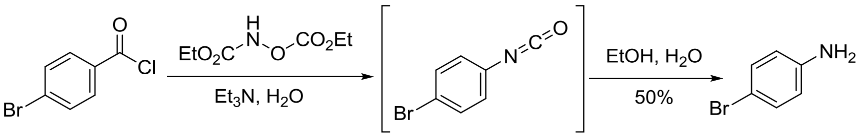
isocyanate intermediate



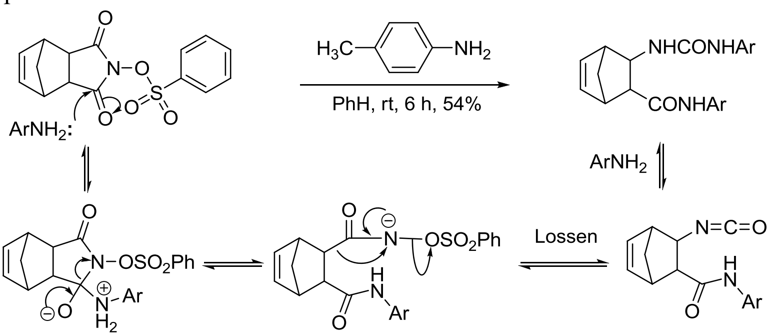
Example 1[6]



Example 2[7]



Example 3[8]



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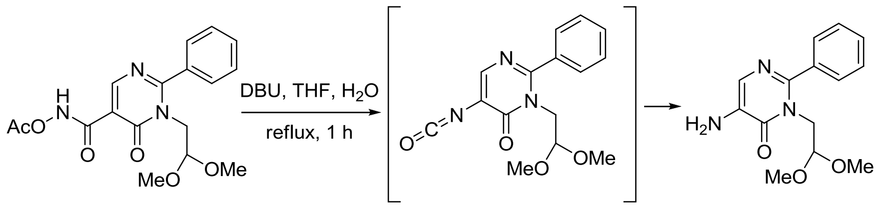
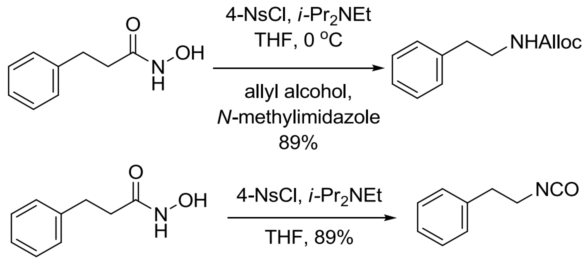
Example 4[9]



Example 5[11]

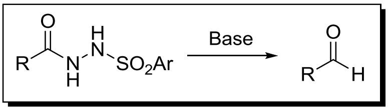


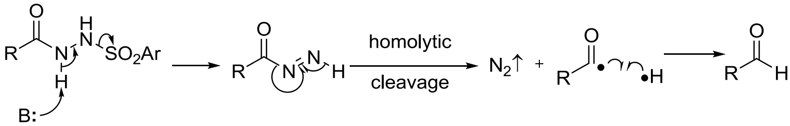
References

1. Lossen, W. *Ann*. **1872,** *161*, 347. Wilhelm C. Lossen (1838−1906) was born in Kreuznach, Germany. After his Ph.D. studies at Göttingen in 1862, he embarked on his independent academic career, and his interests centered on hydroxyamines.
2. Bauer, L.; Exner, O. *Angew. Chem. Int. Ed.* **1974,** *13*, 376.
3. Lipczynska-Kochany, E. *Wiad. Chem.* **1982,** *36*, 735−756.
4. Casteel, D. A.; Gephart, R. S.; Morgan, T. *Heterocycles* **1993,** *36*, 485–495.
5. Zalipsky, S. *Chem. Commun*. **1998,** 69−70.
6. Stafford, J. A.; Gonzales, S. S.; Barrett, D. G.; Suh, E. M.; Feldman, P. L. *J. Org. Chem*. **1998,** 63, 10040–10044.
7. Anilkumar, R.; Chandrasekhar, S.; Sridhar, M. *Tetrahedron Lett*. **2000,** *41*, 5291−5293.
8. Abbady, M. S.; Kandeel, M. M.; Youssef, M. S. K. *Phosphorous, Sulfur and Silicon* **2000,** *163*, 55–64.
9. Ohmoto, K.; Yamamoto, T.; Horiuchi, T.; Kojima, T.; Hachiya, K.; Hashimoto, S.; Kawamura, M.; Nakai, H.; Toda, M. *Synlett* **2001,** 299−301.
10. Choi, C.; Pfefferkorn, J. A. *Lossen rearrangement*. In *Name Reactions for Homologa-tions-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 200–209. (Review).
11. Yoganathan, S.; Miller, S. J. *Org. Lett*. **2013,** *15*, 602–605.

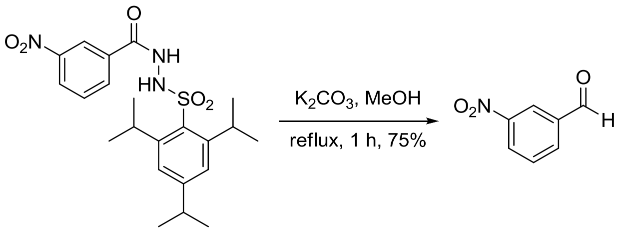
McFadyen–Stevens reduction

Treatment of acylbenzenesulfonylhydrazines with base delivers the corresponding aldehydes.





Example 1[5]



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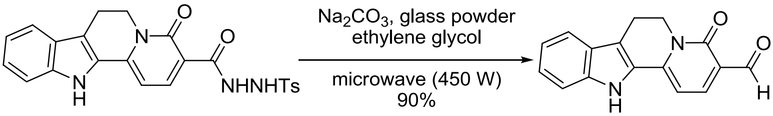

References

1. McFadyen, J. S.; Stevens, T. S. *J. Chem. Soc.* **1936,** 584–587. Thomas S. Stevens (1900–2000) was born in Renfrew, Scotland. After earning his Ph.D. under W. H. Perkin at Oxford University, he became a reader at the University of Sheffield. J. S. McFadyen (1908–) was born in Toronto, Canada. After studying under Stevens at the University of Glasgow, he worked for ICI for 15 years before returning to Canada where he worked for the Canadian Industries, Ltd., Montreal.
2. Graboyes, H.; Anderson, E. L.; Levinson, S. H.; Resnick, T. M. *J. Heterocycl. Chem.* **1975,** *12*, 1225–1231.
3. Eichler, E.; Rooney, C. S.; Williams, H. W. R. *J. Heterocycl. Chem.* **1976,** *13*, 841–844.
4. Nair, M.; Shechter, H. *J. Chem. Soc., Chem. Commun.* **1978,** 793–796.
5. Dudman, C. C.; Grice, P.; Reese, C. B. *Tetrahedron Lett.* **1980,** *21*, 4645–4648.
6. Manna, R. K.; Jaisankar, P.; Giri, V. S. *Synth. Commun.* **1998,** *28*, 9–16.
7. Jaisankar, P.; Pal, B.; Giri, V. S. *Synth. Commun.* **2002,** *32,* 2569–2573.
8. Ma, B.; Banerjee, B.; Litvinov, D. N.; He, L.; Castle, S. L. *J. Am. Chem. Soc.* **2010,** *132,* 1159–1171.
9. Iwai, Y.; Ozaki, T.; Takita, R.; Uchiyama, M.; Shimokawa, J.; Fukuyama, T. *Chem. Sci.* **2013,** *4,* 1111–1119.

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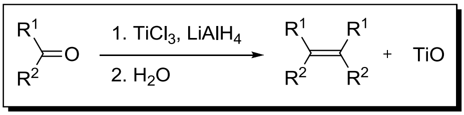
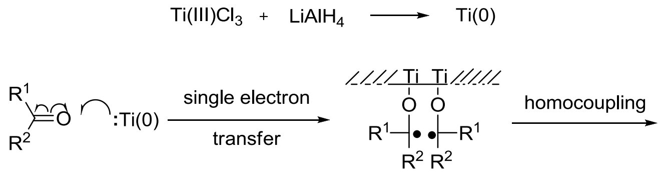
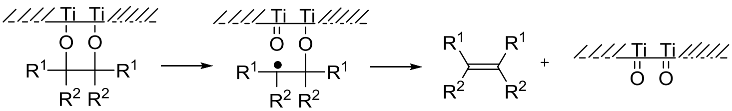
McMurry coupling

Olefination of carbonyls with low-valent titanium such as Ti(0) derived from $TiCl_3$/$LiAlH_4$. A single-electron process.



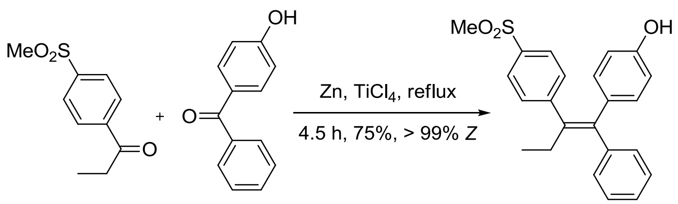


radical anion intermediate

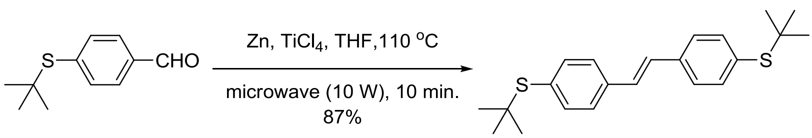


oxide-coated titanium surface

Example 1, Cross-McMurry coupling[7]



Example 2, Homo-McMurry coupling[8]



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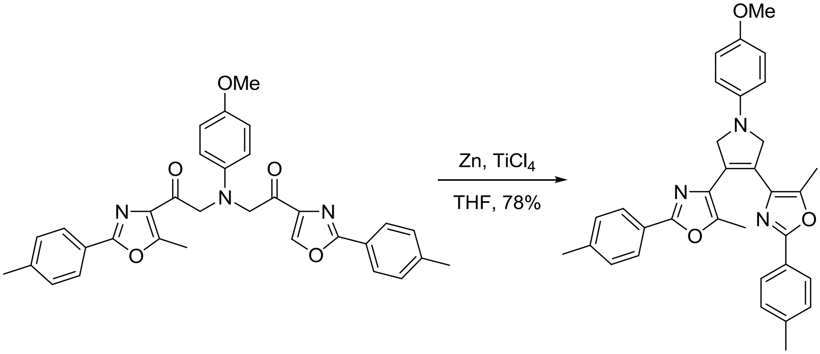
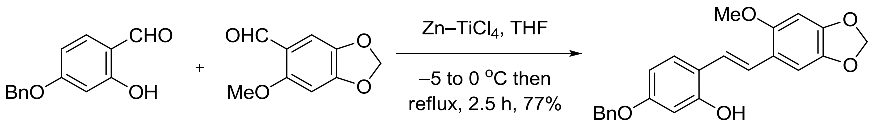
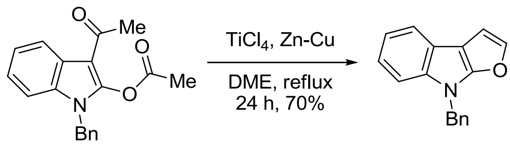
Example 3, Cross-McMurry coupling[9]



Example 4, Cross-McMurry coupling[10]



Example 5[12]

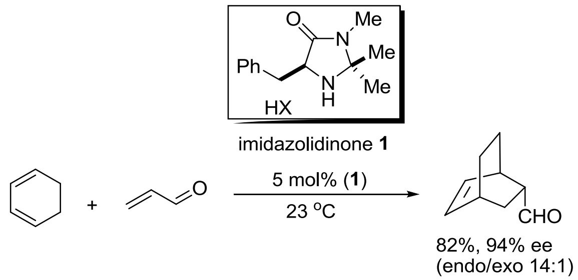


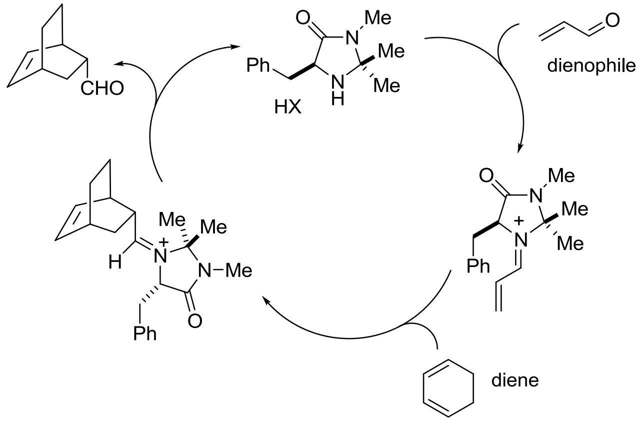
References

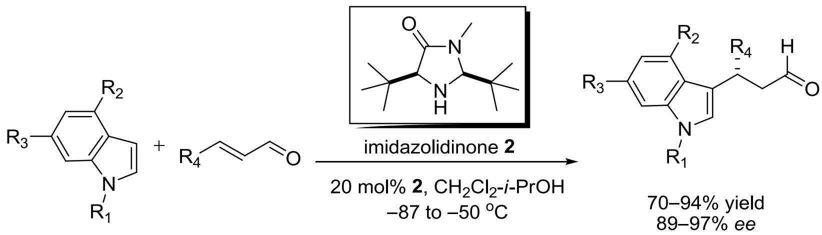
1. (a) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974,** *96*, 4708–4712. (b) McMurry, J. E. *Chem. Rev.* **1989,** *89*, 1513–1524. (Review).
2. Hirao, T. *Synlett* **1999,** 175–181.
3. Sabelle, S.; Hydrio, J.; Leclerc, E.; Mioskowski, C.; Renard, P.-Y. *Tetrahedron Lett.* **2002,** *43*, 3645–3648.
4. Williams, D. R.; Heidebrecht, R. W., Jr. *J. Am. Chem. Soc.* **2003,** *125*, 1843–1850.
5. Honda, T.; Namiki, H.; Nagase, H.; Mizutani, H. *Tetrahedron Lett.* **2003,** *44*, 3035–3038.
6. Ephritikhine, M.; Villiers, C. In *Modern Carbonyl Olefination* Takeda, T., Ed.; Wiley-VCH: Weinheim, Germany, **2004,** 223–285. (Review).
7. Uddin, M. J.; Rao, P. N. P.; Knaus, E. E. *Synlett* **2004,** 1513–1516.
8. Stuhr-Hansen, N. *Tetrahedron Lett.* **2005,** *46*, 5491–5494.
9. Zeng, D. X.; Chen, Y. *Synlett* **2006,** 490–492.
10. Duan, X.-F.; Zeng, J.; Zhang, Z.-B.; Zi, G.-F. *J. Org. Chem.* **2007,** *72*, 10283–10286.
11. Debroy, P.; Lindeman, S. V.; Rathore, R. *J. Org. Chem.* **2009,** *74*, 2080–2087.
12. Kumar, A. S.; Nagarajan, R. *Synthesis* **2013,** *45*, 1235–1246.

MacMillan catalyst

Highly enantioselective and general asymmetric organocatalytic Diels–Alder reaction using α-amino acid-derived imidazolidinones (of type **1**) as catalysts. The first generation of MacMillan catalyst (**1**) has been employed in a variety of organocatalytic enantioselective reactions. Typical examples are: Diels–Alder reaction;[1] nitrone cycloaddition,[2] pyrrole Friedel–Crafts reaction,[3] indole addition,[4] vinylogous Michael addition;[5] α-chlorination;[6] hydride addition;[7] cyclopropanation;[8] α-fluorination.[9] The second generation MacMillan catalyst (**2**) was used to catalyze 1,4-addition of indoles to α,β-unsaturated aldehydes.







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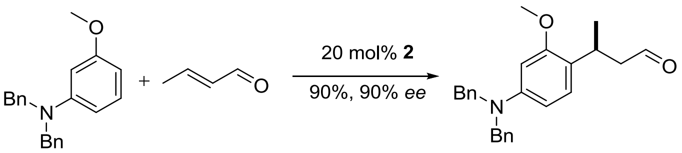
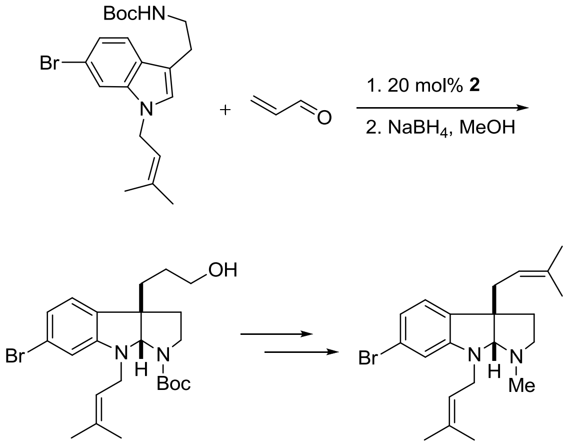
Example 1[11]



Example 2[10]



78% yield
90% *ee*

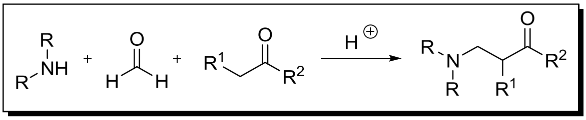
(−)-flustramine B

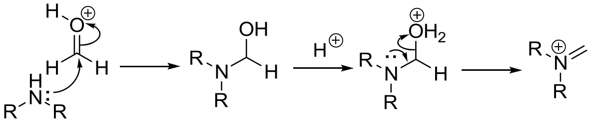
References

1. Ahrendt, K.; Borths, C.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2000,** *122*, 4243.
2. Jen, W.; Wiener, J.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2000,** *122*, 9874.
3. Paras, N.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2001,** *123*, 4370.
4. Austin, J. F.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2002,** *124*, 1172.
5. Brown, S. P.; Goodwin, N. C.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2003,** *125*, 1192.
6. Brochu, M. P.; Brown, S. P.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2004,** *126*, 4108.
7. Ouellet, S. G.; Tuttle, J. B.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2005,** *127*, 32.
8. Kunz, R. K; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2005,** *127*, 3240.
9. Beeson, T. D.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2005,** *127*, 8826.
10. Austin, J. F.; Kim, S.-G.; Sinz, C. J.; Xiao, W.-J.; MacMillan, D. W. C. *Proc. Nat. Acad. Sci. USA*, **2004,** *101*, 5482.
11. Kim, S.-G.; Kim, J.; Jung, H. *Tetrahedron Lett.* **2005,** *46*, 2437.
12. Riente, P.; Yadav, J.; Pericas, M. A. *Org. Lett*. **2012,** *14,* 3668–3671.
13. Zhang, Y.; Wang, S.-Y.; Xu, X.-P.; Jiang, R.; Ji, S.-J. *Org. Biomol. Chem*. **2013,** *11*, 1933−1937.

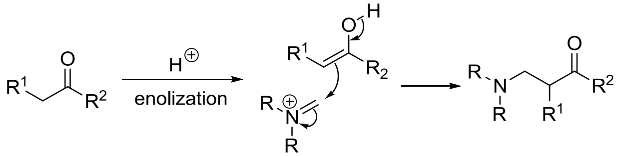
Mannich reaction

Three-component aminomethylation from amine, aldehyde and a compound with an acidic methylene moiety.

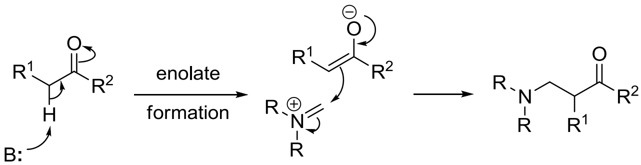




When R = Me, the $^{+}Me_2N{=}CH_2$ salt is known as *Eschenmoser's salt*

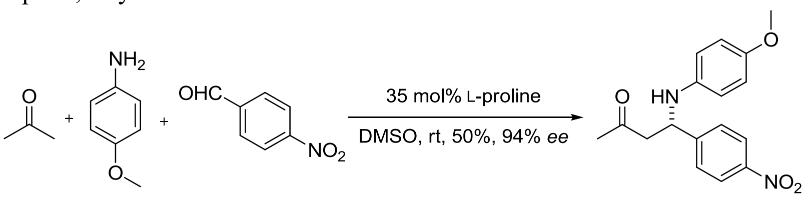


The Mannich reaction can also operate under basic conditions:

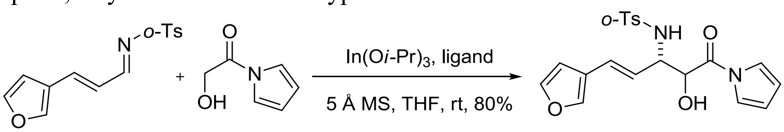


Mannich Base

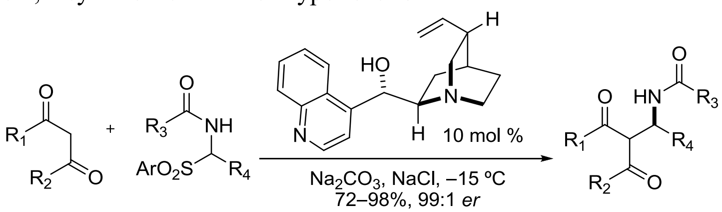
Example 1, Asymmetric Mannich reaction[2]



Example 2, Asymmetric Mannich-type reaction[9]



Example 3, Asymmetric Mannich-type reaction[10]



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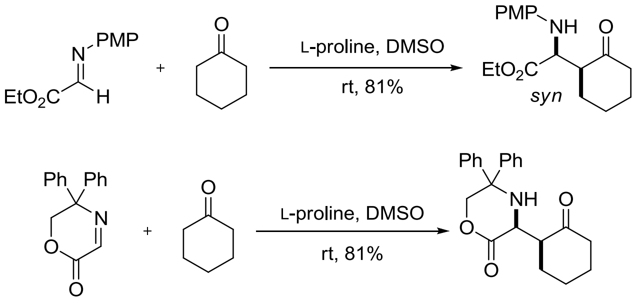
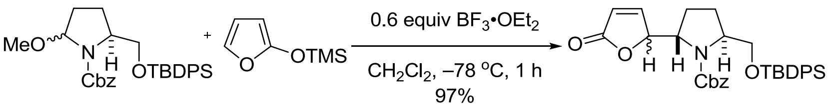
DOI 10.1007/978-3-319-03979-4_162,

Example 4[11]



Example 5, Vinylogous Mannich Reaction (VMR)[13]

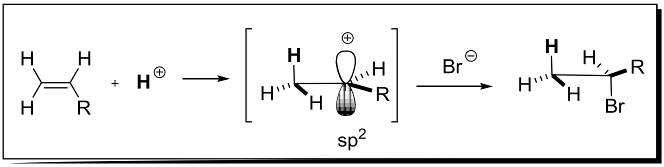


References

1. Mannich, C.; Krösche, W. *Arch. Pharm.* **1912,** *250*, 647–667. Carl U. F. Mannich (1877–1947) was born in Breslau, Germany. After receiving a Ph.D. at Basel in 1903, he served on the faculties of Göttingen, Frankfurt and Berlin. Mannich synthesized many esters of *p*-aminobenzoic acid as local anesthetics.
2. List, B. *J. Am. Chem. Soc*. **2000,** *122*, 9336–9337.
3. Schlienger, N.; Bryce, M. R.; Hansen, T. K. *Tetrahedron* **2000,** *56*, 10023–10030.
4. Bur, S. K.; Martin, S. F. *Tetrahedron* **2001,** *57*, 3221–3242. (Review).
5. Martin, S. F. *Acc. Chem. Res.* **2002,** *35*, 895–904. (Review).
6. Padwa, A.; Bur, S. K.; Danca, D. M.; Ginn, J. D.; Lynch, S. M. *Synlett* **2002,** 851–862. (Review).
7. Notz, W.; Tanaka, F.; Barbas, C. F., III. *Acc. Chem. Res*. **2004,** *37*, 580–591. (Review).
8. Córdova, A. *Acc. Chem. Res*. **2004,** *37*, 102–112. (Review).
9. Harada, S.; Handa, S.; Matsunaga, S.; Shibasaki, M. *Angew. Chem. Int. Ed.* **2005,** *44*, 4365–4368.
10. Lou, S.; Dai, P.; Schaus, S. E. *J. Org. Chem*. **2007,** *72*, 9998–10008.
11. Hahn, B. T.; Fröhlich, R.; Harms, K.; Glorius, F. *Angew. Chem. Int. Ed.* **2008,** *47*, 9985–9988.
12. Galatsis, P. *Mannich reaction*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 653–670. (Review).
13. Liu, X.-K.; Ye, J.-L.; Ruan, Y.-P.; Li, Y.-X.; Huang, P.-Q. *J. Org. Chem*. **2013,** *78*, 35–41.

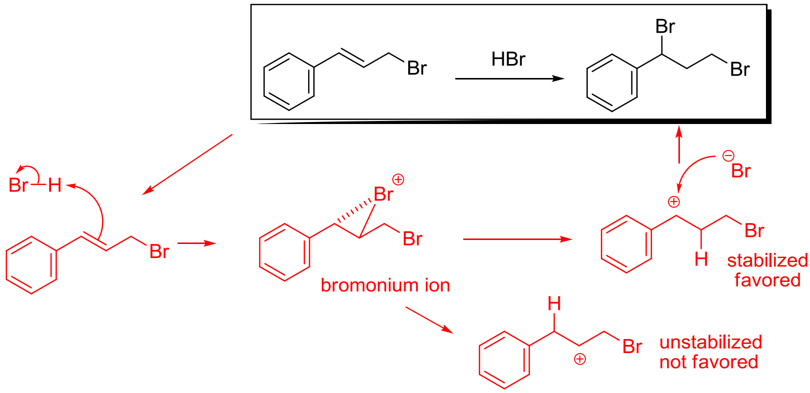
Markovnikov's rule

For addition of HX to olefins, Markovnikov's Rule predicts the regiochemistry of HX addition to unsymmetrically substituted alkenes: The halide component of HX bonds preferentially at the more highly substituted carbon, whereas the hydrogen prefers the carbon which already contains more hydrogen atoms.

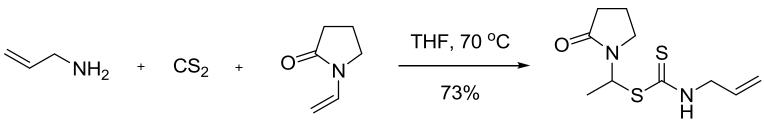


The intermediate is the secondary cation, and the formal charge is on one carbon.

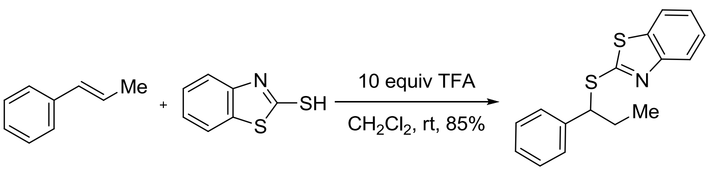
Exception to Markovnikov's Rule:



Example 1[3]



Example 2, Markovnikov-selective hydrothiolation of styrenes[4]



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DOI 10.1007/978-3-319-03979-4_163, © Springer International Publishing Switzerland 2014

References

1 Markownikoff, W. *Ann. Pharm.* **1870,** *153,* 228–259. Vladimir Vasilyevich Markovnikov (1838–1904) fomulated the rule for addition to alkenes at Moscow University. He was one of the most eminant Russian organic chemists in the 19th century. He was a prickly individual with strong opinions, and he had no fear in expressing them. His tactless outspokenness led to his ouster from professorship at Kazan' and Moscow. (Lewis, D. E. *Early Russian Organic Chemists and Their Legacy*, Springer: Heldelberg, Germany, 2012, p 71.).

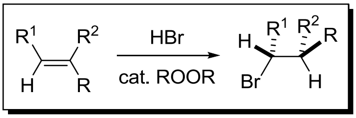
2 Oparina, L. A.; Artem'ev, A. V.; Vysotskaya, O. V.; Kolyvanov, N. A.; Bagryanskaya, Y. I.; Doronina, E. P.; Gusarova, N. K. *Tetrahedron* **2013,** *69*, 6185–6195.

3 Ziyaei Halimehjani, A.; Pasha Zanussi, H. *Synthesis* **2013,** *45*, 1483–1488

4 Savolainen, M. A.; Wu, J. *Org. Lett.* **2013,** *15,* 3802–3804.

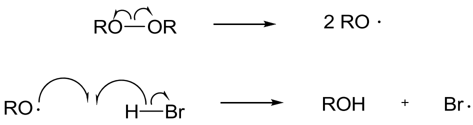
Anti-Markovnikov

Some reactions do not follow Markovnikov's Rule, and *anti*-Markovnikov products are isolated. The outcome of the regioselectivity may be explained by the relative stability of the radical intermediates.

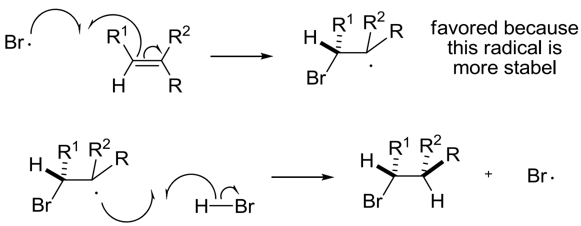


Radical mechanism:

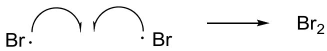
Initiation:



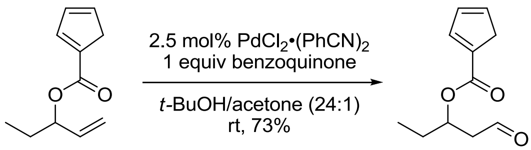
Propagation:



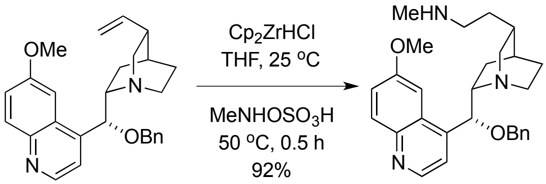
Termination:



Example 1, Anti-Markovnikov oxidation of allylic esters[1]



Example 2, Anti-Markovnikov hydroamination[3]

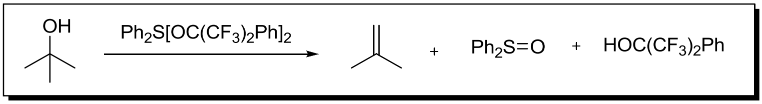


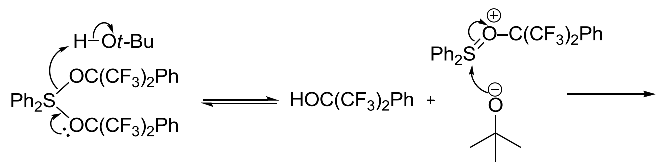
References

1. Nishizawa, M.; Asai, Y.; Imagawa, H. *Org. Lett.* **2006,** *8,* 5793–5796.
2. Dong, J. J.; Fañanás-Mastral, M.; Alsters, P. L.; Browne, W. R.; Feringa, B. L. *Angew. Chem. Int. Ed.* **2008,** *47*, 5561–5565.
3. Strom, A. E.; Hartwig, J. F. *J. Org. Chem.* **2013,** *78*, 8909–8914.

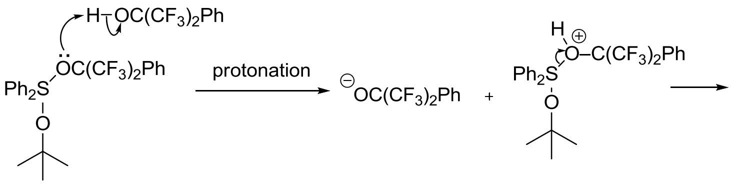
Martin's sulfurane dehydrating reagent

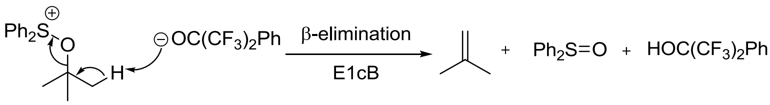
Dehydrates secondary and tertiary alcohols to give olefins, but forms ethers with primary alcohols. *Cf.* Burgess dehydrating reagent.



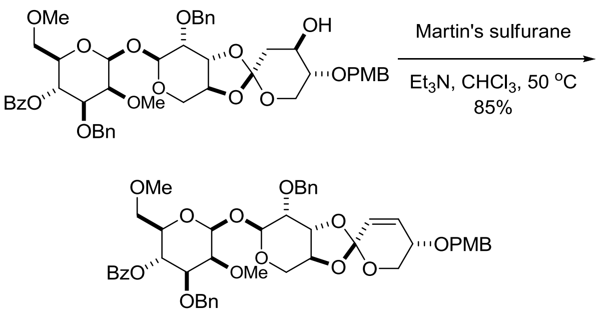


The alcohol is acidic





Example 1[5]



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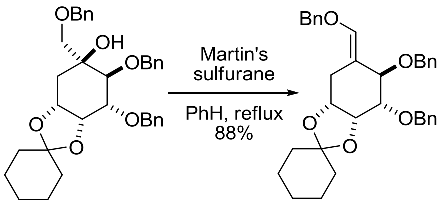
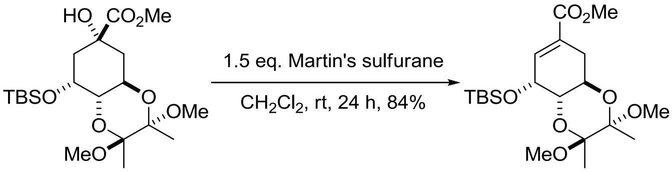
DOI 10.1007/978-3-319-03979-4_164, © Springer International Publishing Switzerland 2014

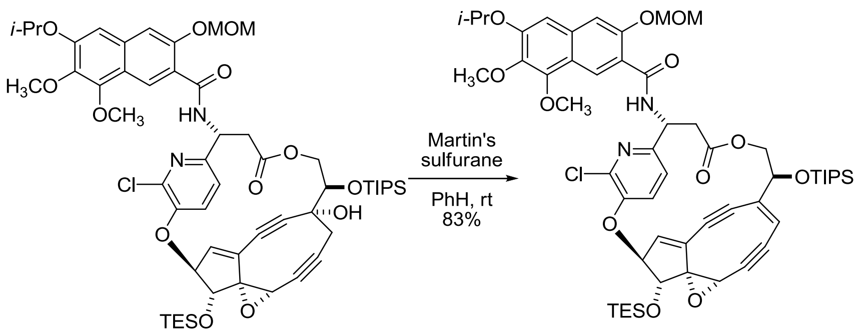
Example 2[6]



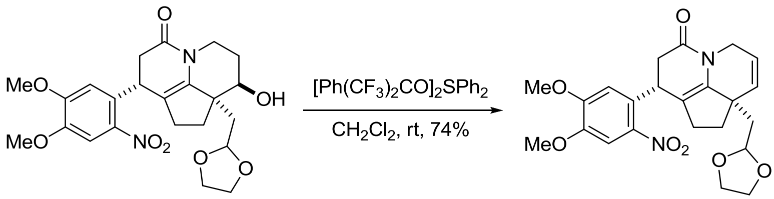
Example 3[7]



Example 4[9]



Example 5[12]



References

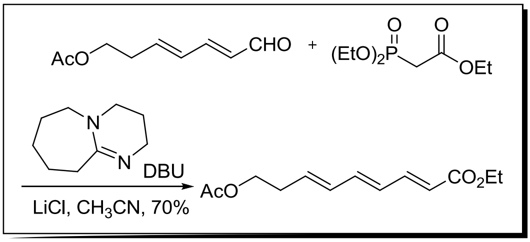
1. (a) Martin, J. C.; Arhart, R. J. *J. Am. Chem. Soc.* **1971,** *93*, 2339–2341; (b) Martin, J. C.; Arhart, R. J. *J. Am. Chem. Soc.* **1971,** *93*, 2341–2342; (c) Martin, J. C.; Arhart, R.

J. *J. Am. Chem. Soc.* **1971,** *93*, 4327–4329. (d) Martin, J. C.; Arhart, R. J.; Franz, J. A.; Perozzi, E. F.; Kaplan, L. J. *Org. Synth*. **1977,** *57*, 22–26.

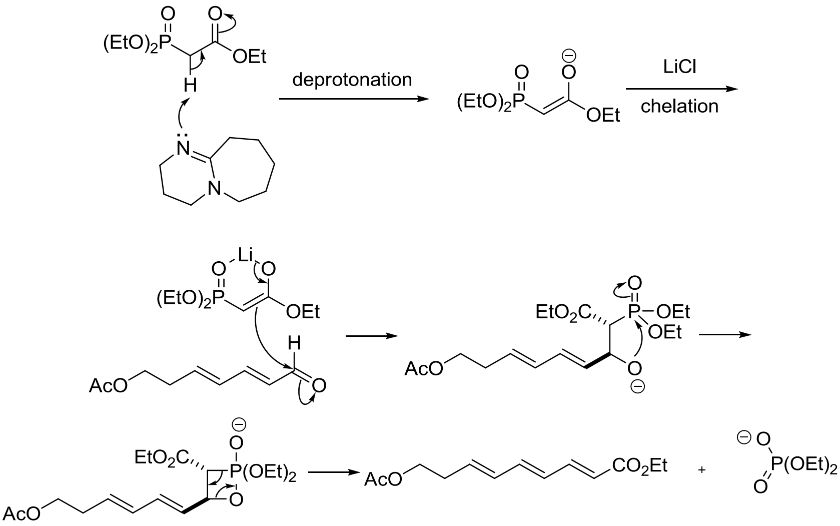
2. Gallagher, T. F.; Adams, J. L. *J. Org. Chem.* **1992,** *57*, 3347–3353.
3. Tse, B.; Kishi, Y. *J. Org. Chem.* **1994,** *59*, 7807–7814.
4. Winkler, J. D.; Stelmach, J. E.; Axten, J. *Tetrahedron Lett*. **1996,** *37*, 4317–4320.
5. Nicolaou, K. C.; Rodríguez, R. M.; Fylaktakidou, K. C.; Suzuki, H.; Mitchell, H. J. *Angew. Chem. Int. Ed.* **1999,** *38*, 3340–3345.
6. Kok, S. H. L.; Lee, C. C.; Shing, T. K. M. *J. Org. Chem.* **2001,** *66,* 7184–7190.
7. Box, J. M.; Harwood, L. M.; Humphreys, J. L.; Morris, G. A.; Redon, P. M.; Whitehead, R. C. *Synlett* **2002,** 358–360.
8. Myers, A. G.; Glatthar, R.; Hammond, M.; Harrington, P. M.; Kuo, E. Y.; Liang, J.; Schaus, S. E.; Wu, Y.; Xiang, J.-N. *J. Am. Chem. Soc.* **2002,** *124*, 5380–5401.
9. Myers, A. G.; Hogan, P. C.; Hurd, A. R.; Goldberg, S. D. *Angew. Chem. Int. Ed.* **2002,** *41,* 1062–1067.
10. Shea, K. M. *Martin's sulfurane dehydrating reagent*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 248–264. (Review).
11. Sparling, B. A.; Moslin, R. M.; Jamison, T. F. *Org. Lett*. **2008,** *10,* 1291–1294.
12. Miura, Y.; Hayashi, N.; Yokoshima, S.; Fukuyama, T. *J. Am. Chem. Soc.* **2012**, *134*, 11995–11997.

Masamune–Roush conditions for the Horner–Emmons reaction

Applicable to base-sensitive aldehydes and phosphonates for the Horner–Wadsworth–Emmons reaction to prepare olefins. α-Keto or α-alkoxycarbonyl phosphonate required.

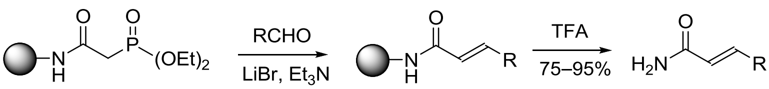


DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene

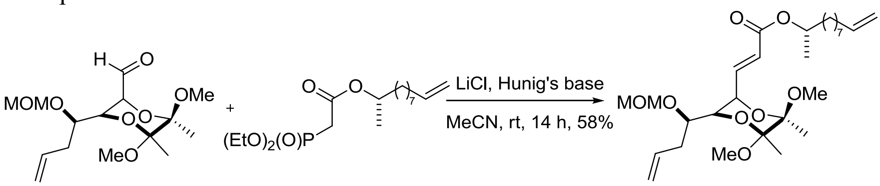


Formation of the P=O is thermodynamically favored, which is the driving force of this reaction.

Example 1[5]



Example 2[6]



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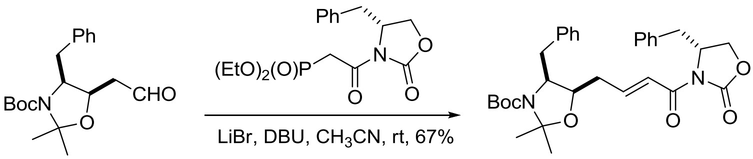
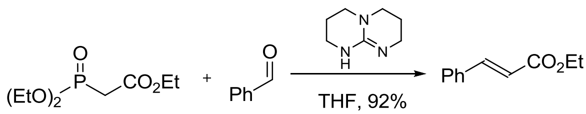
DOI 10.1007/978-3-319-03979-4_165, © Springer International Publishing Switzerland 2014

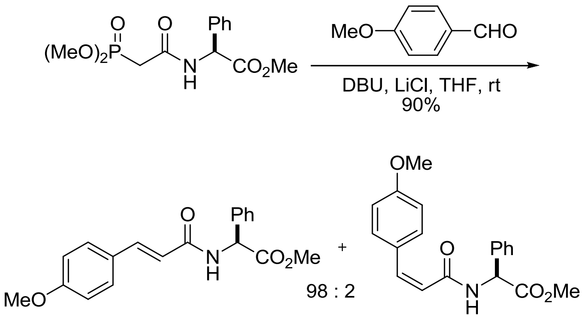
Example 3[7]



Example 4[8]



Example 5[10]

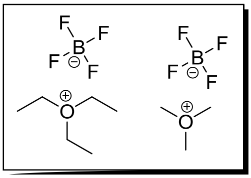


References

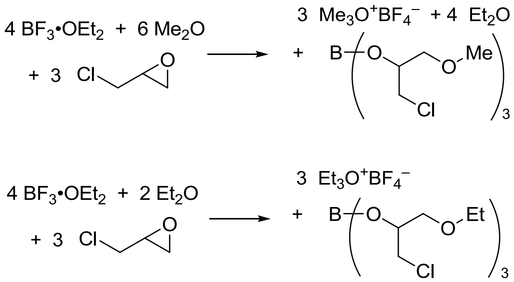
1. Blanchette, M. A.; Choy, W.; Davis, J. T.; Essenfeld, A. P.; Masamune, S.; Roush, W. R.; Sakai, T. *Tetrahedron Lett.* **1984,** *25*, 2183–2186.
2. Rathke, M. W.; Nowak, M. *J. Org. Chem.* **1985,** *50*, 2624–2636.
3. Tius, M. A.; Fauq, A. H. *J. Am. Chem. Soc.* **1986,** *108*, 1035–1039, and 6389–6391.
4. Marshall, J. A.; DuBay, W. J. *J. Org. Chem.* **1994,** *59*, 1703–1708.
5. Johnson, C. R.; Zhang, B. *Tetrahedron Lett.* **1995,** *36*, 9253–9256.
6. Rychnovsky, S. D.; Khire, U. R.; Yang, G. *J. Am. Chem. Soc.* **1997,** *119*, 2058–2059.
7. Dixon, D. J.; Foster, A. C.; Ley, S. V. *Org. Lett.* **2000,** *2*, 123–125.
8. Simoni, D.; Rossi, M.; Rondannin, R.; Mazzali, A.; Baruchello, R.; Malagutti, C.; Roberti, M.; Invidiata, F. P. *Org. Lett.* **2000,** *2*, 3765–3768.
9. Crackett, P.; Demont, E.; Eatherton, A.; Frampton, C. S.; Gilbert, J.; Kahn, I.; Redshaw, S.; Watson, W. *Synlett* **2004,** 679–683.
10. Ordonez, M.; Hernandez-Fernandez, E.; Montiel-Perez, M.; Bautista, R.; Bustos, P.; Rojas-Cabrera, H.; Fernandez-Zertuche, M.; Garcia-Barradas, O. *Tetrahedron: Asymmetry* **2007,** *18*, 2427–2436.
11. Zanato, C.; Pignataro, L.; Hao, Z.; Gennari, C. *Synthesis* **2008,** 2158–2162.
12. Paterson, I.; Fink, S. J.; Blakey, S. B. *Org. Lett.* **2013,** *15*, 3188–3121.

Meerwein's salt

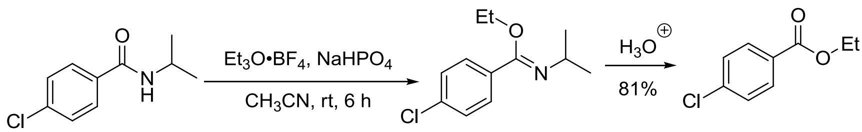
Meerwein's salts, also known as the Meerwein reagents, refer to trimethyloxonium tetrafluoroborate ($Me_3O^+BF_4^-$) and triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$). Named after the inventor Hans Meerwein,[1] these trialkyloxonium salts are powerful alkylating agents.



Preparation:[2]

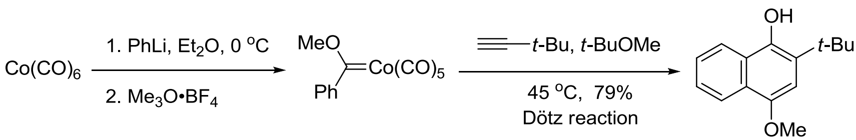


Example 1, The Meerwein reagent is an excellent *O*-alkylating agent:[5]

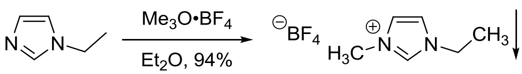


Transforming an amide into its corresponding ethyl or methyl esters

Example 2, *Metal*-methylation[4]



Example 3, *N*-Alkylation, the product is an ionic liquid[8]



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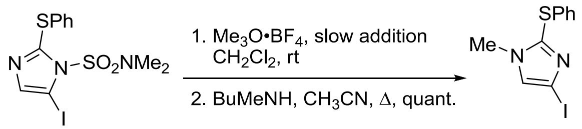
DOI 10.1007/978-3-319-03979-4_166,

Example 4, *N*-Methylation[9]

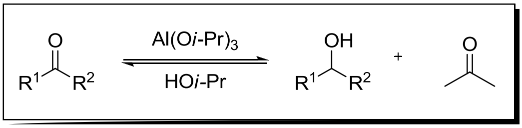


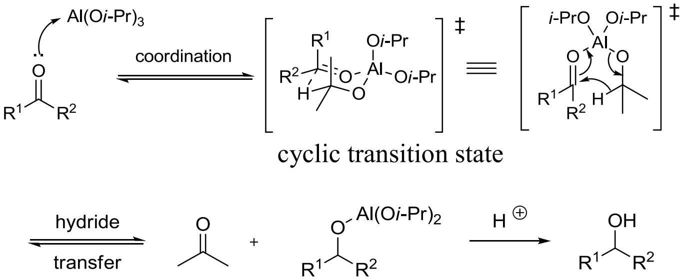
References

1. (a) Meerwein, H.; Hinz, G.; Hofmann, P.; Kroning, E.; Pfeil, E. *J. Prakt. Chem.* **1937,** *147*, 257–285. (b) Meerwein, H.; Bettenberg, E.; Pfeil, E.; Willfang, G. *J. Prakt. Chem.* **1939,** *154*, 83–156.
2. (a) Meerwein, H. *Org. Synth.*; *Coll. Vol. V* **1973,** 1080. Triethyloxonium tetrafluoroborate. (b) Curphey, T. J. *Org. Synth.*; *Coll. Vol. VI*, **1988,** 1019. Trimethyloxonium tetrafluoroborate.
3. Chen, F. M. F.; Benoiton, N. L. *Can. J. Chem.* **1977,** *55*, 1433–1534.
4. Dötz, K. H.; Möhlemeier, J.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983,** *247,* 187–201.
5. Downie, I. M.; Heaney, H.; Kemp, G.; King, D.; Wosley, M. *Tetrahedron* **1992,** *48*, 4005–4016.
6. Kiessling, A. J.; McClure, C. K. *Synth. Commun*. **1997,** *27*, 923–937.
7. Pichlmair, S. *Synlett* **2004,** 195–196. (Review).
8. Egashira, M.; Yamamoto, Y.; Fukutake, T.; Yoshimoto, N.; Morita, M. *J. Fluorine Chem*. **2006,** *127*, 1261–1264.
9. Delest, B.; Nshimyumukiza, P.; Fasbender, O.; Tinant, B.; Marchand-Brynaert, J.; Darro, F.; Robiette, R. *J. Org. Chem.* **2008,** *73*, 6816–6823.
10. Perst, H.; Seapy, D. G. *Triethyloxonium Tetrafluoroborate* In *Encyclopedia of Reagents for Organic Synthesis* Wiley: New York, **2008,**
11. Hari, D. P., König, B. *Angew. Chem. Int. Ed.* **2013,** *52*, 4734–4743. (Review).

Meerwein–Ponndorf–Verley reduction

Reduction of ketones to the corresponding alcohols using $Al(Oi\text{-}Pr)_3$ in iso-propanol. Reverse of the Oppernauer oxidation.





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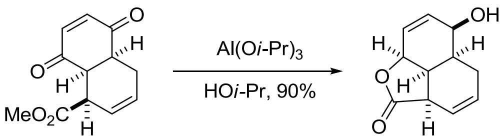

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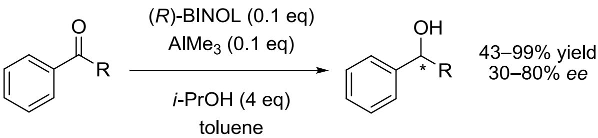
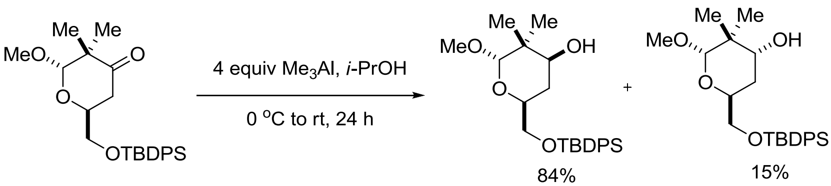


Example 3[7]



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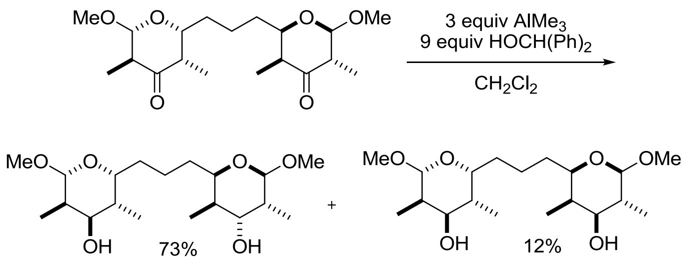
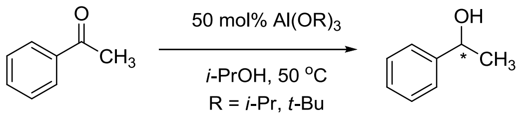
DOI 10.1007/978-3-319-03979-4_167,

Example 4[9]



Example 5[10]

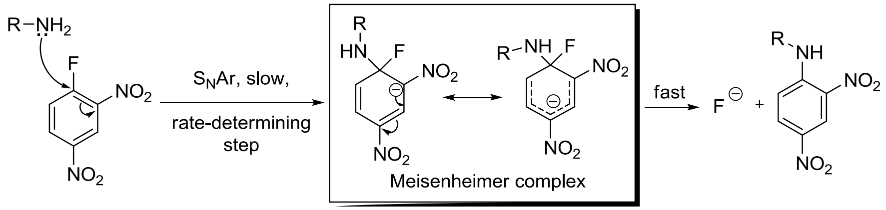


References

1. Meerwein, H.; Schmidt, R. *Ann.* **1925,** *444*, 221–238. Hans L. Meerwein, born in Hamburg Germany in 1879, received his Ph.D. at Bonn in 1903. In his long and productive academic career, Meerwein made many notable contributions in organic chemistry.
2. Woodward, R. B.; Bader, F. E.; Bickel, H.; Frey, A. J.; Kierstead, R. W. *Tetrahedron* **1958,** *2*, 1–57.
3. de Graauw, C. F.; Peters, J. A.; van Bekkum, H.; Huskens, J. *Synthesis* **1994,** 1007–1017. (Review).
4. Campbell, E. J.; Zhou, H.; Nguyen, S. T. *Angew. Chem. Int. Ed.* **2002,** *41*, 1020–1022.
5. Sominsky, L.; Rozental, E.; Gottlieb, H.; Gedanken, A.; Hoz, S. *J. Org. Chem.* **2004,** *69*, 1492–1496.
6. Cha, J. S. *Org. Proc. Res. Dev.* **2006,** *10*, 1032–1053.
7. Manaviazar, S.; Frigerio, M.; Bhatia, G. S.; Hummersone, M. G.; Aliev, A. E.; Hale, K. J. *Org. Lett.* **2006,** *8*, 4477–4480.
8. Clay, J. M. *Meerwein–Ponndorf–Verley reduction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 123–128. (Review).
9. Dilger, A. K.; Gopalsamuthiram, V.; Burke, S. D. *J. Am. Chem. Soc.* **2007,** *129*, 16273–16277.
10. Flack, K.; Kitagawa, K.; Pollet, P.; Eckert, C. A.; Richman, K.; Stringer, J.; Dubay, W.; Liotta, C. L. *Org. Process Res. Dev.* **2012,** *16*, 1301–1306.
11. Lenze, M.; Bauer, E. B. *Chem. Commun.* **2013,** *49*, 5889–5891.

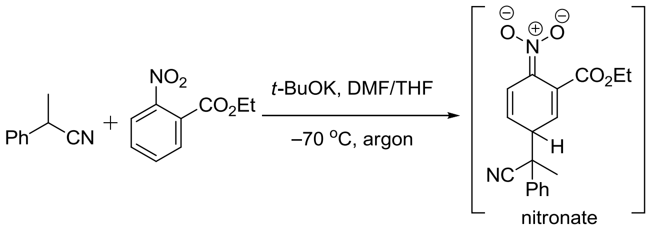
Meisenheimer complex

Also known as **the Meisenheimer–Jackson salt**, the stable intermediate for certain S_NAr reactions.



Sanger's reagent, *ipso* attack *ipso* substitution

Example 1[7]



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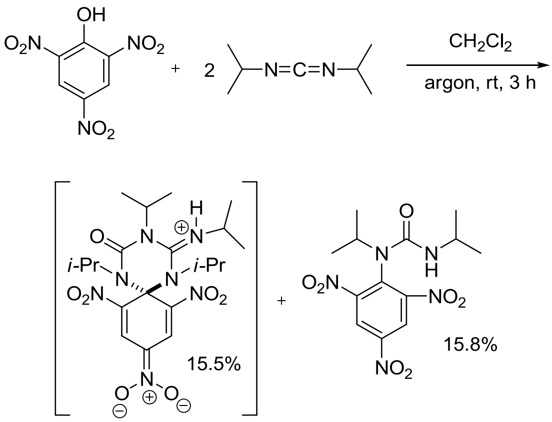

The reaction using Sanger's reagent is faster than using the corresponding chloro-, bromo-, and iododinitrobenzene—the fluoro-Meisenheimer complex is the most stabilized because F is the most electron-withdrawing. The reaction rate does not depend upon the capacity of the leaving group.

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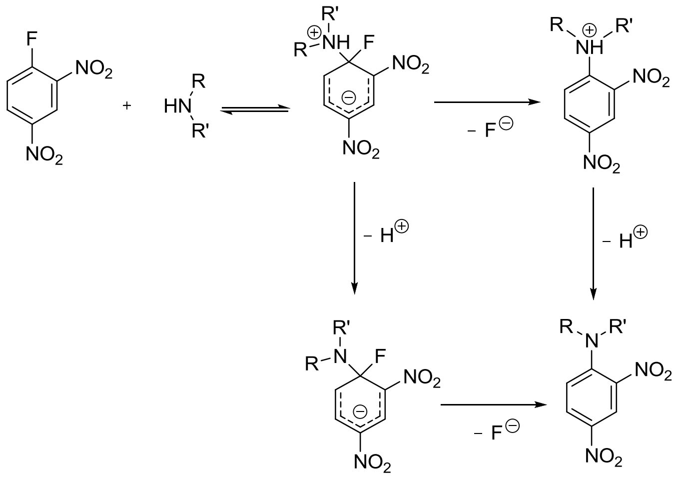
DOI 10.1007/978-3-319-03979-4_168,

Example 3[10]

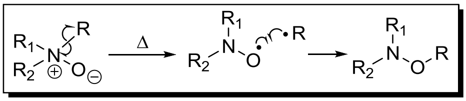


References

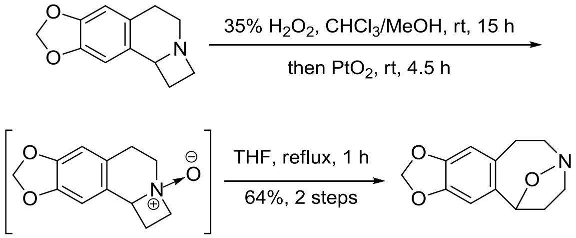
1. Meisenheimer, J. *Ann.* **1902,** *323*, 205–214.
2. Strauss, M. J. *Acc. Chem. Res*. **1974,** *7*, 181–188. (Review).
3. Bernasconi, C. F. *Acc. Chem. Res*. **1978,** *11*, 147–152. (Review).
4. Terrier, F. *Chem. Rev*. **1982,** *82*, 77–152. (Review).
5. Manderville, R. A.; Buncel, E. *J. Org. Chem*. **1997,** *62*, 7614–7620.
6. Hoshino, K.; Ozawa, N.; Kokado, H.; Seki, H.; Tokunaga, T.; Ishikawa, T. *J. Org. Chem*. **1999,** *64*, 4572–4573.
7. Adam, W.; Makosza, M.; Zhao, C.-G.; Surowiec, M. *J. Org. Chem*. **2000,** *65*, 1099–1101.
8. Gallardo, I.; Guirado, G.; Marquet, J. *J. Org. Chem*. **2002,** *67*, 2548–2555.
9. Al-Kaysi, R. O.; Guirado, G.; Valente, E. J. *Eur. J. Org. Chem*. **2004,** 3408–3411.
10. Um, I.-H.; Min, S.-W.; Dust, J. M. *J. Org. Chem*. **2007,** *72*, 8797–8803.
11. Han, T. Y.-J.; Pagoria, P. F.; Gash, A. E.; Maiti, A.; Orme, C. A.; Mitchell, A. R.; Fried, L. E. *New J. Chem*. **2009,** *33*, 50–56.
12. Campodónico, P. R.; Tapia, R. A.; Contreras, R.; Ormazábal-Toledo, R. *Org. Biomol. Chem*. **2013,** *11*, 2302–2309.

[1,2]-Meisenheimer rearrangement

[1,2]-Sigmatropic rearrangement of tertiary amine *N*-oxides to substituted hydroxylamines.



Example 1[7]



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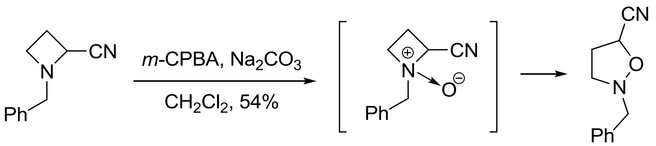

References

1. Meisenheimer, J. *Ber.* **1919,** *52*, 1667–1677.
2. Castagnoli, N., Jr.; Craig, J. C.; Melikian, A. P.; Roy, S. K. *Tetrahedron* **1970,** *26*, 4319–4327.
3. Johnstone, R. A. W. *Mech. Mol. Migr.* **1969,** *2*, 249–266. (Review).
4. Kurihara, T.; Sakamoto, Y.; Tsukamoto, K.; Ohishi, H.; Harusawa, S.; Yoneda, R. *J. Chem. Soc., Perkin Trans. 1*, **1993,** 81–87.
5. Yoneda, R.; Sakamoto, Y.; Oketo, Y.; Minami, K.; Harusawa, S.; Kurihara, T. *Tetrahedron Lett.* **1994,** *35*, 3749–3752.
6. Kurihara, T.; Sakamoto, Y.; Takai, M.; Ohishi, H.; Harusawa, S.; Yoneda, R. *Chem. Pharm. Bull.* **1995,** *43*, 1089–1095.
7. Yoneda, R.; Sakamoto, Y.; Oketo, Y.; Harusawa, S.; Kurihara, T. *Tetrahedron* **1996,** *52*, 14563–14576.
8. Yoneda, R.; Araki, L.; Harusawa, S.; Kurihara, T. *Chem. Pharm. Bull.* **1998,** *46*, 853–856.
9. Menguy, L.; Drouillat, B.; Marrot, J.; Couty, F. *Tetrahedron Lett.* **2012,** *53*, 4697–4699.

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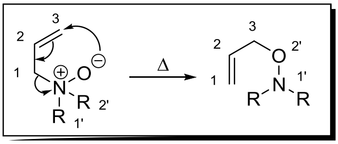
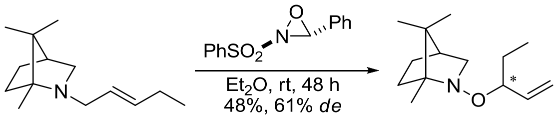
DOI 10.1007/978-3-319-03979-4_169,

[2,3]-Meisenheimer rearrangement

[2,3]-Sigmatropic rearrangement of allylic tertiary amine-*N*-oxides to give *O*-allyl hydroxylamines:



Example 1[7]



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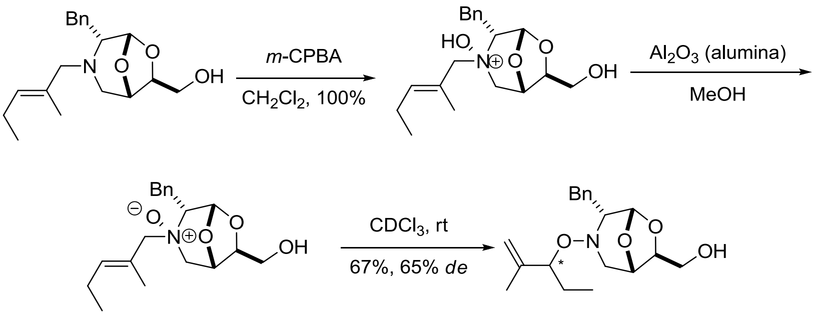

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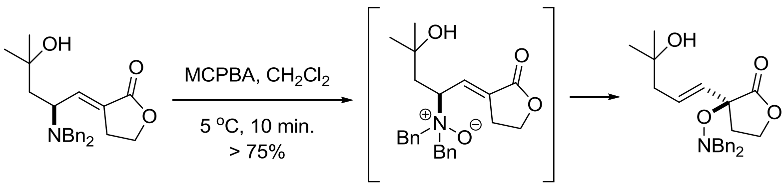


References

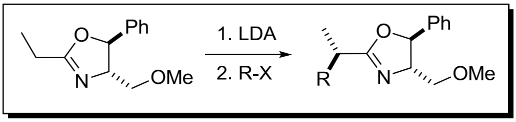
1. Meisenheimer, J. *Ber.* **1919,** *52*, 1667–1677.
2. Yamamoto, Y.; Oda, J.; Inouye, Y. *J. Org. Chem.* **1976,** *41*, 303–306.
3. Johnstone, R. A. W. *Mech. Mol. Migr.* **1969,** *2*, 249–266. (Review).
4. Kurihara, T.; Sakamoto, Y.; Matsumoto, H.; Kawabata, N.; Harusawa, S.; Yoneda, R. *Chem. Pharm. Bull.* **1994,** *42*, 475–480.

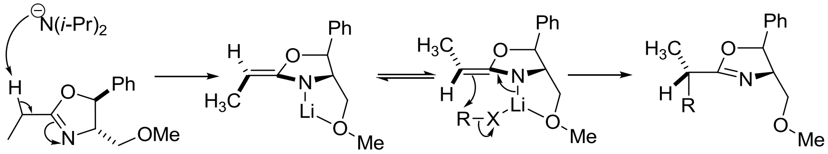
J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_170, © Springer International Publishing Switzerland 2014

5. Blanchet, J.; Bonin, M.; Micouin, L.; Husson, H.-P. *Tetrahedron Lett*. **2000,** *41*, 8279–8283.
6. Enders, D.; Kempen, H. *Synlett* **1994,** 969–971.
7. Buston, J. E. H.; Coldham, I.; Mulholland, K. R. *Synlett* **1997,** 322–324.
8. Guarna, A.; Occhiato, E. G.; Pizzetti, M.; Scarpi, D.; Sisi, S.; van Sterkenburg, M. *Tetrahedron: Asymmetry* **2000,** *11*, 4227–4238.
9. Mucsi, Z.; Szabó, A.; Hermecz, I.; Kucsman, Á.; Csizmadia, I. G. *J. Am. Chem. Soc.* **2005,** *127*, 7615–7621.
10. Bourgeois, J.; Dion, I.; Cebrowski, P. H.; Loiseau, F.; Bedard, A.-C.; Beauchemin, A. M. *J. Am. Chem. Soc.* **2009,** *131*, 874–875.
11. Yang, H.; Sun, M.; Zhao, S.; Zhu, M.; Xie, Y.; Niu, C.; Li, C.*J. Org. Chem.* **2013,** *78*, 339–346.

Meyers oxazoline method

Chiral oxazolines employed as activating groups and/or chiral auxiliaries in nucleophilic addition and substitution reactions that lead to the asymmetric construction of carbon–carbon bonds.





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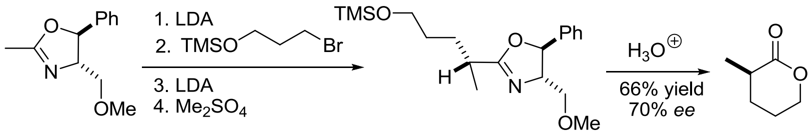

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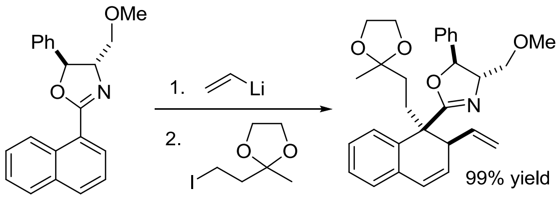
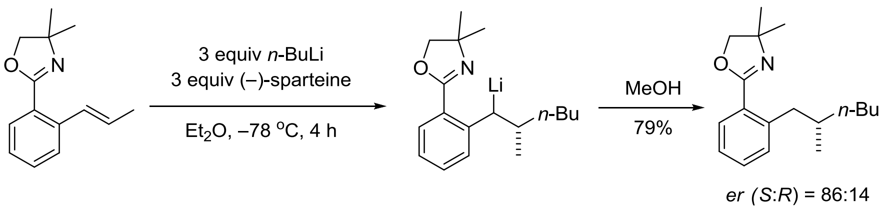


Example 3[9]



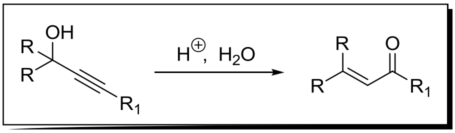
J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_171,

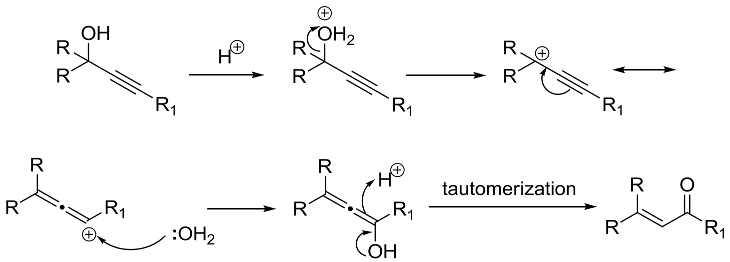
References

1. (a) Meyers, A. I.; Knaus, G.; Kamata, K. *J. Am. Chem. Soc.* **1974,** *96*, 268–270. While Albert I. Meyers was an assistant professor at Wayne State University, neighboring pharmaceutical firm Parke–Davis (Drs. George Moersch and Harry Crooks) donated several kilograms of (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propanediol (Meyers referred to it as the Parke–Davis diol), from which his chemistry with chiral oxazolines began. He taught at Colorado State University since 1972. Meyers passed away in 2007. (b) Meyers, A. I.; Knaus, G. *J. Am. Chem. Soc.* **1974,** *96*, 6508–6510. (c) Meyers, A. I.; Knaus, G. *Tetrahedron Lett.* **1974,** *15,* 1333–1336. (d) Meyers, A. I.; Whitten, C. E. *J. Am. Chem. Soc.* **1975,** *97*, 6266–6267. (e) Meyers, A. I.; Mihelich, E. D. *J. Org. Chem.* **1975,** *40,* 1186–1187. (f) Meyers, A. I.; Mihelich, E. D. *Angew. Chem. Int. Ed.* **1976,** *15*, 270–271. (Review). (g) Meyers, A. I. *Acc. Chem. Res.* **1978,** *11*, 375–381. (Review).
2. Meyers, A. I.; Yamamoto, Y.; Mihelich, E. D.; Bell, R. A. *J. Org. Chem.* **1980,** *45*, 2792–2796.
3. Meyers, A. I., Lutomski, K. A. In *Asymmetric Synthesis*, Morrison, J. D. Ed.; Vol III, Part B, Chapter 3, Academic Press, **1983**. (Review).
4. Reuman, M.; Meyers, A. I. *Tetrahedron* **1985,** *41*, 837–860. (Review).
5. Robichaud, A. J.; Meyers, A. I. *J. Org. Chem.* **1991,** *56*, 2607–2609.
6. Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994,** 50, 2297–2360. (Review).
7. Meyers, A. I. *J. Heterocycl. Chem*. **1998,** 35, 991–1002. (Review).
8. Wolfe, J. P. *Meyers Oxazoline Method*. In *Name Reactions in Heterocycl. Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 237–248. (Review).
9. Hogan, A.-M. L.; Tricotet, T.; Meek, A.; Khokhar, S. S.; O'Shea, D. F. *J. Org. Chem.* **2008,** *73*, 6041–6044.

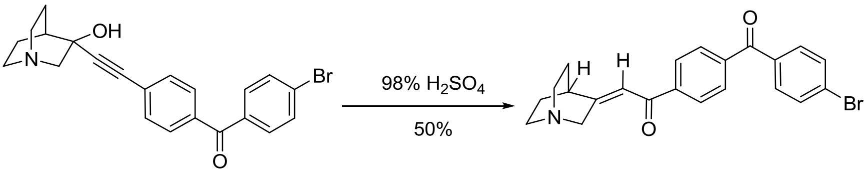
Meyer–Schuster rearrangement

The isomerization of secondary and tertiary α-acetylenic alcohols to α,β-unsaturated carbonyl compounds *via* 1,3-shift. When the acetylenic group is terminal, the products are aldehydes, whereas the internal acetylenes give ketones.
Cf. Rupe rearrangement.

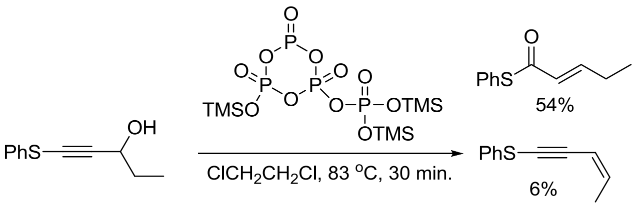




Example 1[6]



Example 2[7]



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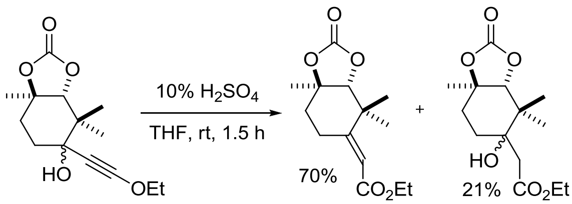

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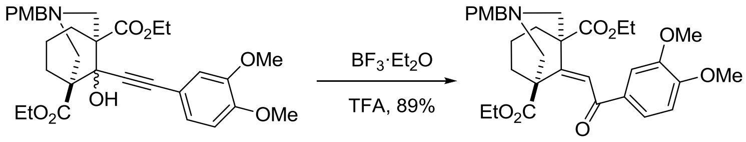
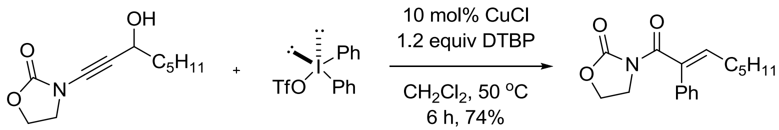
DOI 10.1007/978-3-319-03979-4_172, © Springer International Publishing Switzerland 2014

Example 4[9]



Example 5[11]

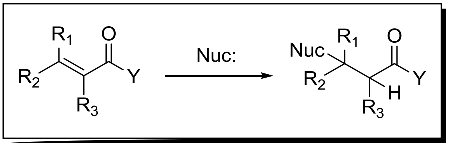


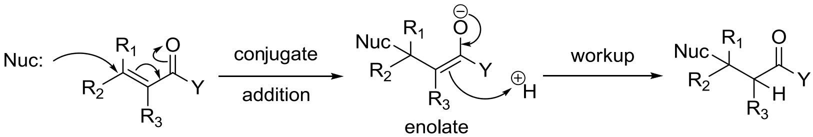
References

1. Meyer, K. H.; Schuster, K. *Ber.* **1922,** *55*, 819–823.
2. Swaminathan, S.; Narayanan, K. V. *Chem. Rev.* **1971,** *71*, 429–438. (Review).
3. Edens, M.; Boerner, D.; Chase, C. R.; Nass, D.; Schiavelli, M. D. *J. Org. Chem.* **1977,** *42*, 3403–3408.
4. Andres, J.; Cardenas, R.; Silla, E.; Tapia, O. *J. Am. Chem. Soc.* **1988,** *110*, 666–674.
5. Tapia, O.; Lluch, J. M.; Cardenas, R.; Andres, J. *J. Am. Chem. Soc.* **1989,** *111*, 829–835.
6. Brown, G. R.; Hollinshead, D. M.; Stokes, E. S.; Clarke, D. S.; Eakin, M. A.; Foubister, A. J.; Glossop, S. C.; Griffiths, D.; Johnson, M. C.; McTaggart, F.; Mirrlees, D. J.; Smith, G. J.; Wood, R. *J. Med. Chem.* **1999,** *42*, 1306–1311.
7. Yoshimatsu, M.; Naito, M.; Kawahigashi, M.; Shimizu, H.; Kataoka, T. *J. Org. Chem.* **1995,** *60*, 4798–4802.
8. Crich, D.; Natarajan, S.; Crich, J. Z. *Tetrahedron* **1997,** *53*, 7139–7158.
9. Williams, C. M.; Heim, R.; Bernhardt, P. V. *Tetrahedron* **2005,** *61*, 3771–3779.
10. Mullins, R. J.; Collins, N. R. *Meyer–Schuster Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 305–318. (Review).
11. Collins, B. S. L.; Suero, M. G.; Gaunt, M. J. *Angew. Chem.* **2013,** *125*, 5911–5914.

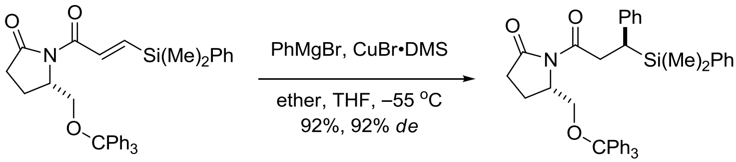
Michael addition

Also known as conjugate addition, Michael addition is the 1,4-addition of a nucleophile to an α,β-unsaturated system.

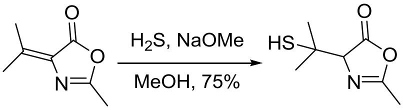




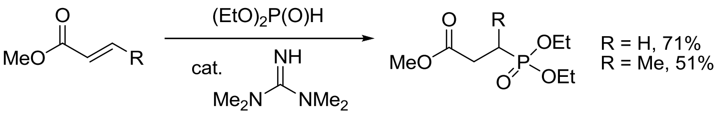
Example 1, Asymmetric Michael addition[2]



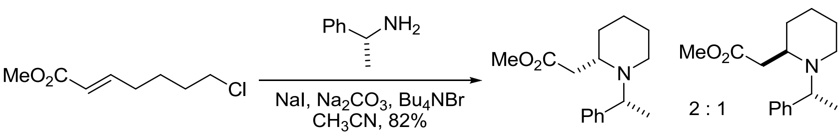
Example 2, Thia-Michael addition[3]



Example 3, Phospha-Michael addition[7]



Example 4, Asymmetric aza-Michael addition[9]



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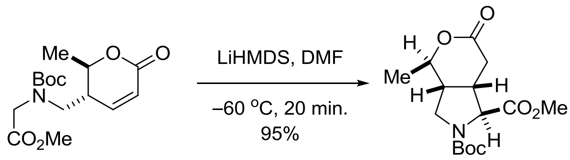
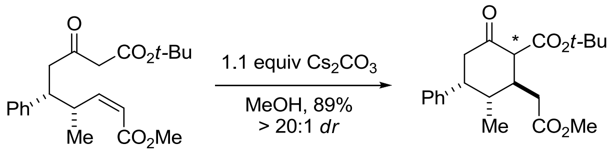
DOI 10.1007/978-3-319-03979-4_173,

Example 5, Intramolecular Michael addition[10]



Example 6, Intramolecular Michael addition[11]

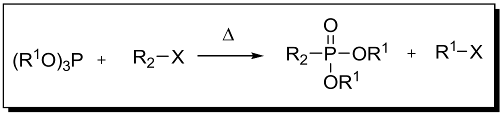


References

1. Michael, A. *J. Prakt. Chem.* **1887,** *35*, 349. Arthur Michael (1853–1942) was born in Buffalo, New York. He studied under Robert Bunsen, August Hofmann, Adolphe Wurtz, and Dimitri Mendeleev, but never bothered to take a degree. Back to the United States, Michael became a Professor of Chemistry at Tufts University, where he married one of his students, Helen Abbott, one of the few female organic chemists in this period. Since he failed miserably as an administrator, Michael and his wife set up their own private laboratory at Newton Center, Massachusetts, where the 1,4-addition was discovered.
2. Hunt, D. A. *Org. Prep. Proced. Int.* **1989,** *21*, 705–749.
3. D'Angelo, J.; Desmaële, D.; Dumas, F.; Guingant, A. *Tetrahedron: Asymmetry* **1992,** *3*, 459–505.
4. Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992,** *41*, 135–631. (Review).
5. Hoz, S. *Acc. Chem. Res.* **1993,** *26*, 69–73. (Review).
6. Ihara, M.; Fukumoto, K. *Angew. Chem. Int. Ed.* **1993,** *32*, 1010–1022. (Review).
7. Simoni, D.; Invidiata, F. P.; Manferdini, M.; Lampronti, I.; Rondanin, R.; Roberti, M.; Pollini, G. P. *Tetrahedron Lett.* **1998,** *39*, 7615–7618.
8. Enders, D.; Saint-Dizier, A.; Lannou, M.-I.; Lenzen, A. *Eur. J. Org. Chem.* **2006,** 29–49. (Review on the phospha-Michael addition).
9. Chen, L.-J.; Hou, D.-R. *Tetrahedron: Asymmetry* **2008,** *19*, 715–720.
10. Sakaguchi, H.; Tokuyama, H.; Fukuyama, T. *Org. Lett.* **2008,** *10*, 1711–1714.
11. Kwan, E. E.; Scheerer, J. R.; Evans, D. A. *J. Org. Chem.* **2013,** *78*, 175–203.

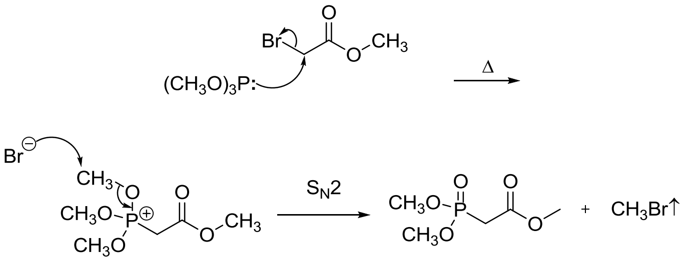
Michaelis–Arbuzov phosphonate synthesis

Aliphatic phosphonate synthesis from the reaction of alkyl halides with phosphites.
General scheme:

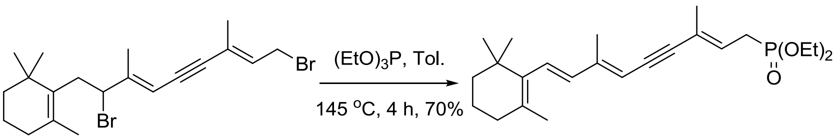


R^1 = alkyl, *etc*.; R_2 = alkyl, acyl, *etc*.; X = Cl, Br, I

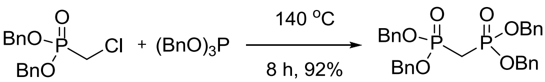
For instance:



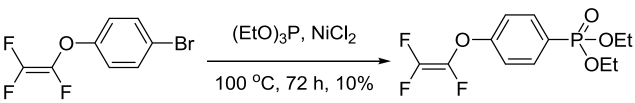
Example 1[2]



Example 2[6]



Example 3, Transition-metal catalyzed coupling, not via S_N2[7]



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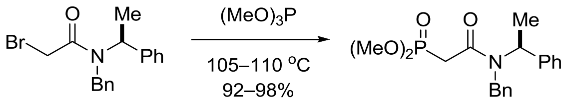
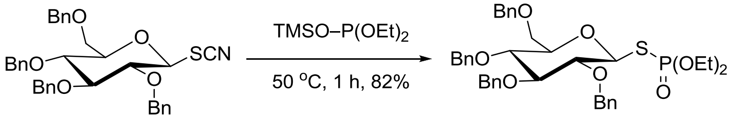
DOI 10.1007/978-3-319-03979-4_174, © Springer International Publishing Switzerland 2014

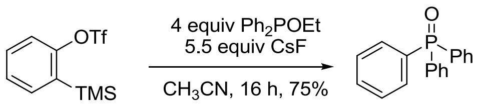
Example 4[9]



Example 5[10]



Example 6, An Approach to prepare aromatic phosphonates[11]

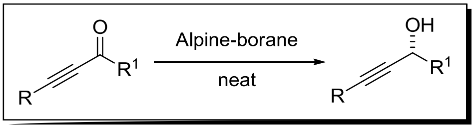


References

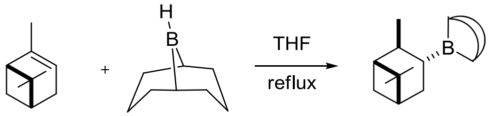
1. (a) Michaelis, A.; Kaehne, R. *Ber.* **1898,** *31,* 1048–1055. (b) Arbuzov, A. E. *J. Russ. Phys. Chem. Soc.* **1906,** *38*, 687.
2. Surmatis, J. D.; Thommen, R. *J. Org. Chem*. **1969,** *34*, 559–560.
3. Gillespie, P.; Ramirez, F.; Ugi, I.; Marquarding, D. *Angew. Chem. Int. Ed.* **1973,** *12*, 91–119. (Review).
4. Waschbűsch, R.; Carran, J.; Marinetti, A.; Savignac, P. *Synthesis* **1997,** 727–743.
5. Bhattacharya, A. K.; Stolz, F.; Schmidt, R. R. *Tetrahedron Lett*. **2001,** *42*, 5393–5395.
6. Erker, T.; Handler, N. *Synthesis* **2004,** 668–670.
7. Souzy, R.; Ameduri, B.; Boutevin, B.; Virieux, D. *J. Fluorine Chem*. **2004,** *125*, 1317–1324.
8. Kadyrov, A. A.; Silaev, D. V.; Makarov, K. N.; Gervits, L. L.; Röschenthaler, G.-V. *J. Fluorine Chem*. **2004,** *125*, 1407–1410.
9. Ordonez, M.; Hernandez-Fernandez, E.; Montiel-Perez, M.; Bautista, R.; Bustos, P.; Rojas-Cabrera, H.; Fernandez-Zertuche, M.; Garcia-Barradas, O. *Tetrahedron: Asymmetry* **2007,** *18*, 2427–2436.
10. Piekutowska, M.; Pakulski, Z. *Carbohydrate Res*. **2008,** *343*, 785–792.
11. Dhokale, R. A.; Mhaske, S. B. *Org. Lett.* **2013,** *15*, 2218–2221.

Midland reduction

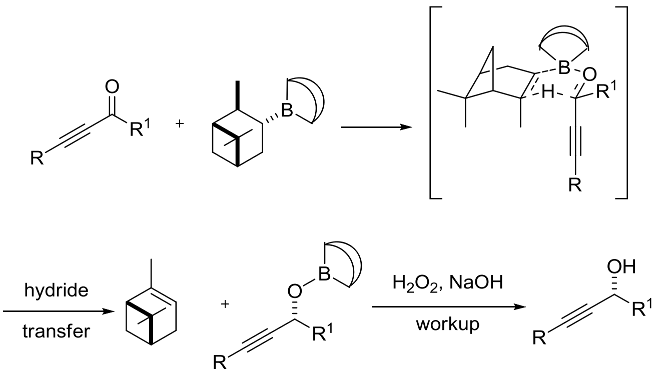
Asymmetric reduction of ketones using Alpine-borane®.
Alpine-borane® = *B*-isopinocampheyl-9-borabicyclo[3.3.1]nonane.



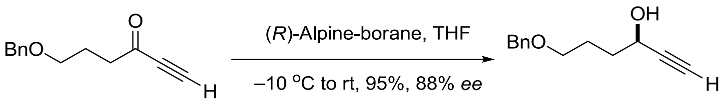
Preparation:



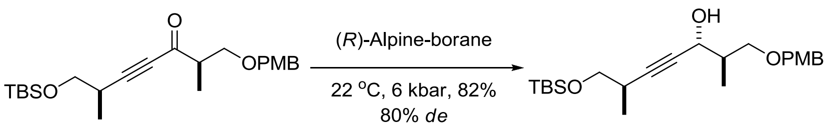
(1*R*)-(+)-α-pinene 9-BBN (*R*)-Alpine-borane
9-BBN = 9-borabicyclo[3.3.1]nonane



Example 1[6]



Example 2[7]



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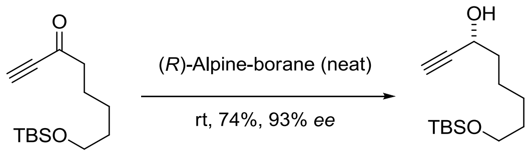
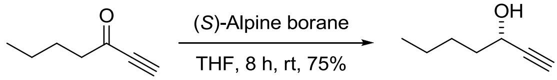
DOI 10.1007/978-3-319-03979-4_175, © Springer International Publishing Switzerland 2014

Example 3[8]



Example 4[10]

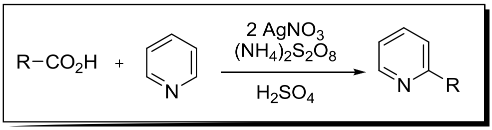


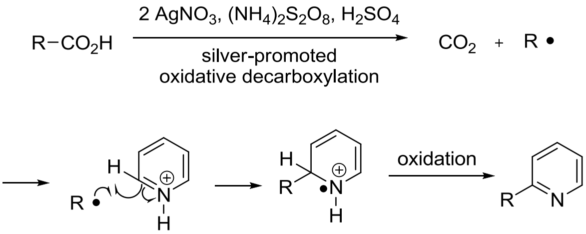
References

1. Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc*. **1979,** *101*, 2352−2355. M. Mark Midland was a professor at the University of California, Riverside.
2. Midland, M. M.; McDowell, D. C.; Hatch, R. L.; Tramontano, A. *J. Am. Chem. Soc*. **1980,** *102*, 867−869.
3. Brown, H. C.; Pai, G. G. *J. Org. Chem*. **1982,** *47*, 1606−1608.
4. Brown, H. C.; Pai, G. G.; Jadhav, P. K. *J. Am. Chem. Soc*. **1984,** *106*, 1531−1533.
5. Singh, V. K. *Synthesis* **1992,** 605−617. (Review).
6. Williams, D. R.; Fromhold, M. G.; Earley, J. D. *Org. Lett.* **2001,** *3*, 2721−2724.
7. Mulzer, J.; Berger, M. *J. Org. Chem*. **2004,** *69*, 891−898.
8. Kiewel, K.; Luo, Z.; Sulikowski, G. A. *Org. Lett.* **2005,** *7*, 5163−5165.
9. Clay, J. M. *Midland reduction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 40–45. (Review).
10. Ramesh, D.; Shekhar, V.; Chantibabu, D.; Rajaram, S.; Ramulu, U.; Venkateswarlu, Y. *Tetrahedron Lett.* **2012,** *53*, 1258−1260.

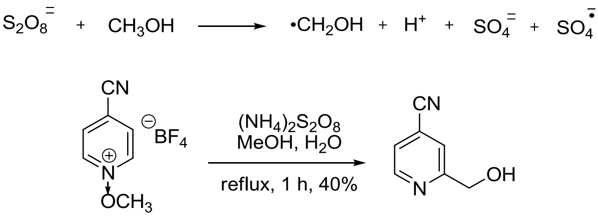
Minisci reaction

Radical-based carbon–carbon bond formation with electron-deficient heteroaromatics. The reaction entails an intermolecular addition of a nucleophilic *radical* to protonated heteroaromatic nucleus.

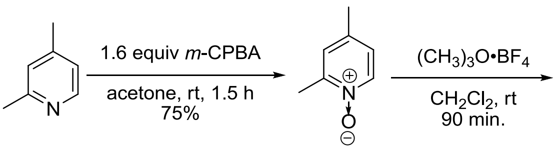




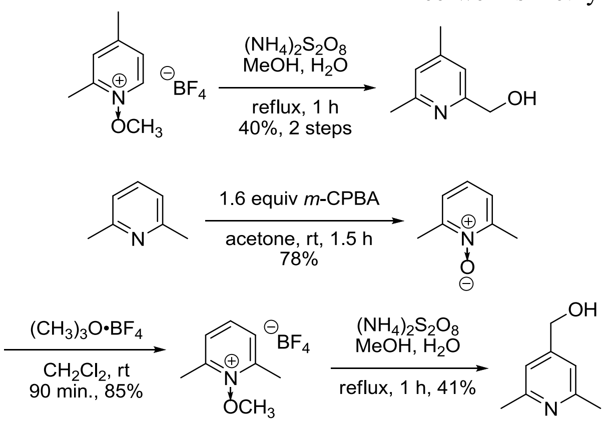
Example 1[4]



Example 2[5]



Meerwein's methylating reagent



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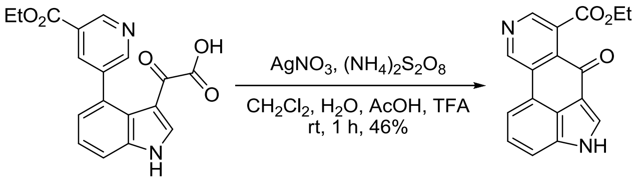
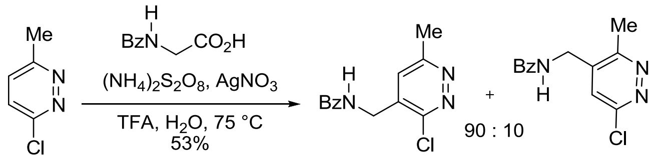
DOI 10.1007/978-3-319-03979-4_176, © Springer International Publishing Switzerland 2014

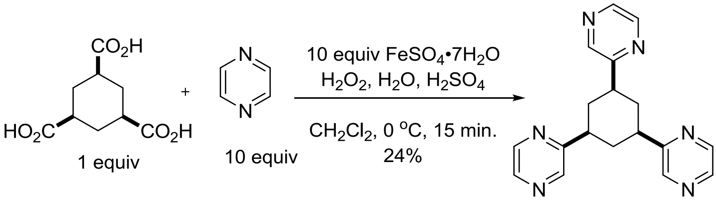
Example 3, Intramolecular Minisci reaction[6]



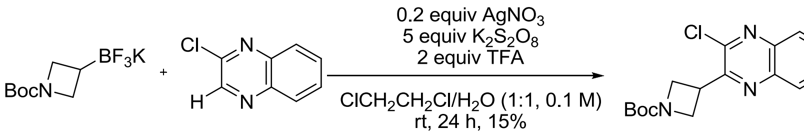
Example 4[7]



Example 5[10]



Example 6[12]

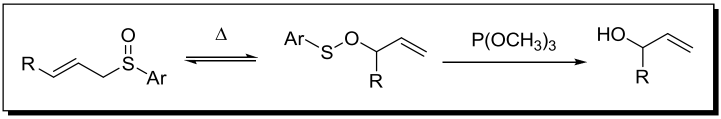


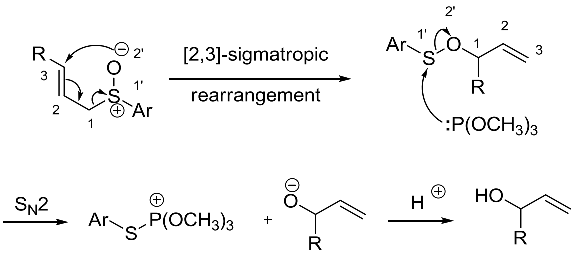
References

1. Minisci, F, Bernardi. R, Bertini, F, Galli, R, Perchinummo, M. *Tetrahedron* **1971,** *27*, 3575–3579.
2. Minisci, F. *Synthesis* **1973,** 1–24. (Review).
3. Minisci, F. *Acc. Chem. Res*. **1983,** *16*, 27–32. (Review).
4. Katz, R. B.; Mistry, J.; Mitchell, M. B. *Synth. Commun*. **1989,** *19*, 317–325.
5. Biyouki, M. A. A.; Smith, R. A. J.; Bedford, J. J.; Leader, J. P. *Synth. Commun*. **1998,** *28*, 3817–3825.
6. Doll, M. K. H. *J. Org. Chem*. **1999,** *64*, 1372–1374.
7. Cowden, C. J. *Org. Lett.* **2003,** *5*, 4497–4499.
8. Kast, O.; Bracher, F. *Synth. Commun*. **2003,** *33*, 3843–3850.
9. Benaglia, M.; Puglisi, A.; Holczknecht, O.; Quici, S.; Pozzi, G. *Tetrahedron* **2005,** *61*, 12058–12064.
10. Palde, P. B.; McNaughton, B. R.; Ross, N. T.; Gareiss, P. C.; Mace, C. R.; Spitale, R. C.; Miller, B. L. *Synthesis* **2007,** 2287–2290.
11. Brebion, F.; Nàjera, F.; Delouvrié, B.; Lacôte, E.; Fensterbank, L.; Malacria, M. *J. Heterocycl. Chem.* **2008,** *45*, 527–532.
12. Presset, M.; Fleury-Brégeot, N.; Oehlrich, D.; Rombouts, F.; Molander, G. A. *J. Org. Chem*. **2013,** *78*, 4615–4619.

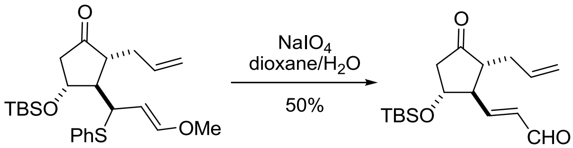
Mislow–Evans rearrangement

[2,3]-Sigmatropic rearrangement followed by reduction of allylic sulfoxide to allylic alcohol.

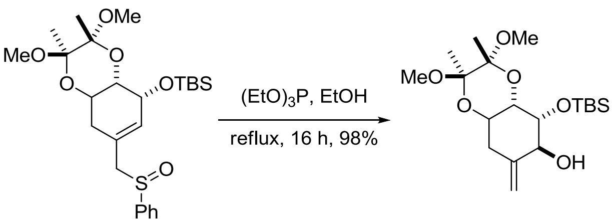




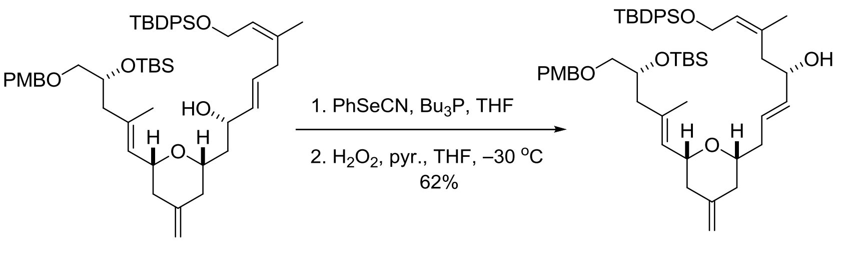
Example 1[2]



Example 2[7]



Example 3, Seleno-Mislow–Evans[8]



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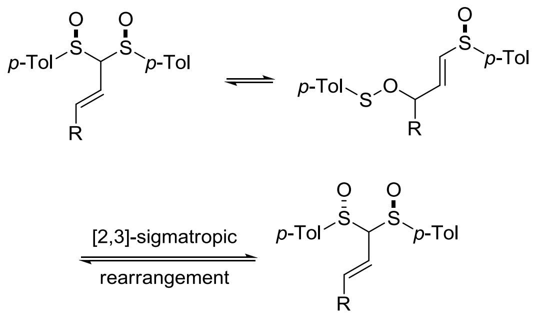
DOI 10.1007/978-3-319-03979-4_177, © Springer International Publishing Switzerland 2014

Example 4[12]

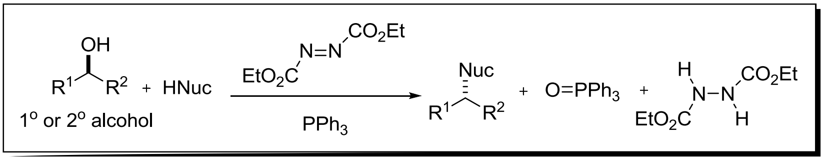


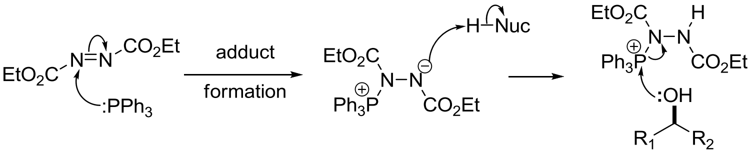
References

1. (a) Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1970,** *92*, 2100–2104. (b) Evans, D. A.; Andrews, G. C.; Sims, C. L. *J. Am. Chem. Soc.* **1971,** *93*, 4956–4957. (c) Evans, D. A.; Andrews, G. C. *J. Am. Chem. Soc.* **1972,** *94*, 3672–3674. (d) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974,** *7*, 147–155. (Review).
2. Sato, T.; Shima, H.; Otera, J. *J. Org. Chem*. **1995,** *60*, 3936–3937.
3. Jones-Hertzog, D. K.; Jorgensen, W. L. *J. Am. Chem. Soc*. **1995,** *117*, 9077–9078.
4. Jones-Hertzog, D. K.; Jorgensen, W. L. *J. Org. Chem*. **1995,** *60*, 6682–6683.
5. Mapp, A. K.; Heathcock, C. H. *J. Org. Chem*. **1999,** *64*, 23–27.
6. Zhou, Z. S.; Flohr, A.; Hilvert, D. *J. Org. Chem*. **1999,** *64*, 8334–8341.
7. Shinada, T.; Fuji, T.; Ohtani, Y.; Yoshida, Y.; Ohfune, Y. *Synlett* **2002,** 1341–1343.
8. Aubele, D. L.; Wan, S.; Floreancig, P. E. *Angew. Chem. Int. Ed.* **2005,** *44*, 3485–3499.
9. Albert, B. J.; Sivaramakrishnan, A.; Naka, T.; Koide, K. *J. Am. Chem. Soc.* **2006,** *128*, 2792–2793.
10. Pelc, M. J.; Zakarian, A. *Tetrahedron Lett.* **2006,** *47*, 7519–7523.
11. Brebion, F.; Najera, F.; Delouvrie, B.; Lacote, E.; Fensterbank, L.; Malacria, M. *Synthesis* **2007,** 2273–2278.
12. Palko, J. W.; Buist, P. H.; Manthorpe, J. M. *Tetrahedron: Assmmetry* **2013,** *24*, 165–168.

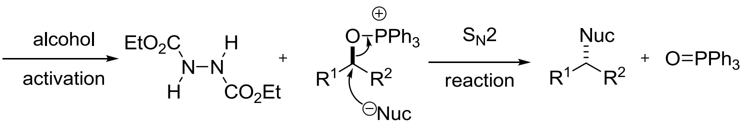
Mitsunobu reaction

S_N2 inversion of an alcohol by a nucleophile using disubstituted azodicarboxylates (originally, diethyl diazodicarboxylate, or DEAD) and trisubstituted phosphines (originally, triphenylphosphine).

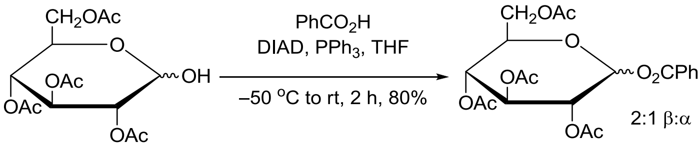




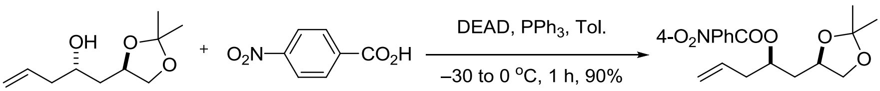
Diethyl azodicarboxylate (DEAD)



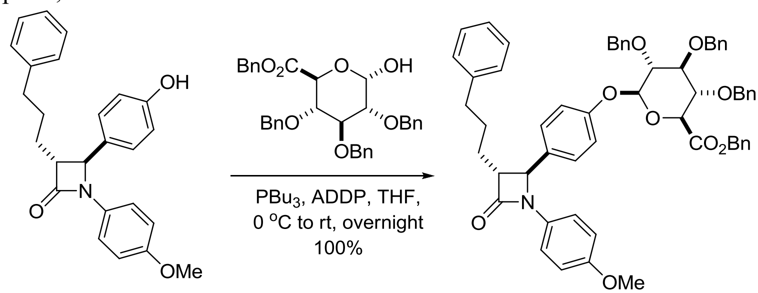
Example 1[2]



Example 2[3]



Example 3, Ether formation[6]



ADDP = 1,1'-(azodicarbonyl)dipiperidine

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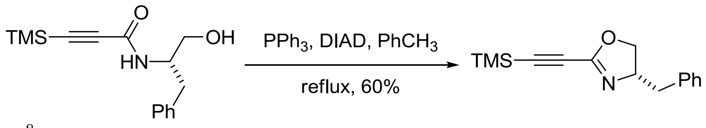
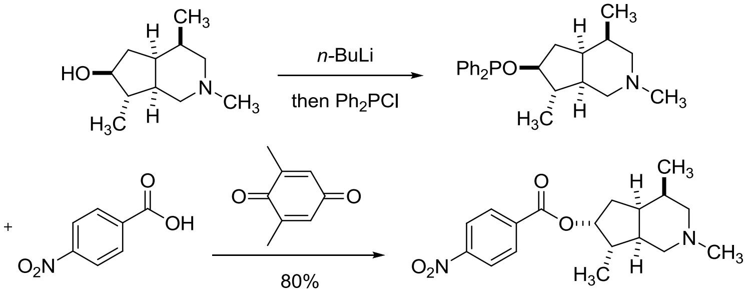
DOI 10.1007/978-3-319-03979-4_178,

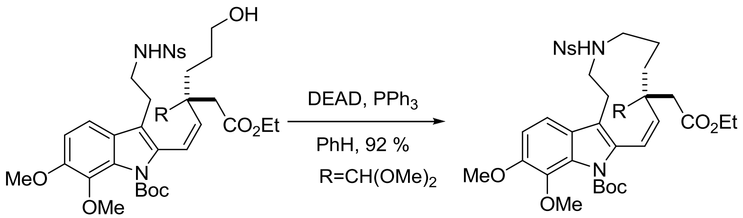
Example 4[7]



Example 5[8]



Example 6, Intramolecular Mitsunobu reaction[9]

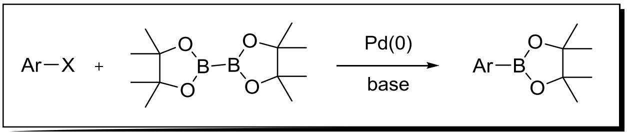


References

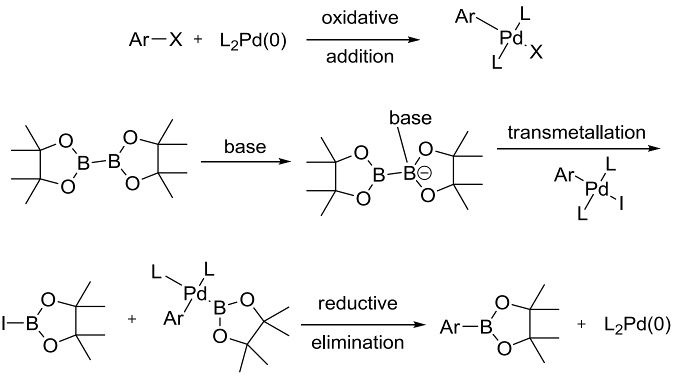
1. (a) Mitsunobu, O.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1967,** *40*, 2380–2382. (b) Mitsunobu, O. *Synthesis* **1981,** 1–28. (Review).
2. Smith, A. B., III; Hale, K. J.; Rivero, R. A. *Tetrahedron Lett*. **1986,** *27*, 5813–5816.
3. Kocieński, P. J.; Yeates, C.; Street, D. A.; Campbell, S. F. *J. Chem. Soc., Perkin Trans. 1*, **1987,** 2183–2187.
4. Hughes, D. L. *Org. React.* **1992,** *42*, 335–656. (Review).
5. Hughes, D. L. *Org. Prep. Proc. Int.* **1996,** *28*, 127–164. (Review).
6. Vaccaro, W. D.; Sher, R.; Davis, H. R., Jr. *Bioorg. Med. Chem. Lett.* **1998,** *8*, 35–40.
7. Cevallos, A.; Rios, R.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron: Asymmetry* **2000,** *11*, 4407–4416.
8. Mukaiyama, T.; Shintou, T.; Fukumoto, K. *J. Am. Chem. Soc.* **2003,** *125*, 10538–10539.
9. Sumi, S.; Matsumoto, K.; Tokuyama, H.; Fukuyama, T. *Tetrahedron* **2003,** *59*, 8571–8587.
10. Christen, D. P. *Mitsunobu reaction*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 671–748. (Review).
11. Ganesan, M.; Salunke, R. V.; Singh, N.; Ramesh, N. G. *Org. Biomol. Chem.* **2013,** *11*, 559–611.

Miyaura borylation

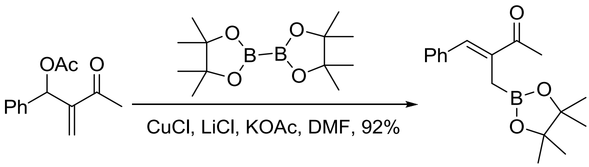
Palladium-catalyzed reaction of aryl halides with diboron reagents to produce arylboronates. Also known as Hosomi–Miyaura borylation.



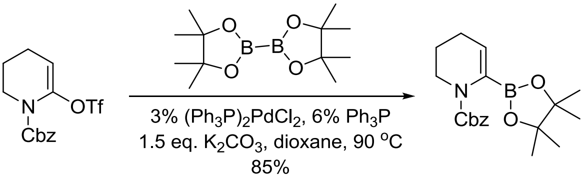
X = I, Br, Cl, OTf.



Example 1[7]



Example 2[8]



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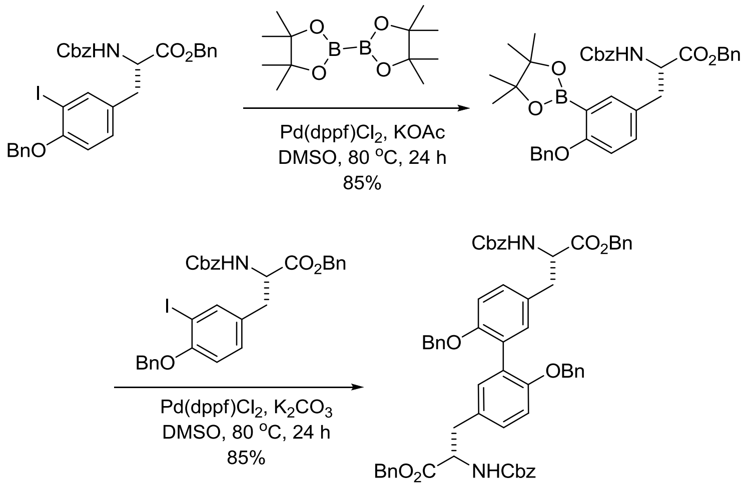
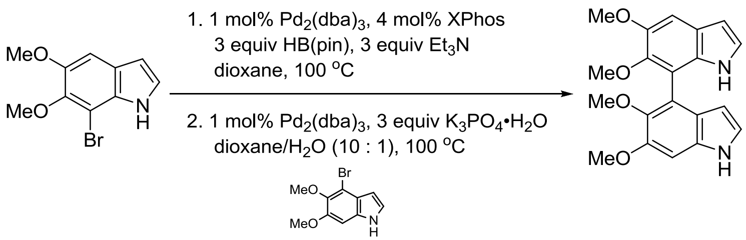
Example 3[9]



Example 4, One-pot synthesis of biindolyl[10]

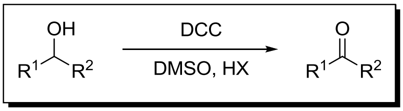


References

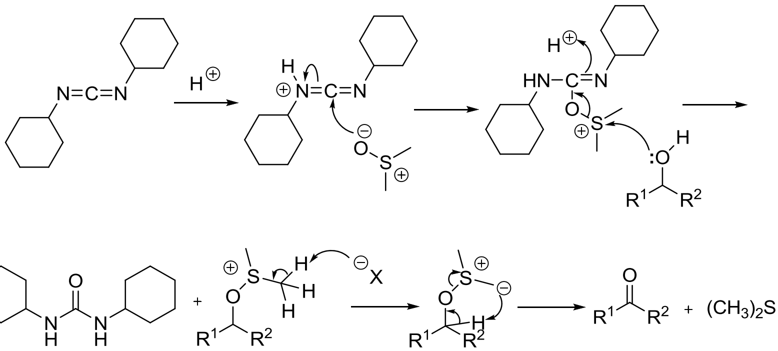
1. Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995,** *60*, 7508–7510.
2. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995,** *95*, 2457–2483. (Review).
3. Suzuki, A. *J. Organomet. Chem.* **1995,** *576*, 147–168. (Review).
4. Carbonnelle, A.-C.; Zhu, J. *Org. Lett.* **2000,** *2*, 3477–3480.
5. Giroux, A. *Tetrahedron Lett.* **2003,** *44*, 233–235.
6. Kabalka, G. W.; Yao, M.-L. *Tetrahedron Lett.* **2003,** *44*, 7885–7887.
7. Ramachandran, P. V.; Pratihar, D.; Biswas, D.; Srivastava, A.; Reddy, M. V. R. *Org. Lett.* **2004,** *6*, 481–484.
8. Occhiato, E. G.; Lo Galbo, F.; Guarna, A. *J. Org. Chem.* **2005,** *70*, 7324–7330.
9. Skaff, O.; Jolliffe, K. A.; Hutton, C. A. *J. Org. Chem.* **2005,** *70*, 7353–7363.
10. Duong, H. A.; Chua, S.; Huleatt, P. B.; Chai, C. L. L. *J. Org. Chem.* **2008,** *73*, 9177–9180.
11. Jo, T. S.; Kim, S. H.; Shin, J.; Bae, C. *J. Am. Chem. Soc.* **2009,** *131*, 1656–1657.
12. Marciasini, L. D.; Richy, N.; Vaultier, M.; Pucheault, M. *Adv. Synth. Cat.* **2013,** *355*, 1083–1088.

Moffatt oxidation

Oxidation of alcohols using DCC and DMSO, aka "Pfitzner–Moffatt oxidation".

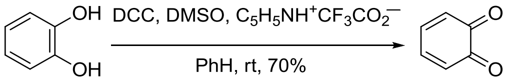


DCC =1,3-dicyclohexylcarbodiimide

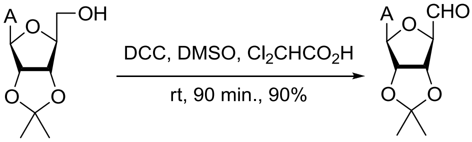


1,3-dicyclohexylurea

Example 1[2]

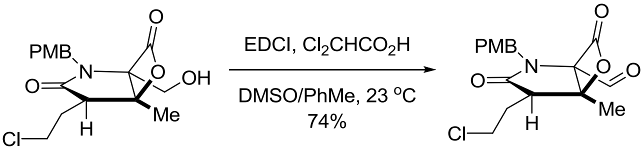


Example 2[8]



A = adenosine

Example 3[10]



EDCI = 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide

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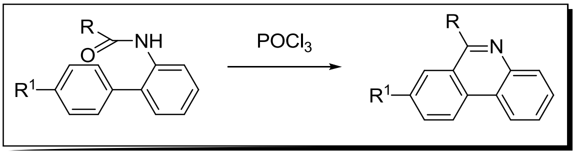
DOI 10.1007/978-3-319-03979-4_180, © Springer International Publishing Switzerland 2014

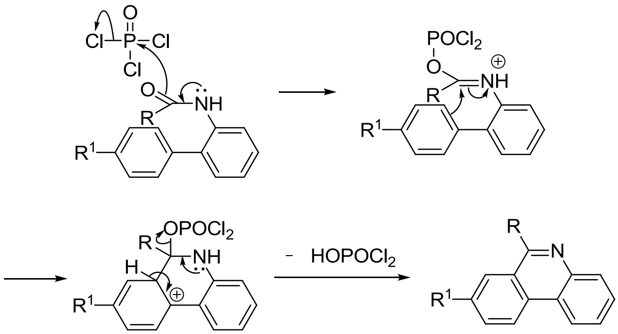
References

1. Pfitzner, K. E.; Moffatt, J. G. *J. Am. Chem. Soc.* **1963,** *85*, 3027–3028.
2. Schobert, R. *Synthesis* **1987,** 741–742.
3. Liu, H. J.; Nyangulu, J. M. *Tetrahedron Lett.* **1988,** *29*, 3167–3170.
4. Tidwell, T. T. *Org. React.* **1990,** *39*, 297–572. (Review).
5. Gordon, J. F.; Hanson, J. R.; Jarvis, A. G.; Ratcliffe, A. H. *J. Chem. Soc., Perkin Trans. 1*, **1992,** 3019–3022.
6. Krysan, D. J.; Haight, A. R. *Org. Prep. Proced. Int.* **1993,** *25*, 437–443.
7. Adak, A. K. *Synlett* **2004,** 1651–1652.
8. Wang, M.; Zhang, J.; Andrei, D.; Kuczera, K.; Borchardt, R. T.; Wnuk, S. F. *J. Med. Chem.* **2005,** *48*, 3649–3653.
9. van der Linden, J. J. M.; Hilberink, P. W.; Kronenburg, C. M. P.; Kemperman, G. J. *Org. Proc. Res. Dev.* **2008,** *12*, 911–920.
10. Nguyen, H.; Ma, G.; Gladysheva, T.; Fremgen, T.; Romo, D. *J. Org. Chem.* **2011,** *76*, 2–12.

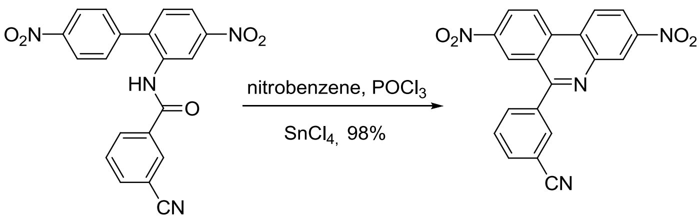
Morgan–Walls reaction

Phenanthridine cyclization by dehydrative ring closure of acyl-*o*-aminobiphenyls with phosphorus oxychloride in boiling nitrobenzene.



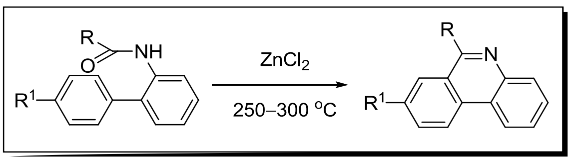


Example 1[6]



Pictet–Hubert reaction

The Pictet-Hubert reaction is a variant of the Morgan-Walls reaction where the phenanthridine cyclization was accomplished by dehydrative ring closure of acyl-*o*-aminobiphenyls on heating with zinc chloride at 250–300 °C.



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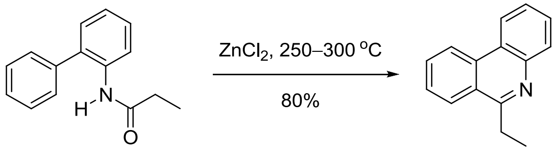
Example 2[4]

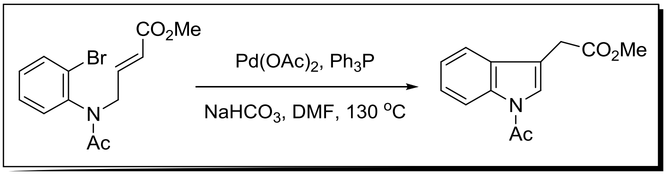


References

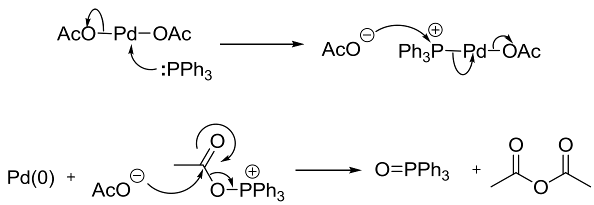
1. (a) Pictet, A.; Hubert, A. *Ber.* **1896,** *29*, 1182–1189. (b) Morgan, C. T.; Walls, L. P. *J. Chem. Soc.* **1931,** 2447–2456. (c) Morgan, C. T.; Walls, L. P. *J. Chem. Soc.* **1932,** 2225–2231.
2. Gilman, H.; Eisch, J. *J. Am. Chem. Soc.* **1957,** *79*, 4423–4426.
3. Hollingsworth, B. L.; Petrow, V. *J. Chem. Soc.* **1961,** 3664–3667.
4. Fodor, G.; Nagubandi, S. *Tetrahedron* **1980,** *36*, 1279–1300.
5. Atwell, G. J.; Baguley, B. C.; Denny, W. A. *J. Med. Chem.* **1988,** *31*, 774–779.
6. Peytou, V.; Condom, R.; Patino, N.; Guedj, R.; Aubertin, A.-M.; Gelus, N.; Bailly, C.; Terreux, R.; Cabrol-Bass, D. *J. Med. Chem.* **1999,** *42*, 4042–4043.
7. Holsworth, D. D. *Pictet–Hubert Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 465–468. (Review).

Mori–Ban indole synthesis

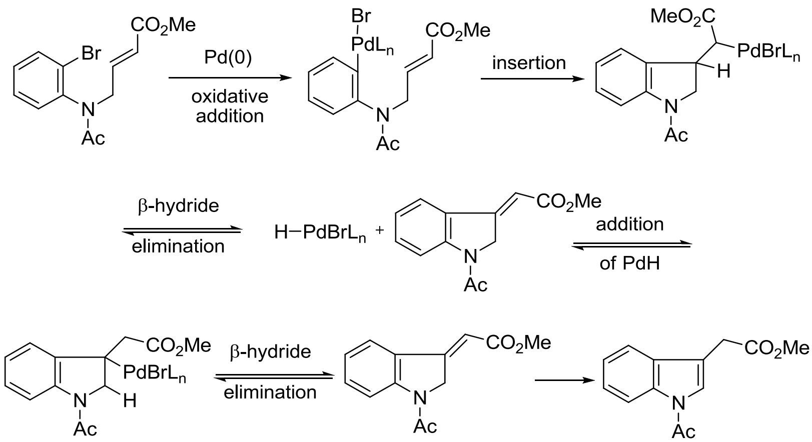
Intramolecular Heck reaction of *o*-halo-aniline with pendant olefin to prepare indole.



Reduction of $Pd(OAc)_2$ to Pd(0) using Ph_3P:



Mori–Ban indole synthesis:



Regeneration of Pd(0):

$$H{-}PdBrL_n + NaHCO_3 \longrightarrow Pd(0) + NaBr + H_2O + CO_2\uparrow$$

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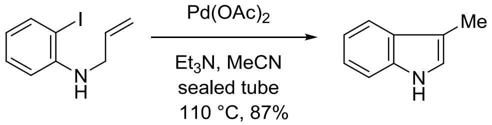
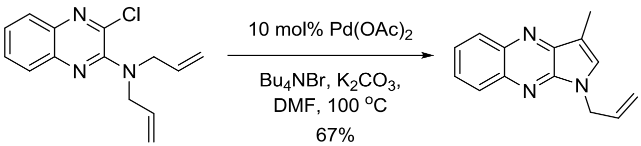
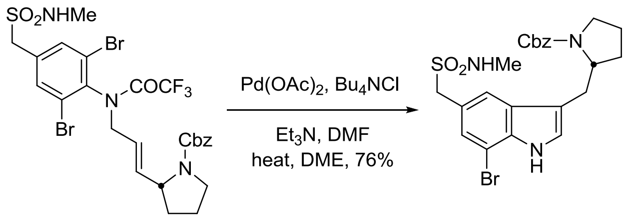
Example 1[1a]



Example 2[4]



Example 3[7]

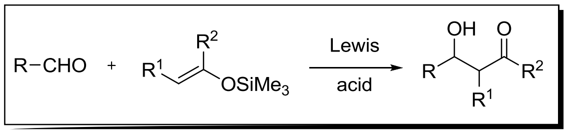


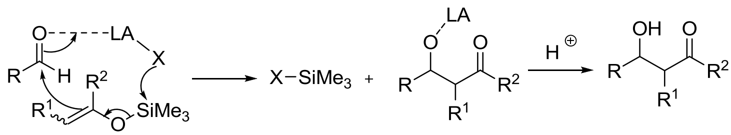
References

1. Mori–Ban indole synthesis, (a) Mori, M.; Chiba, K.; Ban, Y. *Tetrahedron Lett.* **1977,** *18*, 1037–1040; (b) Ban, Y.; Wakamatsu, T.; Mori, M. *Heterocycles* **1977,** *6,* 1711–1715.
2. Reduction of $Pd(OAc)_2$ to Pd(0), (a) Amatore, C.; Carre, E.; Jutand, A.; M'Barki, M. A.; Meyer, G. *Organometallics* **1995,** *14*, 5605–5614; (b) Amatore, C.; Carre, E.; M'Barki, M. A. *Organometallics* **1995,** *14*, 1818–1826; (c) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992,** *11*, 3009–3013; (d) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991,** *113,* 8375–8384.
3. Macor, J. E.; Ogilvie, R. J.; Wythes, M. J. *Tetrahedron Lett.* **1996,** *37*, 4289–4293.
4. Li, J. J. *J. Org. Chem.* **1999,** *64,* 8425–8427.
5. Gelpke, A. E. S.; Veerman, J. J. N.; Goedheijt, M. S.; Kamer, P. C. J.; van Leuwen, P. W. N. M.; Hiemstra, H. *Tetrahedron* **1999,** *55,* 6657–6670.
6. Sparks, S. M.; Shea, K. J. *Tetrahedron Lett.* **2000,** *41*, 6721–6724.
7. Bosch, J.; Roca, T.; Armengol, M.; Fernandez-Forner, D. *Tetrahedron* **2001,** *57,* 1041–1048.
8. Ma, J.; Yin, W.; Zhou, H.; Liao, X.; Cook, J. M. *J. Org. Chem.* **2009,** *74*, 264–273.
9. Platon, M.; Amardeil, R.; Djakovitch, L.; Hierso, J.-C. *Chem. Soc. Rev.* **2012,** *41*, 3929–3968. (Review).

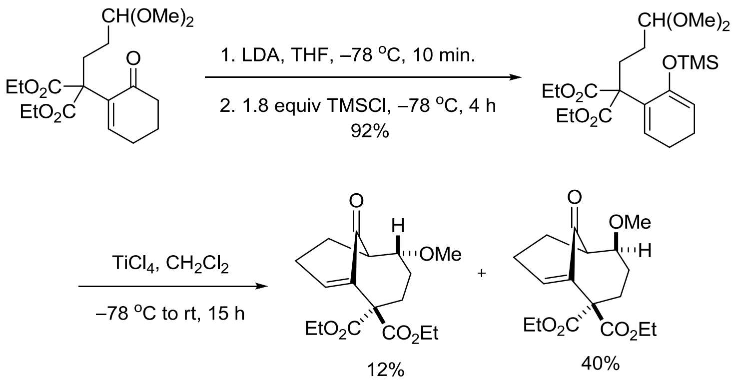
Mukaiyama aldol reaction

Lewis acid-catalyzed aldol condensation of aldehyde and silyl enol ether.

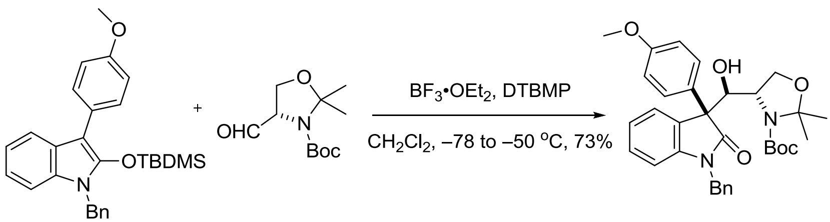




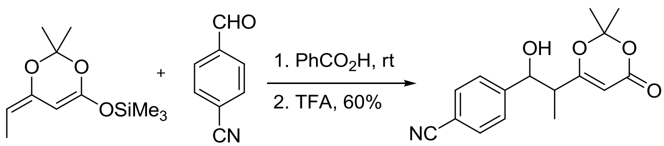
Example 1, Intramolecular Mukaiyama aldol reaction[3]



Example 2, Mukaiyama aldol reaction[7]



Example 3, Vinylogous Mukaiyama aldol reaction[8]



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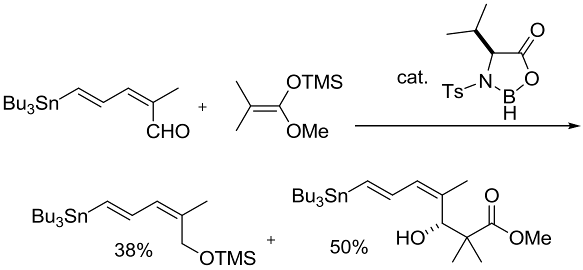
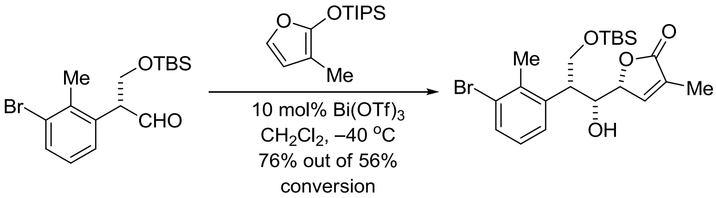
DOI 10.1007/978-3-319-03979-4_183, © Springer International Publishing Switzerland 2014

Example 4, Asymmetric Mukaiyama aldol reaction[10]



Example 5[12]

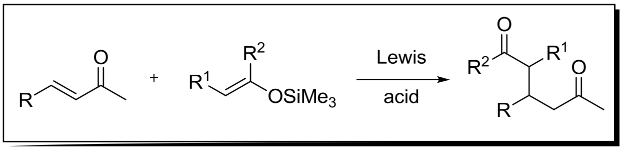


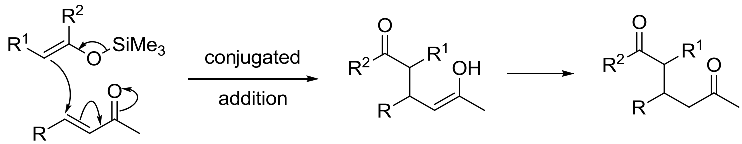
References

1. (a) Mukaiyama, T.; Narasaka, K.; Banno, K. *Chem. Lett.* **1973,** 1011–1014. (b) Mukaiyama, T.; Narasaka, K.; Banno, K. *J. Am. Chem. Soc.* **1974,** *96*, 7503–7509.
2. Ishihara, K.; Kondo, S.; Yamamoto, H. *J. Org. Chem.* **2000,** *65*, 9125–9128.
3. Armstrong, A.; Critchley, T. J.; Gourdel-Martin, M.-E.; Kelsey, R. D.; Mortlock, A. A. *J. Chem. Soc., Perkin Trans. 1* **2002,** 1344–1350.
4. Clézio, I. L.; Escudier, J.-M.; Vigroux, A. *Org. Lett.* **2003,** *5*, 161–164.
5. Ishihara, K.; Yamamoto, H. *Boron and Silicon Lewis Acids for Mukaiyama Aldol Reactions*. In *Modern Aldol Reactions* Mahrwald, R., Ed.; **2004,** 25–68. (Review).
6. Mukaiyama, T. *Angew. Chem. Int. Ed.* **2004,** *43*, 5590–5614. (Review).
7. Adhikari, S.; Caille, S.; Hanbauer, M.; Ngo, V. X.; Overman, L. E. *Org. Lett.* **2005,** *7*, 2795–2797.
8. Acocella, M. R.; Massa, A.; Palombi, L.; Villano, R.; Scettri, A. *Tetrahedron Lett.* **2005,** *46*, 6141–6144.
9. Jiang, X.; Liu, B.; Lebreton, S.; De Brabander, J. K. *J. Am. Chem. Soc.* **2007,** *129*, 6386–6387.
10. Webb, M. R.; Addie, M. S.; Crawforth, C. M.; Dale, J. W.; Franci, X.; Pizzonero, M.; Donald, C.; Taylor, R. J. K. *Tetrahedron* **2008,** *64*, 4778–4791.
11. Frings, M.; Atodiresei, I.; Runsink, J.; Raabe, G.; Bolm, C. *Chem. Eur. J.* **2009,** *15*, 1566–1569.
12. Gao, S.; Wang, Q.; Chen, C. *J. Am. Chem. Soc.* **2009,** *131*, 1410–1412.
13. Matsuo, J.-i.; Murakami, M. *Angew. Chem. Int. Ed.* **2013,** *52*, 9109–9118. (Review).

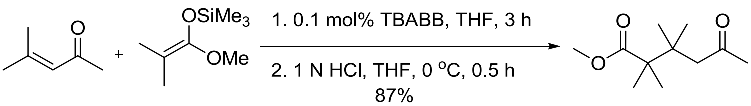
Mukaiyama Michael addition

Lewis acid-catalyzed Michael addition of silyl enol ether to an α,β-unsaturated system.



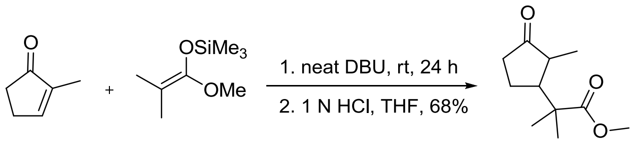


Example 1[2]

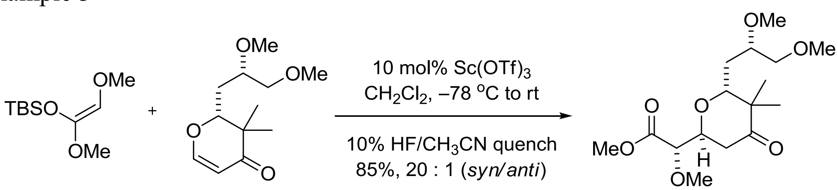


TBABB = tetra-*n*-butylammonium bibenzoate

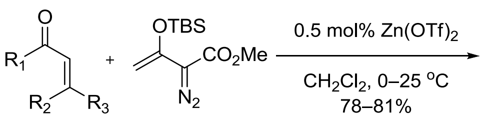
Example 2[5]



Example 3[8]



Example 4[9]



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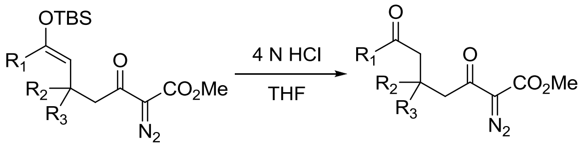
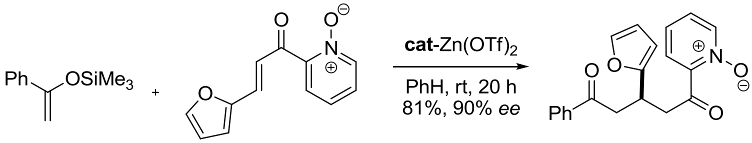
DOI 10.1007/978-3-319-03979-4_184, © Springer International Publishing Switzerland 2014



Example 5, Enantioselective Mukaiyama–Michael reaction[11]



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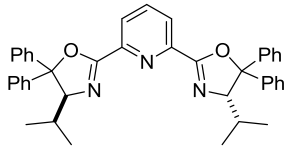
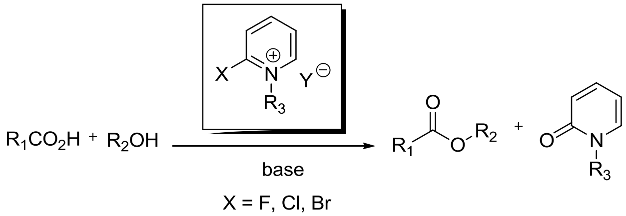


References

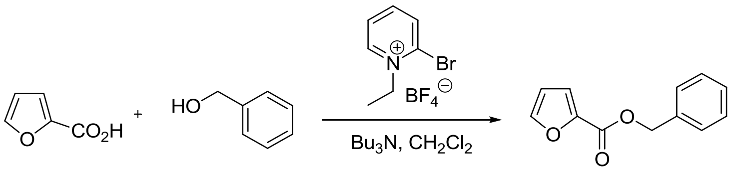
1. (a) Mukaiyama, T.; Narasaka, K.; Banno, K. *Chem. Lett.* **1973,** 1011–1014. (b) Mukaiyama, T.; Narasaka, K.; Banno, K. *J. Am. Chem. Soc.* **1974,** *96*, 7503–7509. (c) Mukaiyama, T. *Angew. Chem. Int. Ed.* **2004,** *43*, 5590–5614. (Review).
2. Gnaneshwar, R.; Wadgaonkar, P. P.; Sivaram, S. *Tetrahedron Lett.* **2003,** *44*, 6047–6049.
3. Wang, X.; Adachi, S.; Iwai, H.; Takatsuki, H.; Fujita, K.; Kubo, M.; Oku, A.; Harada, T. *J. Org. Chem.* **2003,** *68*, 10046–10057.
4. Jaber, N.; Assie, M.; Fiaud, J.-C.; Collin, J. *Tetrahedron* **2004,** *60*, 3075–3083.
5. Shen, Z.-L.; Ji, S.-J.; Loh, T.-P. *Tetrahedron Lett.* **2005,** *46*, 507–508.
6. Wang, W.; Li, H.; Wang, J. *Org. Lett.* **2005,** *7*, 1637–1639.
7. Ishihara, K.; Fushimi, M. *Org. Lett.* **2006,** *8*, 1921–1924.
8. Jewett, J. C.; Rawal, V. H. *Angew. Chem. Int. Ed.* **2007,** *46*, 6502–6504.
9. Liu, Y.; Zhang, Y.; Jee, N.; Doyle, M. P. *Org. Lett.* **2008,** *10*, 1605–1608.
10. Takahashi, A.; Yanai, H.; Taguchi, T. *Chem. Commun.* **2008,** 2385–2387.
11. Rout, S.; Ray, S. K.; Singh, V. K. *Org. Biomol. Chem.* **2013,** *11*, 4537–4545.

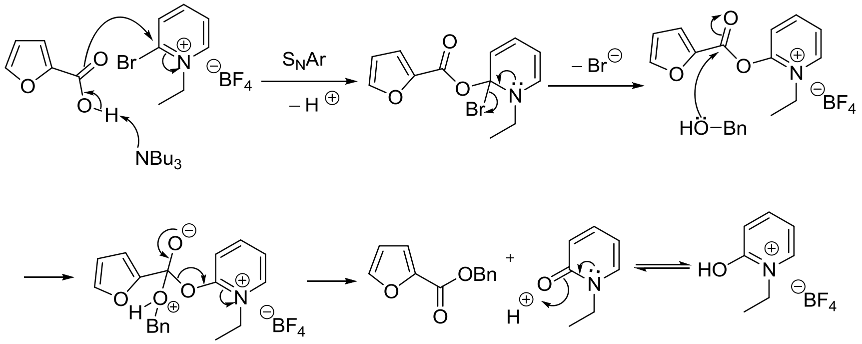
Mukaiyama reagent

Pyridinium halide reagent for esterification or amide formation.
General scheme:

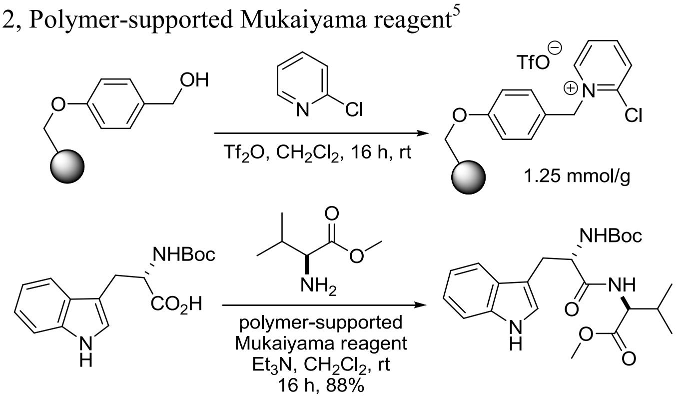


Example 1[1c]





Amide formation using the Mukaiyama reagent follows a similar mechanistic pathway.[1d]
Example 2, Polymer-supported Mukaiyama reagent[5]



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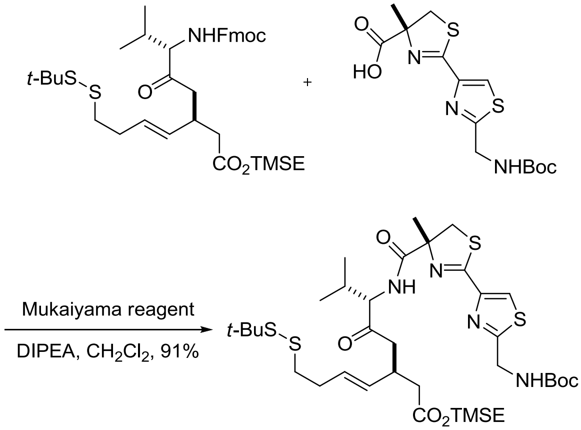
DOI 10.1007/978-3-319-03979-4_185,

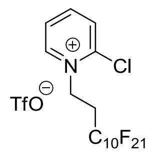
Example 3[9]



Example 4, Fluorous Mukaiyama reagent[10]

$$RCO_2H + R^1NH_2 \text{ or } R^2OH \xrightarrow[\text{2. } H_2O\text{, rt, 5 min., 87–100\%}]{\text{1. Fluorous Mukaiyama reagent, 1 equiv DMAP, 3 equiv } Et_3N\text{, dry DMF, rt, 1h}} RCONHR^1 \text{ or } RCO_2R^2$$

Fluorous Mukaiyama reagent

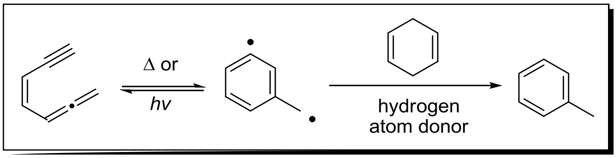


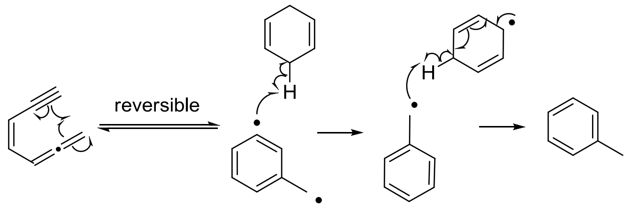
References

1. (a) Mukaiyama, T.; Usui, M.; Shimada, E.; Saigo, K. *Chem. Lett.* **1975,** 1045–1048. (b) Hojo, K.; Kobayashi, S.; Soai, K.; Ikeda, S.; Mukaiyama, T. *Chem. Lett.* **1977,** 635–636. (c) Mukaiyama, T. *Angew. Chem. Int. Ed.* **1979,** *18*, 707–708. (d) For amide formation, see: Huang, H.; Iwasawa, N.; Mukaiyama, T. *Chem. Lett.* **1984,** 1465–1466.
2. Nicolaou, K. C.; Bunnage, M. E.; Koide, K. *J. Am. Chem. Soc*. **1994,** *116*, 8402–8403.
3. Yong, Y. F.; Kowalski, J. A.; Lipton, M. A. *J. Org. Chem*. **1997,** *62*, 1540–1542.
4. Folmer, J. J.; Acero, C.; Thai, D. L.; Rapoport, H. *J. Org. Chem*. **1998,** *63*, 8170–8182.
5. Crosignani, S.; Gonzalez, J.; Swinnen, D. *Org. Lett.* **2004,** *6*, 4579–4582.
6. Mashraqui, S. H.; Vashi, D.; Mistry, H. D. *Synth. Commun*. **2004,** *34*, 3129–3134.
7. Donati, D.; Morelli, C.; Taddei, M. *Tetrahedron Lett.* **2005,** *46*, 2817–2819.
8. Vandromme, L.; Monchaud, D.; Teulade-Fichou, M.-P. *Synlett* **2006,** 3423–3426.
9. Ren, Q.; Dai, L.; Zhang, H.; Tan, W.; Xu, Z.; Ye, T. *Synlett* **2008,** 2379–2383.
10. Matsugi, M.; Suganuma, M.; Yoshida, S.; Hasebe, S.; Kunda, Y.; Hagihara, K.; Oka, S. *Tetrahedron Lett.* **2008,** *49*, 6573–6574.
11. Novosjolova, I. *Synlett* **2013,** *24*, 135–136. (Review).

Myers–Saito cyclization

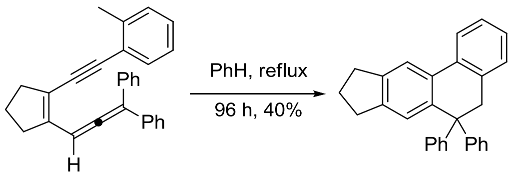
Construction of substituted arenes through the thermal or photochemical cycloaromatization of *allenyl enynes* in the presence of a H· donor such as 1,4-cyclohexadiene. *Cf.* Bergman cyclization and Schmittel cyclization.



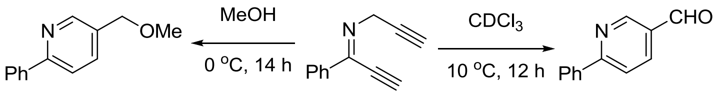


allenyl enyne diradical

Example 1[3]



Example 2, Aza-Myers–Saito reaction[8]



References

1. (a) Myers, A. G.; Proteau, P. J.; Handel, T. M. *J. Am. Chem. Soc.* **1988,** *110,* 7212–7214. (b) Myers, A. G.; Dragovich, P. S.; Kuo, E. Y. *J. Am. Chem. Soc.* **1992,** *114,* 9369–9386.
2. Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995,** *36*, 4975–4978.
3. Schmittel, M.; Steffen, J.-P.; Auer, D.; Maywald, M. *Tetrahedron Lett.* **1997,** *38*, 6177–6180.
4. Bruckner, R.; Suffert, J. *Synlett* **1999,** 657–679. (Review).
5. Stahl, F.; Moran, D.; Schleyer, P. von R.; Prall, M.; Schreiner, P. R. *J. Org. Chem.* **2002,** *67*, 1453–1461.
6. Musch, P. W; Remenyi, C.; Helten, H.; Engels, B. *J. Am. Chem. Soc.* **2002,** *124*, 1823–1828.
7. Bui, B. H.; Schreiner, P. R. *Org. Lett.* **2003,** *5*, 4871–4874.
8. Feng, L.; Kumar, D.; Birney, D. M.; Kerwin, S. M. *Org. Lett.* **2004,** *6*, 2059–2062.
9. Schmittel, M.; Mahajan, A. A.; Bucher, G. *J. Am. Chem. Soc.* **2005,** *127*, 5324–5325.
10. Karpov, G.; Kuzmin, A.; Popik, V. V. *J. Am. Chem. Soc.* **2008,** *130*, 11771–11777.
11. Schmittel, M.; Strittmatter, M.; Vollmann, K. *Tetrahedron Lett.* **2013,** *37*, 999–1002.

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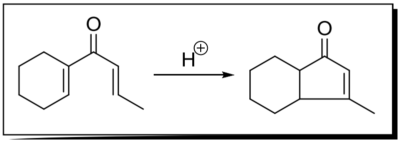
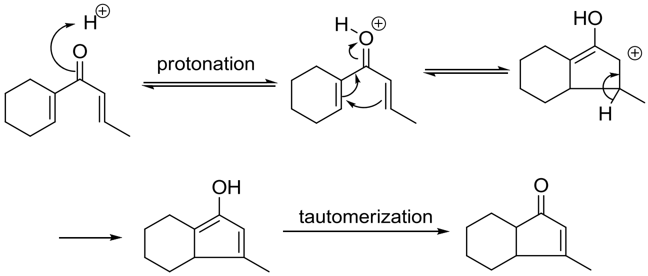
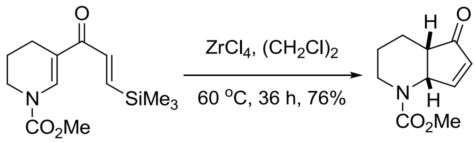
Nazarov cyclization

Acid-catalyzed electrocyclic formation of cyclopentenone from di-vinyl ketone.

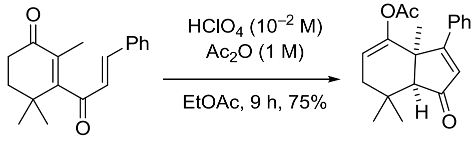




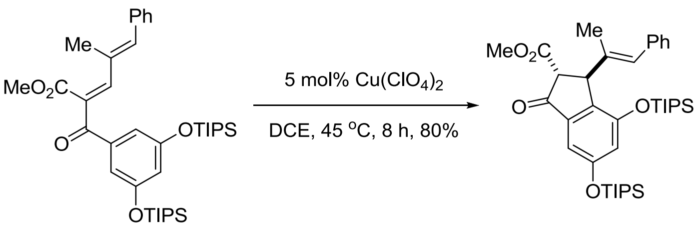
Example 1[2]



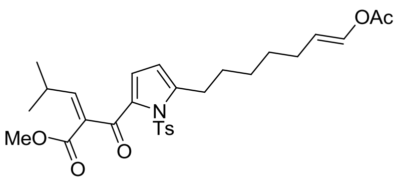
Example 2[6]



Example 3[9]



Example 4[10]



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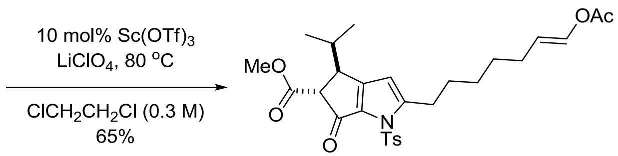
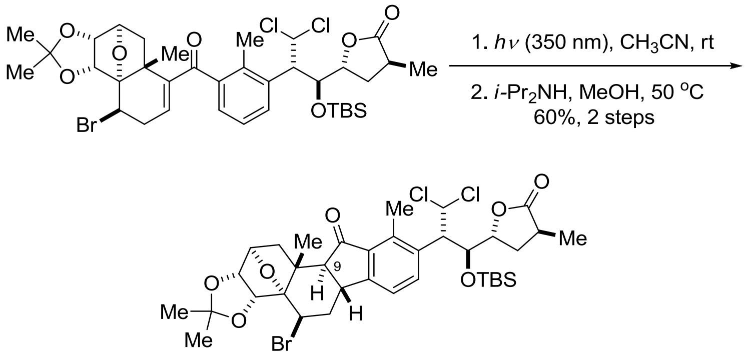
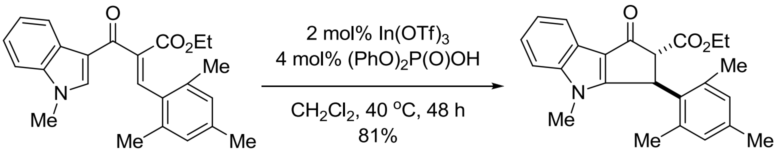
DOI 10.1007/978-3-319-03979-4_187, © Springer International Publishing Switzerland 2014



Example 5, an example with a different mechanism[11]



Example 6[12]

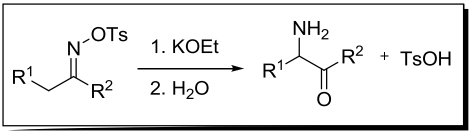


References

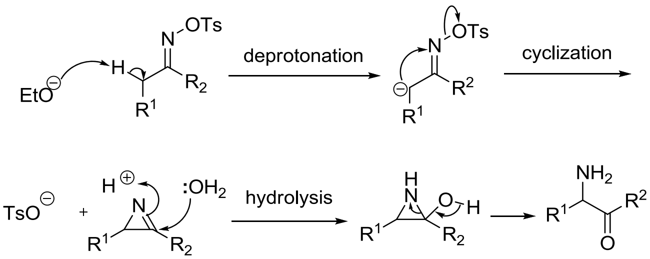
1. Nazarov, I. N.; Torgov, I. B.; Terekhova, L. N. *Bull. Acad. Sci. (USSR)* **1942,** 200. I. N. Nazarov (1900–1957), a Soviet Union Scientist, discovered this reaction in 1942. It was said that almost as many young synthetic chemists have been lost in the pursuit of an asymmetric Nazarov cyclization as of the Bayliss–Hillman reaction.
2. Denmark, S. E.; Habermas, K. L.; Hite, G. A. *Helv. Chim. Acta* **1988,** *71*, 168–194; 195–208.
3. Habermas, K. L.; Denmark, S. E.; Jones, T. K. *Org. React.* **1994,** *45,* 1–158. (Review).
4. Kim, S.-H.; Cha, J. K. *Synthesis* **2000,** 2113–2116.
5. Giese, S.; West, F. G. *Tetrahedron* **2000,** *56*, 10221–10228.
6. Mateos, A. F.; de la Nava, E. M. M.; González, R. R. *Tetrahedron* **2001,** *57*, 1049–1057.
7. Harmata, M.; Lee, D. R. *J. Am. Chem. Soc*. **2002,** *124*, 14328–14329.
8. Leclerc, E.; Tius, M. A. *Org. Lett.* **2003,** *5*, 1171–1174.
9. Marcus, A. P.; Lee, A. S.; Davis, R. L.; Tantillo, D. J.; Sarpong, R. *Angew. Chem. Int. Ed.* **2008,** *47*, 6379–6383.
10. Bitar, A. Y.; Frontier, A. J. *Org. Lett.* **2009,** *11*, 49–52.
11. Gao, S.; Wang, Q.; Chen, C. *J. Am. Chem. Soc*. **2009,** *131*, 1410–1412.
12. Xi, Z.-G.; Zhu, L.; Luo, S.; Cheng, J.-P. *J. Org. Chem.* **2013,** *78*, 606–613.

Neber rearrangement

α-Aminoketone from tosyl ketoxime and base. The net conversion of a ketone into an α-aminoketone *via* the oxime.

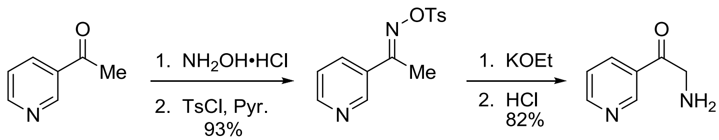


ketoxime α-aminoketone

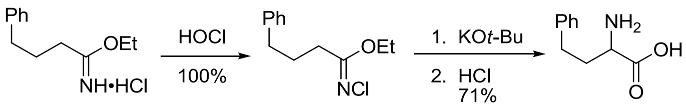


azirine intermediate

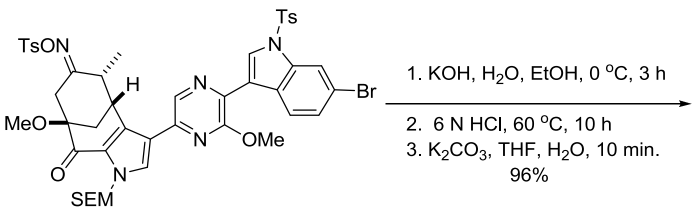
Example 1[3]



Example 2, A variant using iminochloride[5]



Example 3[8]



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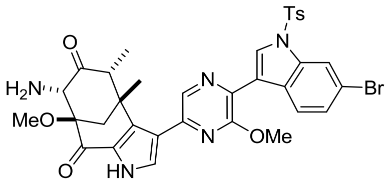
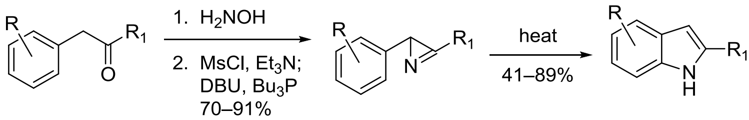
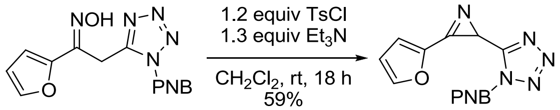


Example 4[9]



Example 5[11]

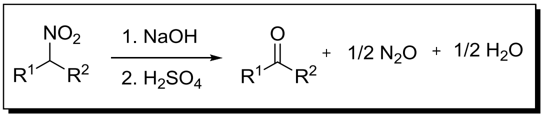


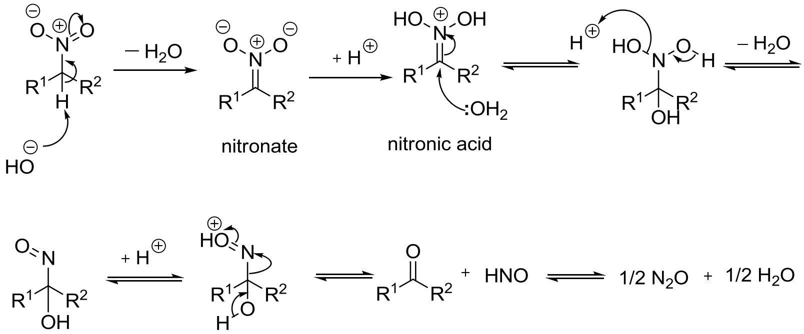
References

1. Neber, P. W.; v. Friedolsheim, A. *Ann.* **1926,** *449*, 109–134.
2. O'Brien, C. *Chem. Rev.* **1964,** *64*, 81–89. (Review).
3. LaMattina, J. L.; Suleske, R. T. *Synthesis* **1980,** 329–330.
4. Verstappen, M. M. H.; Ariaans, G. J. A.; Zwanenburg, B. *J. Am. Chem. Soc.* **1996,** *118*, 8491–8492.
5. Oldfield, M. F.; Botting, N. P. *J. Labeled Compd. Radiopharm.* **1998,** *16*, 29–36.
6. Palacios, F.; Ochoa de Retana, A. M.; Gil, J. I. *Tetrahedron Lett.* **2002,** *41*, 5363-–5366.
7. Ooi, T.; Takahashi, M.; Doda, K.; Maruoka, K. *J. Am. Chem. Soc.* **2002,** *124*, 7640–7641.
8. Garg, N. K.; Caspi, D. D.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005,** *127*, 5970–5978.
9. Taber, D. F.; Tian, W. *J. Am. Chem. Soc.* **2006,** *128*, 1058–1059.
10. Richter, J. M. *Neber Rearrangement*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 464–473. (Review).
11. Cardoso, A. L.; Gimeno, L.; Lemos, A.; Palacios, F.; Teresa, M. V. D.; e Melo, P. *J. Org. Chem.* **2013,** *78*, 6983–6991.

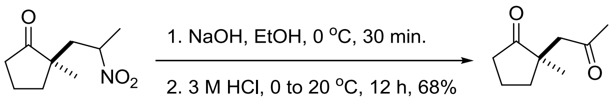
Nef reaction

Conversion of a primary or secondary nitroalkane into the corresponding carbonyl compound.

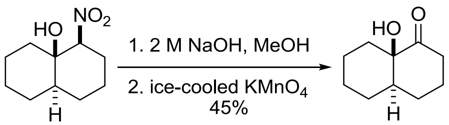




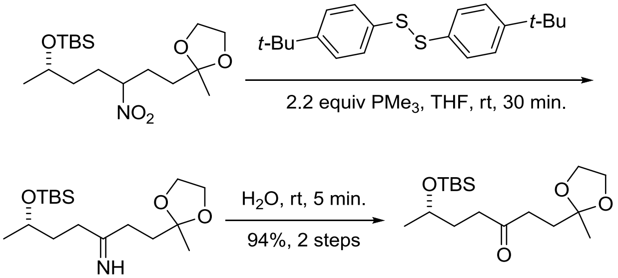
Example 1[4]



Example 2[7]



Example 3[9]



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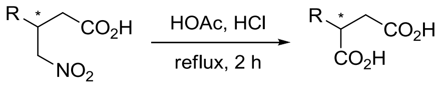
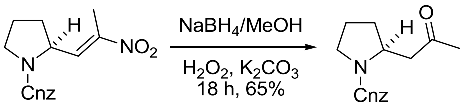
Example 4[10]



Example 5[11]

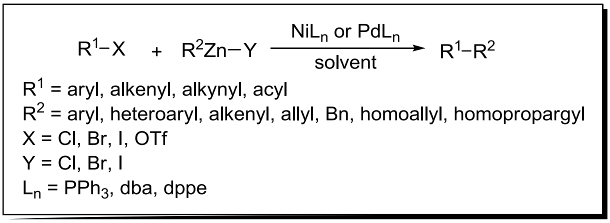


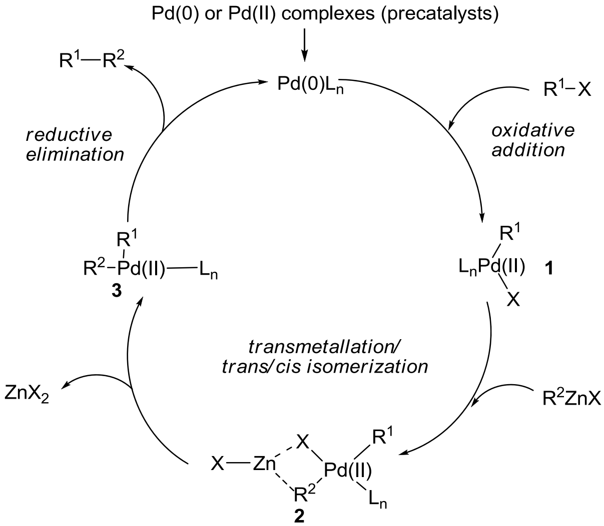
References

1. Nef, J. U. *Ann.* **1894,** *280*, 263–342. John Ulrich Nef (1862–1915) was born in Switzerland and immigrated to the US at the age of four with his parents. He went to Munich, Germany to study with Adolf von Baeyer, earning a Ph.D. In 1886. Back to the States, he served as a professor at Purdue University, Clark University, and the University of Chicago. The Nef reaction was discovered at Clark University in Worcester, Massachusetts. Nef was temperamental and impulsive, suffering from a couple of mental breakdowns. He was also highly individualistic, and had never published with a coworker save for three early articles.
2. Pinnick, H. W. *Org. React.* **1990,** *38*, 655–792. (Review).
3. Adam, W.; Makosza, M.; Saha-Moeller, C. R.; Zhao, C.-G. *Synlett* **1998,** 1335–1336.
4. Thominiaux, C.; Rousse, S.; Desmaele, D.; d'Angelo, J.; Riche, C. *Tetrahedron: Asymmetry* **1999,** *10,* 2015–2021.
5. Capecchi, T.; de Koning, C. B.; Michael, J. P. *J. Chem. Soc., Perkin Trans. 1* **2000,** 2681–2688.
6. Ballini, R.; Bosica, G.; Fiorini, D.; Petrini, M. *Tetrahedron Lett.* **2002,** *43,* 5233–5235.
7. Chung, W. K.; Chiu, P. *Synlett* **2005,** 55–58.
8. Wolfe, J. P. *Nef reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 645–652. (Review).
9. Burés, J.; Vilarrasa, J. *Tetrahedron Lett.* **2008,** *49,* 441–444.
10. Felluga, F.; Pitacco, G.; Valentin, E.; Venneri, C. D. *Tetrahedron: Asymmetry* **2008,** *19,* 945–955.
11. Chinmay Bhat, C.; Tilve, S. G. *Tetrahedron* **2013,** *69,* 6129–6143.

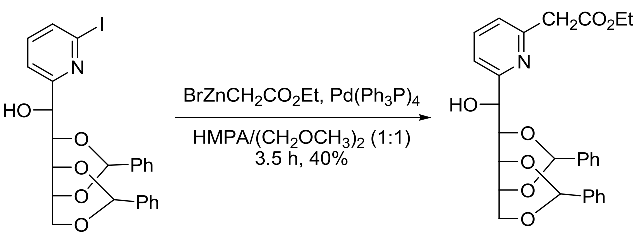
Negishi cross-coupling reaction

The Negishi cross-coupling reaction is the nickel- or palladium-catalyzed coupling of organozinc compounds with various halides or triflates (aryl, alkenyl, alkynyl, and acyl).

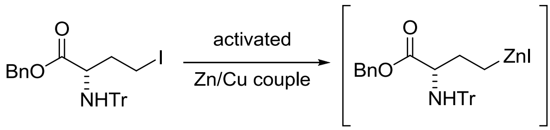




Example 1[3]



Example 2[4]



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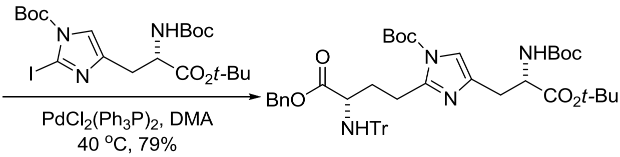
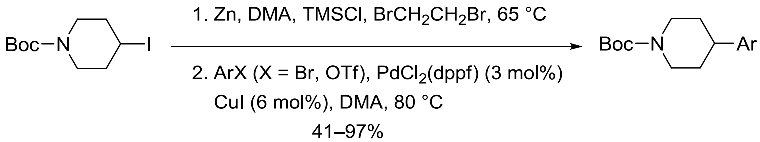
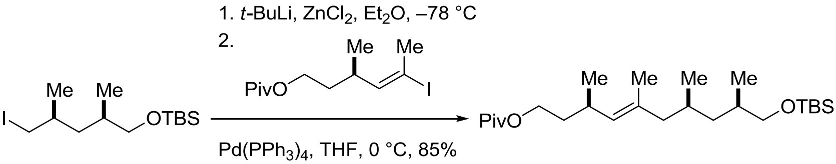
DOI 10.1007/978-3-319-03979-4_190, © Springer International Publishing Switzerland 2014



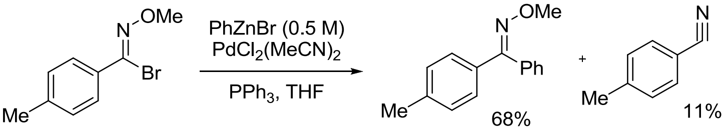
Example 3[8]



Example 4[9]



Example 5[11]

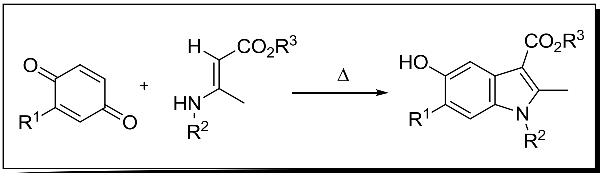


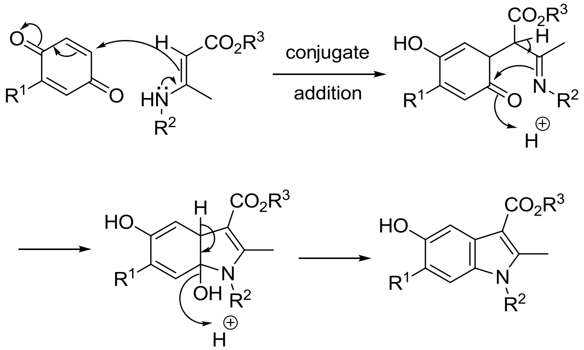
References

1. (a) Negishi, E.-I.; Baba, S. *J. Chem. Soc., Chem. Commun.* **1976,** 596–597. (b) Negishi, E.-I.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977,** *42,* 1821–1823. (c) Negishi, E.-I. *Acc. Chem. Res.* **1982,** *15,* 340–348. (Review). Negishi is a professor at Purdue University. He won Nobel Prize in 2010 along with Richard F. Heck and Akira Suzuki "for palladium-catalyzed cross couplings in organic synthesis".
2. Erdik, E. *Tetrahedron* **1992,** *48,* 9577–9648. (Review).
3. De Vos, E.; Esmans, E. L.; Alderweireldt, F. C.; Balzarini, J.; De Clercq, E. *J. Heterocycl. Chem.* **1993,** *30*, 1245–1252.
4. Evans, D. A.; Bach, T. *Angew. Chem. Int. Ed.* **1993,** *32,* 1326–1327.
5. Negishi, E.-I.; Liu, F. In *Metal-Catalyzed Cross-Coupling Reactions;* Diederich, F.; Stang, P. J., Eds.; Wiley–VCH: Weinheim, Germany, **1998,** pp 1–47. (Review).
6. Arvanitis, A. G.; Arnold, C. R.; Fitzgerald, L. W.; Frietze, W. E.; Olson, R. E.; Gilligan, P. J.; Robertson, D. W. *Bioorg. Med. Chem. Lett.* **2003,** *13*, 289–291.
7. Ma, S.; Ren, H.; Wei, Q. *J. Am. Chem. Soc.* **2003,** *125*, 4817–4830.
8. Corley, E. G.; Conrad, K.; Murry, J. A.; Savarin, C.; Holko, J.; Boice, G. *J. Org. Chem.* **2004,** *69*, 5120–5123.
9. Inoue, M.; Yokota, W.; Katoh, T. *Synthesis* **2007,** 622–637.
10. Yet, L. *Negishi cross-coupling reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 70–99. (Review).
11. Dolliver, D. D.; Bhattarai, B. T.; et al. *J. Org. Chem.* **2013,** *78*, 3676–3687.

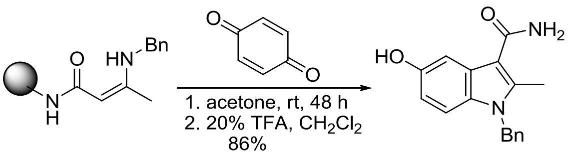
Nenitzescu indole synthesis

5-Hydroxylindole from condensation of *p*-benzoquinone and β-aminocrotonate.

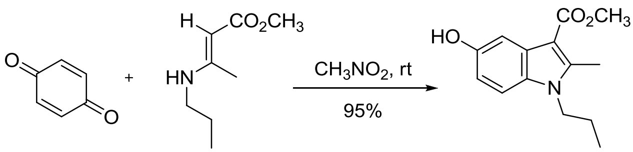




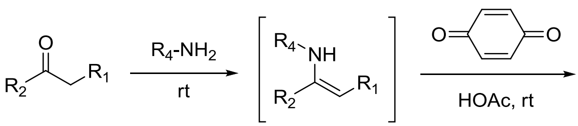
Example 1[5]



Example 2[6]



Example 3[7]



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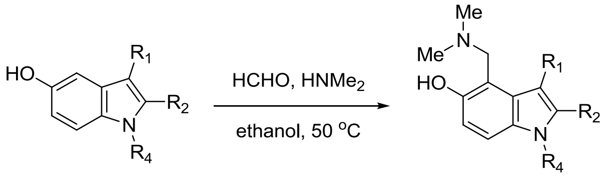
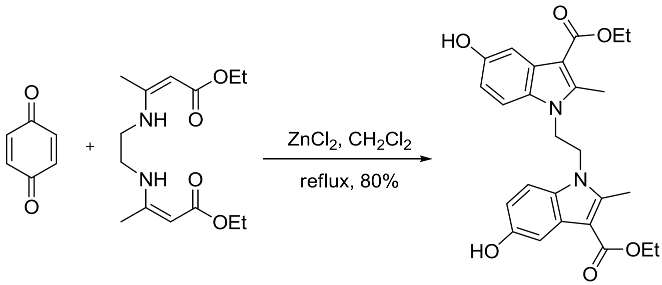
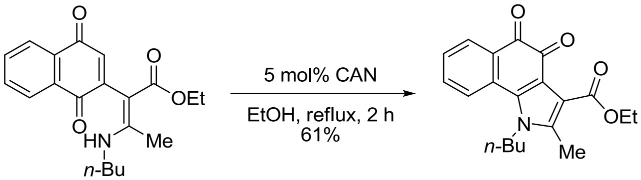
DOI 10.1007/978-3-319-03979-4_191,



Example 4[10]



Example 4[12]

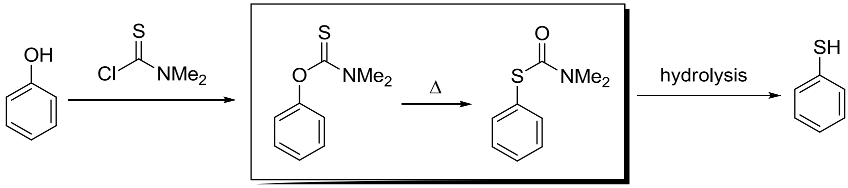


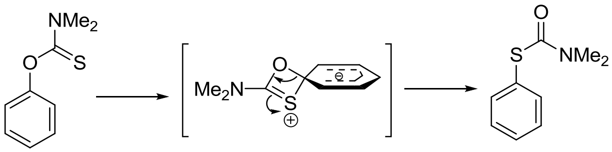
References

1. Nenitzescu, C. D. *Bull. Soc. Chim. Romania* **1929,** *11*, 37–43.
2. Allen, G. R., Jr. *Org. React.* **1973,** *20*, 337–454. (Review).
3. Kinugawa, M.; Arai, H.; Nishikawa, H.; Sakaguchi, A.; Ogasa, T.; Tomioka, S.; Kasai, M. *J. Chem. Soc., Perkin Trans. 1* **1995,** 2677–2681.
4. Mukhanova, T. I.; Panisheva, E. K.; Lyubchanskaya, V. M.; Alekseeva, L. M.; Sheinker, Y. N.; Granik, V. G. *Tetrahedron* **1997,** *53*, 177–184.
5. Ketcha, D. M.; Wilson, L. J.; Portlock, D. E. *Tetrahedron Lett*. **2000,** *41*, 6253–6257.
6. Brase, S.; Gil, C.; Knepper, K. *Bioorg. Med. Chem.* **2002,** *10*, 2415–2418.
7. Böhme, T. M.; Augelli-Szafran, C. E.; Hallak, H.; Pugsley, T.; Serpa, K.; Schwarz, R. D. *J. Med. Chem.* **2002,** *45*, 3094–3102.
8. Schenck, L. W.; Sippel, A.; Kuna, K.; Frank, W.; Albert, A.; Kucklaender, U. *Tetrahedron* **2005,** *61*, 9129–9139.
9. Li, J.; Cook, J. M. *Nenitzescu indole synthesis*. In *Name Reactions in Heterocyclic Chemistry;* Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 145–153. (Review).
10. Velezheva, V. S.; Sokolov, A. I.; Kornienko, A. G.; Lyssenko, K. A.; Nelyubina, Y. V.; Godovikov, I. A.; Peregudov, A. S.; Mironov, A. F. *Tetrahedron Lett.* **2008,** *49,* 7106–7109.
11. Inman, M.; Moody, C. J. *Chem. Sci.* **2013,** *4,* 29–41. (Review).
12. Suryavanshi, P. A.; Sridharan, V.; Menendez, J. C. *Tetrahedron* **2013,** *69,* 5401–5406.

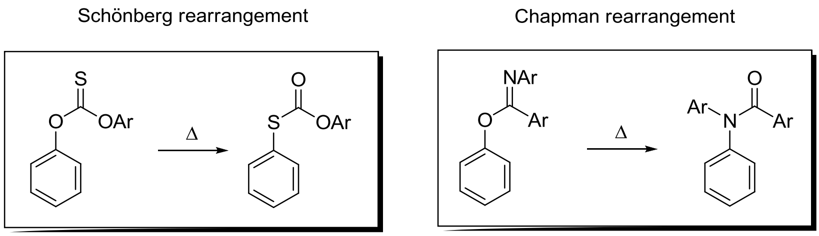
Newman–Kwart rearrangement

Transformation of phenol to the corresponding thiophenol, a variant of the Smiles reaction.

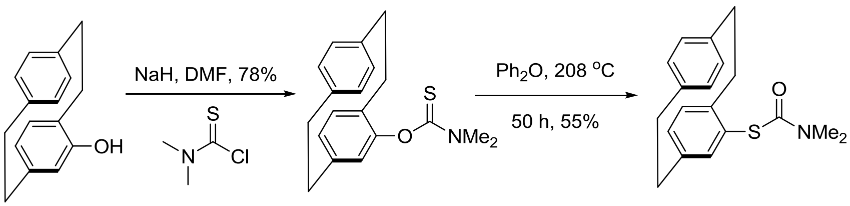




The Newman–Kwart rearrangement is a member of a series of related rearrangements, such as the **Schönberg rearrangement** and the **Chapman rearrangement** (page 105), in which aryl groups migrate intramolecularly between nonadjacent atoms. The Schönberg rearrangement is the most similar and involves the 1,3-migration of an aryl group from oxygen to sulfur in a diarylthiocarbonate. The Chapman rearrangement involves an analogous migration but to nitrogen.



Example 1[5]



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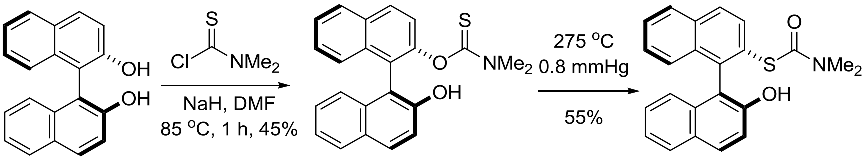
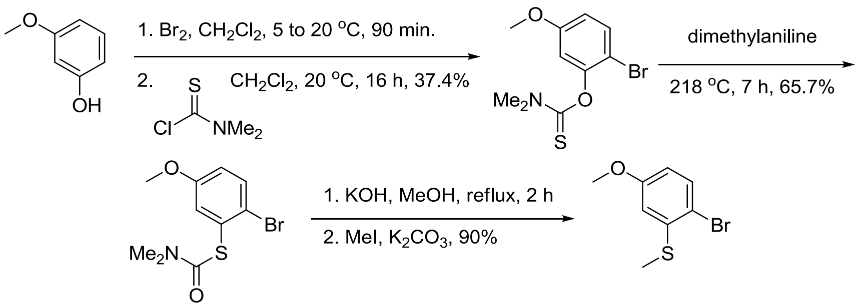
DOI 10.1007/978-3-319-03979-4_192, © Springer International Publishing Switzerland 2014

Example 2[6]



Example 3[7]

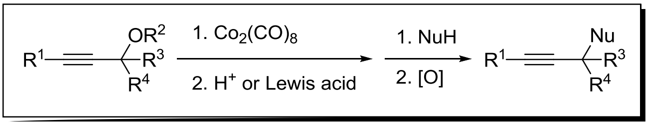


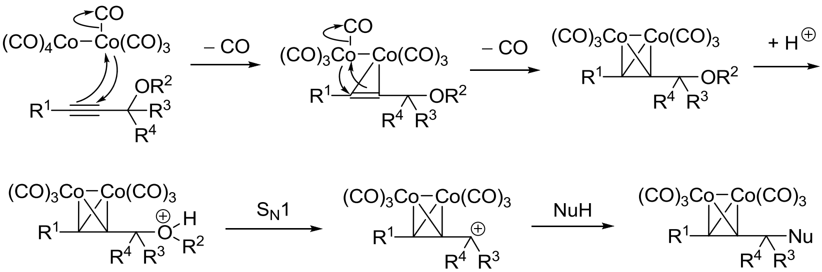
References

1. (a) Kwart, H.; Evans, E. R. *J. Org. Chem.* **1966,** *31*, 410–413. (b) Newman, M. S.; Karnes, H. A. *J. Org. Chem.* **1966,** *31*, 3980–3984. (c) Newman, M. S.; Hetzel, F. W. *J. Org. Chem.* **1969,** *34*, 3604–3606.
2. Cossu, S.; De Lucchi, O.; Fabbri, D.; Valle, G.; Painter, G. F.; Smith, R. A. J. *Tetrahedron* **1997,** *53*, 6073–6084.
3. Lin, S.; Moon, B.; Porter, K. T.; Rossman, C. A.; Zennie, T.; Wemple, J. *Org. Prep. Proc. Int.* **2000,** *32*, 547–555.
4. Ponaras, A. A.; Zain, Ö. In *Encyclopedia of Reagents for Organic Synthesis,* Paquette, L. A., Ed.; Wiley: New York, **1995,** 2174–2176. (Review).
5. Kane, V. V.; Gerdes, A.; Grahn, W.; Ernst, L.; Dix, I.; Jones, P. G.; Hopf, H. *Tetrahedron Lett.* **2001,** *42*, 373–376.
6. Albrow, V.; Biswas, K.; Crane, A.; Chaplin, N.; Easun, T.; Gladiali, S.; Lygo, B.; Woodward, S. *Tetrahedron: Asymmetry* **2003,** *14*, 2813–2819.
7. Bowden, S. A.; Burke, J. N.; Gray, F.; McKown, S.; Moseley, J. D.; Moss, W. O.; Murray, P. M.; Welham, M. J.; Young, M. J. *Org. Proc. Res. Dev.* **2004,** *8*, 33–44.
8. Nicholson, G.; Silversides, J. D.; Archibald, S. J. *Tetrahedron Lett.* **2006,** *47*, 6541–6544.
9. Gilday, J. P.; Lenden, P.; Moseley, J. D.; Cox, B. G. *J. Org. Chem.* **2008,** *73*, 3130–3134.
10. Lloyd-Jones, G. C.; Moseley, J. D.; Renny, J. S. *Synthesis* **2008,** 661–689.
11. Tilstam, U.; Defrance, T.; Giard, T.; Johnson, M. D. *Org. Proc. Res. Dev.* **2009,** *13*, 321–323.
12. Das, J.; Le Cavelier, F.; Rouden, J.; Blanchet, J. *Synthesis* **2012,** *44*, 1349–1352.

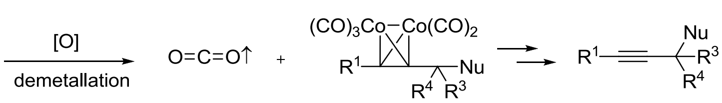
Nicholas reaction

Hexacarbonyldicobalt-stabilized propargyl cation is captured by a nucleophile. Subsequent oxidative demetallation then gives the propargylated product.

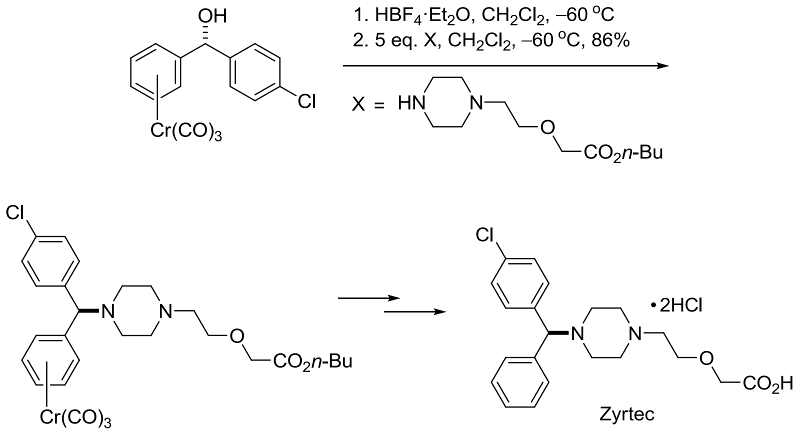




propargyl cation intermediate (stabilized by the hexacarbonyldicobalt complex).



Example 1, A chromium variant of the Nicholas reaction[3]



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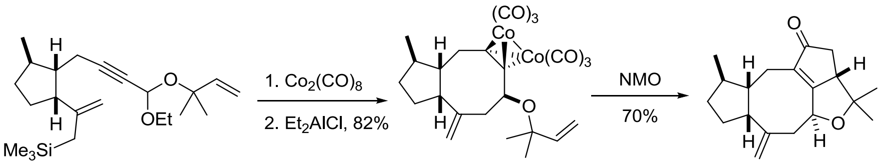
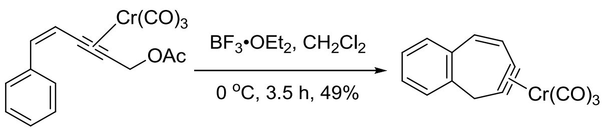
DOI 10.1007/978-3-319-03979-4_193, © Springer International Publishing Switzerland 2014

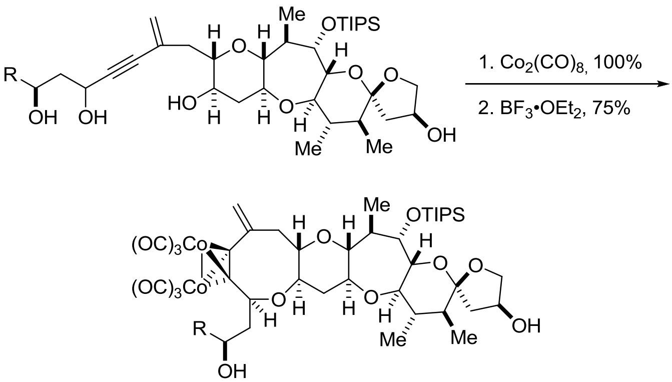
Example 2, A Nicholas-Pauson–Khand sequence[4]



Example 3, Intramolecular Nicholas reaction using chromium[7]



Example 4[9]

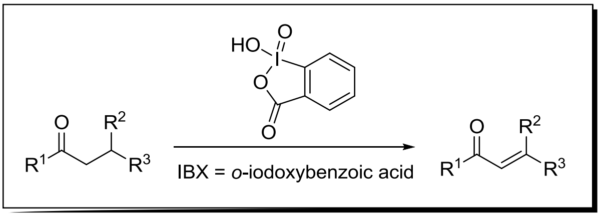


References

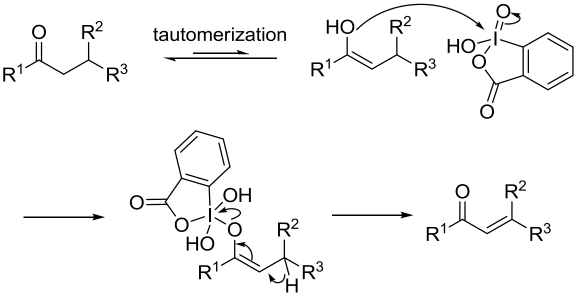
1. Nicholas, K. M.; Pettit, R. *J. Organomet. Chem.* **1972,** *44*, C21–C24.
2. Nicholas, K. M. *Acc. Chem. Res.* **1987,** *20,* 207–214. (Review).
3. Corey, E. J.; Helal, C. J. *Tetrahedron Lett.* **1996,** *37*, 4837–4840.
4. Jamison, T. F.; Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *J. Am. Chem. Soc.* **1997,** *119,* 4353–4363.
5. Teobald, B. J. *Tetrahedron* **2002,** *58*, 4133–4170. (Review).
6. Takase, M.; Morikawa, T.; Abe, H.; Inouye, M. *Org. Lett.* **2003,** *5*, 625–628.
7. Ding, Y.; Green, J. R. *Synlett* **2005,** 271–274.
8. Pinacho Crisóstomo, F. R.; Carrillo, R.; Martin, T.; Martin, V. S. *Tetrahedron Lett.* **2005,** *46*, 2829–2832.
9. Hamajima, A.; Isobe, M. *Org. Lett.* **2006,** *8,* 1205–1208.
10. Shea, K. M. *Nicholas Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 284–298. (Review).
11. Mukai, C.; Kojima, T.; Kawamura, T.; Inagaki, F. *Tetrahedron* **2013,** *69*, 7659–7669.

Nicolaou IBX dehydrogenation

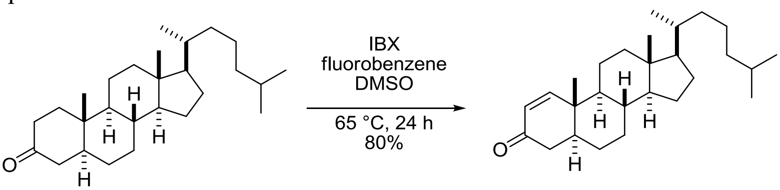
α,β-Unsaturation of aldehydes and ketones mediated by stoichiometric amounts of *o*-iodoxybenzoic acid (IBX), alternative to the Saegusa oxidation.



A SET mechanism has also been proposed. Additionally, silyl enol ethers are also viable substrates.

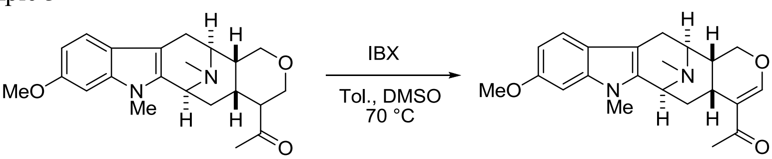


Example 1[1a]



Example 2[3]

Example 3[7]



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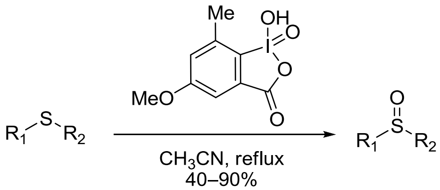
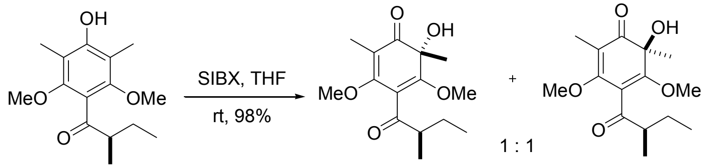
DOI 10.1007/978-3-319-03979-4_194, © Springer International Publishing Switzerland 2014

Example 4, *o*-Methyl-IBX (Me-IBX)[9]



Example 5, Stabilized IBX (SIBX)[10]

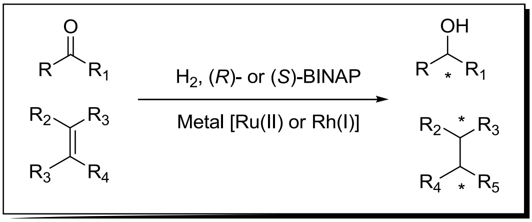


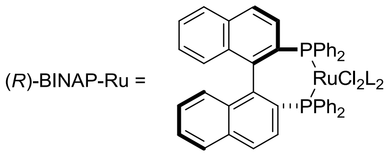
References

1. (a) Nicolaou, K. C.; Zhong, Y.-L.; Baran, P. S. *J. Am. Chem. Soc.* **2000,** *122*, 7596–7597. (b) Nicolaou, K. C.; Montagnon, T.; Baran, P. S. *Angew. Chem. Int. Ed.* **2002,** *41*, 993–996. (c) Nicolaou, K. C.; Gray, D. L.; Montagnon, T.; Harrison, S. T. *Angew. Chem. Int. Ed.* **2002,** *41*, 996–1000.
2. Nagata, H.; Miyazawa, N.; Ogasawara, K. *Org. Lett.* **2001,** *3*, 1737–1740.
3. Ohmori, N. *J. Chem. Soc., Perkin Trans. 1* **2002,** 755–767.
4. Hayashi, Y.; Yamaguchi, J.; Shoji, M. *Tetrahedron* **2002,** *58*, 9839–9846.
5. Shimokawa, J.; Shirai, K.; Tanatani, A.; Hashimoto, Y.; Nagasawa, K. *Angew. Chem. Int. Ed.* **2004,** *43*, 1559–1562.
6. Smith, N. D.; Hayashida. J.; Rawal, V. H. *Org. Lett.* **2005,** *7*, 4309–4312.
7. Liu, X.; Deschamp, J. R.; Cook, J. M. *Org. Lett.* **2002,** *4*, 3339–3342.
8. Herzon, S. B.; Myers, A. G. *J. Am. Chem. Soc.* **2005,** *127*, 5342–5344.
9. Moorthy, J. N.; Singhal, N.; Senapati, K. *Tetrahedron Lett.* **2008,** *49*, 80–84.
10. Pouységu, L.; Marguerit, M.; Gagnepain, J.; Lyvinec, G.; Eatherton, A. J.; Quideau, S. *Org. Lett.* **2008,** *10*, 5211–5214.
11. Raghavan, S.; Babu, Vaddela S. *Tetrahedron* **2011,** *69*, 2044–2050.

Noyori asymmetric hydrogenation

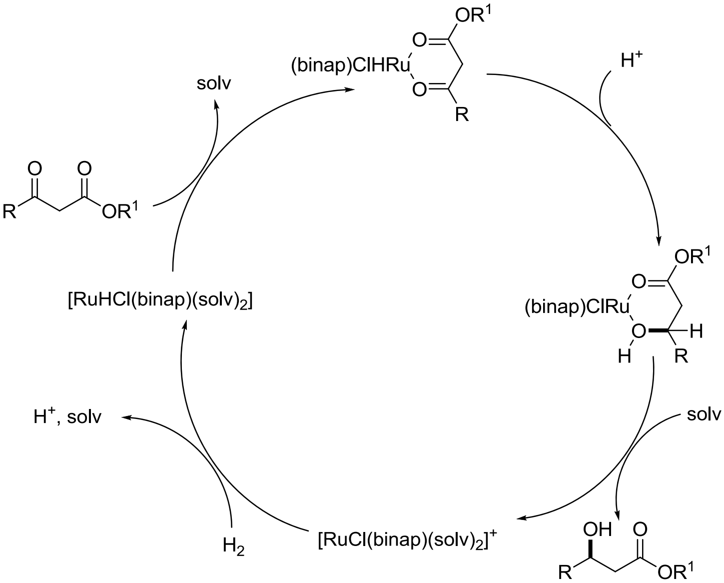
Asymmetric reduction of carbonyls and alkenes *via* hydrogenation, catalyzed by a ruthenium(II) BINAP complex.





$$[RuCl_2(binap)(solv)_2] \xrightarrow[-\,HCl]{H_2} [RuHCl(binap)(solv)_2]$$

The catalytic cycle:



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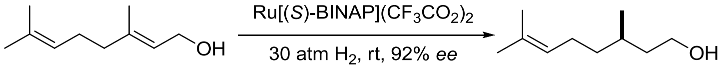
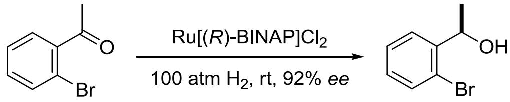
DOI 10.1007/978-3-319-03979-4_195, © Springer International Publishing Switzerland 2014

Example 1[1b]



Example 2[1c]



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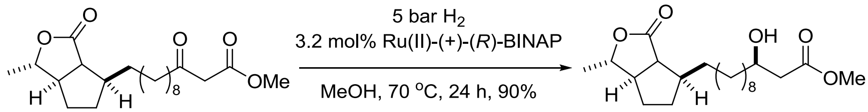
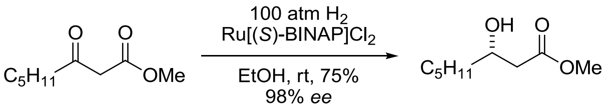
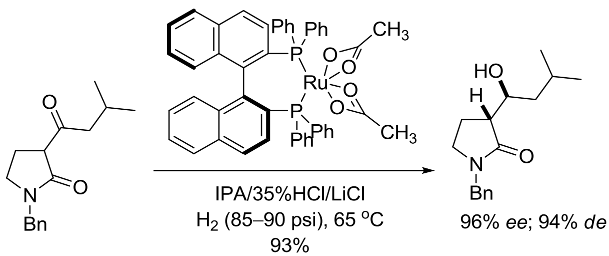


Example 4[10]



Example 5[11]



References

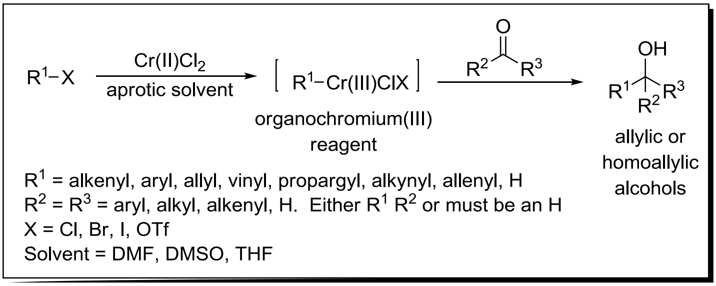
1. (a) Noyori, R.; Ohta, M.; Hsiao, Y.; Kitamura, M.; Ohta, T.; Takaya, H. *J. Am. Chem. Soc*. **1986,** *108*, 7117–7119. Ryoji Noyori (Japan, 1938–) and William S. Knowles (USA, 1917–) shared half of the Nobel Prize in Chemistry in 2001 for their work on chirally catalyzed hydrogenation reactions. K. Barry Sharpless (USA, 1941–) shared the other half for his work on chirally catalyzed oxidation reactions. (b) Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc*. **1987,** *109*, 1596–1598. (c) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *J. Am. Chem. Soc*. **1988,** *110*, 629–631. (d) Noyori, R.; Ohkuma, T.; Kitamura, H.; Ta-

kaya, H.; Sayo, H.; Kumobayashi, S.; Akutagawa, S. *J. Am. Chem. Soc*. **1987,** *109*, 5856−5858. (e) Noyori, R.; Ohkuma, T. *Angew. Chem. Int. Ed.* **2001,** *40*, 40−73. (Review). (f) Noyori, R. *Angew. Chem. Int. Ed.* **2002,** *41*, 2008−2022. (Review, Nobel Prize Address).

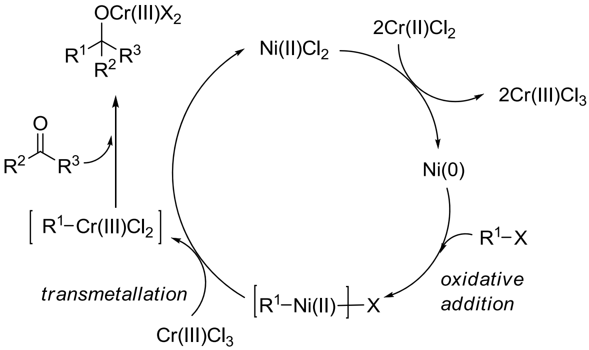
2. Noyori, R. In *Asymmetric Catalysis in Organic Synthesis;* Ojima, I., ed.; Wiley: New York, **1994,** Chapter 2. (Review).
3. Chung, J. Y. L.; Zhao, D.; Hughes, D. L.; McNamara, J. M.; Grabowski, E. J. J.; Reider, P. J. *Tetrahedron Lett*. **1995,** *36*, 7379−7382.
4. Bayston, D. J.; Travers, C. B.; Polywka, M. E. C. *Tetrahedron: Asymmetry* **1998,** *9*, 2015−2018.
5. Berkessel, A.; Schubert, T. J. S.; Mueller, T. N. *J. Am. Chem. Soc*. **2002,** *124*, 8693−8698.
6. Fujii, K.; Maki, K.; Kanai, M.; Shibasaki, M. *Org. Lett.* **2003,** *5*, 733−736.
7. Ishibashi, Y.; Bessho, Y.; Yoshimura, M.; Tsukamoto, M.; Kitamura, M. *Angew. Chem. Int. Ed.* **2005,** *44*, 7287−7290.
8. Lall, M. S. *Noyori Asymmetric Hydrogenation*, In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 46–66. (Review).
9. Bouillon, M. E.; Meyer, H. H. *Tetrahedron* **2007,** *63*, 2712–2723.
10. Case-Green, S. C.; Davies, S. G.; Roberts, P. M.; Russell, A. J.; Thomson, J. E. *Tetrahedron: Asymmetry* **2008,** *19*, 2620–2631.
11. Magnus, N. A.; Astleford, B. A.; Laird, D. L. T.; Maloney, T. D.; McFarland, A. D.; Rizzo, J. R.; Ruble, J. C.; Stephenson, G. A.; Wepsiec, J. P. *J. Org. Chem.* **2013,** *78,* 5768–5774.

Nozaki–Hiyama–Kishi reaction

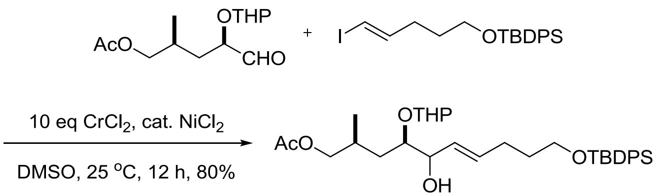
Cr–Ni bimetallic catalyst-promoted redox addition of vinyl- or propargyl-halides to aldehydes.



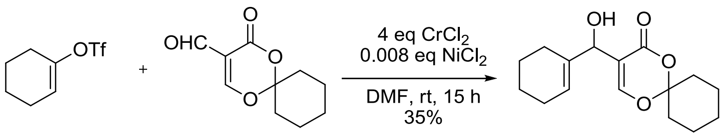
The catalytic cycle:[2]



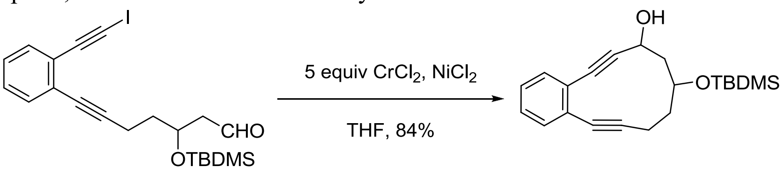
Example 1[3]



Example 2[5]



Example 3, Intramolecular Nozaki–Hiyama–Kishi reaction[8]



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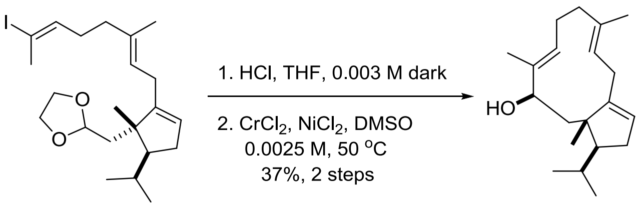
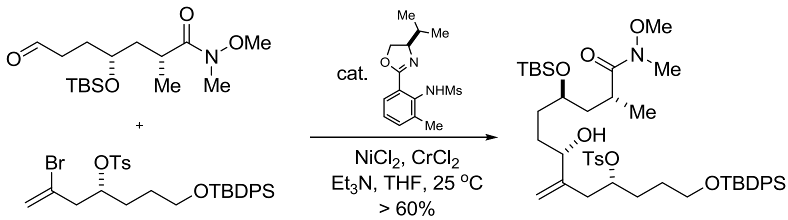
DOI 10.1007/978-3-319-03979-4_196, © Springer International Publishing Switzerland 2014

Example 4, Intramolecular Nozaki–Hiyama–Kishi reaction[9]



Example 5, Asymmetric Nozaki–Hiyama–Kishi reaction[11]

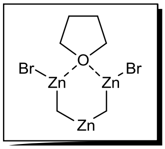


References

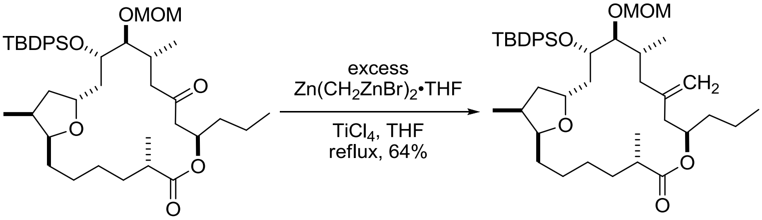
1. (a) Okude, C. T.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc*. **1977,** *99*, 3179−3181. Hitosi Nozaki and T. Hiyama are professors at the Japanese Academy. (b) Takai, K.; Kimura, K.; Kuroda, T.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett*. **1983,** *24*, 5281−5284. Kazuhiko Takai was Prof. Nozaki's student during the discovery of the reaction and is a professor at Okayama University. (c) Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc*. **1986,** *108*, 5644−5646. Yoshito Kishi at Harvard independently discovered the catalytic effect of nickel during his total synthesis of polytoxin. (d) Takai, K.; Tagahira, M.; Kuroda, T.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc*. **1986,** *108*, 6048−6050. (e) Kress, M. H.; Ruel, R.; Miller, L. W. H.; Kishi, Y. *Tetrahedron Lett*. **1993,** *34*, 5999−6002.
2. Fürstner, A.; Shi, N. *J. Am. Chem. Soc*. **1996,** *118*, 12349−12357. (The catalytic cycle).
3. Chakraborty, T. K.; Suresh, V. R. *Chem. Lett.* **1997,** 565−566.
4. Fürstner, A. *Chem. Rev*. **1999,** *99*, 991−1046. (Review).
5. Blaauw, R. H.; Benningshof, J. C. J.; van Ginkel, A. E.; van Maarseveen, J. H.; Hiemstra, H. *J. Chem. Soc., Perkin Trans. 1* **2001,** 2250–2256.
6. Berkessel, A.; Menche, D.; Sklorz, C. A.; Schroder, M.; Paterson, I. *Angew. Chem. Int. Ed*. **2003,** *42*, 1032−1035.
7. Takai, K. *Org. React.* **2004,** *64*, 253−612. (Review).
8. Karpov, G. V.; Popik, V. V. *J. Am. Chem. Soc.* **2007,** *129*, 3792–3793.
9. Valente, C.; Organ, M. G. *Chem. Eur. J*. **2008,** *14*, 8239–8245.
10. Yet, L. *Nozaki–Hiyama–Kishi reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 299–318. (Review).
11. Austad, B. C.; Benayoud, F.; Calkins, T. L.; et al. *Synlett* **2013,** *17*, 327–332.

Nysted reagent

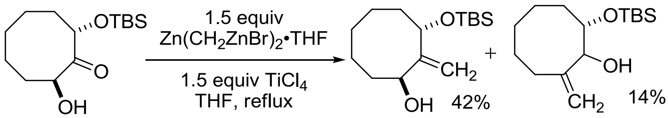
The Nysted reagent, cyclo-dibromodi-μ-methylene(μ-tetrahydrofuran)trizinc, is used for the olefination of ketones and aldehydes.



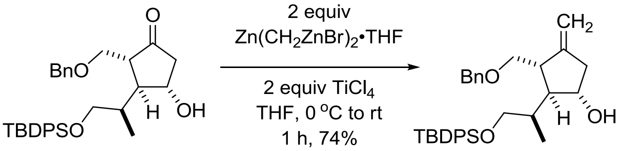
Example 1, The Wittig reagent opened the lactone:[6]



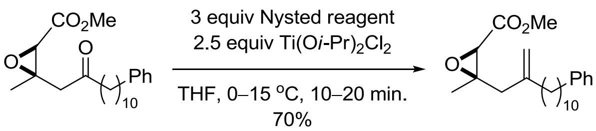
Example 2[8]



Example 3[9]



Example 4[11]



References

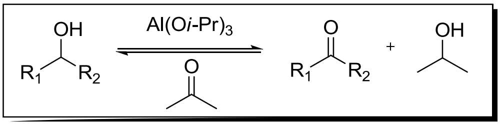
1. Nysted, L. N. US Patent 3,865,848 (**1975**).
2. Tochtermann, W.; Bruhn, S.; Meints, M.; Wolff, C.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Tetrahedron* **1995,** *51*, 1623−1630.

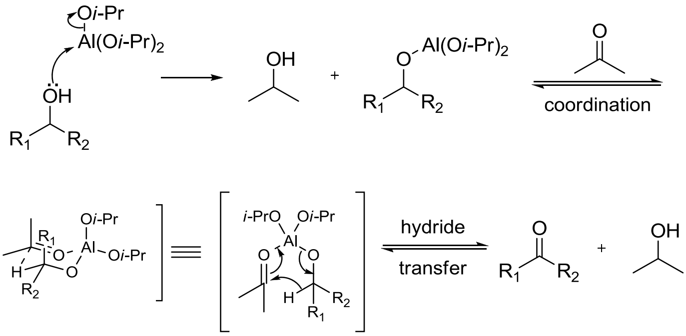
J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_197,

3. Matsubara, S.; Sugihara, M.; Utimoto, K. *Synlett* **1998,** 313−315.
4. Tanaka, M.; Imai, M.; Fujio, M.; Sakamoto, E.; Takahashi, M.; Eto-Kato, Y.; Wu, X. M.; Funakoshi, K.; Sakai, K.; Suemune, H. *J. Org. Chem*. **2000,** *65*, 5806−5816.
5. Tarraga, A.; Molina, P.; Lopez, J. L.; Velasco, M. D. *Tetrahedron Lett*. **2001,** *42*, 8989−8992.
6. Aïssa, C.; Riveiros, R.; Ragot, J.; Fürstner, A. J. *Am. Chem. Soc*. **2003,** *125*, 15512−15520.
7. Clark, J. S.; Marlin, F.; Nay, B.; Wilson, C. *Org. Lett*. **2003,** *5*, 89−92.
8. Paquette, L. A.; Hartung, R. E.; Hofferberth, J. E.; Vilotijevic, I.; Yang, J. *J. Org. Chem.* **2004,** *69*, 2454−2460.
9. Hanessian, S.; Mainetti, E.; Lecomte, F. *Org. Lett*. **2006,** *8*, 4047−4049.
10. Haahr, A.; Rankovic, Z.; Hartley, R. C. *Tetrahedron Lett*. **2011,** *52*, 3020−3022.
11. Barnych, B.; Fenet, B.; Vatele, J.-M. *Tetrahedron* **2013,** *69*, 334−340.

Oppenauer oxidation

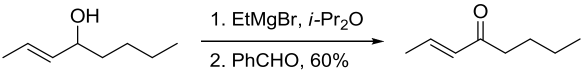
Alkoxide-catalyzed oxidation of secondary alcohols. Reverse of the Meerwein–Ponndorf–Verley reduction.



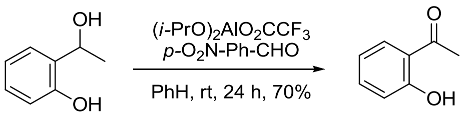


cyclic transition state

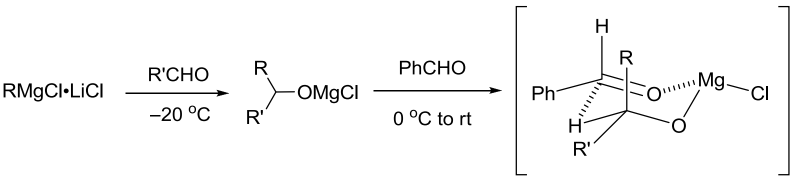
Example 1, Mg-Oppenauer oxidation[3]



Example 2[6]



Example 3, Mg-Oppenauer oxidation[8]



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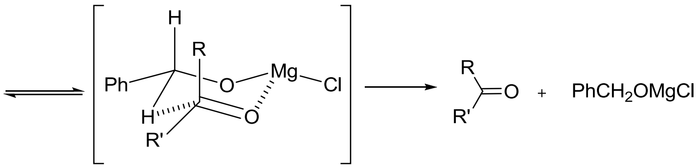
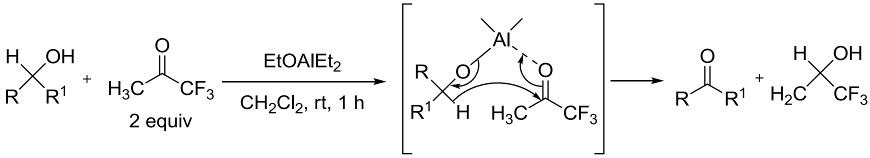
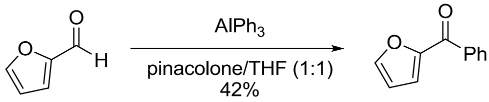


Example 4[10]



Example 5, Tandem nucleophilic addition–Oppenauer oxidation[12]

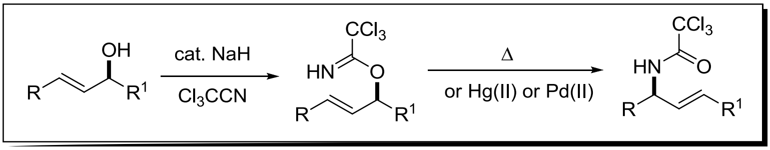


References

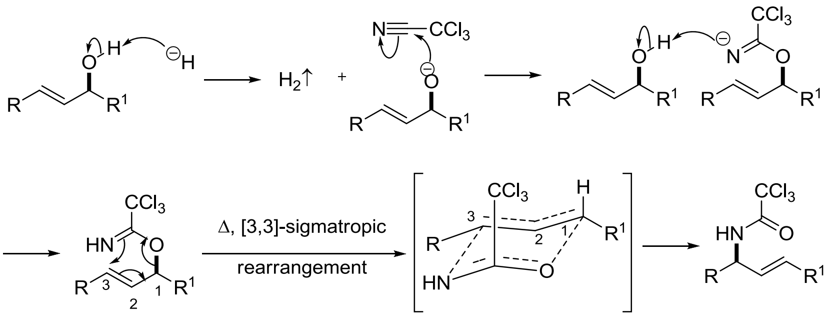
1. Oppenauer, R. V. *Rec. Trav. Chim.* **1937,** *56*, 137–144. Rupert V. Oppenauer (1910–), born in Burgstall, Italy, studied at ETH in Zurich under Ruzicka and Reichstei, both Nobel laureates. After a string of academic appointments around Europe and a stint at Hoffman–La Roche, Oppenauer worked for the Ministry of Public Health in Buenos Aires, Argentina.
2. Djerassi, C. *Org. React.* **1951,** *6*, 207–235. (Review).
3. Byrne, B.; Karras, M. *Tetrahedron Lett.* **1987,** *28*, 769–772.
4. Ooi, T.; Otsuka, H.; Miura, T.; Ichikawa, H.; Maruoka, K. *Org. Lett.* **2002,** *4*, 2669–2672.
5. Suzuki, T.; Morita, K.; Tsuchida, M.; Hiroi, K. *J. Org. Chem.* **2003,** *68*, 1601–1602.
6. Auge, J.; Lubin-Germain, N.; Seghrouchni, L. *Tetrahedron Lett.* **2003,** *44*, 819–822.
7. Hon, Y.-S.; Chang, C.-P.; Wong, Y.-C. Byrne, B.; Karras, M. *Tetrahedron Lett.* **2004,** *45*, 3313–3315.
8. Kloetzing, R. J.; Krasovskiy, A.; Knochel, P. *Chem. Eur. J.* **2007,** *13*, 215–227.
9. Fuchter, M. J. *Oppenauer Oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 265–373. (Review).
10. Mello, R.; Martinez-Ferrer, J.; Asensio, G.; Gonzalez-Nunez, M. E. *J. Org. Chem.* **2008,** *72*, 9376–9378.
11. Borzatta, V.; Capparella, E.; Chiappino, R.; Impala, D.; Poluzzi, E.; Vaccari, A. *Cat. Today* **2009,** *140*, 112–116.
12. Fu, Y.; Yang, Y.; Hügel, H. M.; Du, Z.; Wang, K.; Huang, D.; Hu, Y. *Org. Biomol. Chem.* **2013,** *11,* 4429–4432.

Overman rearrangement

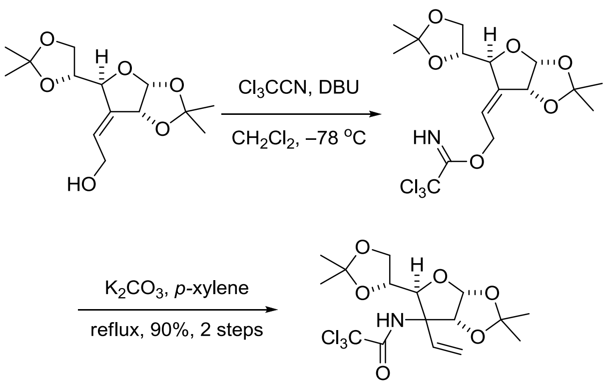
Stereoselective transformation of allylic alcohol to allylic trichloroacetamide *via* trichloroacetimidate intermediate.



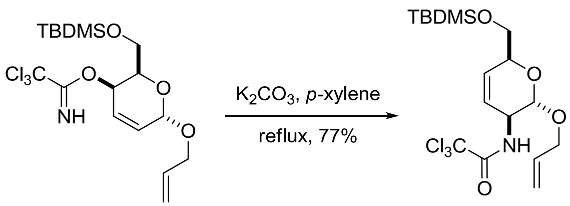
trichloroacetimidate



Example 1[5]



Example 2[6]



Example 3[7]

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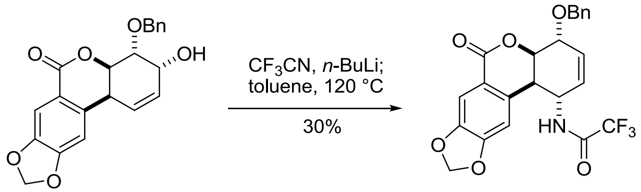
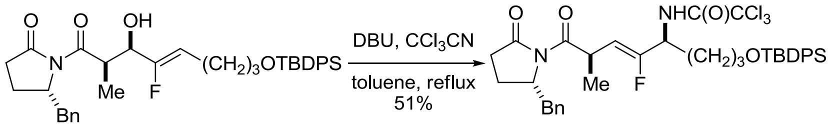
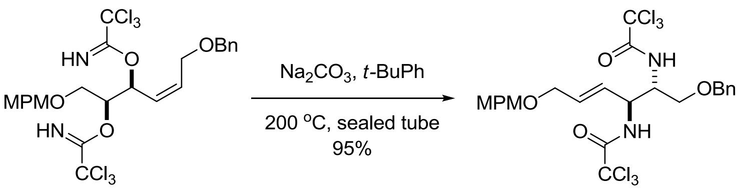
DOI 10.1007/978-3-319-03979-4_199, © Springer International Publishing Switzerland 2014



Example 4[9]



Example 5, Cascade-type Overman rearrangement[11]

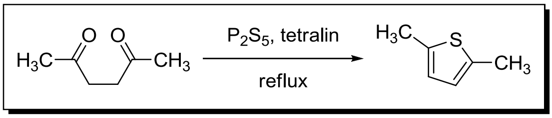


References

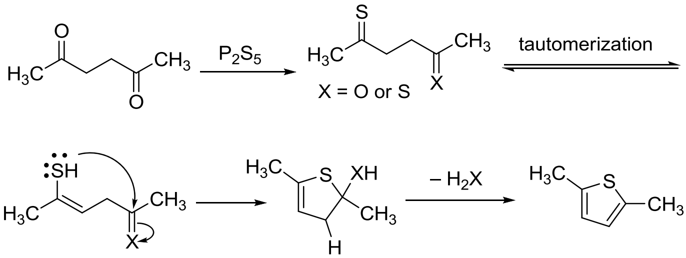
1. (a) Overman, L. E. *J. Am. Chem. Soc*. **1974,** *96*, 597–599. (b) Overman, L. E. *J. Am. Chem. Soc*. **1976,** *98*, 2901–2910. (c) Overman, L. E. *Acc. Chem. Res*. **1980,** *13*, 218–224. (Review).
2. Demay, S.; Kotschy, A.; Knochel, P. *Synthesis* **2001,** 863–866.
3. Oishi, T.; Ando, K.; Inomiya, K.; Sato, H.; Iida, M.; Chida, N. *Org. Lett*. **2002,** *4*, 151–154.
4. Reilly, M.; Anthony, D. R.; Gallagher, C. *Tetrahedron Lett*. **2003,** *44*, 2927–2930.
5. Tsujimoto, T.; Nishikawa, T.; Urabe, D.; Isobe, M. *Synlett* **2005,** 433–436.
6. Montero, A.; Mann, E.; Herradon, B. *Tetrahedron Lett*. **2005,** *46*, 401–405.
7. Hakansson, A. E.; Palmelund, A.; Holm, H.; Madsen, R. *Chem. Eur. J*. **2006,** *12*, 3243–3253.
8. Bøjstrup, M.; Fanejord, M.; Lundt, I. *Org. Biomol. Chem*. **2007,** *5*, 3164–3171.
9. Lamy, C.; Hifmann, J.; Parrot-Lopez, H.; Goekjian, P. *Tetrahedron Lett*. **2007,** *48*, 6177–6180.
10. Wu, Y.-J. *Overman Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, 2009, pp 210–225. (Review).
11. Nakayama, Y.; Sekiya, R.; Oishi, H.; Hama, N.; Yamazaki, M.; Sato, T.; Chida, N. *Chem. Eur. J.* **2013,** *19*, 12052–12058.

Paal thiophene synthesis

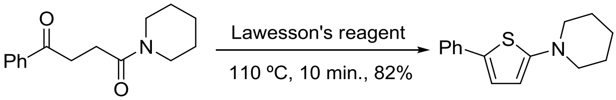
Thiophene synthesis from addition of a sulfur atom to 1,4-diketones and subsequent dehydration.



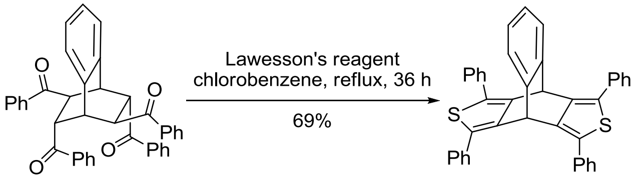
The reaction now is frequently carried out using the Lawesson's reagent. For the mechanism of carbonyl to thiocarbonyl transformation, see Lawesson's reagent.



Example 1[2]



Example 2[3]



References

1. (a) Paal, C. *Ber.* **1885,** *18*, 2251–2254. (b) Paal, C. *Ber.* **1885,** *18*, 367–371.
2. Thomsen, I.; Pedersen, U.; Rasmussen, P. B.; Yde, B.; Andersen, T. P.; Lawesson, S.-O. *Chem. Lett.* **1983,** 809–810.
3. Parakka, J. P.; Sadannandan, E. V.; Cava, M. P. *J. Org. Chem.* **1994,** *59*, 4308–4310.
4. Kikuchi, K.; Hibi, S.; Yoshimura, H.; Tokuhara, N.; Tai, K.; Hida, T.; Yamauchi, T.; Nagai, M. *J. Med. Chem.* **2000,** *43*, 409–423.
5. Sonpatki, V. M.; Herbert, M. R.; Sandvoss, L. M.; Seed, A. J. *J. Org. Chem.* **2001,** *66*, 7283–7286.
6. Kiryanov, A. A.; Sampson, P.; Seed, A. J. *J. Org. Chem.* **2001,** *66*, 7925–7929.
7. Mullins, R. J.; Williams, D. R. *Paal Thiophene Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 207–217. (Review).
8. Kaniskan, N.; Elmali, D.; Civcir, P. U. *ARKIVOC* **2008,** 17–29.

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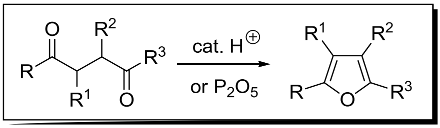
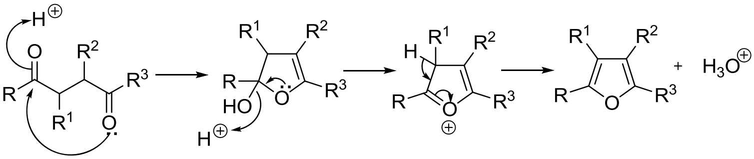
DOI 10.1007/978-3-319-03979-4_200,

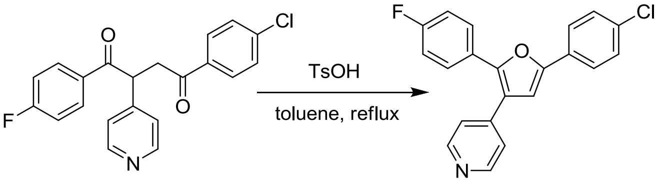
Paal–Knorr furan synthesis

Acid-catalyzed cyclization of 1,4-diketones to form furans.

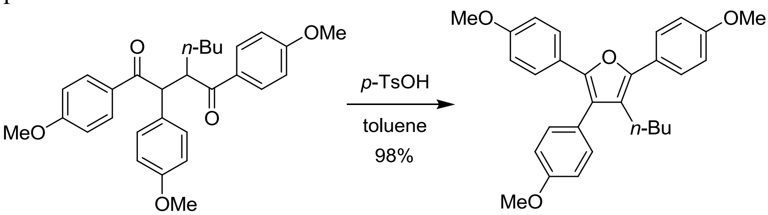




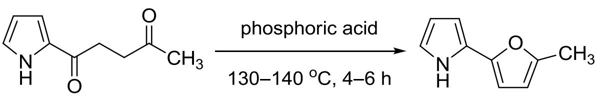
Example 1[3]



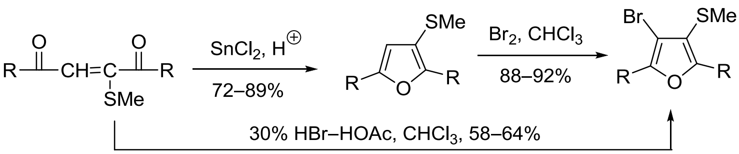
Example 2[6]



Example 3[9]



Example 4[10]



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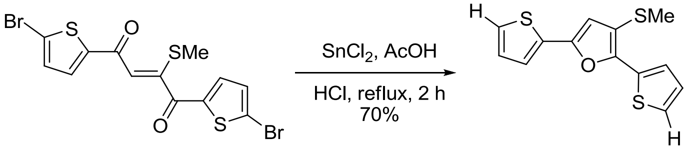
DOI 10.1007/978-3-319-03979-4_201, © Springer International Publishing Switzerland 2014

Example 5, Concurrent debromination along with furan formation[10]

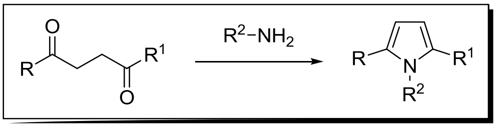


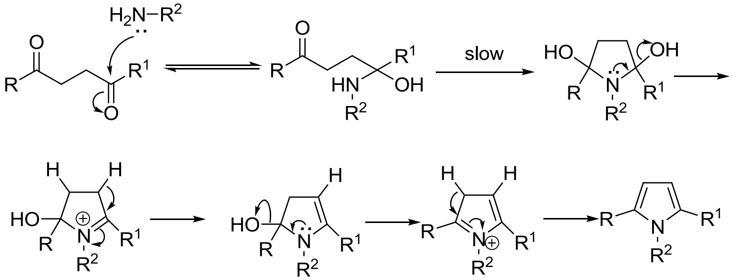
References

1. (a) Paal, C. *Ber.* **1884,** *17*, 2756–2767. (b) Knorr, L. *Ber.* **1885,** *17*, 2863–2870. (c) Paal, C. *Ber.* **1885,** *18*, 367–371.
2. Friedrichsen, W. Furans and Their Benzo Derivatives: Synthesis. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, **1996**; *Vol. 2*, 351–393. (Review).
3. de Laszlo, S. E.; Visco, D.; Agarwal, L.; *et al. Bioorg. Med. Chem. Lett.* **1998,** *8*, 2689–2694.
4. Gupta, R. R.; Kumar, M.; Gupta, V. *Heterocyclic Chemistry*, Springer: New York, **1999**; Vol. 2, 83–84. (Review).
5. Joule, J. A.; Mills, K. *Heterocyclic Chemistry*, 4th ed.; Blackwell Science: Cambridge, **2000**; 308–309. (Review).
6. Mortensen, D. S.; Rodriguez, A. L.; Carlson, K. E.; Sun, J.; Katzenellenbogen, B. S.; Katzenellenbogen, J. A. *J. Med. Chem.* **2001,** *44*, 3838–3848.
7. König, B. *Product Class 9: Furans*. In *Science of Synthesis: Houben–Weyl Methods of Molecular Transformations*; Maas, G., Ed.; Georg Thieme Verlag: New York, **2001**; *Cat. 2, Vol.* 9, 183–278. (Review).
8. Shea, K. M. *Paal–Knorr Furan Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 168–181. (Review).
9. Kaniskan, N.; Elmali, D.; Civcir, P. U. *ARKIVOC* **2008,** 17–29.
10. Yin, G.; Wang, Z.; Chen, A.; Gao, M.; Wu, A.; Pan, Y. *J. Org. Chem.* **2008,** *73*, 3377–3383.
11. Wang, G.; Guan, Z.; Tang, R.; He, Y. *Synth. Commun.* **2010,** *40*, 370–377.

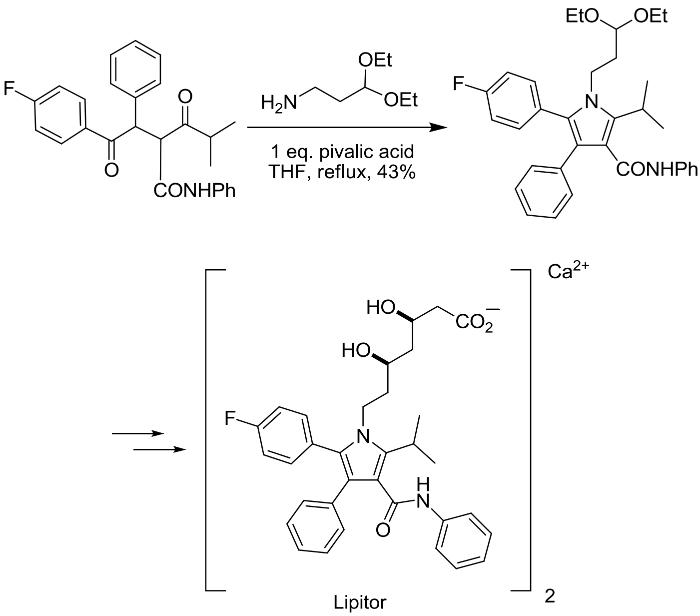
Paal–Knorr pyrrole synthesis

Reaction between 1,4-diketones and primary amines (or ammonia) to give pyrroles. A variation of the Knorr pyrazole synthesis.



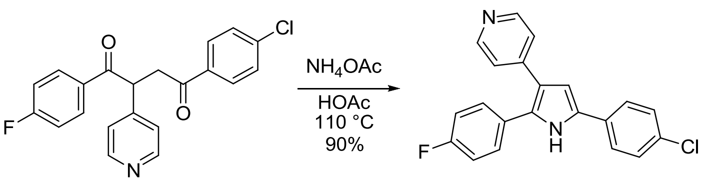


Example 1[4]



Lipitor

Example 2[5]



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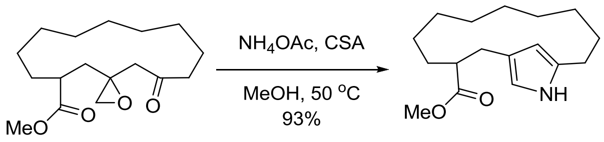
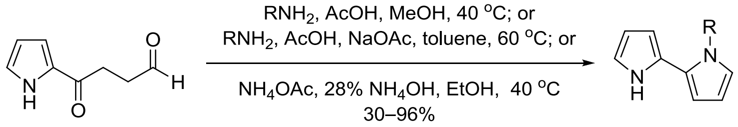
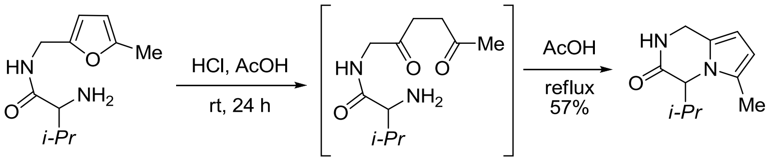
Example 3[9]



Example 4[10]



Example 5, Furan ring opening–pyrrole ring closure[10]

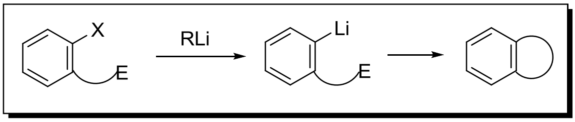


References

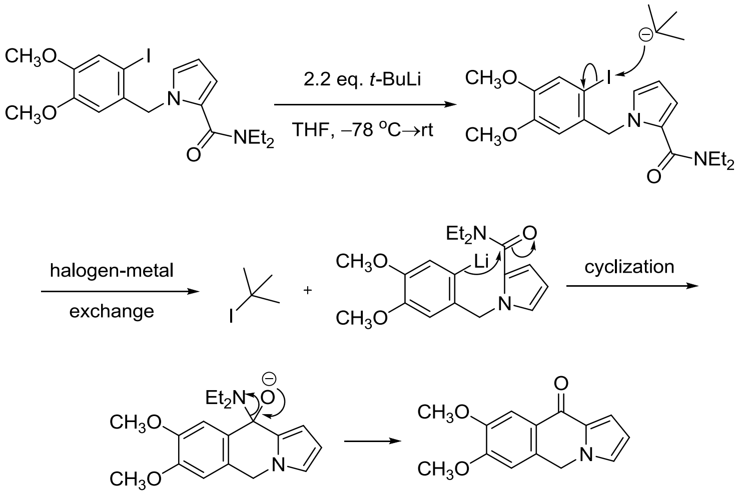
1. (a) Paal, C. *Ber.* **1885,** *18*, 367–371. (b) Paal, C. *Ber.* **1885,** *18*, 2251–2254. (c) Knorr, L. *Ber.* **1885,** *18*, 299–311.
2. Corwin, A. H. *Heterocyclic Compounds Vol. 1*, Wiley, NY, **1950**; Chapter 6. (Review).
3. Jones, R. A.; Bean, G. P. *The Chemistry of Pyrroles*, Academic Press, London, **1977,** pp 51–57, 74–79. (Review).
4. (a) Brower, P. L.; Butler, D. E.; Deering, C. F.; Le, T. V.; Millar, A.; Nanninga, T. N.; Roth, B. D. *Tetrahedron Lett.* **1992,** *33*, 2279-2282. (b) Baumann, K. L.; Butler, D. E.; Deering, C. F.; Mennen, K. E.; Millar, A.; Nanninga, T. N.; Palmer, C. W.; Roth, B. D. *Tetrahedron Lett.* **1992,** *33*, 2279, 2283–2284.
5. de Laszlo, S. E.; Visco, D.; Agarwal, L.; *et al. Bioorg. Med. Chem. Lett.* **1998,** *8*, 2689–2694.
6. Braun, R. U.; Zeitler, K.; Müller, T. J. J. *Org. Lett.* **2001,** *3*, 3297–3300.
7. Quiclet-Sire, B.; Quintero, L.; Sanchez-Jimenez, G.; Zard, Z. *Synlett* **2003,** 75–78.
8. Gribble, G. W. *Knorr and Paal–Knorr Pyrrole Syntheses*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Corey, E. J., Eds, Wiley: Hoboken, NJ, **2005,** 77–88. (Review).
9. Salamone, S. G.; Dudley, G. B. *Org. Lett.* **2005,** *7*, 4443–4445.
10. Fu, L.; Gribble, G. W. *Tetrahedron Lett.* **2008,** *49*, 7352–7354.
11. Trushkov, I. V.; Nevolina, T. A.; Shcherbinin, V. A.; Sorotskaya, L. N.; Butin, A. V. *Tetrahedron Lett.* **2013,** *54*, 3974–3976.

Parham cyclization

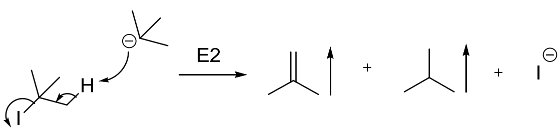
The Parham cyclization is the generation by halogen–lithium exchange of aryllithiums and heteroaryllithiums, and their subsequent intramolecular cyclization onto an electrophilic site.



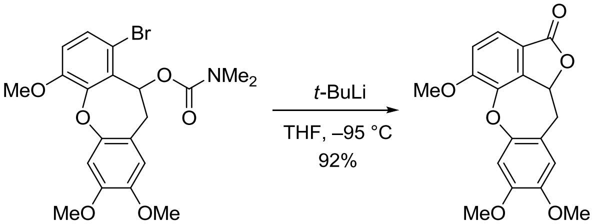
Example 1



The fate of the second equivalent of *t*-BuLi:



Example 2[2]



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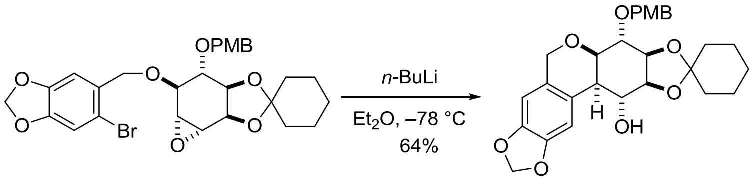
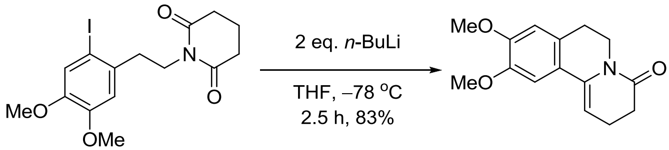
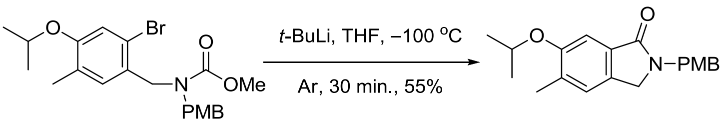
Example 3[4]



Example 4[5]



Example 5[9]

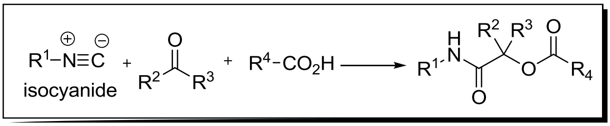


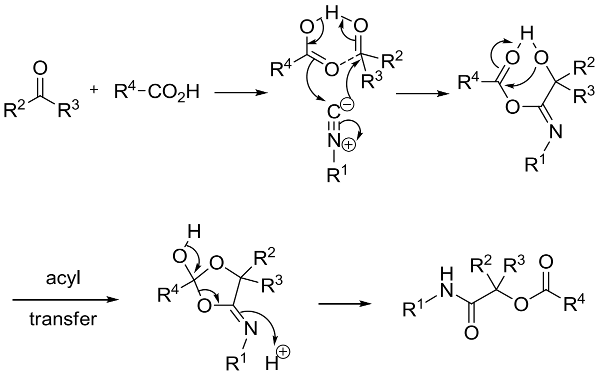
References

1. (a) Parham, W. E.; Jones, L. D.; Sayed, Y. *J. Org. Chem.* **1975,** *40*, 2394–2399. William E. Parham was a professor at Duke University. (b) Parham, W. E.; Jones, L. D.; Sayed, Y. *J. Org. Chem.* **1976,** *41*, 1184–1186. (c) Parham, W. E.; Bradsher, C. K. *Acc. Chem. Res.* **1982,** *15*, 300–305. (Review).
2. Paleo, M. R.; Lamas, C.; Castedo, L.; Domínguez, D. *J. Org. Chem.* **1992,** *57*, 2029–2033.
3. Gray, M.; Tinkl, M.; Snieckus, V. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Exeter, **1995**; Vol. 11; p 66. (Review).
4. Gauthier, D. R., Jr.; Bender, S. L. *Tetrahedron Lett.* **1996,** *37*, 13–16.
5. Collado, M. I.; Manteca, I.; Sotomayor, N.; Villa, M.-J.; Lete, E. *J. Org. Chem.* **1997,** *62*, 2080–2092.
6. Mealy, M. M.; Bailey, W. F. *J. Organomet. Chem.* **2002,** *646*, 59–67. (Review).
7. Sotomayor, N.; Lete, E. *Current Org. Chem.* **2003,** *7*, 275–300. (Review).
8. González-Temprano, I.; Osante, I.; Lete, E.; Sotomayor, N. *J. Org. Chem.* **2004,** *69*, 3875–3885.
9. Moreau, A.; Couture, A.; Deniau, E.; Grandclaudon, P.; Lebrun, S. *Org. Biomol. Chem.* **2005,** *3*, 2305–2309.
10. Gribble, G. W. *Parham cyclization*. In *Name Reactions for Homologations-Part II;* Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 749–764. (Review).
11. Aranzamendi, E.; Sotomayor, N.; Lete, E. *J. Org. Chem.* **2012,** *77*, 2986–2991.
12. Huard, K.; Bagley, S. W.; Menhaji-Klotz, E.; et al. *J. Org. Chem.* **2012,** *77*, 10050–10057.

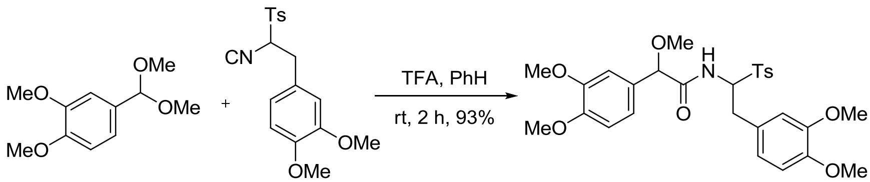
Passerini reaction

Three-component condensation (3CC) of carboxylic acids, *C*-isocyanides, and carbonyl compounds to afford α-acyloxycarboxamides. Also known as three-component reaction (3CR). *Cf*. Ugi reaction.





Example 1[3]



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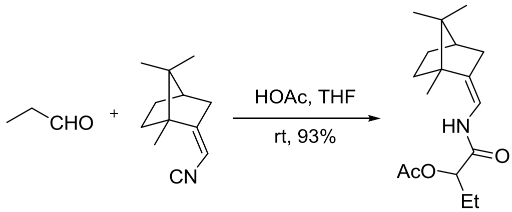
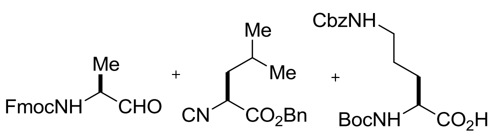


Example 3[6]



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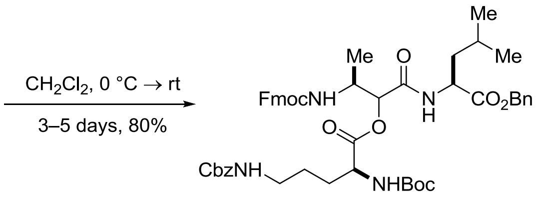
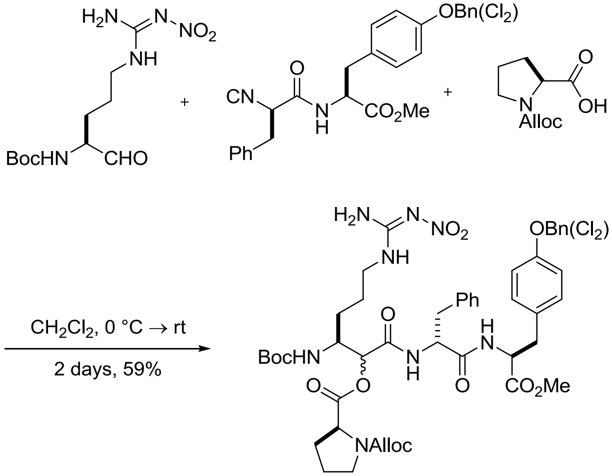


Example 4[7]

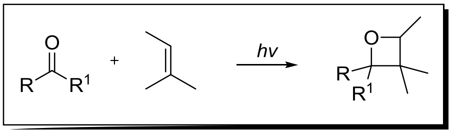


References

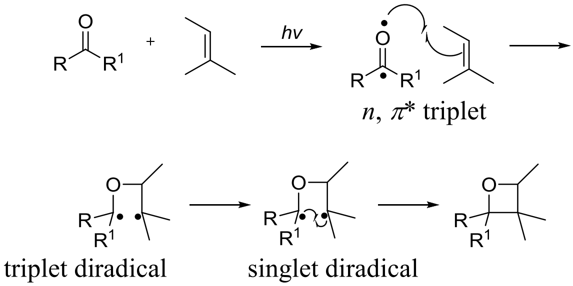
1. Passerini, M. *Gazz. Chim. Ital.* **1921,** *51*, 126–129. (b) Passerini, M. *Gazz. Chim. Ital.* **1921,** *51*, 181–188. Mario Passerini (b, 1891) was born in Scandicci, Italy. He obtained his Ph.D. in chemistry and pharmacy at the University of Florence, where he was a professor for most of his career.
2. Ferosie, I. *Aldrichimica Acta* **1971,** *4*, 21. (Review).
3. Barrett, A. G. M.; Barton, D. H. R.; Falck, J. R.; Papaioannou, D.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1979,** 652–661.
4. Ugi, I.; Lohberger, S.; Karl, R. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, **1991,** *Vol. 2*, p.1083. (Review).
5. Bock, H.; Ugi, I. *J. Prakt. Chem.* **1997,** *339*, 385–389.
6. Banfi, L.; Guanti, G.; Riva, R. *Chem. Commun.* **2000,** 985–986.
7. Owens, T. D.; Semple, J. E. *Org. Lett.* **2001,** *3*, 3301–3304.
8. Xia, Q.; Ganem, B. *Org. Lett.* **2002,** *4*, 1631–1634.
9. Banfi, L.; Riva, R. *Org. React.* **2005,** *65*, 1–140. (Review).
10. Klein, J. C.; Williams, D. R. *Passerini Reaction*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 765–785. (Review).
11. Sato, K.; Ozu, T.; Takenaga, N. *Tetrahedron Lett.* **2013,** *54*, 661–664.

Paternó–Büchi reaction

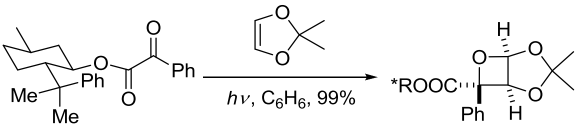
Photoinduced electrocyclization of a carbonyl with an alkene to form polysubstituted oxetane ring systems



Oxetanes



Example 1[2]



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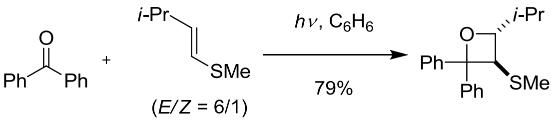
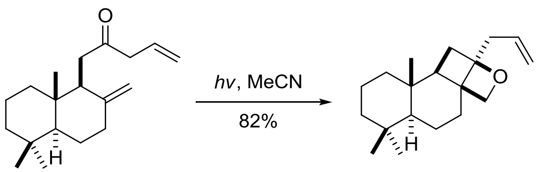


Example 3[6]



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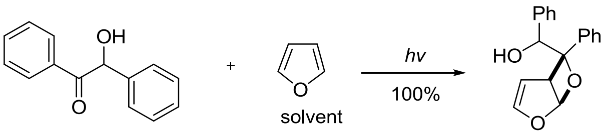
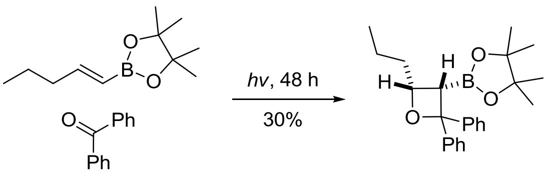
DOI 10.1007/978-3-319-03979-4_205, © Springer International Publishing Switzerland 2014

Example 4[8]



Example 5[9]

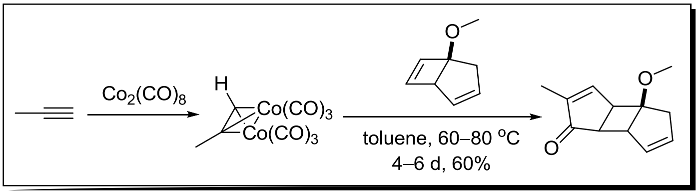


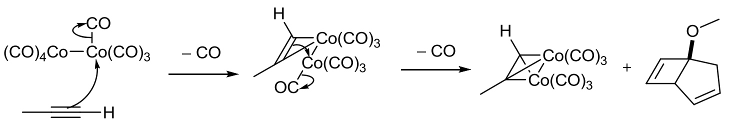
References

1. (a) Paternó, E.; Chieffi, G. *Gazz. Chim. Ital.* **1909,** *39*, 341–361. Emaubuele Paternó (1847–1935) was born in Palermo, Sicily, Italy. It was 104 years ago when he first described photoinduced oxetane formation. (b) Büchi, G.; Inman, C. G.; Lipinsky, E. S. *J. Am. Chem. Soc.* **1954,** *76*, 4327–4331. George H. Büchi (1921–1998) was born in Baden, Switzerland. He was a professor at MIT when he elucidated the structure of oxetanes, the products from the light-catalyzed addition of carbonyl compounds to olefins, which had been observed by E. Paternó in 1909. Büchi died of heart failure while hiking with his wife in his native Switzerland.
2. Koch, H.; Runsink, J.; Scharf, H.-D. *Tetrahedron Lett.* **1983,** *24*, 3217–3220.
3. Carless, H. A. J. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, **1984,** 425. (Review).
4. Morris, T. H.; Smith, E. H.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1987,** 964–965.
5. Porco, J. A., Jr.; Schreiber, S. L. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, **1991,** *Vol. 5*, 151–192. (Review).
6. de la Torre, M. C.; Garcia, I.; Sierra, M. A. *J. Org. Chem.* **2003,** *68*, 6611–6618.
7. Griesbeck, A. G.; Mauder, H.; Stadtmüller, S. *Acc. Chem. Res.* **1994,** *27*, 70–75. (Review).
8. D'Auria, M.; Emanuele, L.; Racioppi, R. *Tetrahedron Lett.* **2004,** *45*, 3877–3880.
9. Liu, C. M. *Paternó–Büchi Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 44–49. (Review).
10. Cho, D. W.; Lee, H.-Y.; Oh, S. W.; Choi, J. H.; Park, H. J.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem.* **2008,** *73*, 4539–4547.
11. D'Annibale, A.; D'Auria, M.; Prati, F.; Romagnoli, C.; Stoia, S.; Racioppi, R.; Viggiani, L. *Tetrahedron* **2013,** *69*, 3782–3795.

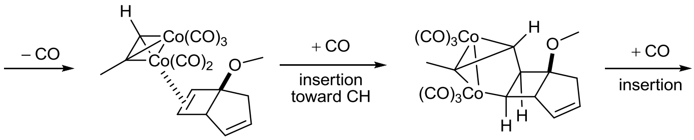
Pauson–Khand reaction

Formal [2 + 2 +1] cycloaddition of an alkene, alkyne, and carbon monoxide mediated by octacarbonyl dicobalt to form cyclopentenones.



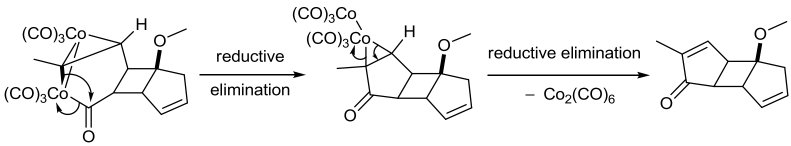


hexacarbonyldicobalt complex

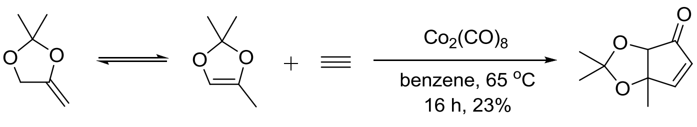


exo complex

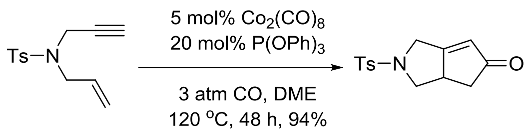
sterically-favored isomer



Example 1[3]



Example 2, A catalytic version[6]



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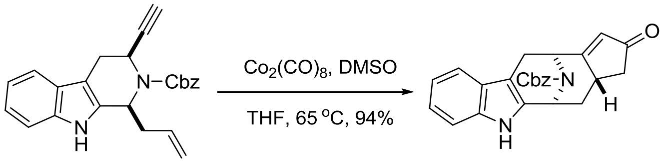
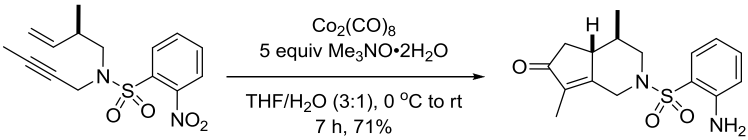
DOI 10.1007/978-3-319-03979-4_206,

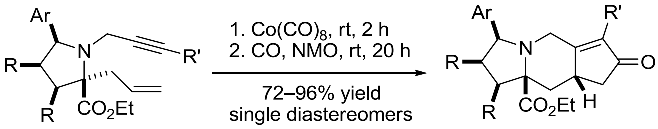
Example 3, Intramolecular Pauson–Khand reaction[9]



Example 4, Intramolecular Pauson–Khand reaction[10]



Example 5[12]

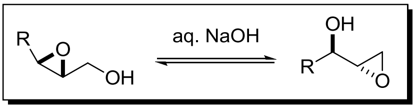


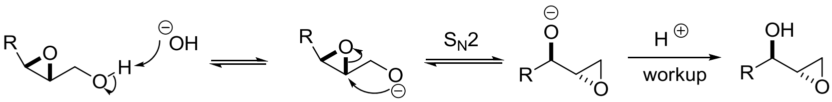
References

1. (a) Pauson, P. L.; Khand, I. U.; Knox, G. R.; Watts, W. E. *J. Chem. Soc., Chem. Commun*. **1971,** 36. Ihsan U. Khand and Peter L. Pauson were at the University of Strathclyde, Glasgow in Scotland. (b) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973,** 975–977. (c) Bladon, P.; Khand, I. U.; Pauson, P. L. *J. Chem. Res. (S)*, **1977,** 9. (d) Pauson, P. L. *Tetrahedron* **1985,** *41*, 5855–5860. (Review).
2. Schore, N. E. *Chem. Rev.* **1988,** *88*, 1081−1119. (Review).
3. Billington, D. C.; Kerr, W. J.; Pauson, P. L.; Farnocchi, C. F. *J. Organomet. Chem.* **1988,** *356*, 213–219.
4. Schore, N. E. In *Comprehensive Organic Synthesis*; Paquette, L. A.; Fleming, I.; Trost, B. M., Eds.; Pergamon: Oxford, **1991,** *Vol. 5*, p.1037. (Review).
5. Schore, N. E. *Org. React.* **1991,** *40*, 1–90. (Review).
6. Jeong, N.; Hwang, S. H.; Lee, Y.; Chung, J. *J. Am. Chem. Soc.* **1994,** *116*, 3159–3160.
7. Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000,** *56*, 3263–3283. (Review).
8. Tsujimoto, T.; Nishikawa, T.; Urabe, D.; Isobe, M. *Synlett* **2005,** 433–436.
9. Miller, K. A.; Martin, S. F. *Org. Lett*. **2007,** *9*, 1113–1116.
10. Kaneda, K.; Honda, T. *Tetrahedron* **2008,** *64*, 11589–11593.
11. Torres, R. R. *The Pauson-Khand Reaction: Scope, Variations and Applications*, Wiley: Hoboken, NJ, 2012. (Review).
12. McCormack, M. P.; Waters, S. P. *J. Org. Chem*. **2013,** *78*, 1127–1137.

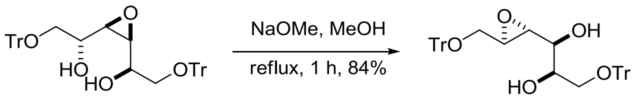
Payne rearrangement

The isomerization of 2,3-epoxy alcohol under the influence of a base to 1,2-epoxy-3-ol is referred to as the Payne rearrangement. Also known as epoxide migration.

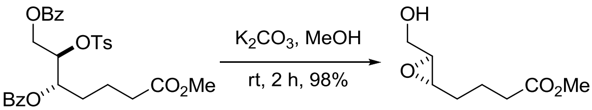




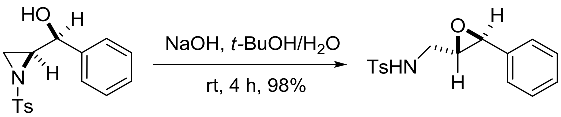
Example 1[2]



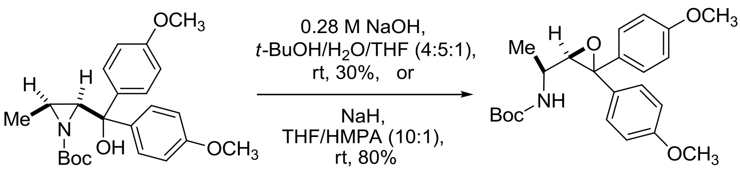
Example 2[3]



Example 3, Aza-Payne rearrangement[8]



Example 4, Aza-Payne rearrangement[9]



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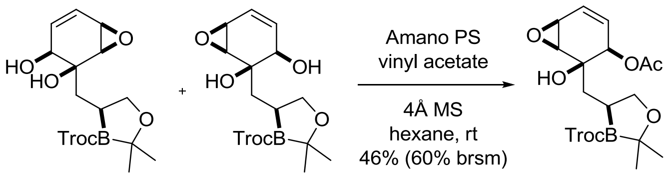
DOI 10.1007/978-3-319-03979-4_207, © Springer International Publishing Switzerland 2014

Example 5, Lipase-mediated dynamic kinetic resolution via a *vinylogous* Payne rearrangement[11]

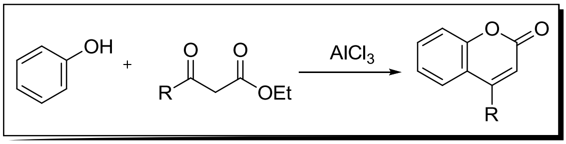


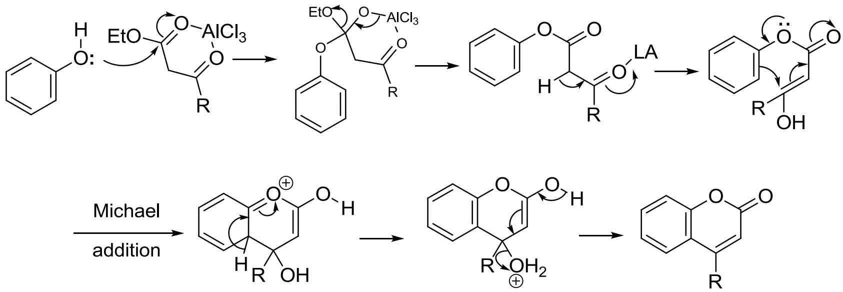
References

1. Payne, G. B. *J. Org. Chem.* **1962,** *27*, 3819–3822. George B. Payne was a chemist at Shell Development Co. in Emeryville, CA.
2. Buchanan, J. G.; Edgar, A. R. *Carbohydr. Res.* **1970,** *10*, 295–302.
3. Corey, E. J.; Clark, D. A.; Goto, G.; Marfat, A.; Mioskowski, C.; Samuelsson, B.; Hammerstrom, S. *J. Am. Chem. Soc.* **1980,** *102*, 1436–1439, and 3663–3665.
4. Ibuka, T. *Chem. Soc. Rev.* **1998,** *27*, 145–154. (Review).
5. Hanson, R. M. *Org. React.* **2002,** *60*, 1–156. (Review).
6. Yamazaki, T.; Ichige, T.; Kitazume, T. *Org. Lett.* **2004,** *6*, 4073–4076.
7. Bilke, J. L.; Dzuganova, M.; Froehlich, R.; Wuerthwein, E.-U. *Org. Lett.* **2005,** *7*, 3267–3270.
8. Feng, X.; Qiu, G.; Liang, S.; Su, J.; Teng, H.; Wu, L.; Hu, X. *Russ. J. Org. Chem.* **2006,** *42*, 514–500.
9. Feng, X.; Qiu, G.; Liang, S.; Teng, H.; Wu, L.; Hu, X. *Tetrahedron*: *Asymmetry* **2006,** *17*, 1394–1401.
10. Kumar, R. R.; Perumal, S. *Payne Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 474–488. (Review).
11. Hoye, T. R.; Jeffrey, C. S.; Nelson, D. P. *Org. Lett.* **2010,** *12*, 52–55.
12. Kulshrestha, A.; Salehi Marzijarani, N.; Dilip Ashtekar, K.; Staples, R.; Borhan, B. *Org. Lett.* **2012,** *14*, 3592–3595.

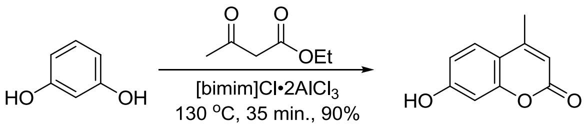
Pechmann coumarin synthesis

Lewis and Brønsted acid-mediated condensation of phenol with β-ketoester to produce coumarin. Some call it the von Pechmann cyclization.

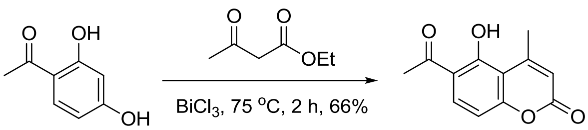




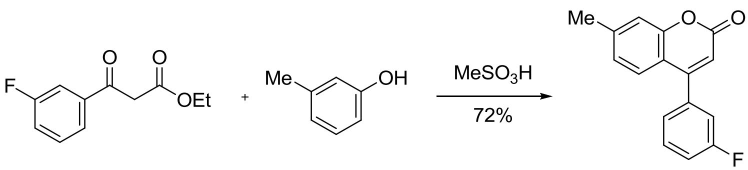
Example 1[6]



Example 2[8]



Example 3[11]



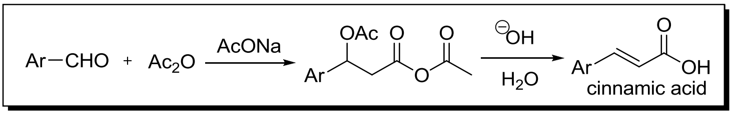
J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4_208,

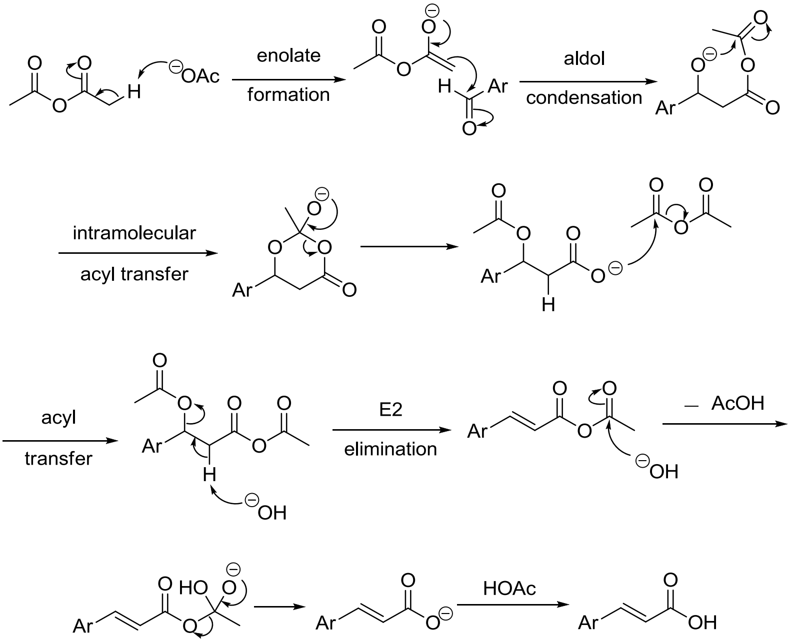
References

1. von Pechmann, H.; Duisberg, C. *Ber*. **1883,** *16*, 2119. Hans von Pechmann (1850–1902) was born in Nürnberg, Germany. After his doctorate, he worked with Frankland and von Baeyer. Pechmann taught at Munich and Tübingen. He committed suicide at 52 by taking cyanide.
2. Corrie, J. E. T. *J. Chem. Soc., Perkin Trans. 1* **1990,** 2151–2997.
3. Hua, D. H.; Saha, S.; Roche, D.; Maeng, J. C.; Iguchi, S.; Baldwin, C. *J. Org. Chem*. **1992,** *57*, 399–403.
4. Li, T.-S.; Zhang, Z.-H.; Yang, F.; Fu, C.-G. *J. Chem. Res., (S)* **1998,** 38–39.
5. Potdar, M. K.; Mohile, S. S.; Salunkhe, M. M. *Tetrahedron Lett*. **2001,** *42*, 9285–9287.
6. Khandekar, A. C.; Khandilkar, B. M. *Synlett*. **2002,** 152–154.
7. Smitha, G.; Sanjeeva Reddy, C. *Synth. Commun*. **2004,** *34*, 3997–4003.
8. De, S. K.; Gibbs, R. A. *Synthesis* **2005,** 1231–1233.
9. Manhas, M. S.; Ganguly, S. N.; Mukherjee, S.; Jain, A. K.; Bose, A. K. *Tetrahedron Lett*. **2006,** *47*, 2423–2425.
10. Rodriguez-Dominguez, J. C.; Kirsch, G. *Synthesis* **2006,** 1895–1897.
11. Ouellet, S. G.; Gauvreau, D.; Cameron, M.; Dolman, S.; Campeau, L.-C.; Hughes, G.; O'Shea, P. D.; Davies, I. W. *Org. Process Res. Dev*. **2012,** *16,* 214–219.

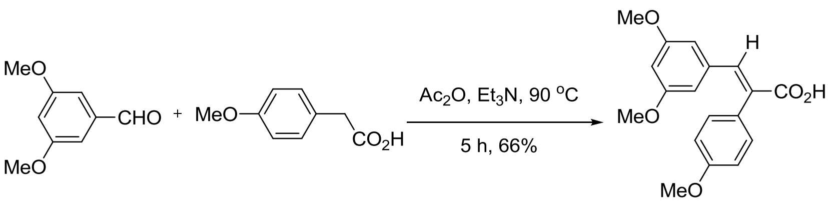
Perkin reaction

Cinnamic acid synthesis from aryl aldehyde and acetic anhydride.

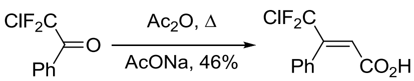




Example 1[7]



Example 2[9]



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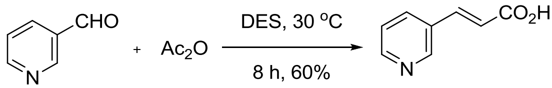
Example 3[12]



DES = Biodegradable deep eutectic solvent generated from choline chloride and urea.

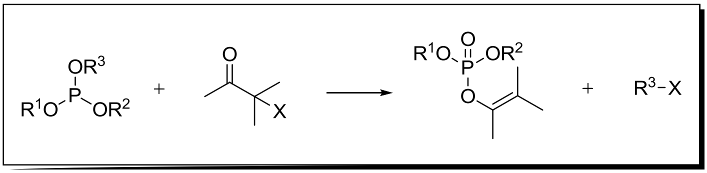
References

1. Perkin, W. H. *J. Chem. Soc.* **1868,** *21,* 53. William Henry Perkin (1838–1907), born in London, England, studied under A. W. von Hofmann at the Royal College of Chemistry. In an attempt to synthesize quinine in his home laboratory in 1856, Perkin synthesized mauve, the purple dye. He then started a factory to manufacture mauve and later other dyes including alizarin. Perkin was the first person to show that organic chemistry was not just mere intellectual curiosity but could be profitable, which catapulted the discipline into a higher level. In addition, Perkin also happened to be an exceptionally talented pianist.
2. Gaset, A.; Gorrichon, J. P. *Synth. Commun.* **1982,** *12,* 71–79.
3. Kinastowski, S.; Nowacki, A. *Tetrahedron Lett.* **1982,** *23,* 3723–3724.
4. Koepp, E.; Vögtle, F. *Synthesis* **1987,** 177–179.
5. Brady, W. T.; Gu, Y.-Q. *J. Heterocycl. Chem.* **1988,** *25,* 969–971.
6. Pálinkó, I.; Kukovecz, A.; Török, B.; Körtvélyesi, T. *Monatsh. Chem.* **2001,** *131,* 1097–1104.
7. Gaukroger, K.; Hadfield, J. A.; Hepworth, L. A.; Lawrence, N. J.; McGown, A. T. *J. Org. Chem.* **2001,** *66*, 8135–8138.
8. Solladié, G.; Pasturel-Jacopé, Y.; Maignan, J. *Tetrahedron* **2003,** *59,* 3315–3321.
9. Sevenard, D. V. *Tetrahedron Lett.* **2003,** *44,* 7119–7126.
10. Chandrasekhar, S.; Karri, P. *Tetrahedron Lett.* **2006,** *47,* 2249–2251.
11. Lacova, M.; Stankovicova, H.; Bohac, A.; Kotzianova, B. *Tetrahedron* **2008,** *64,* 9646–9653.
12. Pawar, P. M.; Jarag, K. J.; Shankarling, G. S. *Green Chem.* **2011,** *13,* 2130–2134.

Perkow vinyl phosphate synthesis

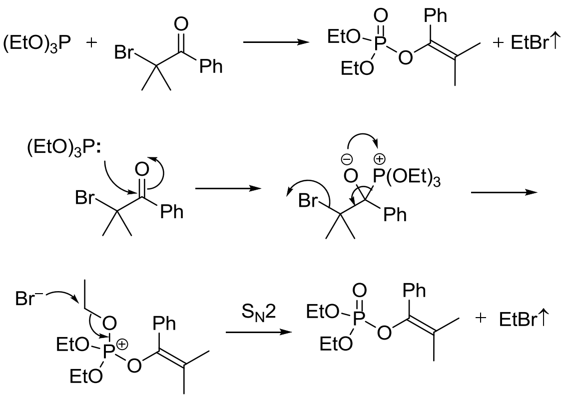
Enol phosphate synthesis from α-halocarbonyls and trialkylphosphites.

General scheme:

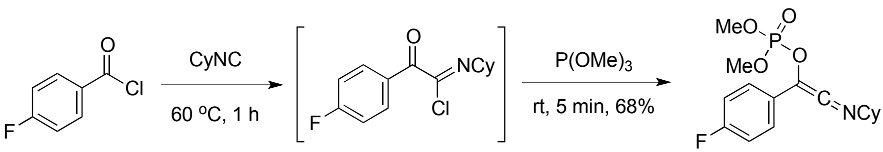


X = Cl, Br, I, secondary or tertiary halides are required to retard the competing Michaelis–Arbuzov reaction.

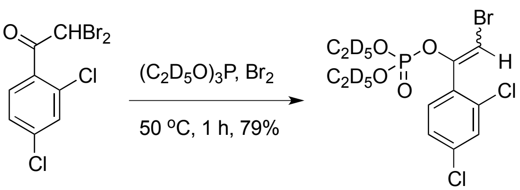
Example 1.



Example 2[7]



Example 3[8]



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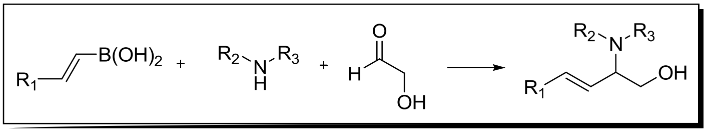
DOI 10.1007/978-3-319-03979-4_210, © Springer International Publishing Switzerland 2014

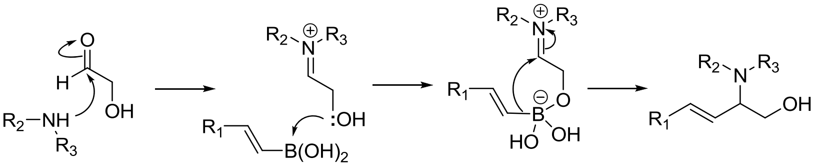
References

1. Perkow, W.; Ullrich, K.; Meyer, F. *Nasturwiss.* **1952,** *39*, 353.
2. Perkow, W. *Ber. Dtsch. Chem. Ges.* **1954,** *87*, 755.
3. Borowitz, G. B.; Borowitz, I. J. *Handb. Organophosphorus Chem.* **1992,** 115. (Review).
4. Hudson, H. R.; Matthews, R. W.; McPartlin, M.; Pryce, M. A.; Shode, O. O. *J. Chem. Soc., Perkin Trans. 2* **1993,** 1433.
5. Janecki, T.; Bodalski, R. *Heteroat. Chem*. **2000,** *11*, 115.
6. Balasubramanian, M. *Perkow Reaction,* in *Name Reactions for Functional Group Transformations,* Li, J. J. Ed., Wiley: Hoboken, NJ, **2007,** pp 369–385. (Review).
7. Coffinier, D.; El Kaim, L.; Grimaud, L. *Org. Lett*. **2009,** *11,* 1825–1827.
8. Huras, B.; Konopski, L.; Zakrzewski, J. *J. Labeled Compd. Radiopharm.* **2011,** *54*, 399–400.
9. Yavari, I.; Hosseinpour, R.; Pashazadeh, R.; Ghanbari, E.; Skoulika, S. *Tetrahedron* **2013,** *69*, 2462–2467.

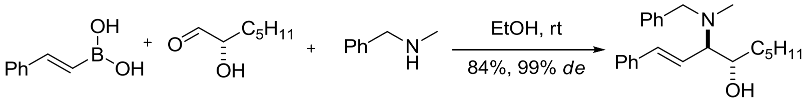
Petasis reaction

Benzylic or allylic amine from the three-component reaction of an aryl- or a vinyl-boronic acid, a carbonyl and an amine. Also known as boronic acid-Mannich or Petasis boronic acid-Mannich reaction. *Cf.* Mannich reaction.

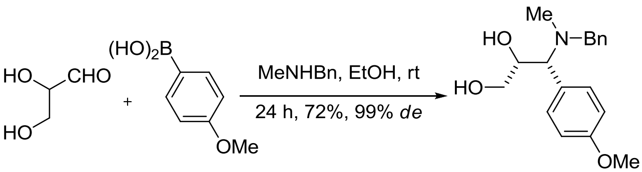




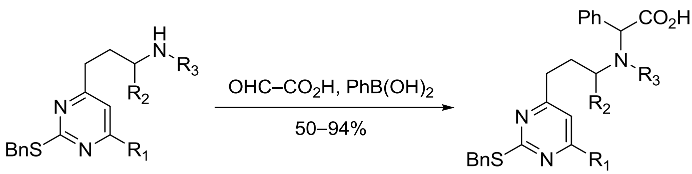
Example 1[2]



Example 2[4]



Example 3[9]



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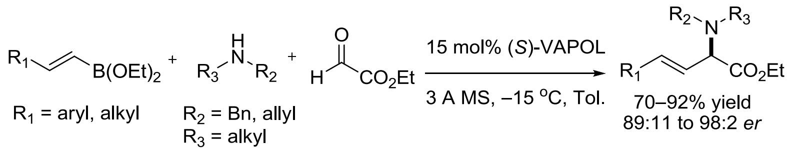
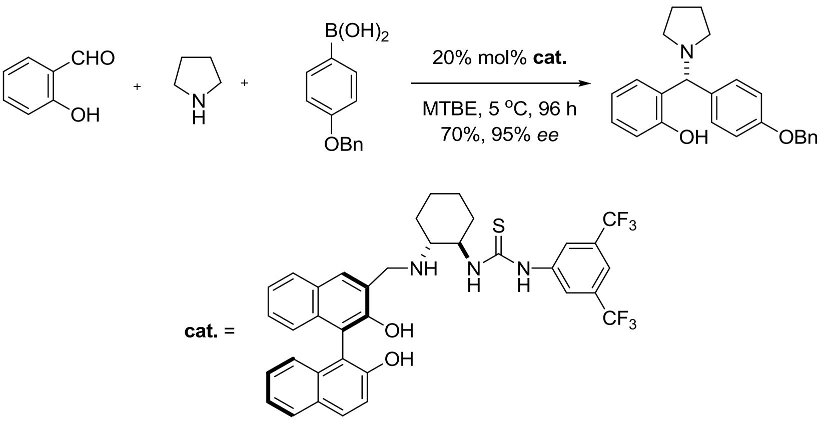
Example 4, Asymmetric Petasis reaction[10]



Example 5, Asymmetric Petasis reaction[11]

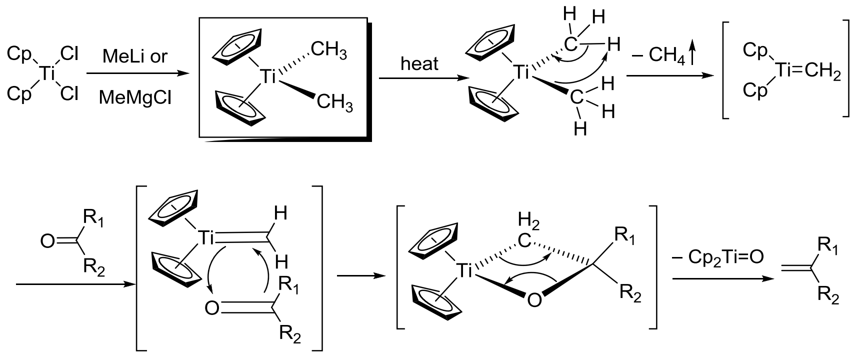


References

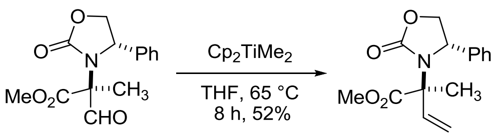
1. (a) Petasis, N. A.; Akritopoulou, I. *Tetrahedron Lett*. **1993,** *34*, 583–586. (b) Petasis, N. A.; Zavialov, I. A. *J. Am. Chem. Soc*. **1997,** *119*, 445–446. (c) Petasis, N. A.; Goodman, A.; Zavialov, I. A. *Tetrahedron* **1997,** *53*, 16463–16470. (d) Petasis, N. A.; Zavialov, I. A. *J. Am. Chem. Soc*. **1998,** *120*, 11798–11799. Nicos A. Petasis is a professor at the University of Southern California in Los Angeles.
2. Koolmeister, T.; Södergren, M.; Scobie, M. *Tetrahedron Lett*. **2002,** *43*, 5969–5970.
3. Orru, R. V. A.; deGreef, M. *Synthesis* **2003,** 1471–1499. (Review).
4. Sugiyama, S.; Arai, S.; Ishii, K. *Tetrahedron: Asymmetry* **2004,** *15*, 3149–3153.
5. Chang, Y. M.; Lee, S. H.; Nam, M. H.; Cho, M. Y.; Park, Y. S.; Yoon, C. M. *Tetrahedron Lett.* **2005**, *46*, 3053–3056.
6. Follmann, M.; Graul, F.; Schaefer, T.; Kopec, S.; Hamley, P. *Synlett* **2005,** 1009–1011.
7. Danieli, E.; Trabocchi, A.; Menchi, G.; Guarna, A. *Eur. J. Org. Chem*. **2007,** 1659–1668.
8. Konev, A. S.; Stas, S.; Novikov, M. S.; Khlebnikov, A. F.; Abbaspour Tehrani, K. *Tetrahedron* **2007,** *64*, 117–123.
9. Font, D.; Heras, M.; Villalgordo, J. M. *Tetrahedron* **2007,** *64*, 5226–5235.
10. Lou, S.; Schaus, S. E. *J. Am. Chem. Soc*. **2008,** *130*, 6922–6923.
11. Abbaspour Tehrani, K.; Stas, S.; Lucas, B.; De Kimpe, N. *Tetrahedron* **2009,** *65*, 1957–1966.
12. Han, W.-Y.; Zuo, J.; Zhang, X.-M.; Yuan, W.-C. *Tetrahedron* **2013,** *69*, 537–541.

Petasis reagent

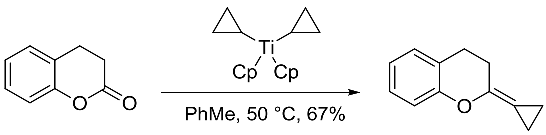
The Petasis reagent (Cp_2TiMe_2, dimethyltitanocene) undergoes similar olefination reactions with ketones and aldehydes as does the Tebbe reagent. The originally proposed mechanism[5] was very different from that of Tebbe olefination. However, later experimental data seem to suggest that both Petasis and Tebbe olefination share the same mechanism, i.e., the carbene mechanism involving a four-membered titanium oxide ring intermediate.[9] Petasis reagent is easier to make than the Tebbe reagent.



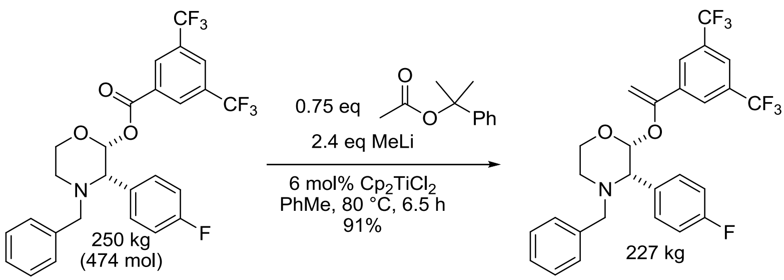
Example 1[2]



Example 2[3]



Example 3[5]



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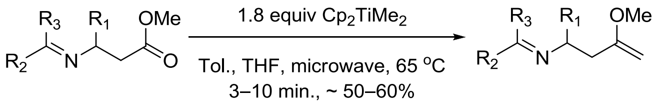
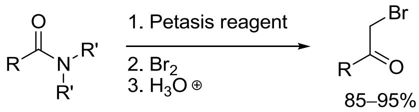
Example 4[8]



Example 5[11]

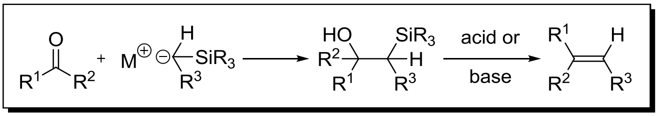


References

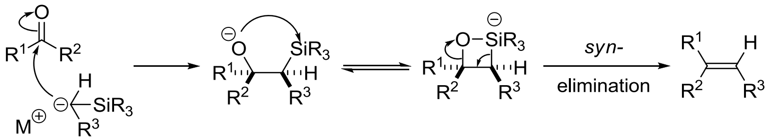
1. Petasis, N. A.; Bzowej, E. I. *J. Am. Chem. Soc.* **1990,** *112*, 6392–6394. Nicos A. Petasis is a professor at the University of Southern California in Los Angeles.
2. Colson, P. J.; Hegedus, L. S. *J. Org. Chem*. **1993,** *58*, 5918–5924.
3. Petasis, N. A.; Bzowej, E. I. *Tetrahedron Lett*. **1993,** *34*, 943–946.
4. Payack, J. F.; Hughes, D. L.; Cai, D.; Cottrell, I. F.; Verhoeven, T. R. *Org. Synth*. **2002,** *79*, 19.
5. Payack, J. F.; Huffman, M. A.; Cai, D. W.; Hughes, D. L.; Collins, P. C.; Johnson, B. K.; Cottrell, I. F.; Tuma, L. D. *Org. Pro. Res. Dev*. **2004,** *8*, 256–259.
6. Cook, M. J.; Fleming, E. I. *Tetrahedron Lett*. **2005,** *46*, 297–300.
7. Morency, L.; Barriault, L. *J. Org. Chem*. **2005,** *70*, 8841–8853.
8. Adriaenssens, L. V.; Hartley, R. C. *J. Org. Chem*. **2007,** *72*, 10287–10290.
9. Naskar, D.; Neogi, S.; Roy, A.; Mandal, A. B. *Tetrahedron Lett*. **2008,** *49*, 6762–6764.
10. Zhang, J. *Tebbe Reagent*. In *Name Reactions for Homologations-Part I,* Li, J. J. Ed., Wiley: Hoboken, NJ, **2009,** pp 319–333. (Review).
11. Kobeissi, M.; Cherry, K.; Jomaa, W. *Synth. Commun*. **2013,** *43*, 2955–2965.

Peterson olefination

Alkenes from α-silyl carbanions and carbonyl compounds. Also known as the sila-Wittig reaction.

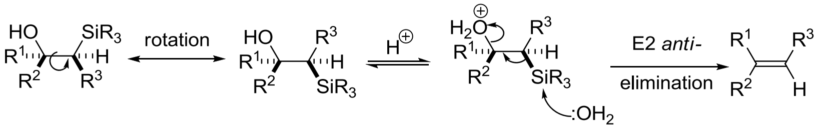


Basic conditions:



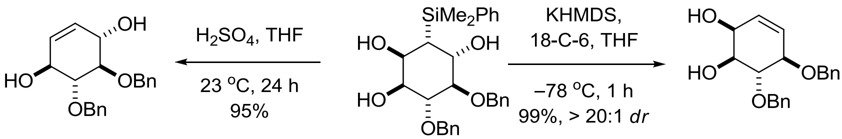
β-silylalkoxide intermediate

Acidic conditions:

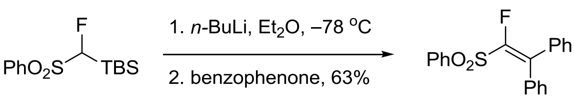


β-hydroxysilane

Example 1[6]



Example 2[7]



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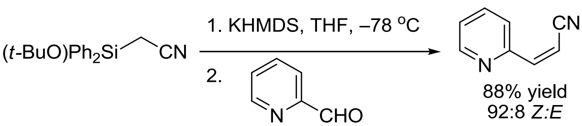

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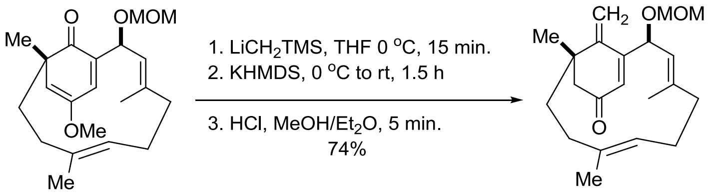
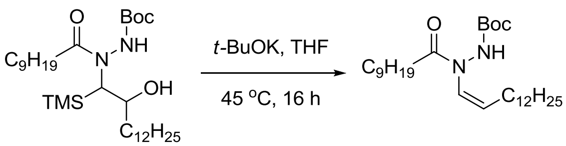
DOI 10.1007/978-3-319-03979-4_213, © Springer International Publishing Switzerland 2014

Example 4[10]



Example 5[12]

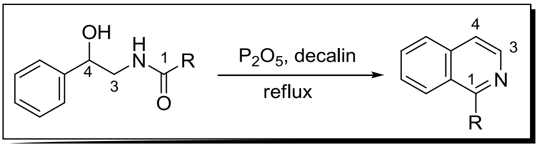


References

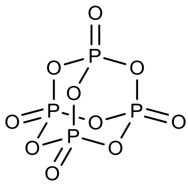
1. Peterson, D. J. *J. Org. Chem*. **1968,** *33*, 780–784.
2. Ager, D. J. *Org. React.* **1990,** *38*, 1–223. (Review).
3. Barrett, A. G. M.; Hill, J. M.; Wallace, E. M.; Flygare, J. A. *Synlett* **1991,** 764–770. (Review).
4. van Staden, L. F.; Gravestock, D.; Ager, D. J. *Chem. Soc. Rev.* **2002,** *31*, 195–200. (Review).
5. Ager, D. J. *Science of Synthesis* **2002,** *4*, 789–809. (Review).
6. Heo, J.-N.; Holson, E. B.; Roush, W. R. *Org. Lett*. **2003,** *5*, 1697–1700.
7. Asakura, N.; Usuki, Y.; Iio, H. *J. Fluorine Chem*. **2003,** *124*, 81–84.
8. Kojima, S.; Fukuzaki, T.; Yamakawa, A.; Murai, Y. *Org. Lett*. **2004,** *6,* 3917–3920.
9. Kano, N.; Kawashima, T. *The Peterson and Related Reactions* in *Modern Carbonyl Olefination;* Takeda, T., Ed.; Wiley-VCH: Weinheim, Germany, **2004,** 18–103. (Review).
10. Huang, J.; Wu, C.; Wulff, W. D. *J. Am. Chem. Soc*. **2007,** *129*, 13366.
11. Ahmad, N. M. *Peterson Olefination*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed., Wiley: Hoboken, NJ, **2009,** pp 521–538. (Review).
12. Beveridge, R. E.; Batey, R. A. *Org. Lett*. **2013,** *15,* 3086–3089.

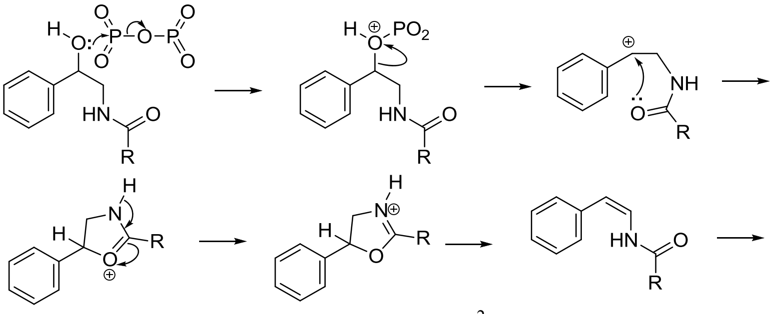
Pictet–Gams isoquinoline synthesis

The isoquinoline framework is derived from the corresponding acyl derivatives of β-hydroxy-β-phenylethylamines. Upon exposure to a dehydrating agent such as phosphorus pentoxide, or phosphorus oxychloride, under reflux and in an inert solvent such as decalin, isoquinoline frameworks are formed.

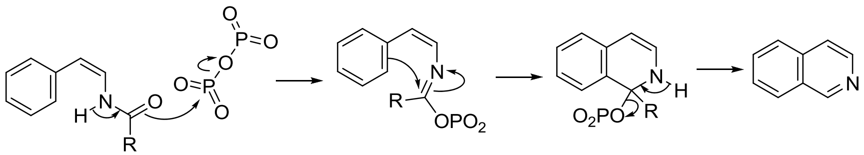


P_2O_5 actually exists as P_4O_{10}, an adamantane-like structure:

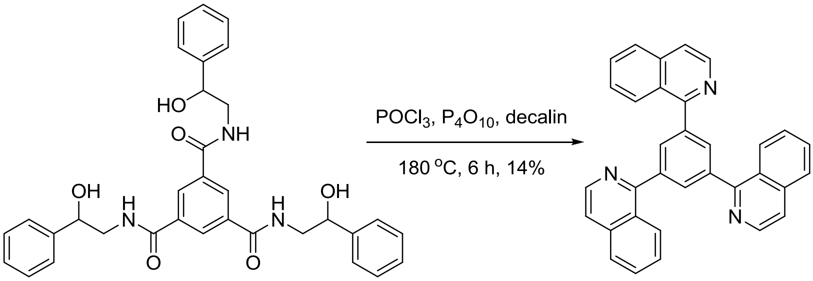




Oxazoline intermediate[2]



Example 1[4]



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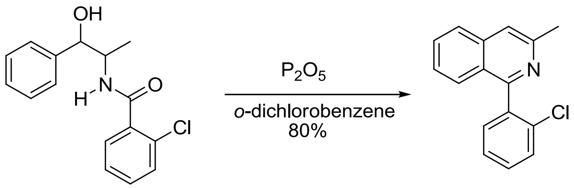
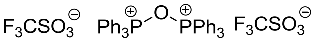
DOI 10.1007/978-3-319-03979-4_214, © Springer International Publishing Switzerland 2014

Example 2[7]



Example 3[9]

An Alternative to Pictet—Gams Reaction Triggered by Hendrickson Reagent: Isoquinolines and β-Carbolines from amides:



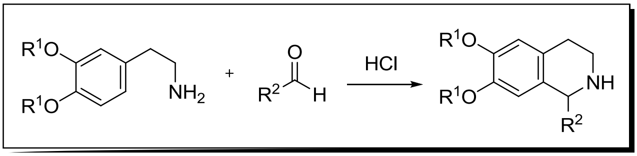
Hendrickson reagent

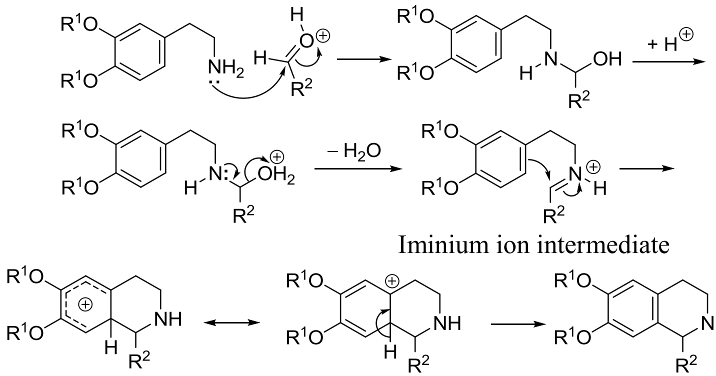
Reference

1. (a) Pictet, A.; Kay, F. W. *Ber*. **1909,** *42*, 1973–1979. (b) Pictet, A.; Gams, A. *Ber*. **1909,** *42*, 2943–2952. Amé Pictet (1857–1937), born in Geneva, Switzerland, carried out a tremendous amount of work on alkaloids.
2. Fritton, A. O.; Frost, J. R.; Zakaria, M. M.; Andrew, G. *J. Chem. Soc., Chem. Commun*., **1973,** 889.
3. (a) Ardabilchi, N.; Fitton, A. O.; Frost, J. R.; Oppong-Boachie, F. *Tetrahedron Lett.* **1977,** *18,* 4107–4110. (b) Ardabilchi, N.; Fitton, A. O.; Frost, J. R.; Oppong-Boachie, F. K.; Hadi, A. H. A.; Sharif, A. M. *J. Chem. Soc., Perkin Trans. 1* **1979,** 539–543.
4. Dyker, G.; Gabler, M.; Nouroozian, M.; Schulz, P. *Tetrahedron Lett*. **1994,** *35,* 9697–9700.
5. Poszávácz, L.; Simig, G. *J. Heterocycl. Chem*. **2000,** *37*, 343–348.
6. Poszávácz, L.; Simig, G. *Tetrahedron* **2001,** *57*, 8573–8580.
7. Manning, H. C.; Goebel, T.; Marx, J. N.; Bornhop, D. J. *Org. Lett*. **2002,** *4*, 1075–1081.
8. Holsworth, D. D. *Pictet–Gams Isoquinoline Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 457–465. (Review).
9. Wu, M.; Wang, S. *Synthesis* **2010,** 587–592.
10. Caille, F.; Buron, F.; Toth, E.; Suzenet, F. *E. J. Org. Chem.* **2011,** 2120–2127, S2120/1-S2120/25.
11. Blair, A.; Stevenson, L.; Sutherland, A. *Tetrahedron Lett*. **2012,** *53*, 4084–4086.

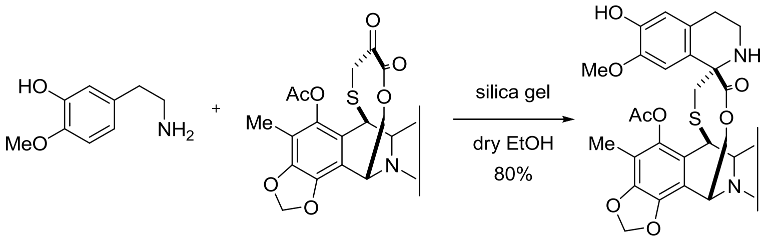
Pictet–Spengler tetrahydroisoquinoline synthesis

Tetrahydroisoquinolines from condensation of β-arylethylamines and carbonyl compounds followed by cyclization.

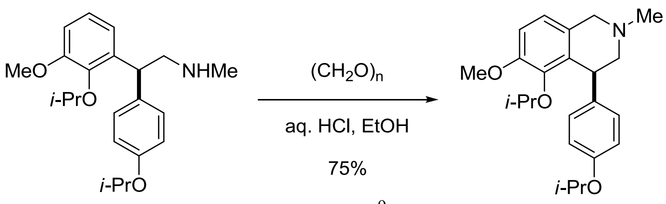




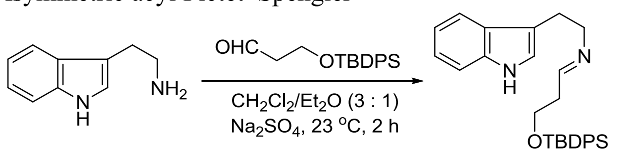
Example 1[4]



Example 2[7]



Example 3, Asymmetric acyl Pictet–Spengler[9]



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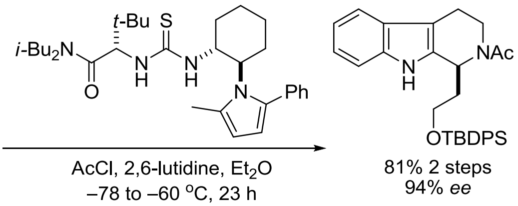
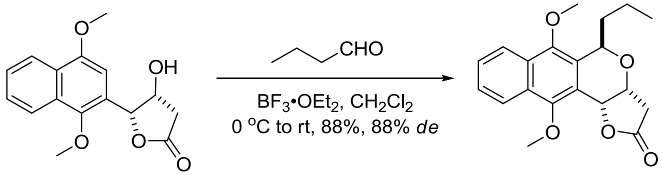
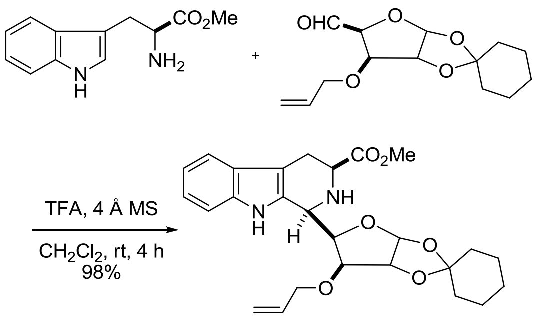


Example 4, Oxa-Pictet–Spengler[10]



Example 5,

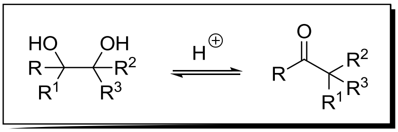


References

1. Pictet, A.; Spengler, T. *Ber.* **1911,** *44*, 2030–2036.
2. Cox, E. D.; Cook, J. M. *Chem. Rev.* **1995,** *95*, 1797–1842. (Review).
3. Corey, E. J.; Gin, D. Y.; Kania, R. S. *J. Am. Chem. Soc*. **1996,** *118*, 9202–9203.
4. Zhou, B.; Guo, J.; Danishefsky, S. J. *Org. Lett*. **2002,** *4*, 43–46.
5. Yu, J.; Wearing, X. Z.; Cook, J. M. *Tetrahedron Lett.* **2003,** *44*, 543–547.
6. Tsuji, R.; Nakagawa, M.; Nishida, A. *Tetrahedron: Asymmetry* **2003,** *14*, 177–180.
7. Couture, A.; Deniau, E.; Grandclaudon, P.; Lebrun, S. *Tetrahedron: Asymmetry* **2003,** *14*, 1309–1320.
8. Tinsley, J. M. *Pictet–Spengler Isoquinoline Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 469–479. (Review).
9. Mergott, D. J.; Zuend, S. J.; Jacobsen, E. N. *Org. Lett*. **2008,** *10*, 745–748.
10. Eid, C. N.; Shim, J.; Bikker, J.; Lin, M. *J. Org. Chem*. **2009,** *74*, 423–426.
11. Pradhan, P.; Nandi, D.; Pradhan, S. D.; Jaisankar, P.; Giri, V. S. *Synlett* **2013,** *24*, 85–89.

Pinacol rearrangement

Acid-catalyzed rearrangement of vicinal diols (pinacols) to carbonyl compounds.

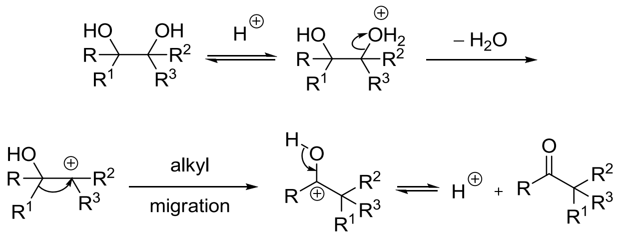


The most electron-rich alkyl group (more substituted carbon) migrates first. The general migration order:

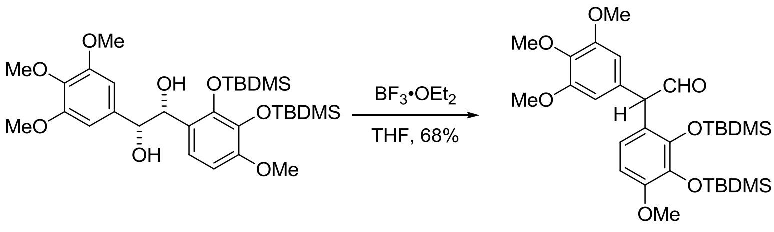
tertiary alkyl > cyclohexyl > secondary alkyl > benzyl > phenyl > primary alkyl > methyl >> H.

For substituted aryls:

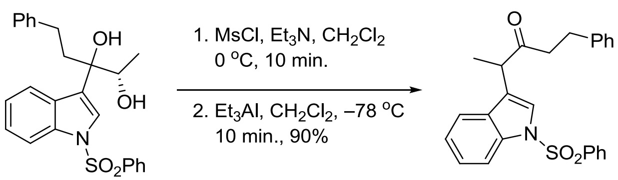
p-MeO-Ar > *p*-Me-Ar > *p*-Cl-Ar > *p*-Br-Ar > *p*-O_2N-Ar



Example 1[4]



Example 2[5]



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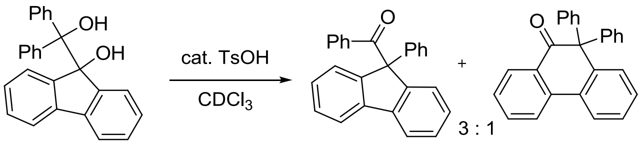
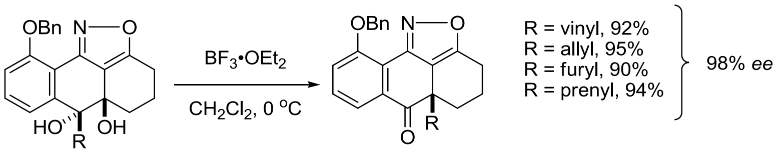
DOI 10.1007/978-3-319-03979-4_216, © Springer International Publishing Switzerland 2014

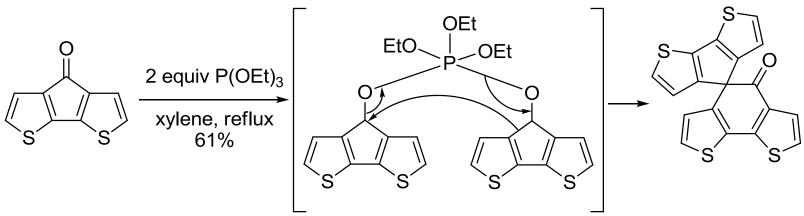
Example 3[7]



Example 4[9]



Example 5, A Trivalent organophosphorus reagent induced pinacol rearrangement[11]

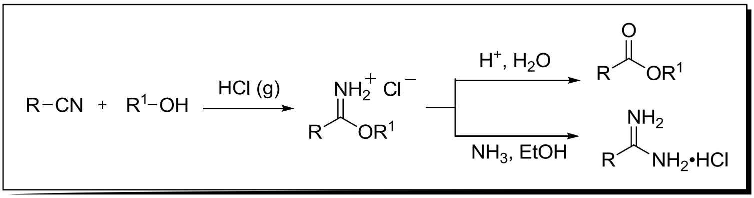


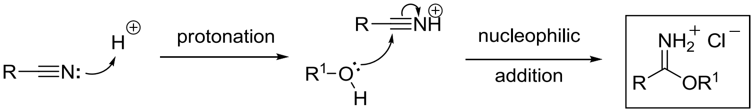
References

1. Fittig, R. *Ann.* **1860,** *114*, 54–63.
2. Magnus, P.; Diorazio, L.; Donohoe, T. J.; Giles, M.; Pye, P.; Tarrant, J.; Thom, S. *Tetrahedron* **1996,** *52*, 14147–14176.
3. Razavi, H.; Polt, R. *J. Org. Chem.* **2000,** *65*, 5693–5706.
4. Pettit, G. R.; Lippert III, J. W.; Herald, D. L. *J. Org. Chem.* **2000,** *65*, 7438–7444.
5. Shinohara, T.; Suzuki, K. *Tetrahedron Lett.* **2002,** *43*, 6937–6940.
6. Overman, L. E.; Pennington, L. D. *J. Org. Chem.* **2003,** *68*, 7143–7157. (Review).
7. Mladenova, G.; Singh, G.; Acton, A.; Chen, L.; Rinco, O.; Johnston, L. J.; Lee-Ruff, E. *J. Org. Chem.* **2004,** *69*, 2017–2023.
8. Birsa, M. L.; Jones, P. G.; Hopf, H. *Eur. J. Org. Chem.* **2005,** 3263–3270.
9. Suzuki, K.; Takikawa, H.; Hachisu, Y.; Bode, J. W. *Angew. Chem. Int. Ed.* **2007,** *46*, 3252–3254.
10. Goes, B. *Pinacol Rearrangement*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed., Wiley: Hoboken, NJ, **2009,** pp 319–333. (Review).
11. Marin, L.; Zhang, Y.; Robeyns, K.; Champagne, B.; Adriaensens, P.; Lutsen, L.; Vanderzande, D.; Bevk, D.; Maes, W. *Tetrahedron Lett.* **2013,** *54*, 526–529.

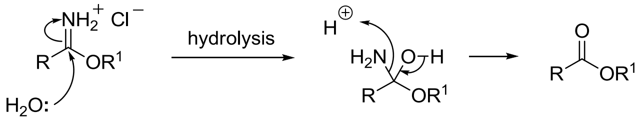
Pinner reaction

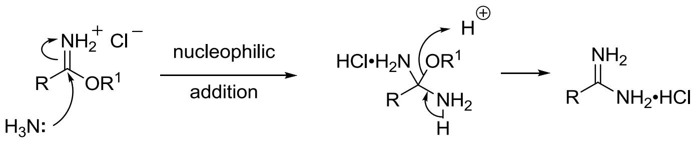
Transformation of a nitrile into an imino ether, which can be converted to either an ester or an amidine.





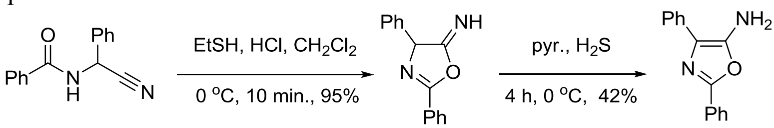
common intermediate



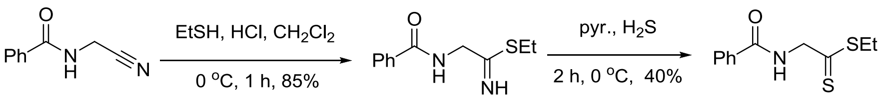


imidate hydrochloride

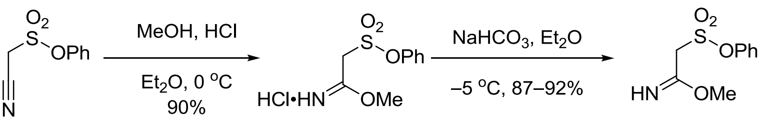
Example 1[2]



Example 2[2]



Example 3[6]



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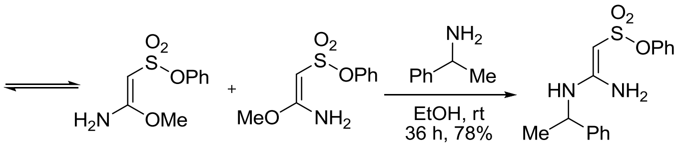
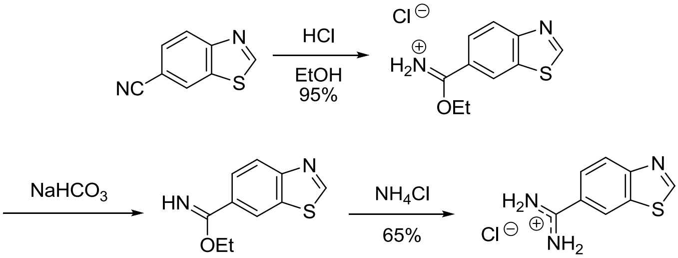
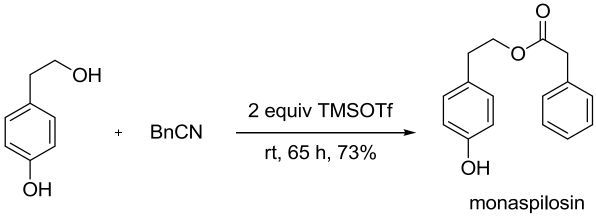
DOI 10.1007/978-3-319-03979-4_217, © Springer International Publishing Switzerland 2014



Example 4[10]



Example 5[11]

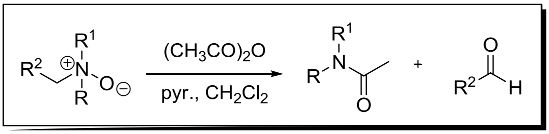


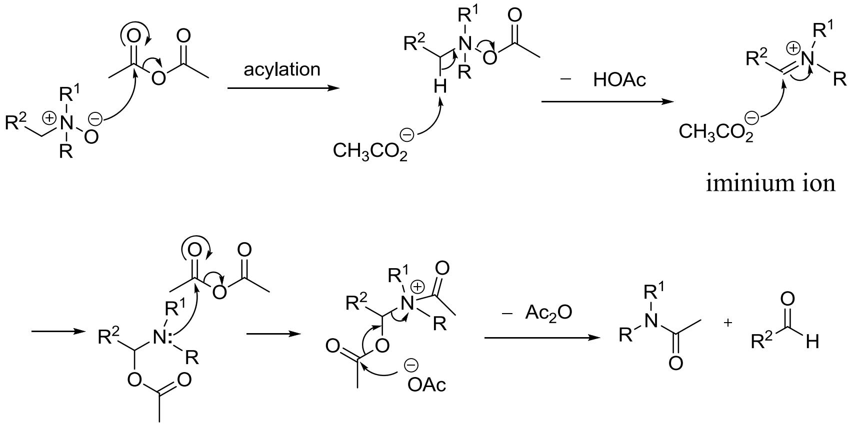
References

1. (a) Pinner, A.; Klein, F. *Ber.* **1877,** *10*, 1889–1897. (b) Pinner, A.; Klein, F. *Ber.* **1878,** *11*, 1825.
2. Poupaert, J.; Bruylants, A.; Crooy, P. *Synthesis* **1972,** 622–624.
3. Lee, Y. B.; Goo, Y. M.; Lee, Y. Y.; Lee, J. K. *Tetrahedron Lett.* **1990,** *31*, 1169–1170.
4. Cheng, C. C. *Org. Prep. Proced. Int.* **1990,** *22*, 643–645.
5. Siskos, A. P.; Hill, A. M. *Tetrahedron Lett.* **2003,** *44*, 789–794.
6. Fischer, M.; Troschuetz, R. *Synthesis* **2003,** 1603–1609.
7. Fringuelli, F.; Piermatti, O.; Pizzo, F. *Synthesis* **2003,** 2331–2334.
8. Cushion, M. T.; Walzer, P. D.; Collins, M. S.; Rebholz, S.; Vanden Eynde, J. J.; Mayence, A.; Huang, T. L. *Antimicrob. Agents Chemoth.* **2004,** *48*, 4209–4216.
9. Li, J.; Zhang, L.; Shi, D.; Li, Q.; Wang, D.; Wang, C.; Zhang, Q.; Zhang, L.; Fan, Y. *Synlett* **2008,** 233–236.
10. Racané, L.; Tralic-Kulenovic, V.; Mihalic, Z.; Pavlovic, G.; Karminski-Zamola, G. *Tetrahedron* **2008,** *64*, 11594–11602.
11. Pfaff, D.; Nemecek, G.; Podlech, J. *Beilstein J. Org. Chem.* **2013,** *9*, 1572–1577.

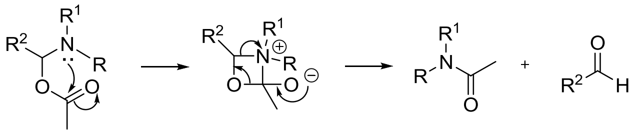
Polonovski reaction

Treatment of a tertiary *N*-oxide with an activating agent such as acetic anhydride, resulting in rearrangement where an *N,N*-disubstituted acetamide and an aldehyde are generated.

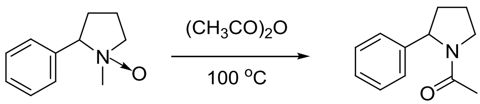




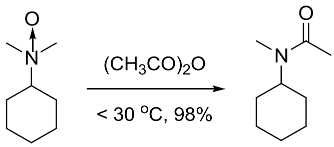
The intramolecular pathway is also operative:



Example 1[1]



Example 2[2]



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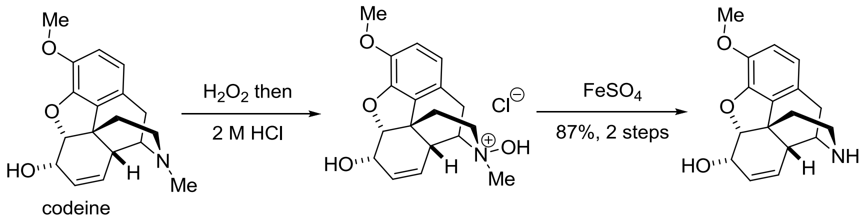
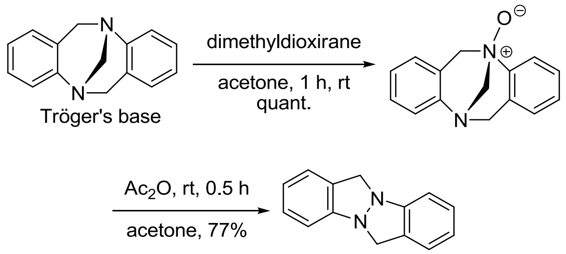
Example 3, Iron salt-mediated Polonovski reaction[9]



Example 4[11]

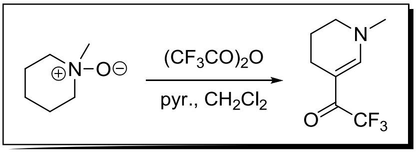


References

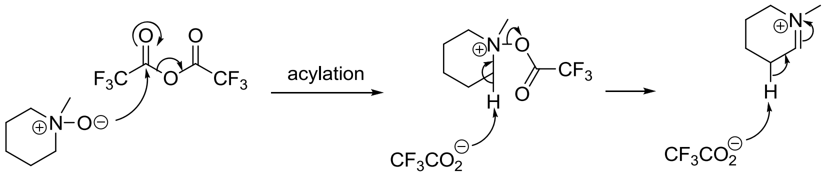
1. Polonovski, M.; Polonovski, M. *Bull. Soc. Chim. Fr.* **1927,** *41*, 1190–1208.
2. Michelot, R. *Bull. Soc. Chim. Fr.* **1969,** 4377–4385.
3. Lounasmaa, M.; Karvinen, E.; Koskinen, A.; Jokela, R. *Tetrahedron* **1987,** *43*, 2135–2146.
4. Tamminen, T.; Jokela, R.; Tirkkonen, B.; Lounasmaa, M. *Tetrahedron* **1989,** *45*, 2683–2692.
5. Grierson, D. *Org. React.* **1990,** *39*, 85–295. (Review).
6. Morita, H.; Kobayashi, J. *J. Org. Chem.* **2002,** *67*, 5378–5381.
7. McCamley, K.; Ripper, J. A.; Singer, R. D.; Scammells, P. J. *J. Org. Chem.* **2003,** *68*, 9847–9850.
8. Nakahara, S.; Kubo, A. *Heterocycles* **2004,** *63*, 1849–1854.
9. Thavaneswaran, S.; Scammells, P. J. *Bioorg. Med. Chem. Lett.* **2006,** *16*, 2868–2871.
10. Volz, H.; Gartner, H. *Eur. J. Org. Chem.* **2007,** 2791–2801.
11. Pacquelet, S.; Blache, Y.; Kimny, T.; Dubois, M.-A. L.; Desbois, N. *Synth. Commun.* **2013,** *43*, 1092–1100.

Polonovski–Potier reaction

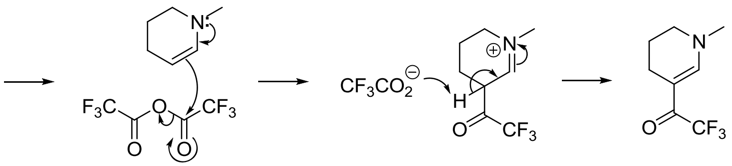
A modification of the Polonovski reaction where trifluoroacetic anhydride is used in place of acetic anhydride. Because the reaction conditions for the Polonovski–Potier reaction are mild, it has largely replaced the Polonovski reaction.



tertiary *N*-oxide

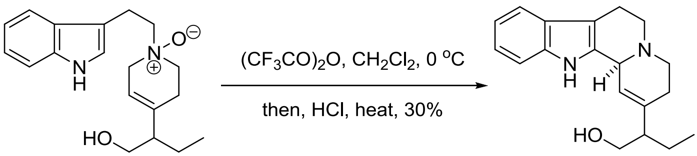


iminium ion

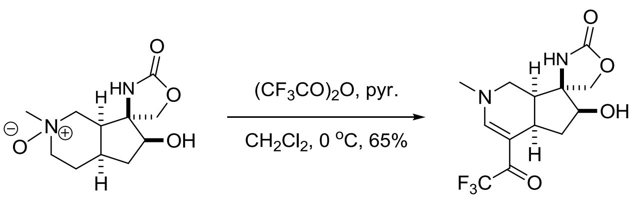


enamine

Example 1[2]



Example 2[5]



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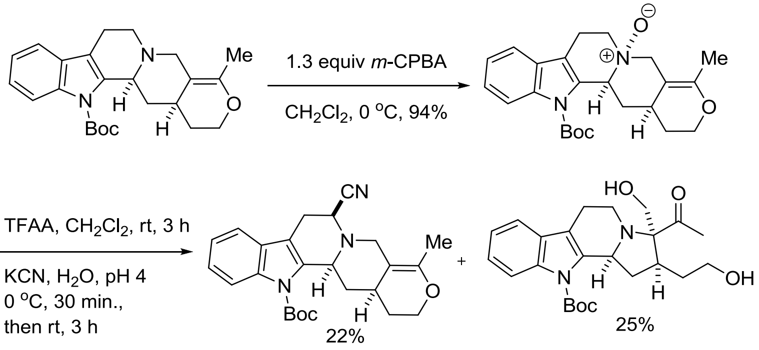
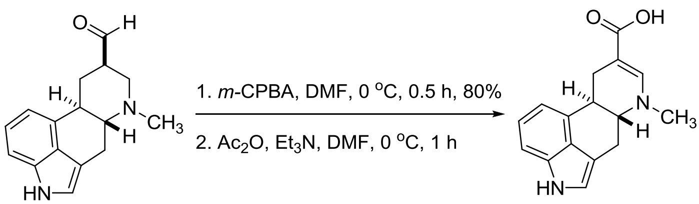
DOI 10.1007/978-3-319-03979-4_219, © Springer International Publishing Switzerland 2014

Example 3[8]



Example 4, *m*-CPBA also concurrently oxidized the aldehyde[10]

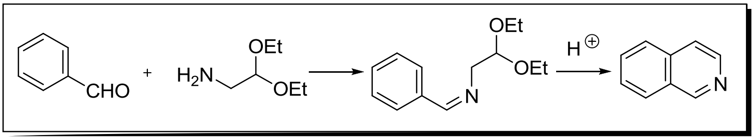


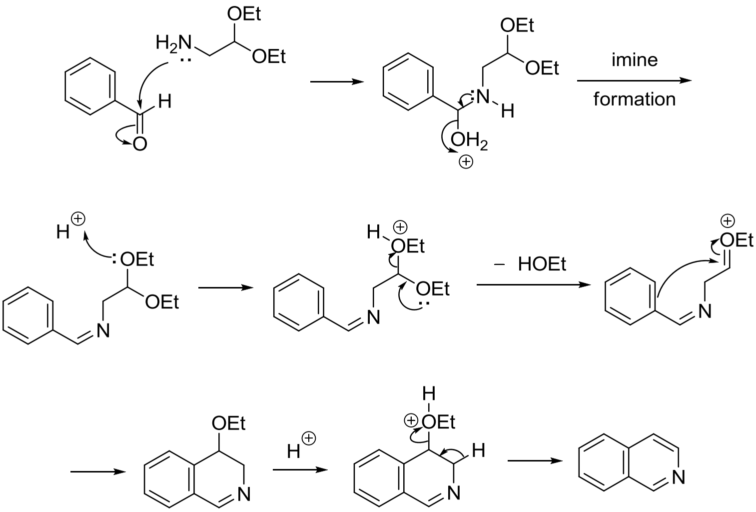
References

1. Ahond, A.; Cavé, A.; Kan-Fan, C.; Husson, H.-P.; de Rostolan, J.; Potier, P. *J. Am. Chem. Soc*. **1968,** *90,* 5622–5623.
2. Husson, H.-P.; Chevolot, L.; Langlois, Y.; Thal, C.; Potier, P. *J. Chem. Soc., Chem. Commun*. **1972,** 930–931.
3. Grierson, D. *Org. React.* **1990,** *39*, 85–295. (Review).
4. Sundberg, R. J.; Gadamasetti, K. G.; Hunt, P. J. *Tetrahedron* **1992,** *48*, 277–296.
5. Kende, A. S.; Liu, K.; Brands, J. K. M. *J. Am. Chem. Soc*. **1995,** *117*, 10597–10598.
6. Renko, D.; Mary, A.; Guillou, C.; Potier, P.; Thal, C. *Tetrahedron Lett*. **1998,** *39*, 4251–4254.
7. Suau, R.; Nájera, F.; Rico, R. *Tetrahedron* **2000,** *56*, 9713–9720.
8. Thomas, O. P.; Zaparucha, A.; Husson, H.-P. *Tetrahedron Lett*. **2001,** *42*, 3291–3293.
9. Lim, K.-H.; Low, Y.-Y.; Kam, T.-S. *Tetrahedron Lett*. **2006,** *47*, 5037–5039.
10. Gazak, R.; Kren, V.; Sedmera, P.; Passarella, D.; Novotna, M.; Danieli, B. *Tetrahedron* **2007,** *63*, 10466–10478.
11. Nishikawa, Y.; Kitajima, M.; Kogure, N.; Takayama, H. *Tetrahedron* **2009,** *65*, 1608–1617.
12. Perry, M. A.; Morin, M. D.; Slafer, B. W.; Rychnovsky, S. D. **2012,** *77*, 3390–3400.

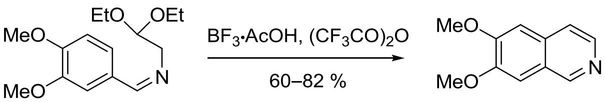
Pomeranz–Fritsch reaction

Isoquinoline and saturated variants synthesis *via* acid-mediated cyclization of the appropriate aminoacetal intermediate.

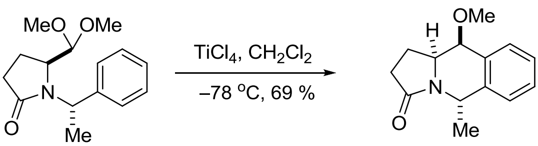




Example 1[3]



Example 2[4]



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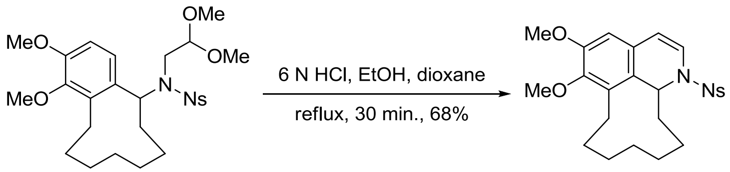
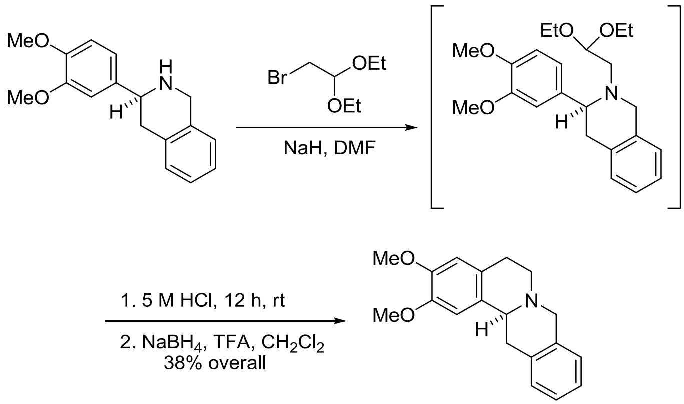
Example 3[9]



Example 4, **Bobbitt modification**[10]

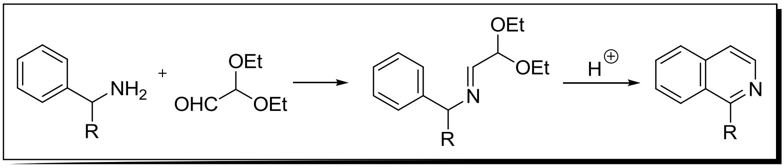


References

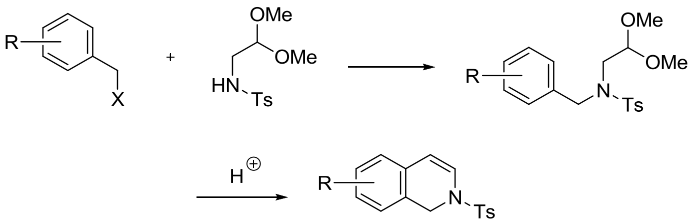
1. (a) Pomeranz, C. *Monatsh.* **1893,** *14*, 116–119. Cesar Pomeranz (1860–1926) received his Ph.D. degree at Vienna, where he was employed as an associate professor of chemistry. (b) Fritsch, P. *Ber.* **1893,** *26*, 419–422. Paul Fritsch (1859–1913) was born in Oels, Silesia. He studied at Munich where he received his doctorate in 1884. Fritsch eventually became a professor at Marburg after several junior positions.
2. Gensler, W. J. *Org. React.* **1951,** *6*, 191–206. (Review).
3. Bevis, M. J.; Forbes, E. J.; Naik, N. N.; Uff, B. C. *Tetrahedron* **1971,** *27*, 1253–1259.
4. Ishii, H.; Ishida, T. *Chem. Pharm. Bull.* **1984,** *32*, 3248–3251.
5. Bobbitt, J. M.; Bourque, A. J. *Heterocycles* **1987,** *25*, 601–616. (Review).
6. Gluszyńska, A.; Rozwadowska, M. D. *Tetrahedron: Asymmetry* **2000,** *11*, 2359–2368.
7. Capilla, A. S.; Romero, M.; Pujol, M. D.; Caignard, D. H.; Renard, P. *Tetrahedron* **2001,** *57*, 8297–8303.
8. Hudson, A. *Pomeranz–Fritsch Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 480–486. (Review).
9. Bracca, A. B. J.; Kaufman, T. S. *Eur. J. Org. Chem.* **2007,** 5284–5293.
10. Grajewska, A.; Rozwadowska, M. D. *Tetrahedron: Asymmetry* **2007,** *18*, 2910–2914.
11. Chrzanowska, M.; Grajewska, A.; Rozwadowska, M. D. *Heterocycles* **2012,** *86*, 1119–1127.

Schlittler–Müller modification

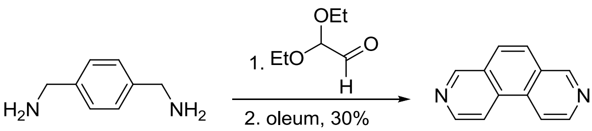
Simple permutation where the amine and the aldehyde switch places for the two reactants in comparison to the Pomeranz–Fritsch reaction.



Example 1[3]



Example 2[4]

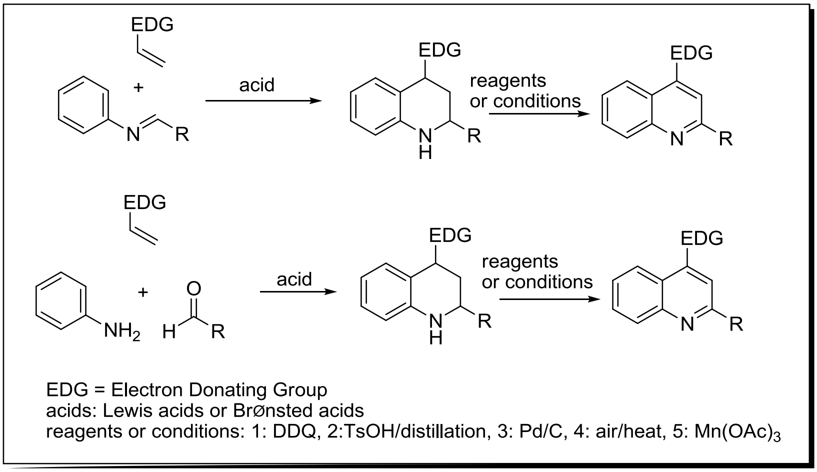


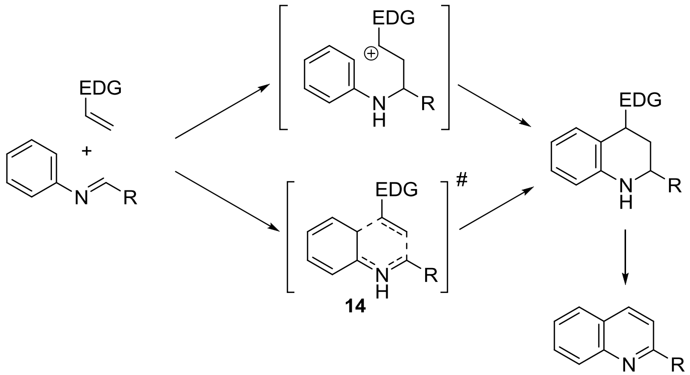
References

1. Schlittler, E.; Müller, J. *Helv. Chim. Acta* **1948,** *31,* 914–924, 1119–1132.
2. Guthrie, D. A.; Frank, A. W.; Purves, C. B. *Can. J. Chem.* **1955,** *33*, 729–742.
3. Boger, D. L.; Brotherton, C. E.; Kelley, M. D. *Tetrahedron* **1981,** *37*, 3977–3980.
4. Gill, E. W.; Bracher, A. W. *J. Heterocycl. Chem.* **1983,** *20*, 1107–1109.
5. Hudson, A. *Pomeranz–Fritsch Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 480–486. (Review).

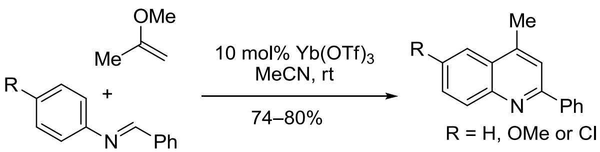
Pavorov reaction

The Povarov reaction is the inverse electron-demand aza-Diels–Alder reaction, a [4 + 2] cycloaddition between an *N*-arylimine (as the diene) and an electron-rich olefin (as the dienophile), which gives tetrahydroquinolines or substituted quinolines as the product.





Example 1[2]



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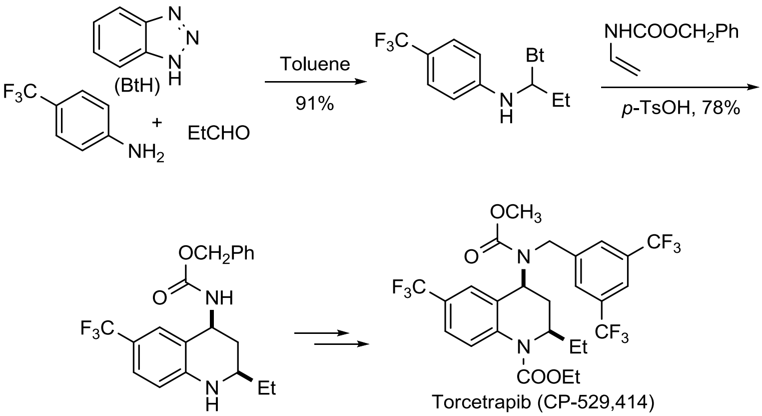
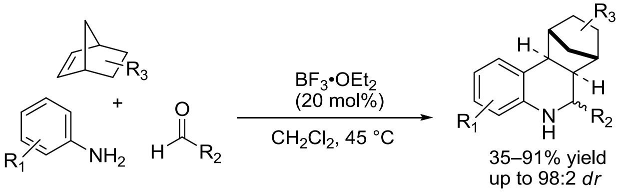
Example 2, Katritzky variation[3,5]



Example 3[7]

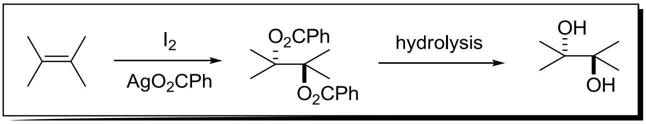


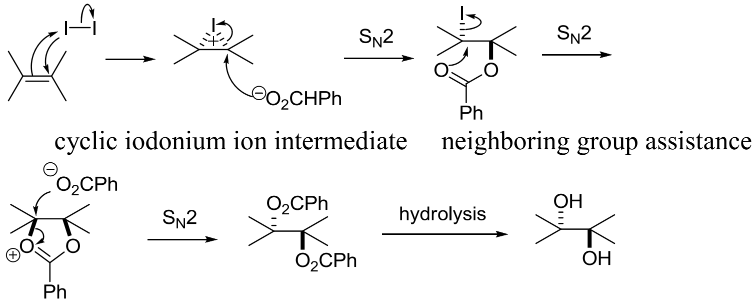
References

1. Povarov, L. S.; Mikhailov, B. M. *Izv. Akad. Nauk SSR, Ser. Khim.* **1963,** 953–956.
2. Makioka, Y.; Shindo, T.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Synthesis* **1995,** *7*, 801–804.
3. Katrizky, A. R.; Belyakov, S. A. *Aldrichimica Acta* **1998,** *31*, 35–45. (Review).
4. Buonora, P.; Olsen, J.-C.; Oh, T. *Tetrahedron* **2001,** *57*, 6099–6138. (Review).
5. Damon, D. B.; Dugger, R. W.; Magnus-Aryitey, G.; Ruggeri, R. B.; Wester, R. T.; Tu, M.; Abramov, Y. *Org. Process Res. Dev.* **2006,** *10*, 464–471.
6. Kouznetsov, V. V. *Tetrahedron* **2009,** *65*, 2721–2750. (Review).
7. Smith, C. D.; Gavrilyuk, J. I.; Lough, A. J.; Batey, R. A. *J. Org. Chem.* **2010,** *75*, 702–715.
8. Xu, H.; Zuend, S. J.; Woll, M. G.; Tao, Y.; Jacobsen, E. N. *Science* **2010,** *327*, 986–990.
9. Zhang, J. *Povarov Reaction*. In *Name Reactions in Heterocyclic Chemistry II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2011,** 385–399. (Review).

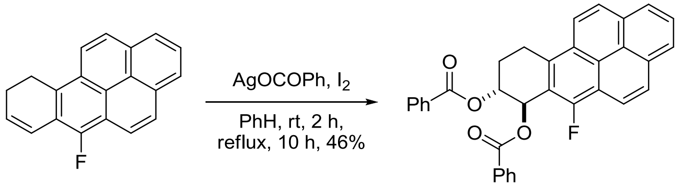
Prévost *trans*-dihydroxylation

Cf. Woodward *cis*-dihydroxylation.

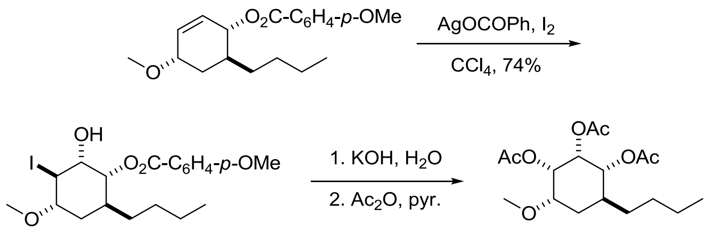




Example 1[5]



Example 2[9]



References

1. Prévost, C. *Compt. Rend.* **1933,** *196,* 1129–1131.
2. Campbell, M. M.; Sainsbury, M.; Yavarzadeh, R. *Tetrahedron* **1984,** *40*, 5063–5070.
3. Ciganek, E.; Calabrese, J. C. *J. Org. Chem*. **1995,** *60*, 4439–4443.
4. Brimble, M. A.; Nairn, M. R. *J. Org. Chem.* **1996,** *61*, 4801–4805.
5. Zajc, B. *J. Org. Chem.* **1999,** *64*, 1902–1907.
6. Hamm, S.; Hennig, L.; Findeisen, M.; Muller, D. *Tetrahedron* **2000,** *56*, 1345–1348.
7. Ray, J. K.; Gupta, S.; Kar, G. K.; Roy, B. C.; Lin, J.-M. *J. Org. Chem.* **2000,** *65*, 8134–8138.
8. Sabat, M.; Johnson, C. R. *Tetrahedron Lett*. **2001,** *42*, 1209–1212.
9. Hodgson, R.; Nelson, A. *Org. Biomol. Chem*. **2004,** *2*, 373–386.
10. Emmanuvel, L.; Shaikh, T. M. A.; Sudalai, A. *Org. Lett*. **2005,** *7*, 5071–5074.

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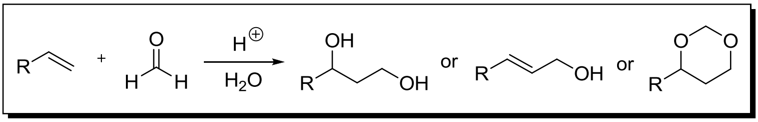
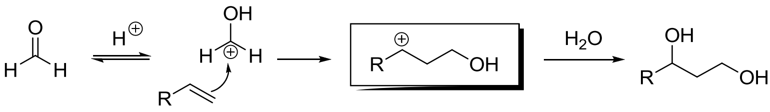
DOI 10.1007/978-3-319-03979-4_222,

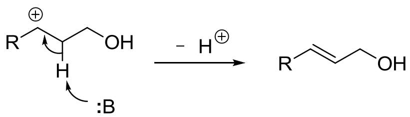
Prins reaction

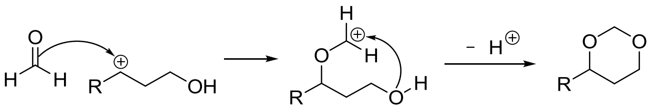
The Prins reaction is the acid-catalyzed addition of aldehydes to alkenes and gives different products depending on the reaction conditions.



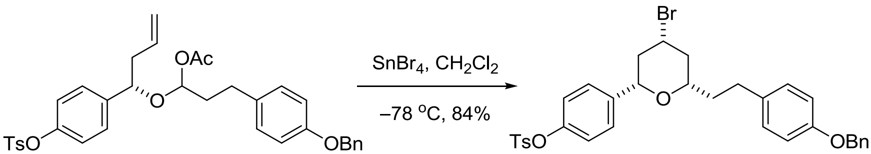


the common intermediate

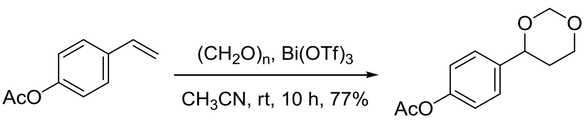




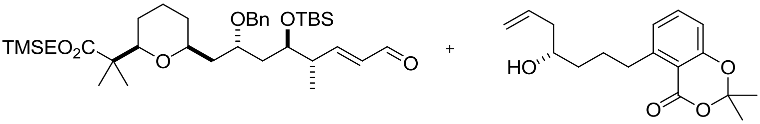
Example 1[5]



Example 2[7]



Example 3[9]



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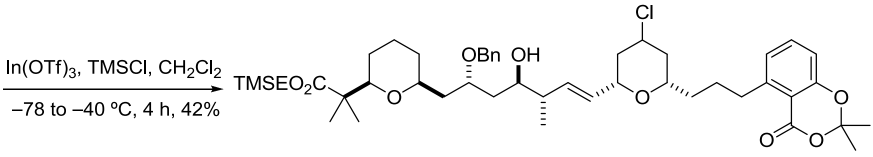
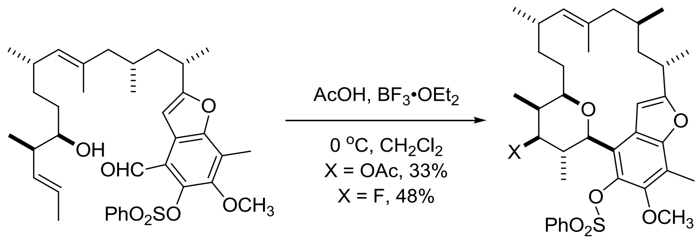
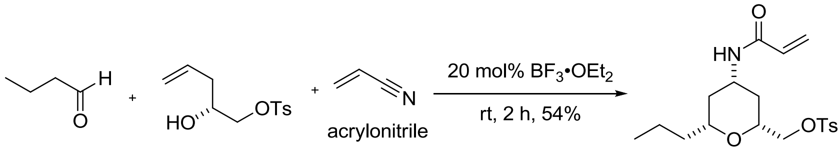


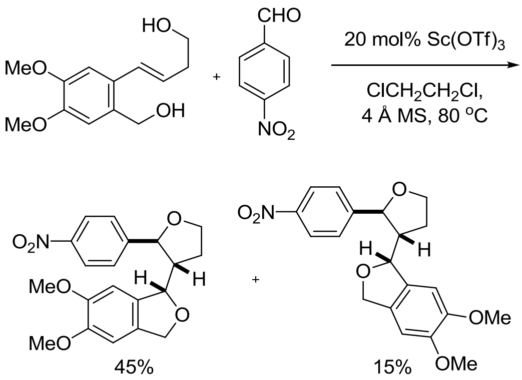
Example 4[10]



Example 5, A cascade of the Prins/Ritter amidation reaction[11]



Example 6[12]



References

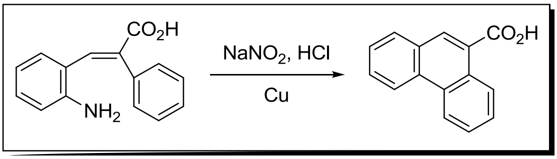
1. Prins, H. J. *Chem. Weekblad* **1919,** *16*, 1072–1023. Born in Zaandam, The Netherlands, Hendrik J. Prins (1889–1958) was not even an organic chemist *per se*. After obtaining a doctorate in chemical engineering, Prins worked for an essential oil company and then a company dealing with the rendering of condemned meats and carcasses. But he had a small laboratory near his house where he carried out his experiments

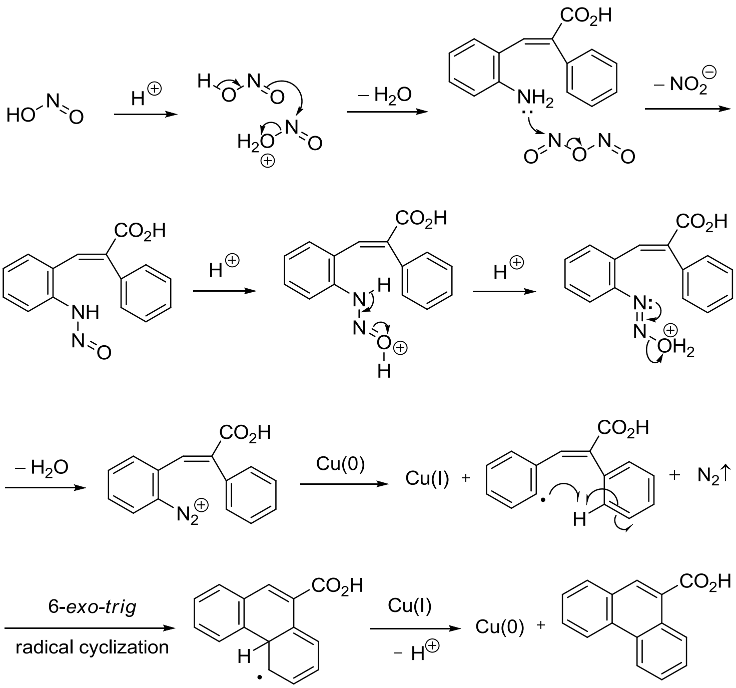
in his spare time, which obviously was not a big distraction—for he rose to be the president-director of the firm he worked for.

2. Adam, D. R.; Bhatnagar, S. P. *Synthesis* **1977,** 661–672. (Review).
3. Hanaki, N.; Link, J. T.; MacMillan, D. W. C.; Overman, L. E.; Trankle, W. G.; Wurster, J. A. *Org. Lett.* **2000,** *2*, 223–226.
4. Davis, C. E.; Coates, R. M. *Angew. Chem. Int. Ed.* **2002,** *41*, 491–493.
5. Marumoto, S.; Jaber, J. J.; Vitale, J. P.; Rychnovsky, S. D. *Org. Lett.* **2002,** *4*, 3919–3922.
6. Braddock, D. C.; Badine, D. M.; Gottschalk, T.; Matsuno, A.; Rodriguez-Lens, M. *Synlett* **2003,** 345–348.
7. Sreedhar, B.; Swapna, V.; Sridhar, Ch.; Saileela, D.; Sunitha, A. *Synth. Commun.* **2005,** *35*, 1177–1182.
8. Aubele, D. L.; Wan, S.; Floreancig, P. E. *Angew. Chem. Int. Ed.* **2005,** *44*, 3485–3488.
9. Chan, K.-P.; Ling, Y. H.; Loh, T.-P. *Chem. Commun.* **2007,** 939–941.
10. Bahnck, K. B.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **2008,** *130*, 13177–13181.
11. Yadav, J. S.; Reddy, Y. J.; Reddy, P. A. N.; Reddy, B. V. S. *Org. Lett.* **2013,** *15*, 546–549.
12. Subba Reddy, B. V.; Jalal, S.; Borkar, P.; Yadav, J. S.; Gurava Reddy, P.; Sarma, A.V.S. *Tetrahedron Lett.* **2013,** *54*, 1519–1523.

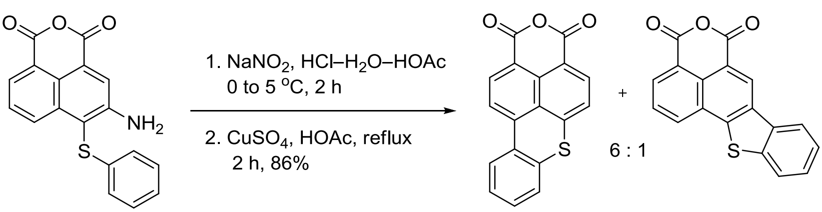
Pschorr cyclization

The intramolecular version of the Gomberg–Bachmann reaction.





Example 1[7]



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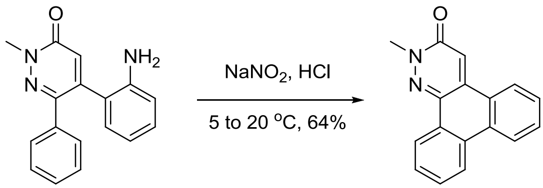
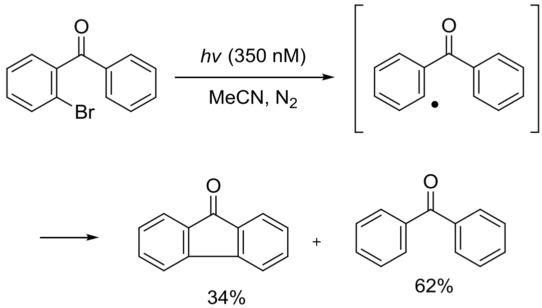
Example 2[8]



Example 3[10]

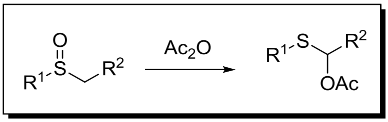


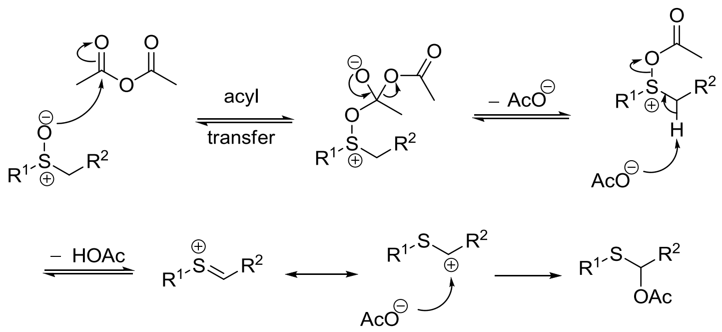
References

1. Pschorr, R. *Ber.* **1896,** *29*, 496–501. Robert Pschorr (1868–1930), born in Munich, Germany, studied under von Baeyer, Bamberger, Knorr, and Fischer. He became an assistant professor in 1899 at Berlin where he discovered the phenanthrene synthesis. During WWI, Pschorr served as a major in the German Army.
2. Kupchan, S. M.; Kameswaran, V.; Findlay, J. W. A. *J. Org. Chem.* **1973,** *38,* 405–406.
3. Wassmundt, F. W.; Kiesman, W. F. *J. Org. Chem.* **1995,** *60*, 196–201.
4. Qian, X.; Cui, J.; Zhang, R. *Chem. Commun.* **2001,** 2656–2657.
5. Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002,** *102*, 1359–1469. (Review).
6. Karady, S.; Cummins, J. M.; Dannenberg, J. J.; del Rio, E.; Dormer, P. G.; Marcune, B. F.; Reamer, R. A.; Sordo, T. L. *Org. Lett.* **2003,** *5*, 1175–1178.
7. Xu, Y.; Qian, X.; Yao, W.; Mao, P.; Cui, J. *Bioorg. Med. Chem.* **2003,** *11*, 5427–5433.
8. Tapolcsányi, P.; Maes, B. U. W.; Monsieurs, K.; Lemière, G. L. F.; Riedl, Z.; Hajós, G.; Van der Driessche, B.; Dommisse, R. A.; Mátyus, P. *Tetrahedron* **2003,** *59*, 5919–5926.
9. Mátyus, P.; Maes, B. U. W.; Riedl, Z.; Hajós, G.; Lemière, G. L. F.; Tapolcśanyi, P.; Monsieurs, K.; Éliás, O.; Dommisse, R. A.; Krajsovszky, G. *Synlett* **2004,** 1123–1139. (Review).
10. Moorthy, J. N.; Samanta, S. *J. Org. Chem.* **2007,** *72*, 9786–9789.
11. Lockner, J. W.; Dixon, D. D.; Risgaard, R.; Baran, P. S. *Org. Lett.* **2011,** *13*, 5628–5631.

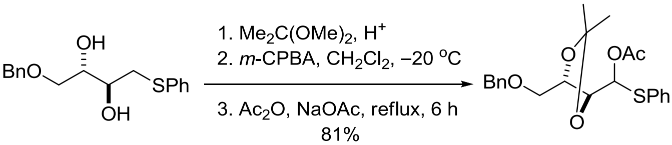
Pummerer rearrangement

The transformation of sulfoxides into α-acyloxythioethers using acetic anhydride.

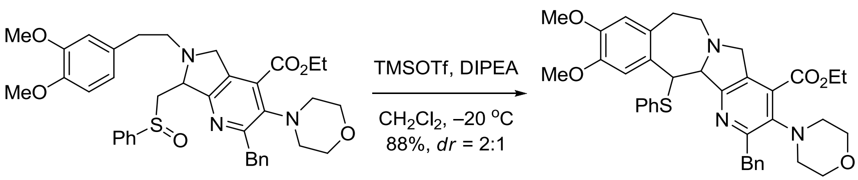




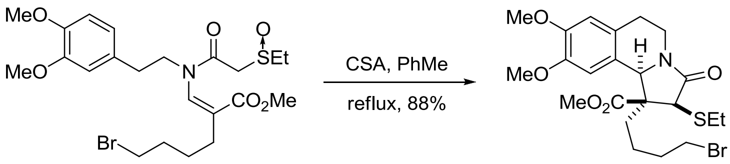
Example 1[2]



Example 2[7]



Example 3[8]



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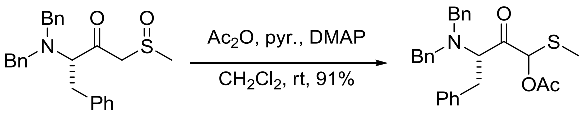
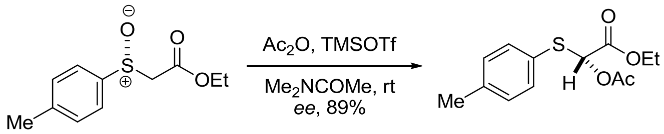
DOI 10.1007/978-3-319-03979-4_225, © Springer International Publishing Switzerland 2014

Example 4[9]



Example 5, Stereoselective Pummerer rearrangement[10,12]

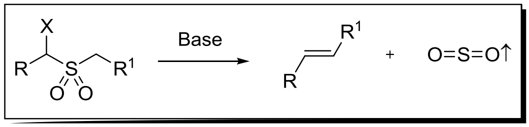


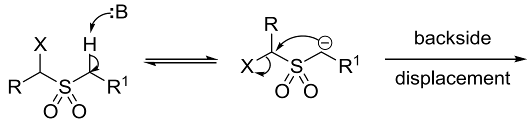
References

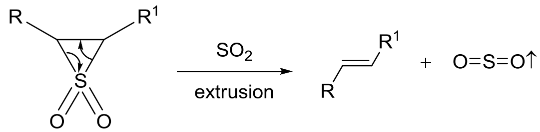
1. Pummerer, R. *Ber.* **1910,** *43*, 1401–1412. Rudolf Pummerer, born in Austria in 1882, studied under von Baeyer, Willstätter, and Wieland. He worked for BASF for a few years and in 1921 he was appointed head of the organic division of the Munich Laboratory, fulfilling his long-desired ambition.
2. Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Tuddenham, D.; Walker, F. J. *J. Org. Chem.* **1982,** *47*, 1373–1378.
3. De Lucchi, O.; Miotti, U.; Modena, G. *Org. React.* **1991,** *40*, 157–406. (Review).
4. Padwa, A.; Gunn, D. E., Jr.; Osterhout, M. H. *Synthesis* **1997,** 1353–1378. (Review).
5. Padwa, A.; Waterson, A. G. *Curr. Org. Chem.* **2000,** *4*, 175–203. (Review).
6. Padwa, A.; Bur, S. K.; Danca, D. M.; Ginn, J. D.; Lynch, S. M. *Synlett* **2002,** 851–862. (Review).
7. Gámez Montaño, R.; Zhu, J. *Chem. Commun.* **2002,** 2448–2449.
8. Padwa, A.; Danca, M. D.; Hardcastle, K.; McClure, M. *J. Org. Chem.* **2003,** *68*, 929–941.
9. Suzuki, T.; Honda, Y.; Izawa, K.; Williams, R. M. *J. Org. Chem.* **2005,** *70*, 7317–7323.
10. Nagao, Y.; Miyamoto, S.; Miyamoto, M.; Takeshige, H.; Hayashi, K.; Sano, S.; Shiro, M.; Yamaguchi, K.; Sei, Y. *J. Am. Chem. Soc.* **2006,** *128*, 9722–9729.
11. Ahmad, N. M. *Pummerer Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 334–352. (Review).
12. Patil, M.; Loerbroks, C.; Thiel, W. *Org. Lett.* **2013,** *15*, 1682–1685.

Ramberg–Bäcklund reaction

Olefin synthesis *via* α-halosulfone extrusion.

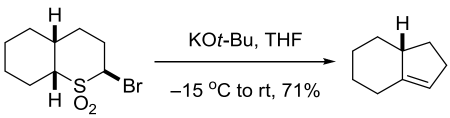




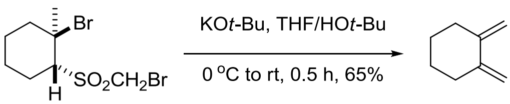


episulfone intermediate

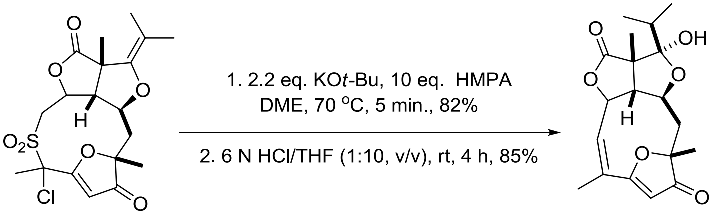
Example 1[4]



Example 2[5]



Example 3[6]



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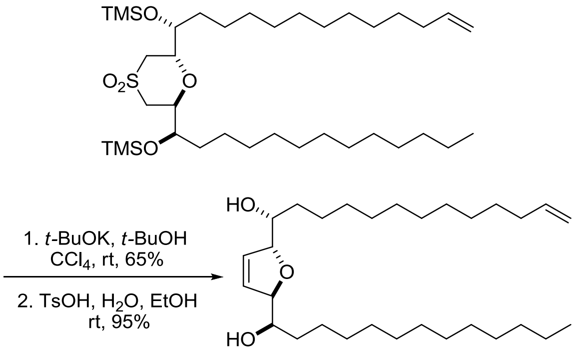
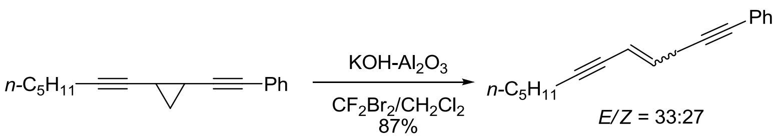
Example 4, *in situ* chlorination[7]



Example 5[8]

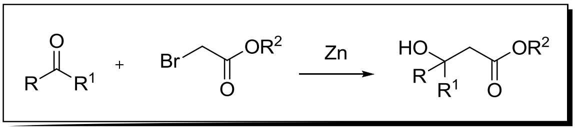


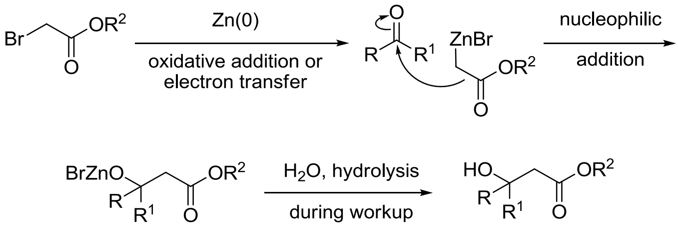
References

1. Ramberg, L.; Bäcklund, B. *Arkiv. Kemi, Mineral Geol.* **1940,** *13A*, 1–50.
2. Paquette, L. A. *Acc. Chem. Res.* **1968,** *1*, 209–216. (Review).
3. Paquette, L. A. *Org. React.* **1977,** *25*, 1–71. (Review).
4. Becker, K. B.; Labhart, M. P. *Helv. Chim. Acta* **1983,** *66*, 1090–1100.
5. Block, E.; Aslam, M.; Eswarakrishnan, V.; Gebreyes, K.; Hutchinson, J.; Iyer, R.; Laffitte, J. A.; Wall, A. *J. Am. Chem. Soc.* **1986,** *108,* 4568–4580.
6. Boeckman, R. K., Jr.; Yoon, S. K.; Heckendorn, D. K. *J. Am. Chem. Soc.* **1991,** *113,* 9682–9684.
7. Trost, B. M.; Shi, Z. *J. Am. Chem. Soc.* **1994,** *116,* 7459–7460.
8. Cao, X.-P.; Chan, T.-L.; Chow, H.-F. *Tetrahedron Lett.* **1996,** *37*, 1049–1052.
9. Taylor, R. J. K. *Chem. Commun.* **1999,** 217–227. (Review).
10. Taylor, R. J. K.; Casy, G. *Org. React.* **2003,** *62*, 357–475. (Review).
11. Li, J. J. *Ramberg–Bäcklund olefin synthesis*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 386–404. (Review).
12. Pal, T. K.; Pathak, T. *Carbohydrate Res.* **2008,** *343*, 2826–2829.
13. Baird, L. J.; Timmer, M. S. M.; Teesdale-Spittle, P. H.; Harvey, J. E. *J. Org. Chem.* **2009,** *74*, 2271–2277.

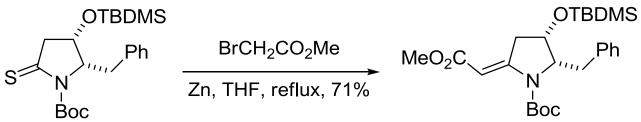
Reformatsky reaction

Nucleophilic addition of organozinc reagents generated from α-haloesters to carbonyls.

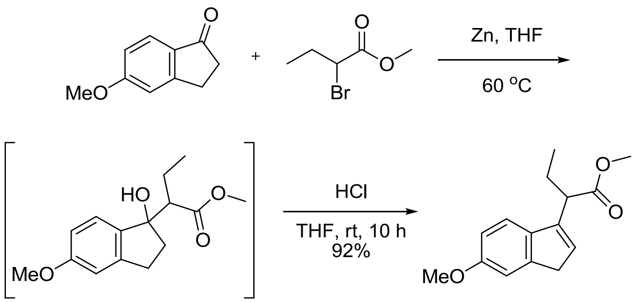




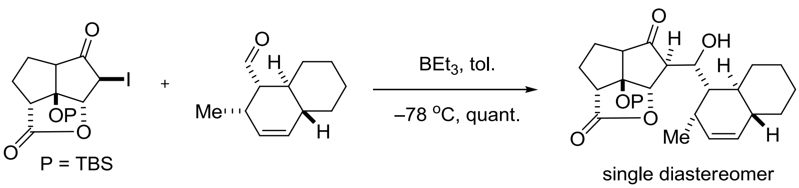
Example 1[4]



Example 2[6]



Example 3, Boron-mediated Reformatsky reaction[8]



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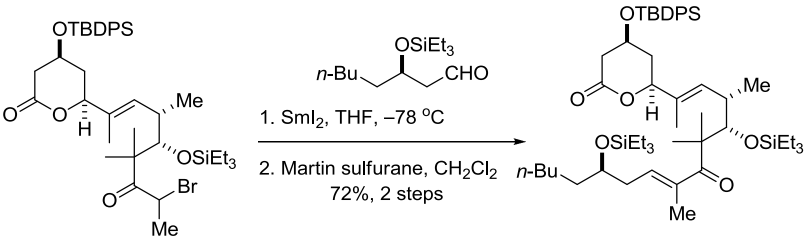
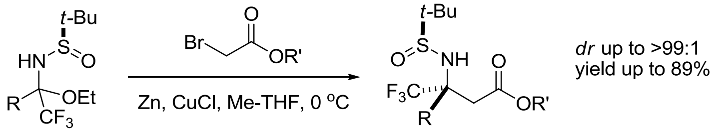
DOI 10.1007/978-3-319-03979-4_227, © Springer International Publishing Switzerland 2014

Example 4, SmI_2-mediated Reformatsky reaction[9]



Example 2[6]

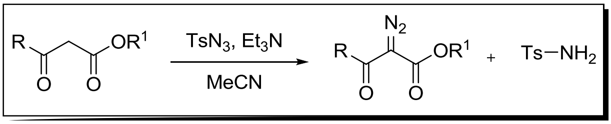


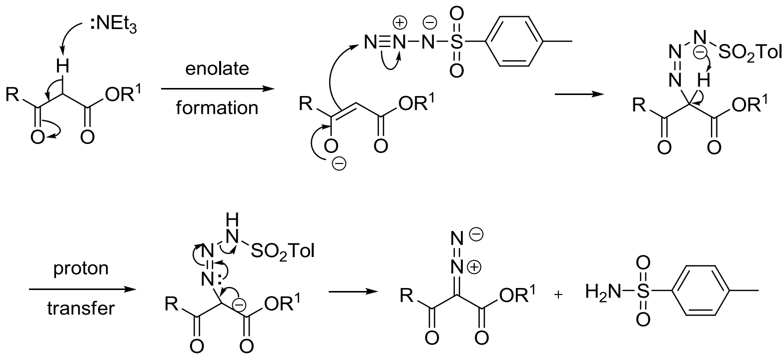
References

1. Reformatsky, S. *Ber.* **1887,** *20,* 1210–1211. Sergei Reformatsky (1860–1934) was born in Russia. He studied at the University of Kazan in Russia, the cradle of Russian chemistry professors, where he found competent guidance of a distinguished chemist, Alexander M. Zaĭtsev. Reformatsky then studied at Göttingen, Heidelberg, and Leipzig in Germany. After returning to Russia, Reformatsky became the Chair of Organic Chemistry at the University of Kiev.
2. Rathke, M. W. *Org. React.* **1975,** *22*, 423–460. (Review).
3. Fürstner, A. *Synthesis* **1989,** 571–590. (Review).
4. Lee, H. K.; Kim, J.; Pak, C. S. *Tetrahedron Lett.* **1999,** *40*, 2173–2174.
5. Fürstner, A. In *Organozinc Reagents* Knochel, P., Jones, P., Eds.; Oxford University Press: New York, **1999,** pp 287–305. (Review).
6. Zhang, M.; Zhu, L.; Ma, X. *Tetrahedron: Asymmetry* **2003,** *14*, 3447–3453.
7. Ocampo, R.; Dolbier, W. R., Jr. *Tetrahedron* **2004,** *60*, 9325–9374. (Review).
8. Lambert, T. H.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2006,** *128*, 426–427.
9. Moslin, R. M.; Jamison, T. F. *J. Am. Chem. Soc.* **2006,** *128*, 15106–15107.
10. Cozzi, P. G. *Angew. Chem. Int. Ed.* **2007,** *46*, 2568–2571. (Review).
11. Ke, Y.-Y.; Li, Y.-J.; Jia, J.-H.; Sheng, W.-J.; Han, L.; Gao, J.-R. *Tetrahedron Lett.* **2009,** *50*, 1389–1391.
12. Grellepois, F. *J. Org. Chem.* **2013,** *78*, 1127–1137.
13. Schulze, T. M.; Grunenberg, J.; Schulz, S. *Tetrahedron Lett.* **2013,** *54*, 921–924.

Regitz diazo synthesis

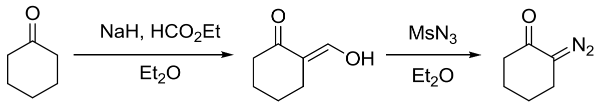
Synthesis of 2-diazo-1,3-diketones or 2-diazo-3-oxoesters using sulfonyl azides.

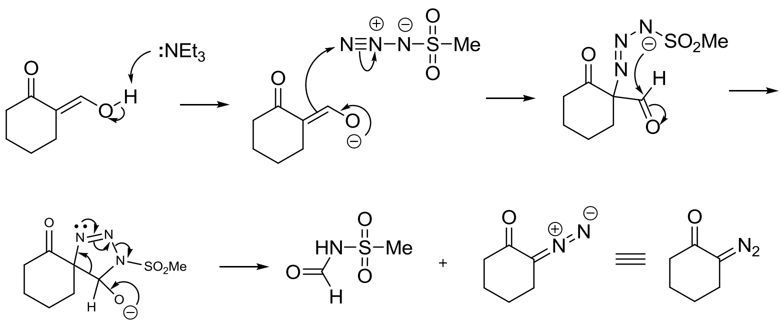




tosyl amide is the by-product

When only one carbonyl is present, ethylformate can be used as an activating auxiliary:[6–9]





Alternatively, the triazole intermediate may be assembled *via* a 1,3-dipolar cycloaddition of the enol and mesyl azide:

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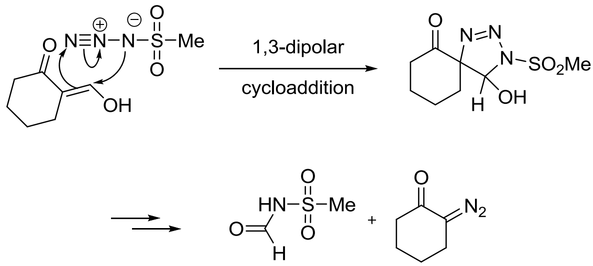
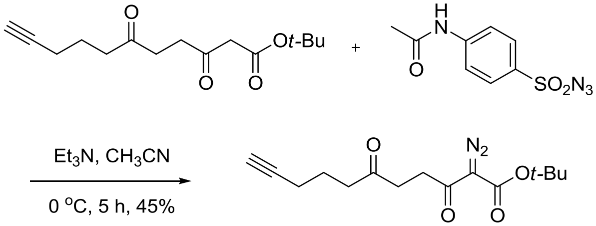
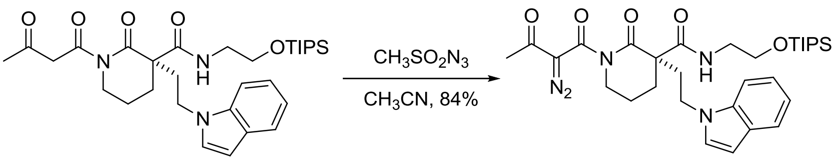
DOI 10.1007/978-3-319-03979-4_228,



Example 1[5]



Example 2[10]

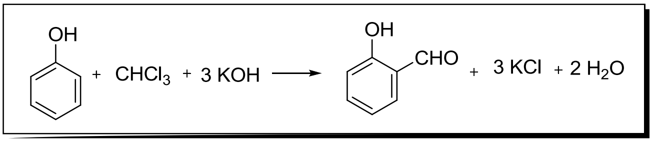


References

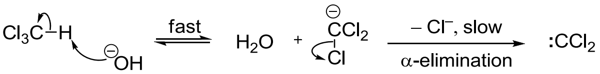
1. (a) Regitz, M. *Angew. Chem. Int. Ed.* **1967,** *6*, 733–741. (b) Regitz, M.; Anschütz, W.; Bartz, W.; Liedhegener, A. *Tetrahedron Lett.* **1968,** *9*, 3171–3174. (c) Regitz, M. *Synthesis* **1972,** 351–373. (Review).
2. Pudleiner, H.; Laatsch, H. *Ann.* **1990,** 423–426.
3. Evans, D. A.; Britton, T. C.; Ellman, J. A.; Dorow, R. L. *J. Am. Chem. Soc.* **1990,** *112*, 4011–4030.
4. Charette, A. B.; Wurz, R. P.; Ollevier, T. *J. Org. Chem.* **2000,** *65*, 9252–9254.
5. Hodgson, D. M.; Labande, A. H.; Pierard, F. Y. T. M.; Expésito Castro, M. A. *J. Org. Chem.* **2003,** *68*, 6153–6159.
6. Sarpong, R.; Su, J. T.; Stoltz, B. M. *J. Am. Chem. Soc.* **2003,** *125*, 13624–13628.
7. Mejía-Oneto, J. M.; Padwa, A. *Org. Lett.* **2004,** *6*, 3241–3244.
8. Muroni, D.; Saba, A.; Culeddu, N. *Tetrahedron: Asymmetry* **2004,** *15*, 2609–2614.
9. Davies, J. R.; Kane, P. D.; Moody, C. J. *Tetrahedron* **2004,** *60*, 3967–3977.
10. Oguri, H.; Schreiber, S. L. *Org. Lett.* **2005,** *7*, 47–50.
11. Balasubramanian, M. *Regitz diazo synthesis* In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 658–688. (Review).

Reimer–Tiemann reaction

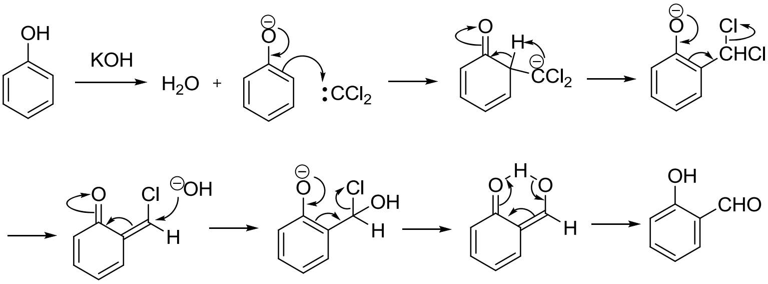
Synthesis of *o*-formylphenol from phenols and chloroform in alkaline medium.



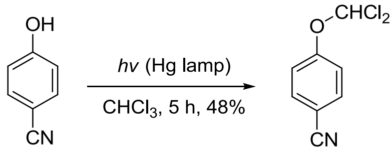
a. Carbene generation:



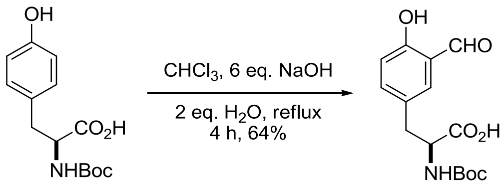
b. Addition of dichlorocarbene and hydrolysis:



Example 1, Photo-Reimer–Tiemann reaction without base[7]



Example 2[8]



References

1. Reimer, K.; Tiemann, F. *Ber.* **1876,** *9*, 824–828.
2. Wynberg, H.; Meijer, E. W. *Org. React.* **1982,** *28*, 1–36. (Review).
3. Bird, C. W.; Brown, A. L.; Chan, C. C. *Tetrahedron* **1985,** *41*, 4685–4690.
4. Neumann, R.; Sasson, Y. *Synthesis* **1986,** 569–570.
5. Cochran, J. C.; Melville, M. G. *Synth. Commun.* **1990,** *20*, 609–616.
6. Langlois, B. R. *Tetrahedron Lett.* **1991,** *32*, 3691–3694.
7. Jiménez, M. C.; Miranda, M. A.; Tormos, R. *Tetrahedron* **1995,** *51*, 5825–5828.
8. Jung, M. E.; Lazarova, T. I. *J. Org. Chem.* **1997,** *62*, 1553–1555.
9. Bhunia, S. C.; Patra, G. C.; Pal, S. C. *Synth. Commun.* **2011,** *41*, 3678–3682.

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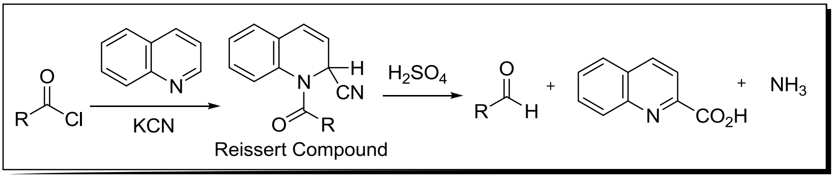
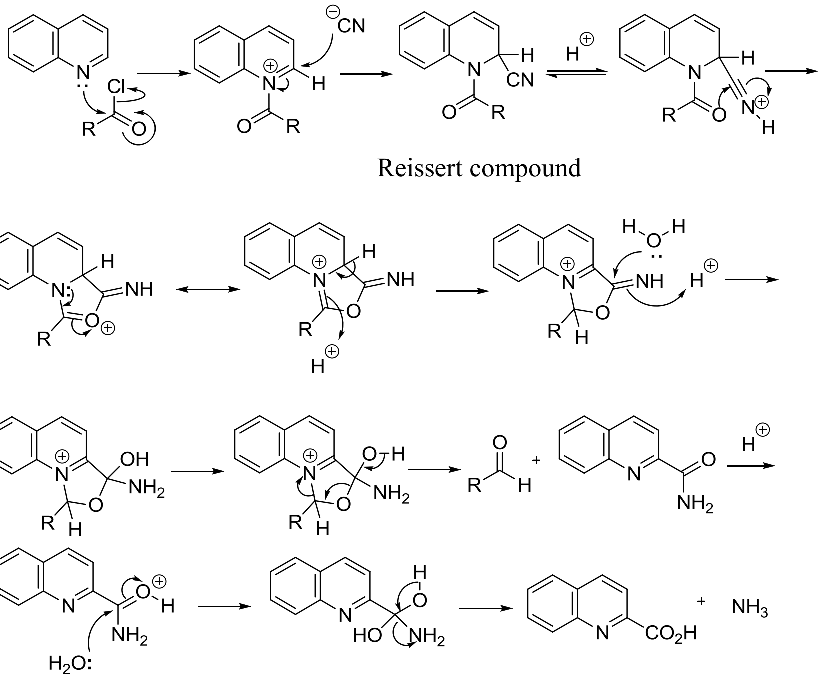
DOI 10.1007/978-3-319-03979-4_229,

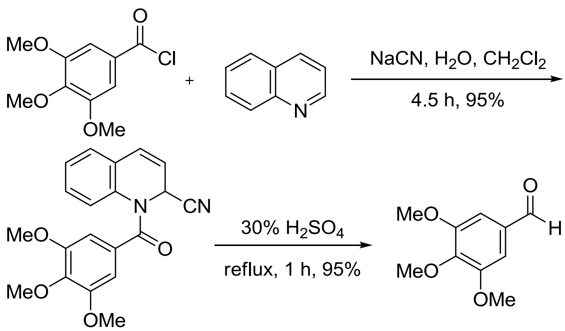
Reissert reaction

Treatment of quinoline or isoquinoline with acid chloride and KCN gives quinaldic acid, aldehyde, and NH_3.





Example 1[3]



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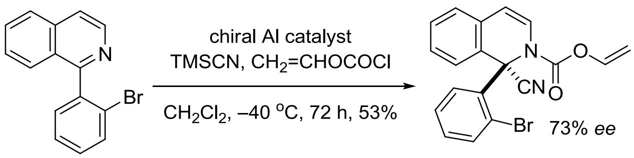
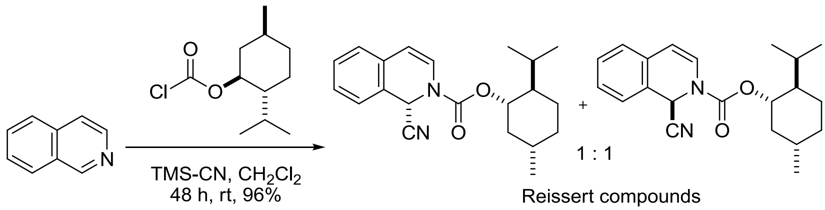
DOI 10.1007/978-3-319-03979-4_230, © Springer International Publishing Switzerland 2014

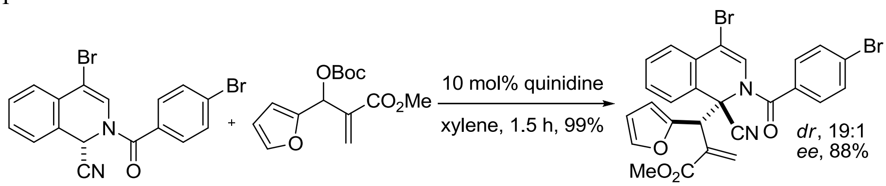
Example 2, Reissert compound from isoquinoline[7]



Example 3, Reissert compound from isoquinoline[10]



Example 4, Asymmetric organocatalytic allylic alkylation of Reissert compounds[12]

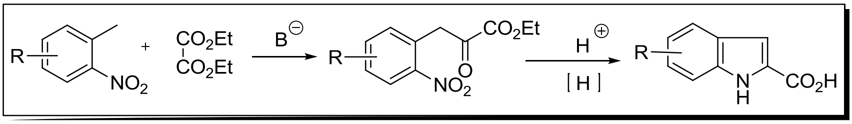


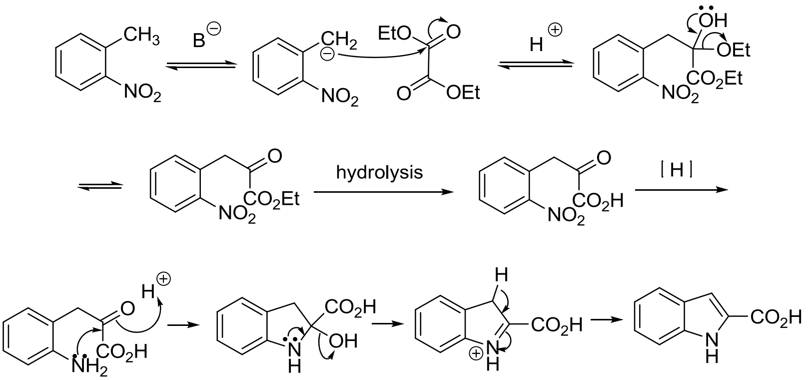
References

1. (a) Reissert, A. *Ber.* **1905,** *38*, 1603–1614. (b) Reissert, A. *Ber.* **1905,** *38*, 3415–3435. Carl Arnold Reissert was born in 1860 in Powayen, Germany. He received his Ph.D. In 1884 at Berlin, where he became an assistant professor. He collaborated with Tiemann. Reissert later joined the faculty at Marburg in 1902.
2. Popp, F. D. *Adv. Heterocycl. Chem.* **1979,** *24*, 187–214. (Review).
3. Schwartz, A. *J. Org. Chem.* **1982,** *47*, 2213–2215.
4. Lorsbach, B. A.; Bagdanoff, J. T.; Miller, R. B.; Kurth, M. J. *J. Org. Chem.* **1998,** *63*, 2244–2250.
5. Perrin, S.; Monnier, K.; Laude, B.; Kubicki, M.; Blacque, O. *Eur. J. Org. Chem.* **1999,** 297–303.
6. Takamura, M.; Funabashi, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2001,** *123*, 6801–6808.
7. Shibasaki, M.; Kanai, M.; Funabashi, K. *Chem. Commun.* **2002,** 1989–1999.
8. Sieck, O.; Schaller, S.; Grimme, S.; Liebscher, J. *Synlett* **2003,** 337–340.
9. Kanai, M.; Kato, N.; Ichikawa, E.; Shibasaki, M. *Synlett* **2005,** 1491–1508. (Review).
10. Gibson, H. W.; Berg, M. A. G.; Clifton Dickson, J.; Lecavalier, P. R.; Wang, H.; Merola, J. S. *J. Org. Chem.* **2007,** *72*, 5759–5770.
11. Fuchs, C.; Bender, C.; Ziemer, B.; Liebscher, J. *J. Heterocycl. Chem.* **2008,** *45*, 1651–1658.
12. Qin, T.Y.; Liao, W.-W.; Zhang, Y.-J.; Zhang, S. X.-A. *Org. Biomol. Chem.* **2013,** *11*, 984–990.

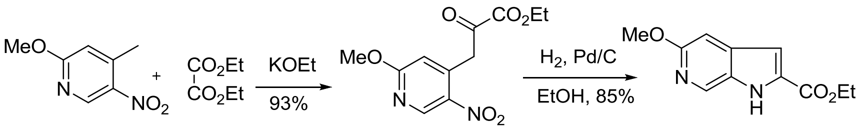
Reissert indole synthesis

The Reissert indole synthesis involves base-catalyzed condensation of an *o*-nitrotoluene derivative with an ethyl oxalate, which is followed by reductive cyclization to an indole-2-carboxylic acid derivative.

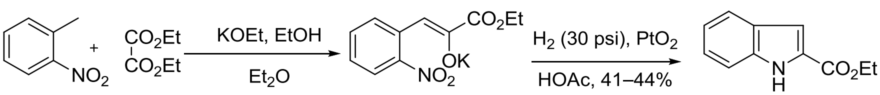




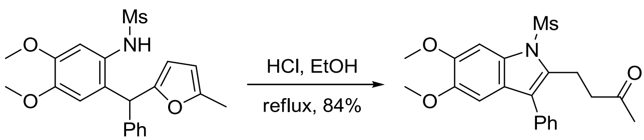
Example 1[2]



Example 2[3]



Example 3, Furan ring as the masked carbonyl[10]



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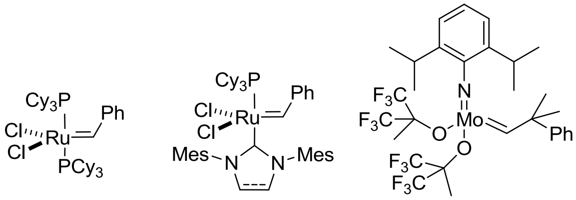
DOI 10.1007/978-3-319-03979-4_231, © Springer International Publishing Switzerland 2014

References

1. Reissert, A. *Ber.* **1897,** *30*, 1030–1053.
2. Frydman, B.; Despuy, M. E.; Rapoport, H. *J. Am. Chem. Soc.* **1965,** *87*, 3530–3531.
3. Noland, W. E.; Baude, F. J. *Org. Synth.* **1973**; *Coll. Vol.* 567–571.
4. Leadbetter, G.; Fost, D. L.; Ekwuribe, N. N.; Remers, W. A. *J. Org. Chem.* **1974,** *39*, 3580–3583.
5. Cannon, J. G.; Lee, T.; Ilhan, M.; Koons, J.; Long, J. P. *J. Med. Chem.* **1984,** *27*, 386–389.
6. Suzuki, H.; Gyoutoku, H.; Yokoo, H.; Shinba, M.; Sato, Y.; Yamada, H.; Murakami, Y. *Synlett* **2000,** 1196–1198.
7. Butin, A. V.; Stroganova, T. A.; Lodina, I. V.; Krapivin, G. D. *Tetrahedron Lett.* **2001,** *42*, 2031–2036.
8. Katayama, S.; Ae, N.; Nagata, R. *J. Org. Chem.* **2001,** *66*, 3474–3483.
9. Li, J.; Cook, J. M. *Reissert Indole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 154–158. (Review).
10. Butin, A. V.; Smirnov, S. K.; Stroganova, T. A.; Bender, W.; Krapivin, G. D. *Tetrahedron* **2006,** *63*, 474–491.
11. Colombo, E.; Ratel, P.; Mounier, L.; Guillier, F. *J. Flow Chem.* **2011,** *1*, 68–73.

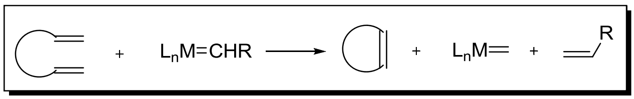
Ring-closing metathesis (RCM)



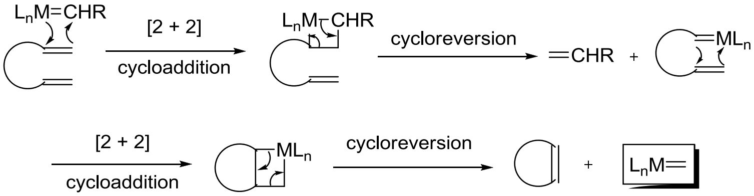
Grubbs' catalysts Schrock's catalyst
Mes = mesityl

All three catalysts are illustrated as "L_nM=CHR" in the mechanism below.

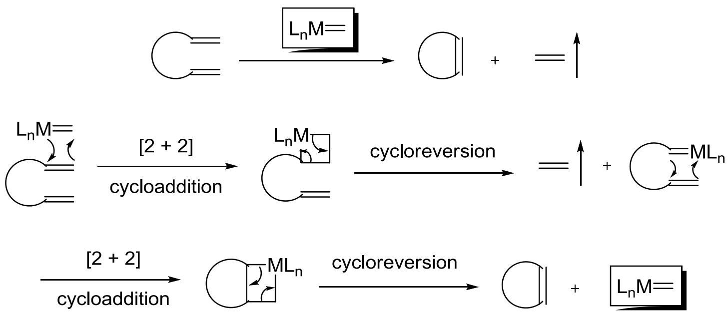
Generation of the real catalyst from the precatalysts:



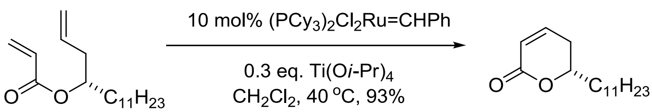
the active catalyst



Catalytic cycle:



Example 1[3]



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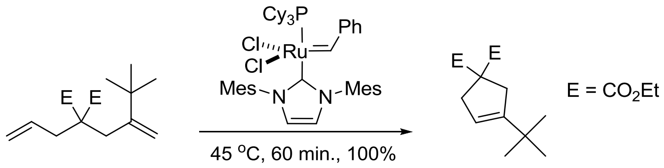
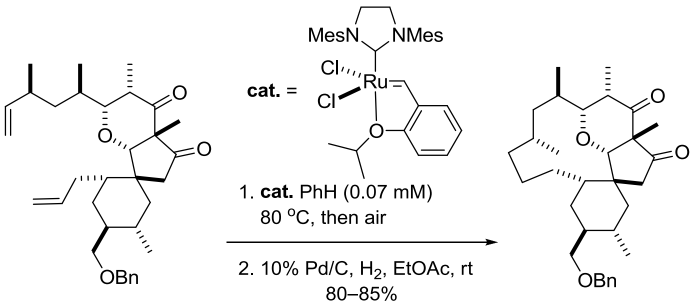
DOI 10.1007/978-3-319-03979-4_232,

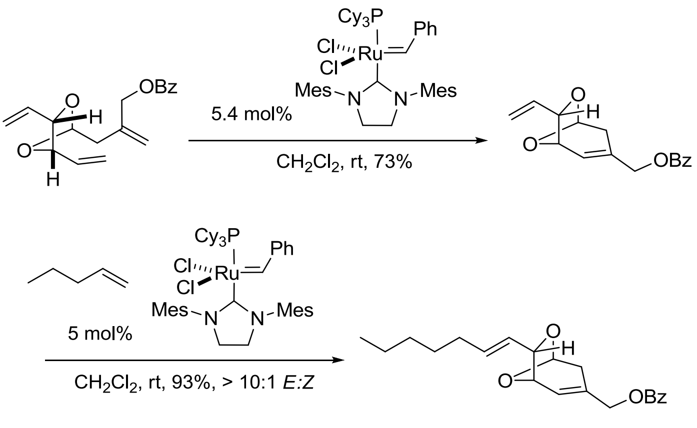
Example 2[4]



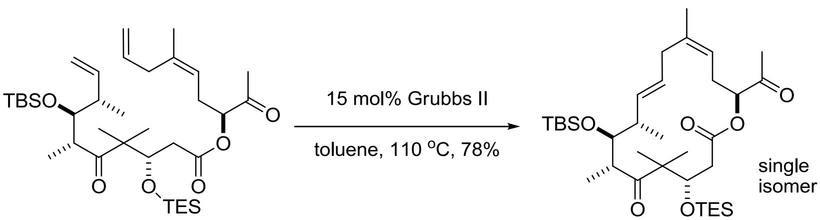
Example 3[7]



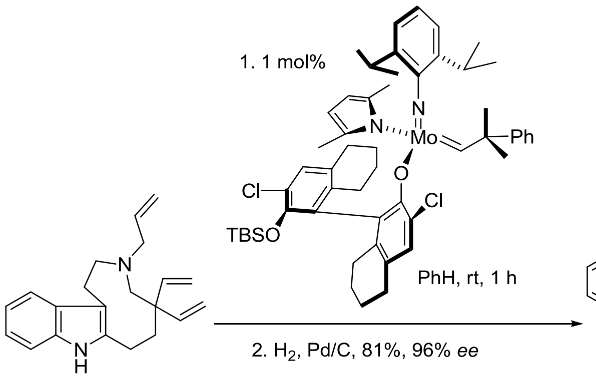
Example 4[9]



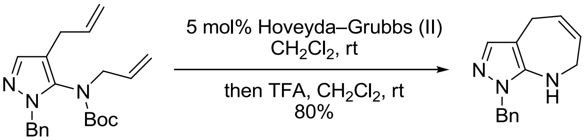
Example 5[10]



Example 6[12]



Example 7[13]

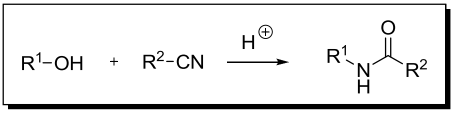


References

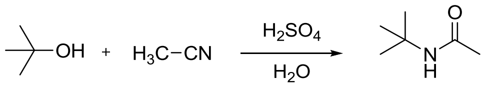
1. Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990,** *112*, 3875–3886. Richard Schrock is a professor at MIT. He shared the 2005 Nobel Prize in Chemistry with Robert Grubbs of Caltech and Yves Chauvin of Institut Français du Pétrole in France for their contributions to metathesis.
2. Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995,** *28,* 446–452. (Review).
3. Scholl, M.; Tunka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999,** *40,* 2247–2250.
4. Fellows, I. M.; Kaelin, D. E., Jr.; Martin, S. F. *J. Am. Chem. Soc.* **2000,** *122*, 10781–10787.
5. Timmer, M. S. M.; Ovaa, H.; Filippov, D. V.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron Lett.* **2000,** *41*, 8635–8638.
6. Thiel, O. R. *Alkene and alkyne metathesis in organic synthesis*. In *Transition Metals for Organic Synthesis (2nd Edn.)*, **2004,** *1*, pp 321–333. (Review).
7. Smith, A. B., III; Basu, K.; Bosanac, T. *J. Am. Chem. Soc.* **2007,** *129*, 14872–14874.
8. Hoveyda, A.H.; Zhugralin, A. R. *Nature* **2007,** *450*, 243–251. (Review).
9. Marvin, C. C.; Clemens, A. J. L.; Burke, S. D. *Org. Lett.* **2007,** *9*, 5353–5356.
10. Keck, G. E.; Giles, R. L.; Cee, V. J.; Wager, C. A.; Yu, T.; Kraft, M. B. *J. Org. Chem.* **2008,** *73*, 9675–9691.
11. Donohoe, T. J.; Fishlock, L. P.; Procopiou, P. A. *Chem. Eur. J.* **2008,** *14*, 5716–5726. (Review).
12. Sattely, E. S.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009,** *131*, 943–953.
13. Moss, T. A. *Tetrahedron Lett.* **2013,** *54*, 993–997.

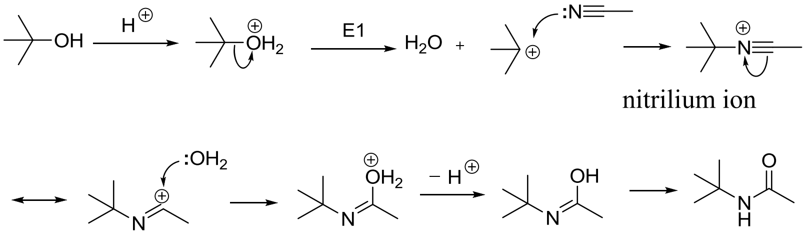
Ritter reaction

Amides from nitriles and alcohols in strong acids.
General scheme:

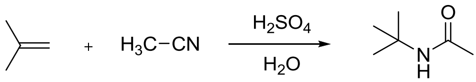


Example 1

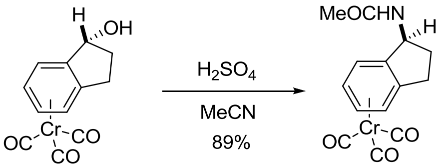




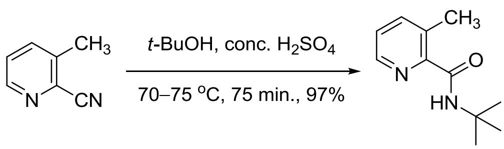
Similarly:



Example 2[3]



Example 3[4]



Example 4[5]

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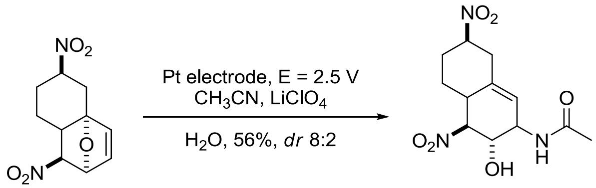
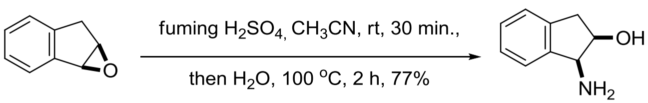
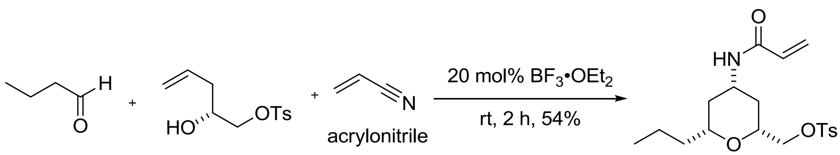
DOI 10.1007/978-3-319-03979-4_233,



Example 5[6]



Example 6, A cascade of the Prins/Ritter amidation reaction[12]

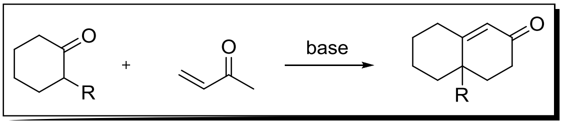


References

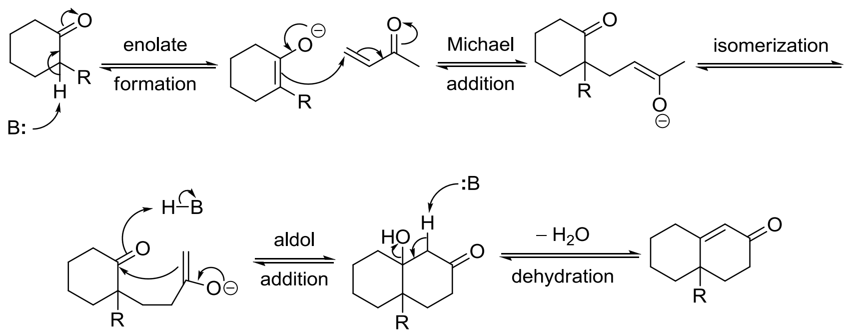
1. (a) Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948,** *70*, 4045–4048. (b) Ritter, J. J.; Kalish, J. *J. Am. Chem. Soc.* **1948,** *70*, 4048–4050.
2. Krimen, L. I.; Cota, D. J. *Org. React.* **1969,** *17*, 213–329. (Review).
3. Top, S.; Jaouen, G. *J. Org. Chem.* **1981,** *46*, 78–82.
4. Schumacher, D. P.; Murphy, B. L.; Clark, J. E.; Tahbaz, P.; Mann, T. A. *J. Org. Chem.* **1989,** *54,* 2242–2244.
5. Le Goanvic, D; Lallemond, M.-C.; Tillequin, F.; Martens, T. *Tetrahedron Lett.* **2001,** *42*, 5175–5176.
6. Tanaka, K.; Kobayashi, T.; Mori, H.; Katsumura, S. *J. Org. Chem*. **2004,** *69*, 5906–5925.
7. Nair, V.; Rajan, R.; Rath, N. P. *Org. Lett.* **2002,** *4*, 1575−1577.
8. Concellón, J. M.; Riego, E.; Suárez, J. R.; García-Granda, S.; Díaz, M. R. *Org. Lett.* **2004,** *6*, 4499–4501.
9. Brewer, A. R. E. *Ritter reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 471–476. (Review).
10. Baum, J. C.; Milne, J. E.; Murry, J. A.; Thiel, O. R. *J. Org. Chem*. **2009,** *74*, 2207–2209.
11. Yadav, J. S.; Reddy, Y. J.; Reddy, P. A. N.; Reddy, B. V. S. *Org. Lett.* **2013,** *15*, 546–549.

Robinson annulation

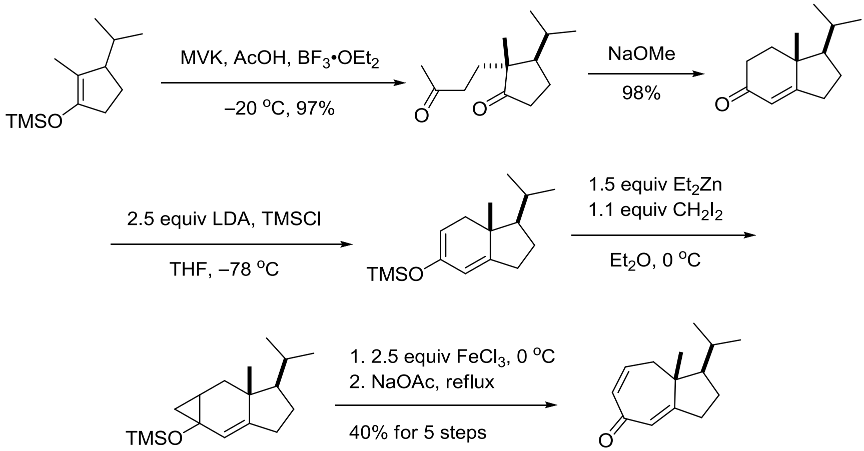
Michael addition of cyclohexanones to methyl vinyl ketone followed by intramolecular aldol condensation to afford six-membered α,β-unsaturated ketones.



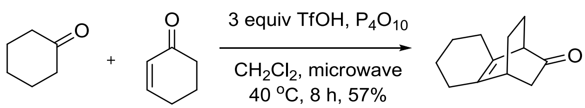
methyl vinyl ketone (MVK)



Example 1, Homo-Robinson[7]



Example 2[8]



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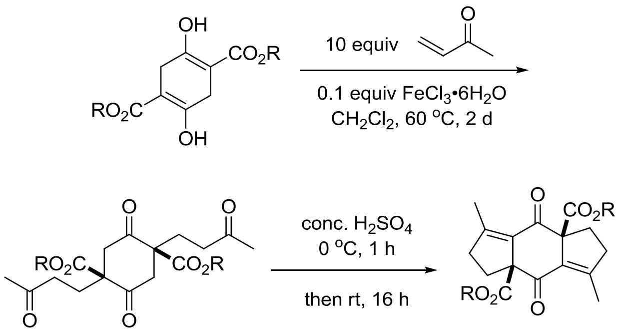
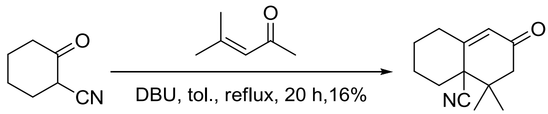
DOI 10.1007/978-3-319-03979-4_234, © Springer International Publishing Switzerland 2014

Example 3, Double Robinson-type cyclopentene annulation[9]



Example 4[10]

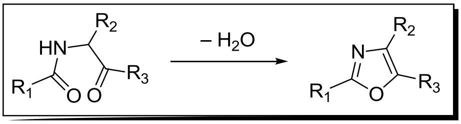


References

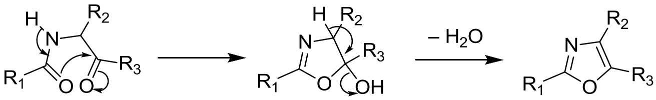
1. Rapson, W. S.; Robinson, R. *J. Chem. Soc.* **1935,** 1285–1288. Robert Robinson used the Robinson annulaton in his total synthesis of cholesterol. Here is a story told by Derek Barton about Robinson and Woodward: "By pure chance, the two great men met early in a Monday morning on an Oxford train station platform in 1951. Robinson politely asked Woodward what kind of research he was doing these days; Woodward replied that he thought that Robinson would be interested in his recent total synthesis of cholesterol. Robinson, incensed and shouting 'Why do you always steal my research topic?', hit Woodward with his umbrella."—An excerpt from Barton, Derek, H. R. *Some Recollections of Gap Jumping,* American Chemical Society, Washington, D.C., **1991**.
2. Gawley, R. E. *Synthesis* **1976,** 777–794. (Review).
3. Guarna, A.; Lombardi, E.; Machetti, F.; Occhiato, E. G.; Scarpi, D. *J. Org. Chem.* **2000,** *65*, 8093–8096.
4. Tai, C.-L.; Ly, T. W.; Wu, J.-D.; Shia, K.-S.; Liu, H.-J. *Synlett* **2001,** 214–217.
5. Jung, M. E.; Piizzi, G. *Org. Lett.* **2003,** *5*, 137–140.
6. Singletary, J. A.; Lam, H.; Dudley, G. B. *J. Org. Chem.* **2005,** *70*, 739–741.
7. Yun, H.; Danishefsky, S. J. *Tetrahedron Lett.* **2005,** *46*, 3879–3882.
8. Jung, M. E.; Maderna, A. *Tetrahedron Lett.* **2005,** *46*, 5057–5061.
9. Zhang, Y.; Christoffers, J. *Synthesis* **2007,** 3061–3067.
10. Jahnke, A.; Burschka, C.; Tacke, R.; Kraft, P. *Synthesis* **2009,** 62–68.
11. Bradshaw, B.; Parra, C.; Bonjoch, J. *Org. Lett.* **2013,** *15*, 2458–2461.

Robinson–Gabriel synthesis

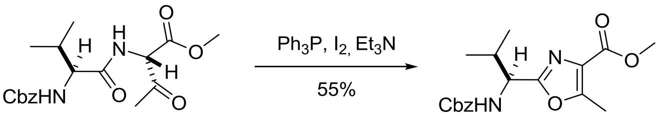
Cyclodehydration of 2-acylamidoketones to give 2,5-di- and 2,4,5-trialkyl-, aryl-, heteroaryl-, and aralkyl-oxazoles.



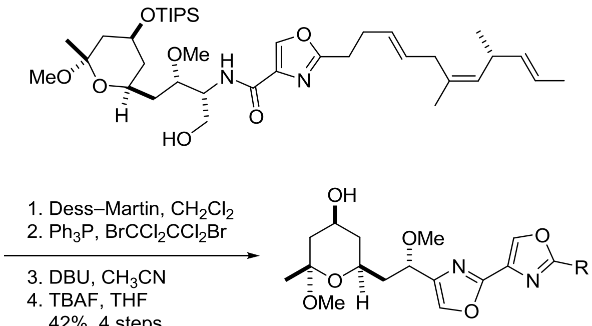
R_1, R_2, R_3 = alkyl, aryl, heteroaryl



Example 1[3]

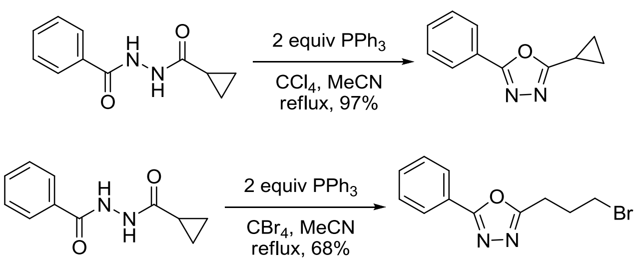


Example 2[4]



(+)-hennoxazole A

Example 3, Halogen effect[9]



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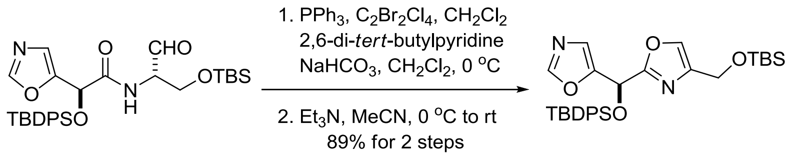
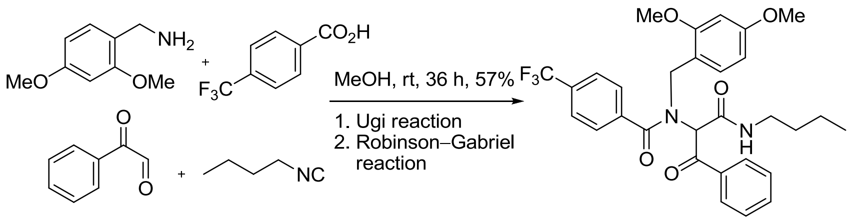
Example 4[10]



Example 5, A cascade Ugi/Robinson-Gabriel reactions[11]

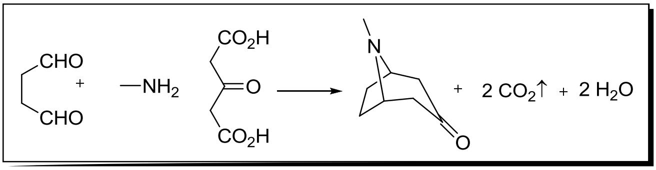


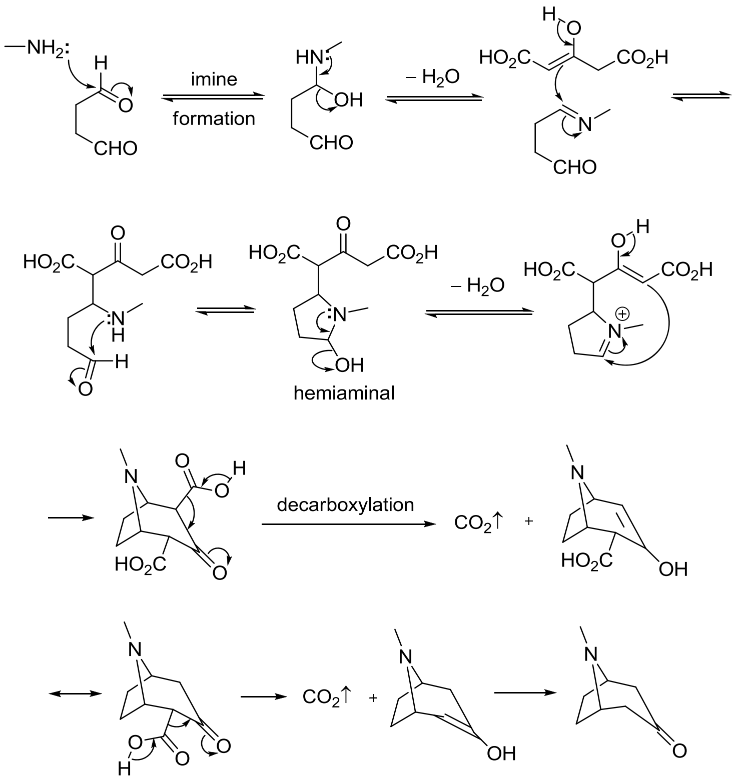
References

1. (a) Robinson, R. *J. Chem. Soc.* **1909,** *95*, 2167–2174. (b) Gabriel, S. *Ber.* **1910,** *43*, 134–138. (c) Gabriel, S. *Ber.* **1910,** *43*, 1283–1287.
2. Turchi, I. J. In *The Chemistry of Heterocyclic Compounds*, *45*; Wiley: New York, **1986**; pp 1–342. (Review).
3. Wipf, P.; Miller, C. P. *J. Org. Chem.* **1993,** *58*, 3604–3606.
4. Wipf, P.; Lim, S. *J. Am. Chem. Soc.* **1995,** *117*, 558–559.
5. Morwick, T.; Hrapchak, M.; DeTuri, M.; Campbell, S. *Org. Lett.* **2002,** *4*, 2665–2668.
6. Nicolaou, K. C.; Rao, P. B.; Hao, J.; Reddy, M. V.; Rassias, G.; Huang, X.; Chen, D. Y.-K.; Snyder, S. A. *Angew. Chem. Int. Ed.* **2003,** *42*, 1753–1758.
7. Godfrey, A. G.; Brooks, D. A.; Hay, L. A.; Peters, M.; McCarthy, J. R.; Mitchell, D. *J. Org. Chem.* **2003,** *68*, 2623–2632.
8. Brooks, D. A. *Robinson–Gabriel Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 249–253. (Review).
9. Yang, Y.-H.; Shi, M. *Tetrahedron Lett*. **2005,** *46*, 6285–6288.
10. Bull, J. A.; Balskus, E. P.; Horan, R. A. J.; Langner, M.; Ley, S. V. *Angew. Chem. Int. Ed.* **2006,** *45*, 6714–6718.
11. Shaw, A. Y.; Xu, Z.; Hulme, C. *Tetrahedron Lett*. **2012,** *53*, 1998–2000.

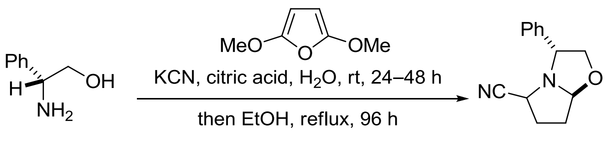
Robinson–Schöpf reaction

1,4-Diketone condensations with primary amines to give tropinones.





Example 1[5]



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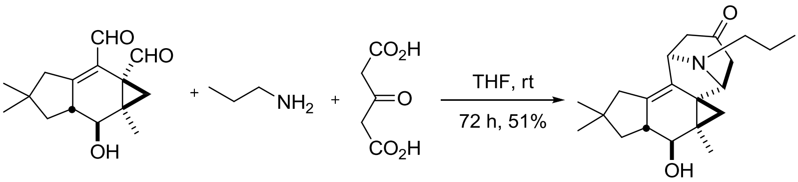
DOI 10.1007/978-3-319-03979-4_236, © Springer International Publishing Switzerland 2014

Example 2[9]

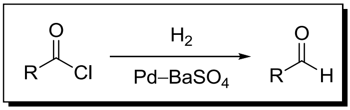


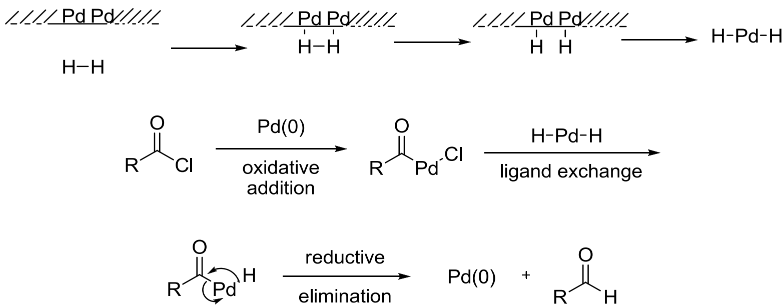
References

1. Robinson, R. *J. Chem. Soc.* **1917,** *111*, 762–768.
2. Paquette, L. A.; Heimaster, J. W. *J. Am. Chem. Soc.* **1966,** *88*, 763–768.
3. Büchi, G.; Fliri, H.; Shapiro, R. *J. Org. Chem*. **1978,** *43*, 4765–4769.
4. Guerrier, L.; Royer, J.; Grierson, D. S.; Husson, H. P. *J. Am. Chem. Soc*. **1983,** *105*, 7754–7755.
5. Royer, J.; Husson, H. P. *Tetrahedron Lett*. **1987,** *28*, 6175–6178.
6. Villacampa, M.; Martínez, M.; González-Trigo, G.; Söllhuber, M. M. *J. Heterocycl. Chem*. **1992,** *29*, 1541–1544.
7. Bermudez, J.; Gregory, J. A.; King, F. D.; Starr, S.; Summersell, R. J. *Bioorg. Med. Chem. Lett.* **1992,** *2*, 519–522.
8. Langlois, M.; Yang, D.; Soulier, J. L.; Florac, C. *Synth. Commun*. **1992,** *22*, 3115–3116.
9. Jarevång, T.; Anke, H.; Anke, T.; Erkel, G.; Sterner, O. *Acta Chem. Scand*. **1998,** *52*, 1350–1352.
10. Amedjkouh, M.; Westerlund, K. *Tetrahedron Lett*. **2004,** *45*, 5175–5177.
11. Eastman, K. J. *Robinson-Schoepf condensation* In *Name Reactions in Heterocyclic Chemistry II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2011,** pp 470–476. (Review).

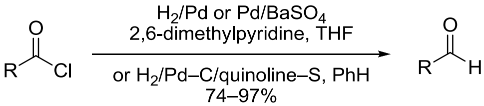
Rosenmund reduction

Hydrogenation reduction of acid chloride to aldehyde using $BaSO_4$-poisoned palladium catalyst. Without this poisoning, the resulting aldehyde may be further reduced to the corresponding alcohol. The possible by-products are alcohol, ester and alkane.

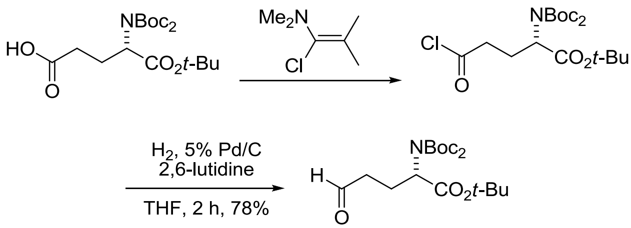




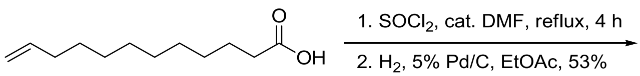
Example 1[4]



Example 2[6]



Example 3[9]



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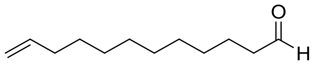
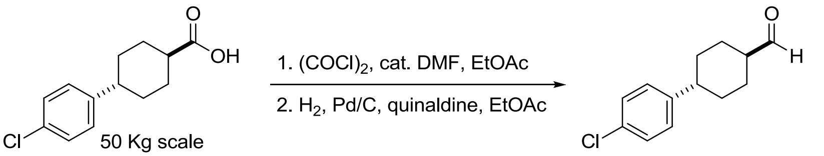
DOI 10.1007/978-3-319-03979-4_237, © Springer International Publishing Switzerland 2014



Example 4[11]

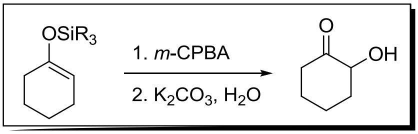


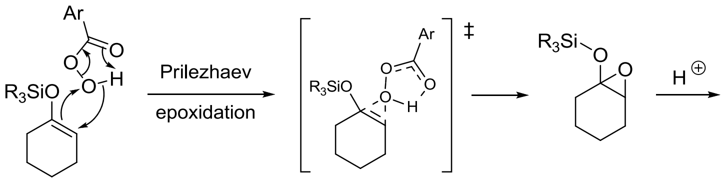
References

1. Rosenmund, K. W. *Ber.* **1918,** *51*, 585–594. Karl Wilhelm Rosenmund was born in Berlin, Germany in 1884. He was a student of Otto Diels and received his Ph.D. In 1906. Rosenmund became professor and director of the Pharmaceutical Institute in Kiel in 1925.
2. Mosettig, E.; Mozingo, R. *Org. React.* **1948,** *4*, 362–377. (Review).
3. Tsuji, J.; Ono, K.; Kajimoto, T. *Tetrahedron Lett*. **1965,** *6,* 4565–4568.
4. Burgstahler, A. W.; Weigel, L. O.; Schäfer, C. G. *Synthesis* **1976,** 767–768.
5. McEwen, A. B.; Guttieri, M. J.; Maier, W. F.; Laine, R. M.; Shvo, Y. *J. Org. Chem.* **1983,** *48*, 4436–4438.
6. Bold, V. G.; Steiner, H.; Moesch, L.; Walliser, B. *Helv. Chim. Acta* **1990,** *73*, 405–410.
7. Yadav, V. G.; Chandalia, S. B. *Org. Proc. Res. Dev.* **1997,** *1*, 226–232.
8. Chandnani, K. H.; Chandalia, S. B. *Org. Proc. Res. Dev.* **1999,** *3*, 416–424.
9. Chimichi, S.; Boccalini, M.; Cosimelli, B. *Tetrahedron* **2002,** *58*, 4851–4858.
10. Ancliff, R. A.; Russell, A. T.; Sanderson, A. J. *Chem. Commun*. **2006,** 3243–3245.
12. Britton, H.; Catterick, D.; Dwyer, A. N.; Gordon, A. H.; et al. *Org. Process Res. Dev.* **2012,** *16,* 1607−1617.

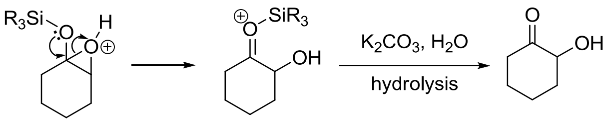
Rubottom oxidation

α-Hydroxylation of enolsilanes.

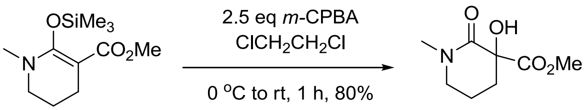




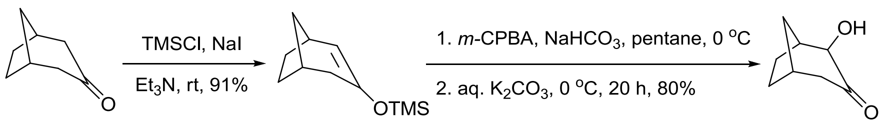
The "butterfly" transition state



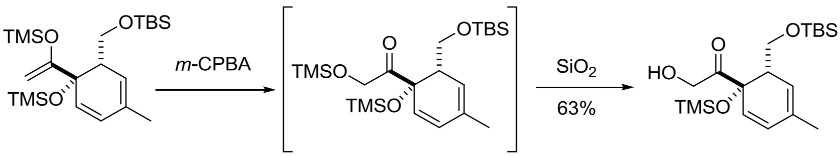
Example 1[2]



Example 2[3]



Example 3[4]



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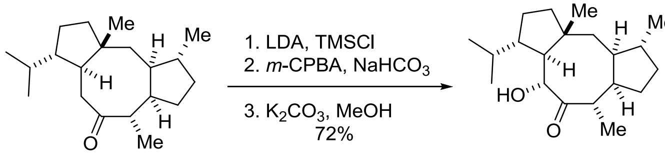
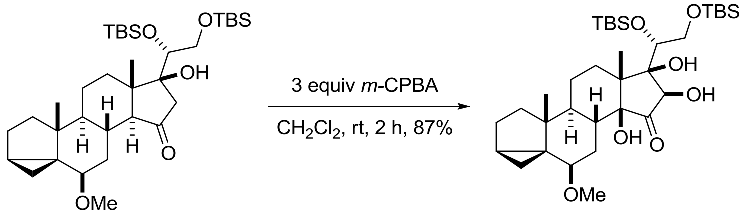
Example 4[5]



Example 5, Double Rubottom oxidation[11]

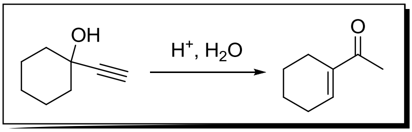


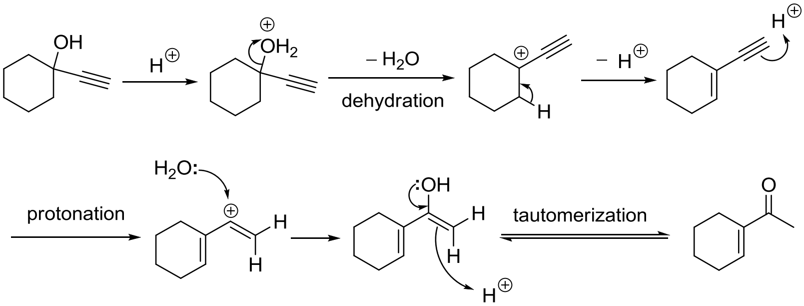
References

1. Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett*. **1974,** *15,* 4319–4322. George Rubottom discovered the Rubottom oxidation when he was an assistant professor at the University of Puerto Rico. He is now a grant officer at the National Science Foundation.
2. Andriamialisoa, R. Z.; Langlois, N.; Langlois, Y. *Tetrahedron Lett*. **1985,** *26*, 3563–2366.
3. Jauch, J. *Tetrahedron* **1994,** *50*, 12903−12912.
4. Crimmins, M. T.; Al-awar, R. S.; Vallin, I. M.; Hollis, W. G., Jr.; O'Mahoney, R.; Lever, J. G.; Bankaitis-Davis, D. M. *J. Am. Chem. Soc.* **1996,** *118*, 7513–7528.
5. Paquette, L. A.; Sun, L.-Q.; Friedrich, D.; Savage, P. B. *Tetrahedron Lett.* **1997,** *38*, 195–198.
6. Paquette, L. A.; Hartung, R. E.; Hofferberth, J. E.; Vilotijevic, I.; Yang, J. *J. Org. Chem*. **2004,** *69*, 2454–2460.
7. Christoffers, J.; Baro, A.; Werner, T. *Adv. Synth. Cat*. **2004,** *346*, 143−151. (Review).
8. He, J.; Tchabanenko, K.; Adlington, R. M.; Cowley, A. R.; Baldwin, J. E. *Eur. J. Org. Chem*. **2006,** 4003−4013.
9. Wolfe, J. P. *Rubottom oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 282–290. (Review).
10. Wang, H.; Andemichael, Y. W.; Vogt, F. G. *J. Org. Chem*. **2009,** *74*, 478–481.
11. Isaka, N.; Tamiya, M.; Hasegawa, A.; Ishiguro, M. *Eur. J. Org. Chem*. **2012,** 665–668.
12. Fujiwara, H.; Kurogi, T.; Okaya, S.; Okano, K.; Tokuyama, H. *Angew. Chem. Int. Ed.* **2012,** *51*, 13062–13065.

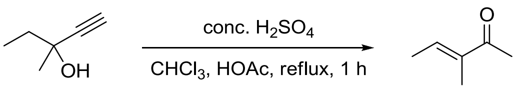
Rupe rearrangement

Acid-catalyzed rearrangement of tertiary α-acetylenic (terminal) alcohols, leading to the formation of α,β-unsaturated ketones rather than the corresponding α,β-unsaturated aldehydes. *Cf.* Meyer–Schuster rearrangement.

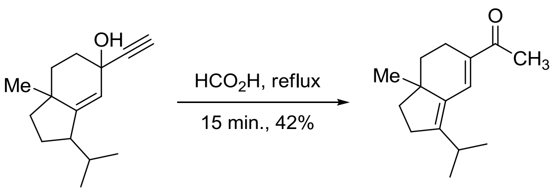




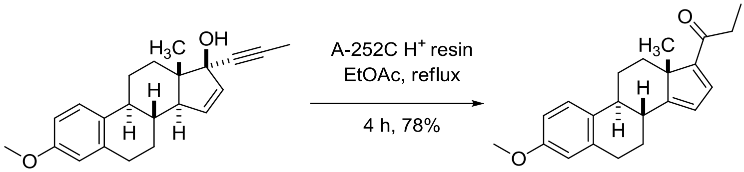
Example 1[4]



Example 2[8]



Example 3[9]



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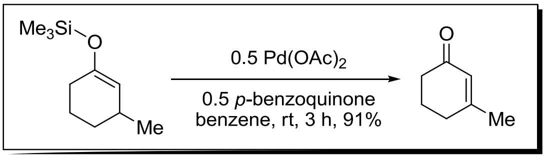
DOI 10.1007/978-3-319-03979-4_239, © Springer International Publishing Switzerland 2014

References

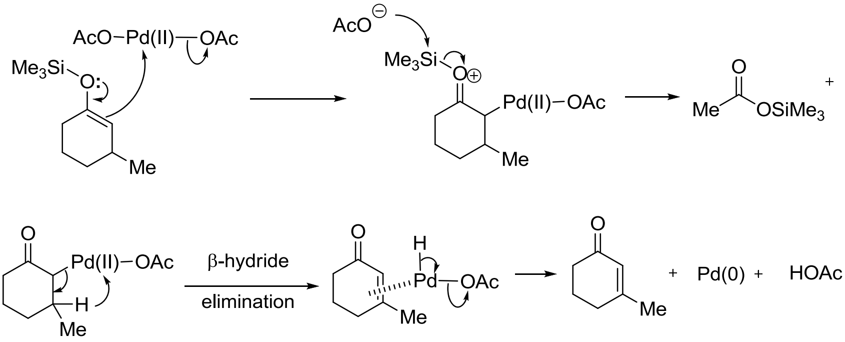
1. Rupe, H.; Kambli, E. *Helv. Chim. Acta* **1926,** *9*, 672.
2. Swaminathan, S.; Narayanan, K. V. *Chem. Rev.* **1971,** *71*, 429–438. (Review).
3. Hasbrouck, R. W.; Anderson Kiessling, A. D. *J. Org. Chem*. **1973,** *38*, 2103–2106.
4. Baran, J.; Klein, H.; Schade, C.; Will, E.; Koschinsky, R.; Bäuml, E.; Mayr, H. *Tetrahedron* **1988,** *44,* 2181–2184.
5. Barre, V.; Massias, F.; Uguen, D. *Tetrahedron Lett*. **1989,** *30*, 7389–7392.
6. An, J.; Bagnell, L.; Cablewski, T.; Strauss, C. R.; Trainor, R. W. *J. Org. Chem*. **1997,** *62*, 2505–2511.
7. Yadav, J. S.; Prahlad, V.; Muralidhar, B. *Synth. Commun*. **1997,** *27*, 3415–3418.
8. Takeda, K.; Nakane, D.; Takeda, M. *Org. Lett.* **2000,** *2*, 1903–1905.
9. Weinmann, H.; Harre, M.; Neh, H.; Nickisch, K.; Skötsch, C.; Tilstam, U. *Org. Proc. Res. Dev.* **2002,** *6*, 216–219.
10. Mullins, R. J.; Collins, N. R. *Meyer–Schuster Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 305–318. (Review).
11. Chang, Y.-J.; Wang, Z.-Z.; Luo, L.-G.; Dai, L.-Y. *Chem. Papers* **2012,** *66*, 33–38.

Saegusa oxidation

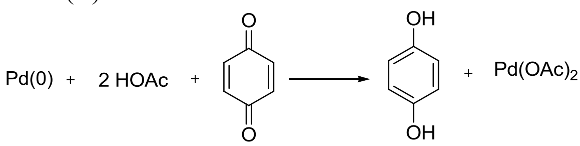
Palladium-catalyzed conversion of enol silanes to enones, also known as the Saegusa enone synthesis or the Saegusa–Ito oxidation.



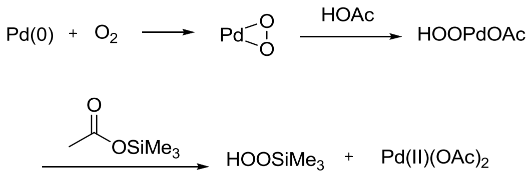
The mechanism is similar to that of the Wacker oxidation.



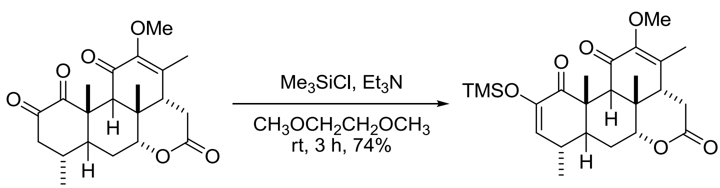
Regenerating the Pd(II) oxidant:



Larock reported regeneration of the Pd(II) oxidant using oxygen:[4]



Example 1[3]



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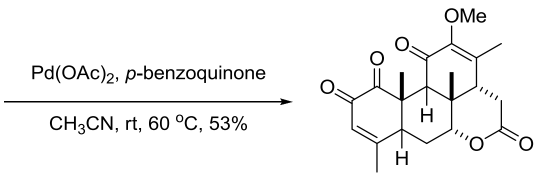
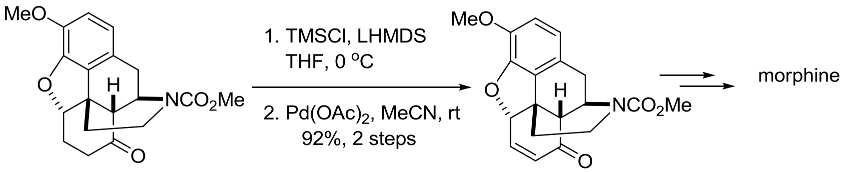
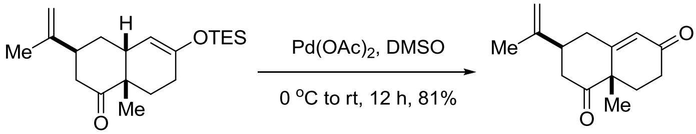
DOI 10.1007/978-3-319-03979-4_240, © Springer International Publishing Switzerland 2014



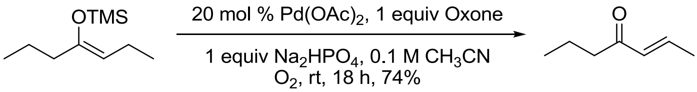
Example 2[9]



Example 3[10]



Example 4[11]

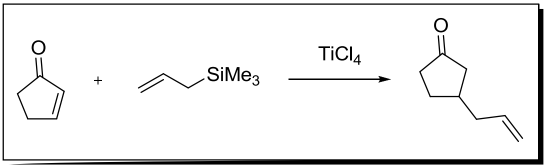


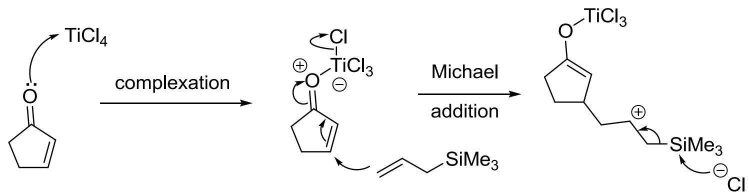
References

1. Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978,** *43*, 1011–1013. Takeo Saegusa was a professor at Kyoto University in Japan.
2. Dickson, J. K., Jr.; Tsang, R.; Llera, J. M.; Fraser-Reid, B. *J. Org. Chem.* **1989,** *54*, 5350–5356.
3. Kim, M.; Applegate, L. A.; Park, O.-S.; Vasudevan, S.; Watt, D. S. *Synth. Commun.* **1990,** *20*, 989–997.
4. Larock, R. C.; Hightower, T. R.; Kraus, G. A.; Hahn, P.; Zheng, D. *Tetrahedron Lett.* **1995,** 36, 2423–2426.
5. Porth, S.; Bats, J. W.; Trauner, D.; Giester, G.; Mulzer, J. *Angew. Chem. Int. Ed.* **1999,** *38*, 2015–2016. The authors proposed a sandwiched Pd(II) as a possible alternative pathway.
6. Williams, D. R.; Turske, R. A. *Org. Lett.* **2000,** *2*, 3217–3220.
7. Nicolaou, K. C.; Zhong, Y.-L.; Baran, P. S. *J. Am. Chem. Soc.* **2000,** *122*, 7596–7597.
8. Sha, C.-K.; Huang, S.-J.; Zhan, Z.-P. *J. Org. Chem.* **2002,** *67*, 831–836.
9. Uchida, K.; Yokoshima, S.; Kan, T.; Fukuyama, T. *Org. Lett.* **2006,** *8*, 5311–5313.
10. Angeles A. R; Waters, S. P.; Danishefsky S. J. *J. Am. Chem. Soc.* **2008,** *130*, 13765–13770.
11. Lu, Y.; Nguyen, P. L.; Lévaray, N.; Lebel, H. *J. Org. Chem.* **2013,** *78,* 776−779.

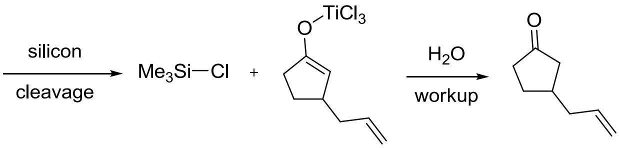
Sakurai allylation reaction

Lewis acid-mediated addition of allylsilanes to carbon nucleophiles. Also known as the Hosomi–Sakurai reaction. The allylsilane will add to the carbonyl compound directly if the electrophile (carbonyl group) is not part of an α,β-unsaturated system (Example 2), giving rise to an alcohol.

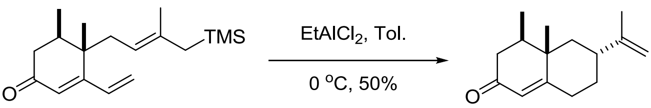




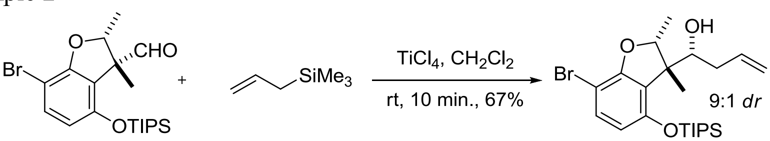
The β-carbocation is stabilized by the β-silicon effect



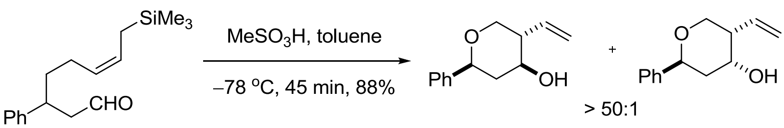
Example 1[2]



Example 2[6]



Example 3[9]



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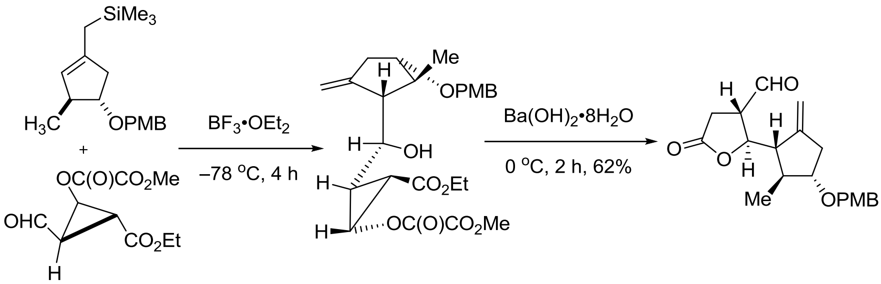
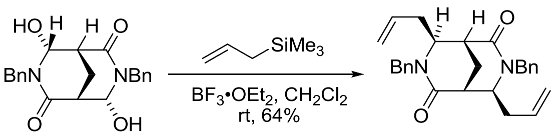
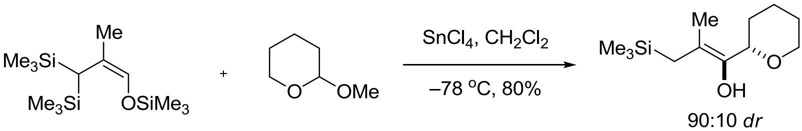
Example 4[10]



Example 5[11]



Example 6[12]

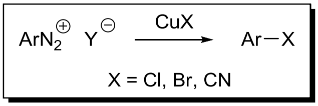


References

1. Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976,** 1295–1298. Hideki Sakurai was a professor at Tohuko University in Japan. This reaction is also known as the Hosomi–Sakurai reaction.
2. Majetich, G.; Behnke, M.; Hull, K. *J. Org. Chem.* **1985,** *50*, 3615–3618.
3. Tori, M.; Makino, C.; Hisazumi, K.; Sono, M.; Nakashima, K. *Tetrahedron: Asymmetry* **2001,** *12*, 301–307.
4. Leroy, B.; Markó, I. E. *J. Org. Chem.* **2002,** *67*, 8744–8752.
5. Itsuno, S.; Kumagai, T. *Helv. Chim. Acta* **2002,** *85*, 3185–3196.
6. Trost, B. M.; Thiel, O. R.; Tsui, H.-C. *J. Am. Chem. Soc.* **2003,** *125*, 13155–13164.
7. Knepper, K.; Ziegert, R. E.; Bräse, S. *Tetrahedron* **2004,** *60*, 8591–8603.
8. Rikimaru, K.; Mori, K.; Kan, T.; Fukuyama, T. *Chem. Commun.* **2005,** 394–396.
9. Jervis, P. J.; Kariuki, B. M.; Cox, L. R. *Org. Lett.* **2006,** *8*, 4649–4652.
10. Kalidindi, S.; Jeong, W. B.; Schall, A.; Bandichhor, R.; Nosse, B.; Reiser, O. *Angew. Chem. Int. Ed.* **2007,** *46*, 6361–6363.
11. Norcross, N. R.; Melbardis, J. P.; Solera, M. F.; Sephton, M. A.; Kilner, C.; Zakharov, L. N.; Astles, P. C.; Warriner, S. L.; Blakemore, P. R. *J. Org. Chem.* **2008,** *73*, 7939–7951.
12. Li, L.; Ye, X.; Wu, Y.; Gao, L.; Song, Z.; Yin, Z.; Xu, Y. *Org. Lett.* **2013,** *15,* 1068–1071.

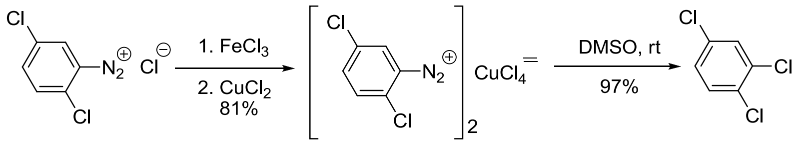
Sandmeyer reaction

Haloarenes from the reaction of a diazonium salt with CuX.

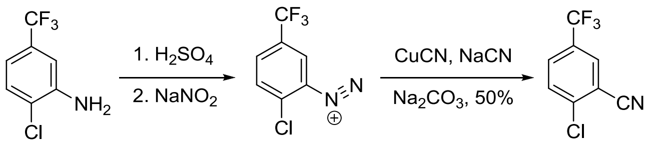


Mechanism:

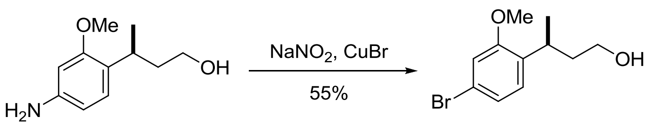
Example 1[4]



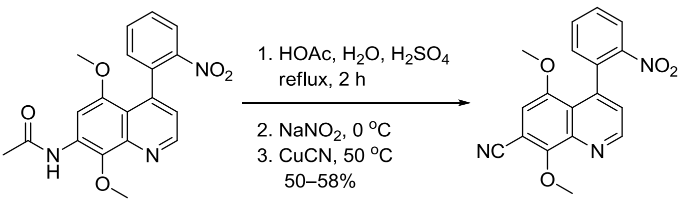
Example 2[7]



Example 3[8]



Example 4[9]



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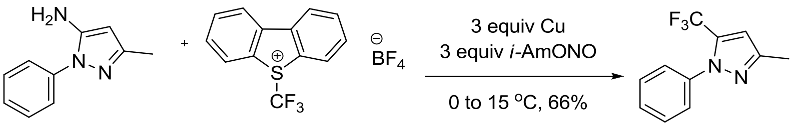
Example 5[11]

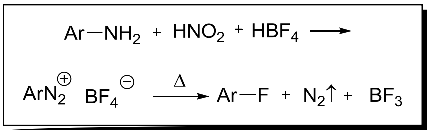


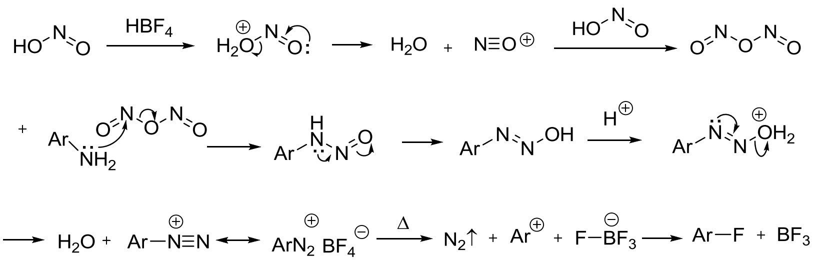
References

1. Sandmeyer, T. *Ber.* **1884,** *17*, 1633. Traugott Sandmeyer (1854–1922) was born in Wettingen, Switzerland. He apprenticed under Victor Meyer and Arthur Hantzsch although he never took a doctorate. He later spent 31 years at the company J. R. Geigy, which is now part of Novartis.
2. Suzuki, N.; Azuma, T.; Kaneko, Y.; Izawa, Y.; Tomioka, H.; Nomoto, T. *J. Chem. Soc., Perkin Trans. 1* **1987,** 645–647.
3. Merkushev, E. B. *Synthesis* **1988,** 923–937. (Review).
4. Obushak, M. D.; Lyakhovych, M. B.; Ganushchak, M. I. *Tetrahedron Lett.* **1998,** *39*, 9567–9570.
5. Hanson, P.; Jones, J. R.; Taylor, A. B.; Walton, P. H.; Timms, A. W. *J. Chem. Soc., Perkin Trans. 2* **2002,** 1135–1150.
6. Daab, J. C.; Bracher, F. *Monatsh. Chem.* **2003,** *134*, 573–583.
7. Nielsen, M. A.; Nielsen, M. K.; Pittelkow, T. *Org. Proc. Res. Dev.* **2004,** *8*, 1059–1064.
8. Kim, S.-G.; Kim, J.; Jung, H. *Tetrahedron Lett.* **2005,** *46*, 2437–2439.
9. LaBarbera, D. V.; Bugni, T. S.; Ireland, C. M. *J. Org. Chem.* **2007,** *72*, 8501–8505.
10. Gehanne, K.; Lancelot, J.-C.; Lemaitre, S.; El-Kashef, H.; Rault, S. *Heterocycles* **2008,** *75*, 3015–3024.
11. Dai, J.-J.; Fang, C.; Xiao, B.; Yi, J.; Xu, J.; Liu, Z.-J.; Lu, X.; Liu, L.; Fu, Y. *J. Am. Chem. Soc.* **2013,** *135*, 8436–8439.

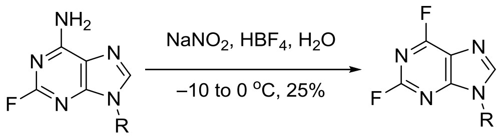
Schiemann reaction

Fluoroarene formation from arylamines. Also known as the Balz–Schiemann reaction.



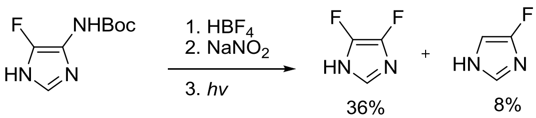


Example 1[4]

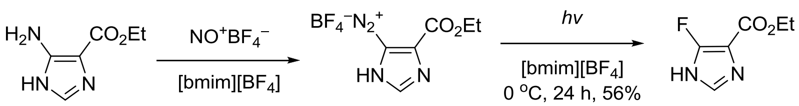


R = 2,3-5-tri-*O*-acetyl-β-*D*-ribofuranose

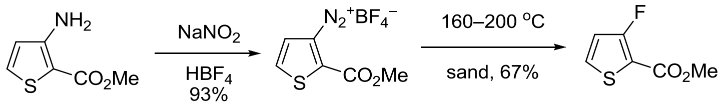
Example 2, Photo-Schiemann reaction[6]



Example 3, Photo-Schiemann reaction[8]



Example 4[10]



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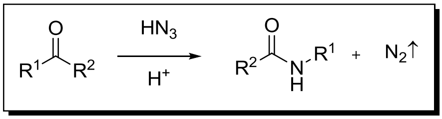
DOI 10.1007/978-3-319-03979-4_243, © Springer International Publishing Switzerland 2014

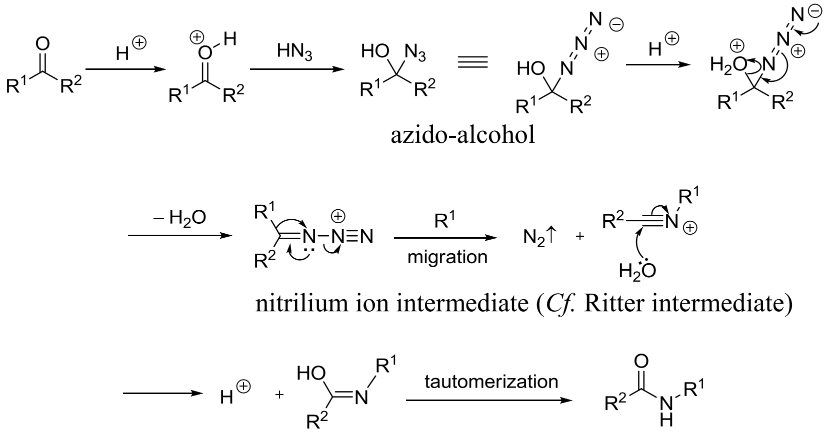
References

1. Balz, G.; Schiemann, G. *Ber.* **1927,** *60*, 1186–1190. Günther Schiemann was born in Breslau, Germany in 1899. In 1925, he received his doctorate at Breslau, where he became an assistant professor. In 1950, he became the Chair of Technical Chemistry at Istanbul, where he extensively studied aromatic fluorine compounds.
2. Roe, A. *Org. React.* **1949,** *5*, 193–228. (Review).
3. Sharts, C. M. *J. Chem. Educ.* **1968,** *45*, 185–192. (Review).
4. Montgomery, J. A.; Hewson, K. *J. Org. Chem.* **1969,** *34*, 1396–1399.
5. Laali, K. K.; Gettwert, V. J. *J. Fluorine Chem.* **2001,** *107*, 31–34.
6. Dolensky, B.; Takeuchi, Y.; Cohen, L. A.; Kirk, K. L. *J. Fluorine Chem.* **2001,** *107*, 147–152.
7. Gronheid, R.; Lodder, G.; Okuyama, T. *J. Org. Chem.* **2002,** *67*, 693–720.
8. Heredia-Moya, J.; Kirk, K. L. *J. Fluorine Chem.* **2007,** *128*, 674–678.
9. Gribble, G. W. *Balz-Schiemann reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 552–563. (Review).
10. Pomerantz, M.; Turkman, N. *Synthesis* **2008,** 2333–2336.

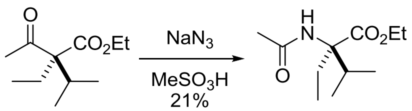
Schmidt rearrangement

The Schmidt reactions refer to the acid-catalyzed reactions of hydrazoic acid with electrophiles, such as carbonyl compounds, tertiary alcohols and alkenes. These substrates undergo rearrangement and extrusion of nitrogen to furnish amines, nitriles, amides or imines.

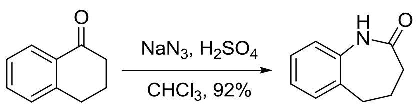




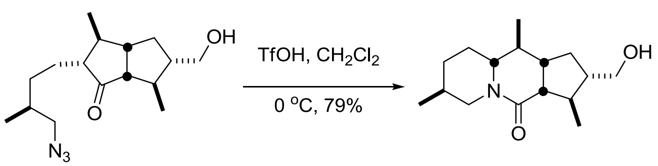
Example 1, A classic example[3]



Example 2[5]



Example 3, Intramolecular Schmidt rearrangement[6]



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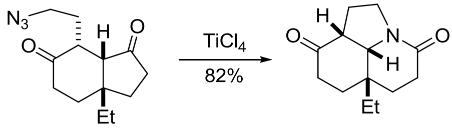
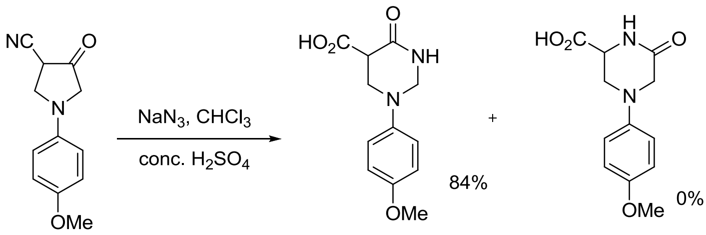
DOI 10.1007/978-3-319-03979-4_244, © Springer International Publishing Switzerland 2014

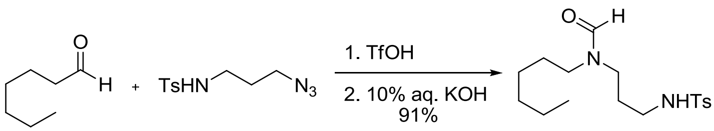
Example 4, Intramolecular Schmidt rearrangement[8]



Example 5, Intermolecular Schmidt rearrangement[9]



Example 6[11]

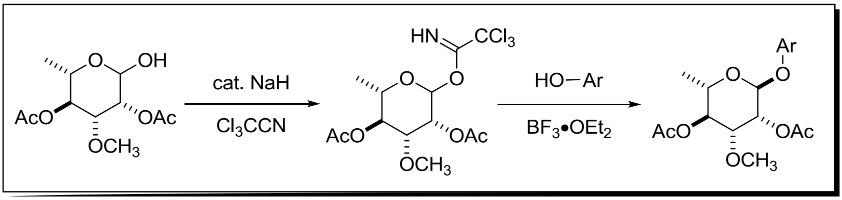


References

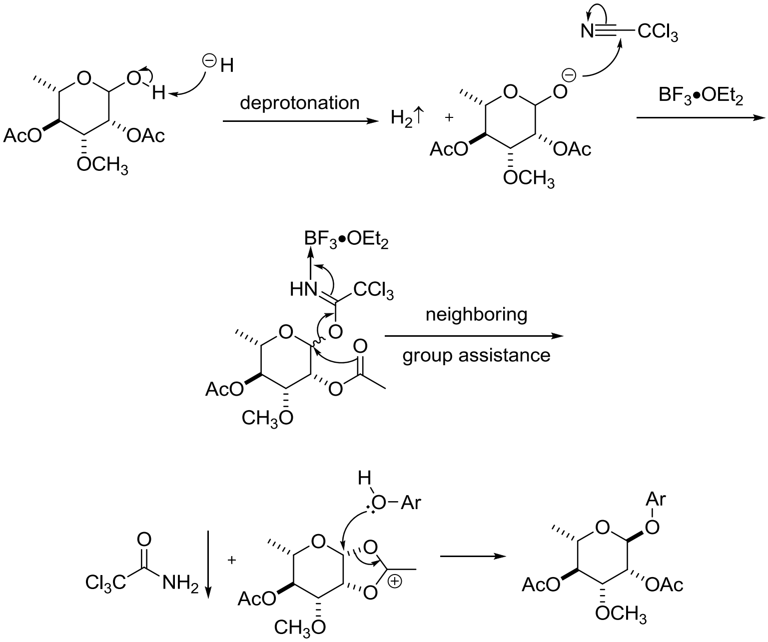
1. (a) Schmidt, K. F. *Angew. Chem.* **1923,** *36*, 511. Karl Friedrich Schmidt (1887–1971) collaborated with Curtius at the University of Heidelberg, where Schmidt became a Professor of Chemistry after 1923. (b) Schmidt, K. F. *Ber.* **1924,** *57*, 704–706.
2. Wolff, H. *Org. React.* **1946,** *3*, 307–336. (Review).
3. Tanaka, M.; Oba, M.; Tamai, K.; Suemune, H. *J. Org. Chem*. **2001,** *66*, 2667–2573.
4. Golden, J. E.; Aubé, J. *Angew. Chem. Int. Ed.* **2002,** *41*, 4316–4318.
5. Johnson, P. D.; Aristoff, P. A.; Zurenko, G. E.; Schaadt, R. D.; Yagi, B. H.; Ford, C. W.; Hamel, J. C.; Stapert, D.; Moerman, J. K. *Bioorg. Med. Chem. Lett*. **2003,** *13*, 4197–4200.
6. Wrobleski, A.; Sahasrabudhe, K.; Aubé, J. *J. Am. Chem. Soc*. **2004,** *126*, 5475–5481.
7. Gorin, D. J.; Davis, N. R.; Toste, F. D. *J. Am. Chem. Soc*. **2005,** *127*, 11260–11261.
8. Iyengar, R.; Schidknegt, K.; Morton, M.; Aubé, J. *J. Org. Chem*. **2005,** *70*, 10645–10652.
9. Amer, F. A.; Hammouda, M.; El-Ahl, A. A. S.; Abdel-Wahab, B. F. *Synth. Commun*. **2009,** *39*, 416–425.
10. Wu, Y.-J. *Schmidt Reactions*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 353–372. (Review).
11. Gu, P.; Sun, J.; Kang, X.-Y.; Yi, M.; Li, X.-Q.; Xue, P.; Li, R. *Org. Lett.* **2013,** *15*, 1124–1127

Schmidt's trichloroacetimidate glycosidation

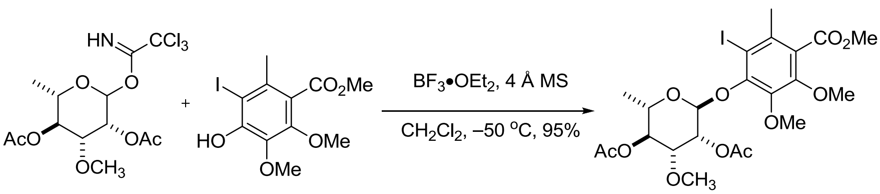
Lewis acid-promoted glycosidation of trichloroacetimidates with alcohols or phenols.



trichloroacetimidate



Example 1[5]



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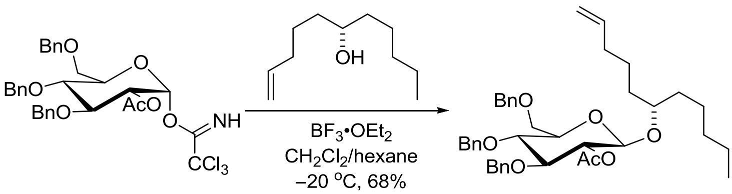
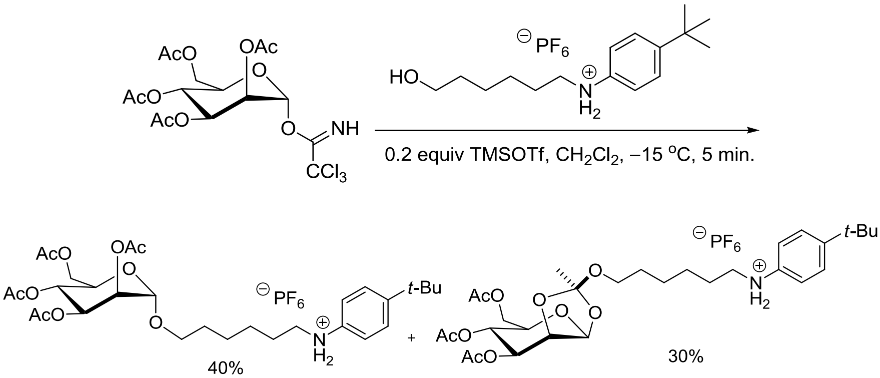
DOI 10.1007/978-3-319-03979-4_245, © Springer International Publishing Switzerland 2014

Example 2[7]



Example 3[9]

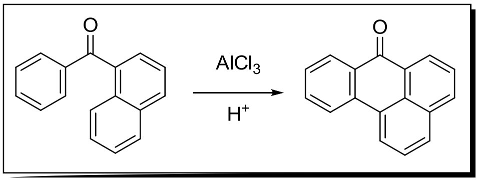


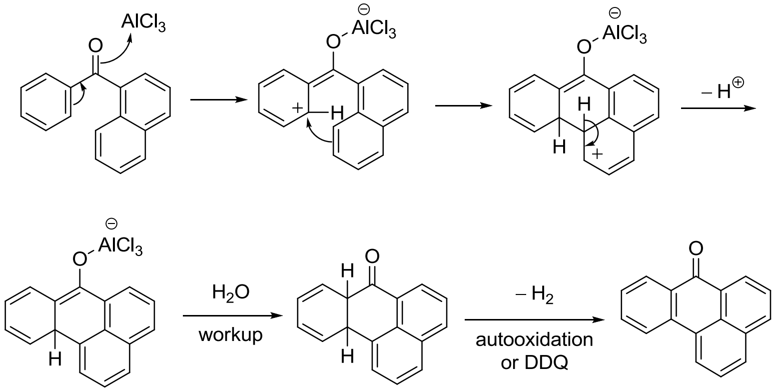
References

1. (a) Grundler, G.; Schmidt, R. R. *Carbohydr. Res.* **1985,** *135*, 203–218. (b) Schmidt, R. R. *Angew. Chem. Int. Ed.* **1986,** *25*, 212–235. (Review).
2. Smith, A. L.; Hwang, C.-K.; Pitsinos, E.; Scarlato, G. R.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1992,** *114*, 3134–3136.
3. Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993,** *93*, 1503–1531. (Review).
4. Nicolaou, K. C. *Angew. Chem. Int. Ed.* **1993,** *32*, 1377–1385. (Review).
5. Groneberg, R. D.; Miyazaki, T.; Stylianides, N. A.; Schulze, T. J.; Stahl, W.; Schreiner, E. P.; Suzuki, T.; Iwabuchi, Y.; Smith, A. L.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1993,** *115*, 7593–611.
6. Fürstner, A.; Jeanjean, F.; Razon, P. *Angew. Chem. Int. Ed.* **2002,** *41*, 2097–2101.
7. Yan, L. Z.; Mayer, J. P. *J. Org. Chem.* **2003,** *68*, 1161–1162.
8. Harding, J. R.; King, C. D.; Perrie, J. A.; Sinnott, D.; Stachulski, A. V. *Org. Biomol. Chem.* **2005,** *3*, 1501–1507.
9. Steinmann, A.; Thimm, J.; Thiem, J. *Eur. J. Org. Chem.* **2007,** *66*, 5506–5513.
10. Coutrot, F.; Busseron, E.; Montero, J.-L. *Org. Lett.* **2008,** *10*, 753–756.
11. Geng, Y.; Kumar, A.; Faidallah, H. M.; Albar, H. A.; Mhkalid, I. A.; Schmidt, R. R. *Angew. Chem. Int. Ed.* **2013,** *52*, 10089–10092.

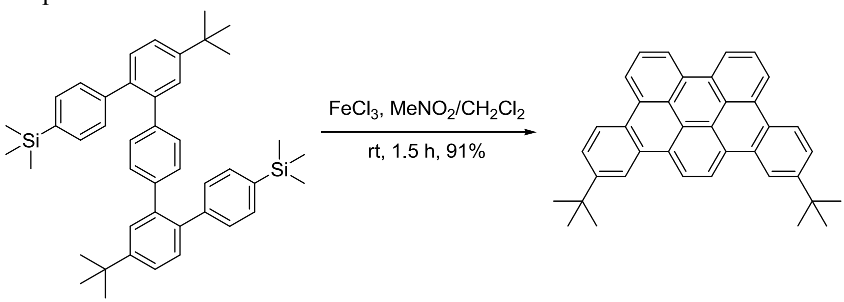
Scholl reaction

The elimination of two aryl-bound hydrogens accompanied by the formation of an aryl-aryl bond under the influence of Friedel–Crafts catalysts. *Cf.* Friedel–Crafts reaction.





Example 1[7]



References

1. Scholl, R.; Seer, C. *Ann,* **1912,** *394*, 111.
2. Olah, G. A.; Schilling, P.; Gross, I. M. *J. Am. Chem. Soc.* **1974,** *96*, 876.
3. Dopper, J. H.; Oudman, D.; Wynberg, H. *J. Org. Chem.* **1975,** *40*, 3398.
4. Rozas, M. F.; Piro, O. E.; Castellano, E. E.; et al. *Synthesis* **2002,** 2399.
5. King, B. T. *J. Am. Chem. Soc.* **2004,** *126*, 15002−15003. (Mechanism).
6. King, B. T. *J. Org. Chem.* **2006,** *71*, 5067–5081. (Mechanism).
7. Pradhan, A.; Dechambenoit, P.; Bock, H.; Durola, F. *J. Org. Chem.* **2013,** *78*, 2266–2274.

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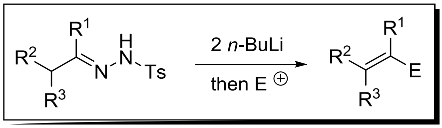
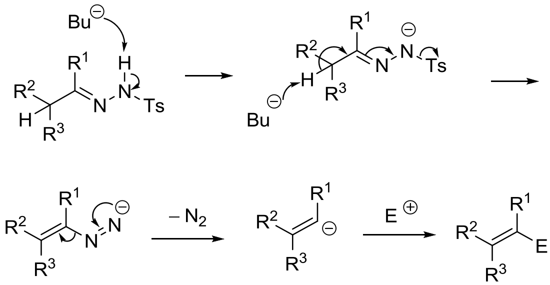
DOI 10.1007/978-3-319-03979-4_246, © Springer International Publishing Switzerland 2014

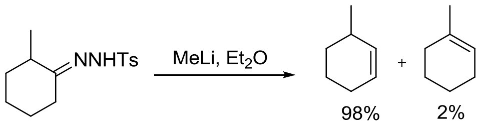
Shapiro reaction

The Shapiro reaction is a variant of the Bamford–Stevens reaction. The former uses bases such as alkyl lithium and Grignard reagents whereas the latter employs bases such as Na, NaOMe, LiH, NaH, $NaNH_2$, *etc*. Consequently, the Shapiro reaction generally affords the less-substituted olefins (the kinetic products), while the Bamford–Stevens reaction delivers the more-substituted olefins (the thermodynamic products).

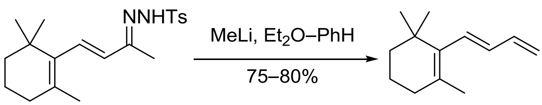




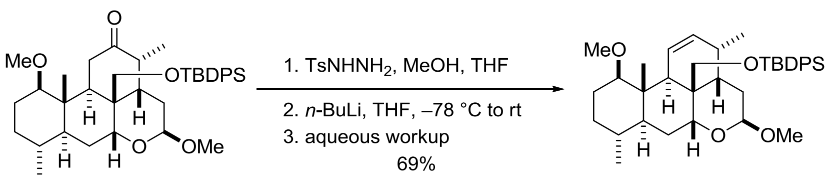
Example 1[2]



Example 2[3]



Example 3[7]



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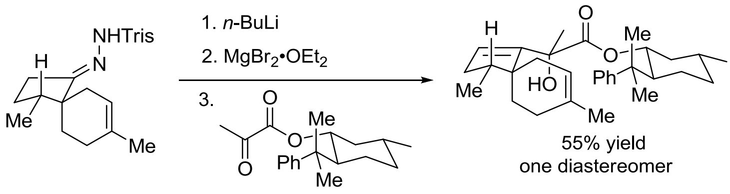
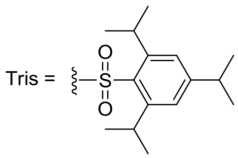
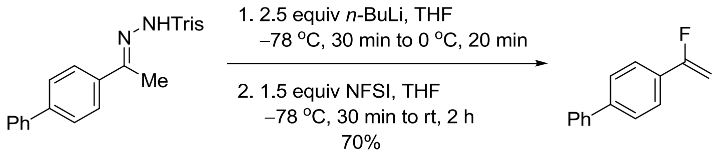
DOI 10.1007/978-3-319-03979-4_247, © Springer International Publishing Switzerland 2014

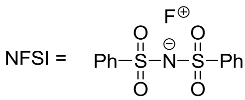
Example 4[8]





Example 5[11]



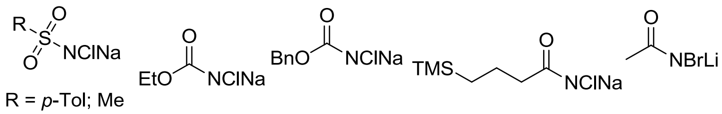


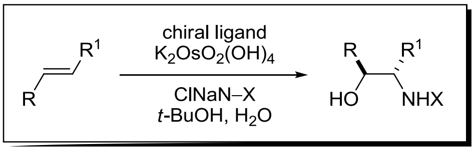
References

1. Shapiro, R. H.; Duncan, J. H.; Clopton, J. C. *J. Am. Chem. Soc.* **1967,** *89*, 471–472. Robert H. Shapiro published this 1967 JACS paper when he was an assistant professor at the University of Colorado. He was denied tenure despite having been immortalized with a reaction named after him.
2. Shapiro, R. H.; Heath, M. J. *J. Am. Chem. Soc.* **1967,** *89*, 5734–5735.
3. Dauben, W. G.; Lorber, M. E.; Vietmeyer, N. D.; Shapiro, R. H.; Duncan, J. H.; Tomer, K. *J. Am. Chem. Soc.* **1968,** *90*, 4762–4763.
4. Shapiro, R. H. *Org. React.* **1976,** *23*, 405–507. (Review).
5. Adlington, R. M.; Barrett, A. G. M. *Acc. Chem. Res.* **1983,** *16*, 55–59. (Review).
6. Chamberlin, A. R.; Bloom, S. H. *Org. React.* **1990,** *39*, 1–83. (Review).
7. Grieco, P. A.; Collins, J. L.; Moher, E. D.; Fleck, T. J.; Gross, R. S. *J. Am. Chem. Soc.* **1993,** *115*, 6078–6093.
8. Tamiya, J.; Sorensen, E. J. *Tetrahedron* **2003,** *59*, 6921–6932.
9. Wolfe, J. P. *Shapiro reaction.* In *Name Reactions for Functional Group Transformations*; Li, J. J., Corey, E. J., eds, Wiley: Hoboken, NJ, **2007,** pp 405–413.
10. Bettinger, H. F.; Mondal, R.; Toenshoff, C. *Org. Biomol. Chem.* **2008,** *6*, 3000–3004.
11. Yang, M.-H.; Matikonda, S. S.; Altman, R. A. *Org. Lett.* **2013,** *15*, 3894–3897.

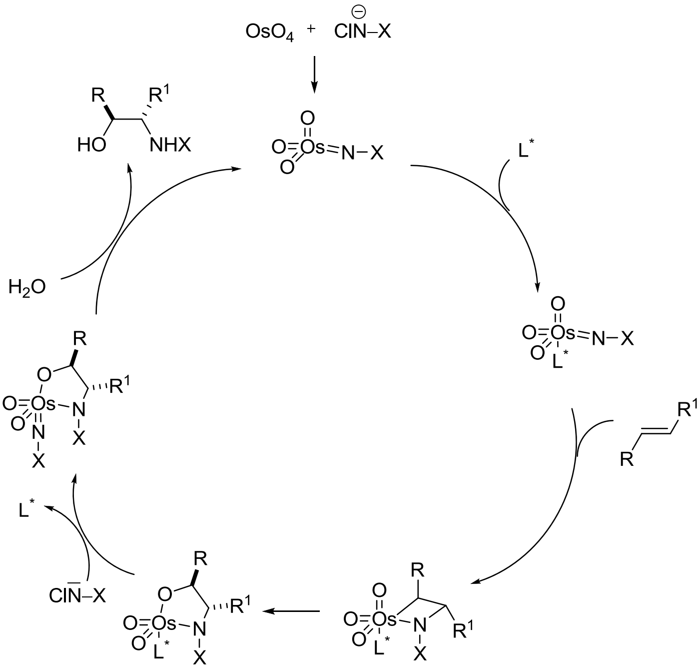
Sharpless asymmetric amino-hydroxylation

Osmium-mediated *cis*-addition of nitrogen and oxygen to olefins. Regio-selectivity may be controlled by ligand. Nitrogen sources (X–NClNa) include:

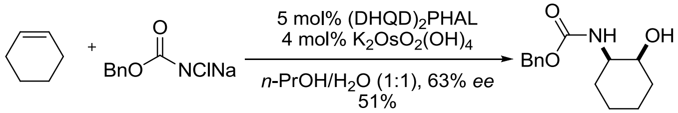




The catalytic cycle:



Example 1[1b]



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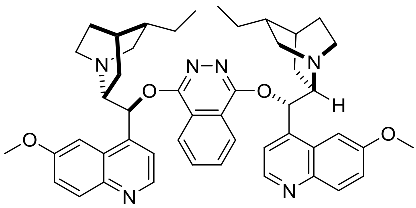
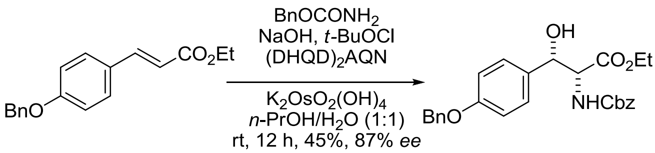
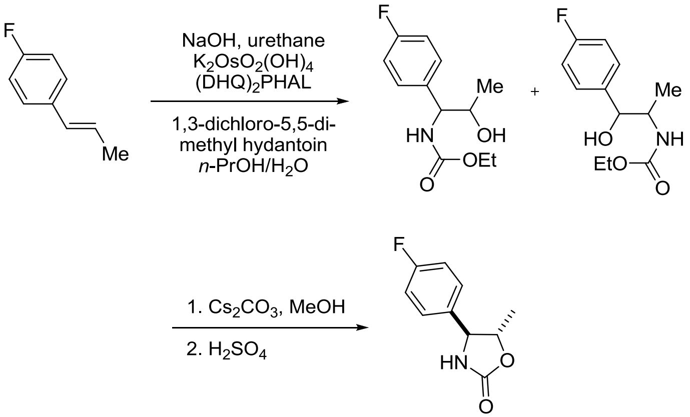
(DHQD)$_2$-PHAL = 1,4-bis(9-*O*-dihydroquinidine)phthalazine:



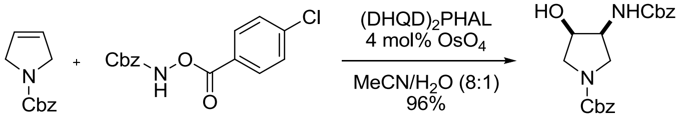
Example 2[2]



Example 3[6]



Example 4[13]



References

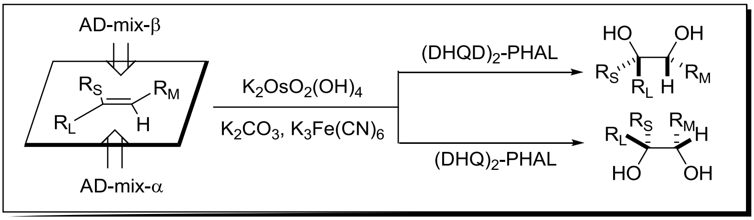
1. (a) Herranz, E.; Sharpless, K. B. *J. Org. Chem*. **1978,** *43*, 2544–2548. K. Barry Sharpless (USA, 1941–) shared the Nobel Prize in Chemistry in 2001 with Herbert William S. Knowles (USA, 1917–) and Ryoji Noyori (Japan, 1938–) for his work on

chirally catalyzed oxidation reactions. (b) Li, G.; Angert, H. H.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **1996,** *35*, 2813–2817. (c) Rubin, A. E.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **1997,** *36*, 2637–2640. (d) Kolb, H. C.; Sharpless, K. B. *Transition Met. Org. Synth*. **1998,** *2*, 243–260. (Review). (e) Thomas, A.; Sharpless, K. B. *J. Org. Chem*. **1999,** *64*, 8379–8385. (f) Gontcharov, A. V.; Liu, H.; Sharpless, K. B. *Org. Lett*. **1999,** *1*, 783–786.

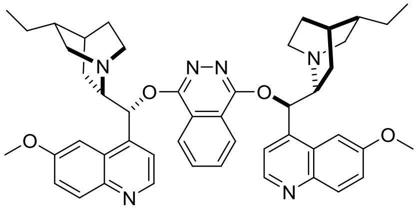
2. Nicolaou, K. C.; Boddy, C. N. C.; Li, H.; Koumbis, A. E.; Hughes, R.; Natarajan, S.; Jain, N. F.; Ramanjulu, J. M.; Braese, S.; Solomon, M. E. *Chem. Eur. J.* **1999,** *5*, 2602–2621.
3. Lohr, B.; Orlich, S.; Kunz, H. *Synlett* **1999,** 1139–1141.
4. Boger, D. L.; Lee, R. J.; Bounaud, P.-Y.; Meier, P. *J. Org. Chem*. **2000,** *65*, 6770–6772.
5. Demko, Z. P.; Bartsch, M.; Sharpless, K. B. *Org. Lett*. **2000,** *2*, 2221–2223.
6. Barta, N. S.; Sidler, D. R.; Somerville, K. B.; Weissman, S. A.; Larsen, R. D.; Reider, P. J. *Org. Lett*. **2000,** *2*, 2821–2824.
7. Bolm, C.; Hildebrand, J. P.; Muñiz, K. In *Catalytic Asymmetric Synthesis;* 2nd edn., Ojima, I., Ed.; Wiley–VCH: New York, **2000,** 399. (Review).
8. Bodkin, J. A.; McLeod, M. D. *J. Chem. Soc., Perkin 1* **2002,** 2733–2746. (Review).
9. Rahman, N. A.; Landais, Y. *Cur. Org. Chem*. **2000,** *6*, 1369–1395. (Review).
10. Nilov, D.; Reiser, O. *Recent Advances on the Sharpless Asymmetric Aminohydroxylation*. In *Organic Synthesis Highlights* Schmalz, H.-G.; Wirth, T., eds.; Wiley–VCH: Weinheim, Germany **2003,** 118–124. (Review).
11. Bodkin, J. A.; Bacskay, G. B.; McLeod, M. D. *Org. Biomol. Chem*. **2008,** *6,* 2544–2553.
12. Wong, D.; Taylor, C. M. *Tetrahedron Lett*. **2009,** *50*, 1273–1275.
13. Harris, L.; Mee, S. P. H.; Furneaux, R. H.; Gainsford, G. J.; Luxenburger, A. *J. Org. Chem*. **2011,** *76*, 358–372.
14. Kumar, J. N.; Das, B. *Tetrahedron Lett*. **2013,** *54*, 3865–3867.

Sharpless asymmetric dihydroxylation

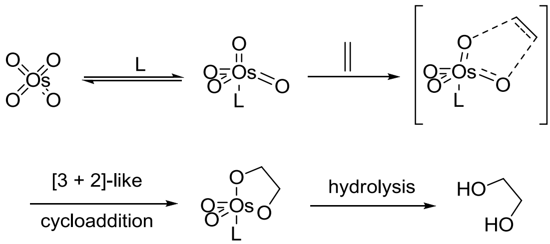
Enantioselective *cis*-dihydroxylation of olefins using osmium catalyst in the presence of cinchona alkaloid ligands.



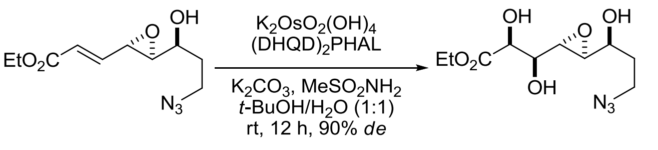
$(DHQ)_2$-PHAL = 1,4-bis(9-*O*-dihydroquinine)phthalazine:



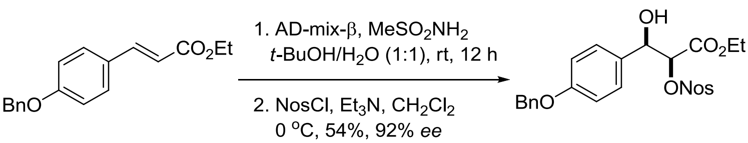
The concerted [3 + 2] cycloaddition mechanism:[5]



Example 1[2]



Example 2[4]



Nos = nosylate = 4-nitrobenzenesulfonyl

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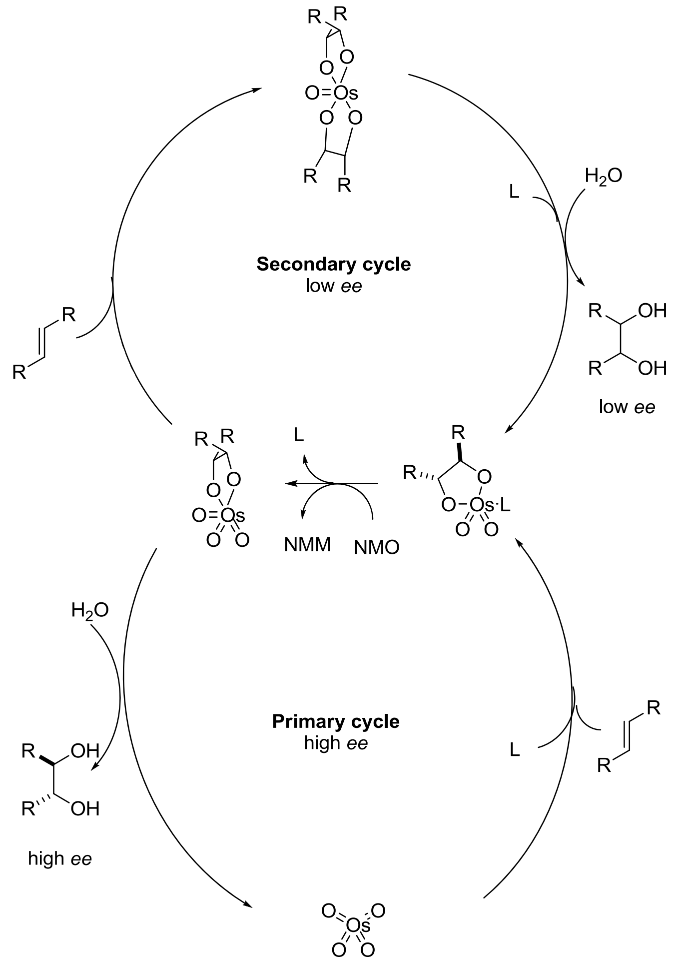
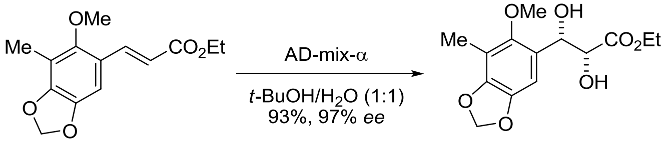
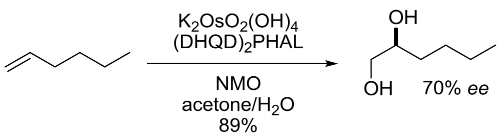
The catalytic cycle: (the secondary cycle is shut off by maintaining a low concentration of olefin):



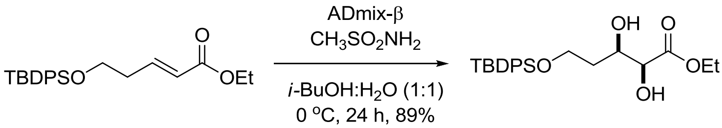
Example 3[9]



Example 4[10]



Example 5[13]

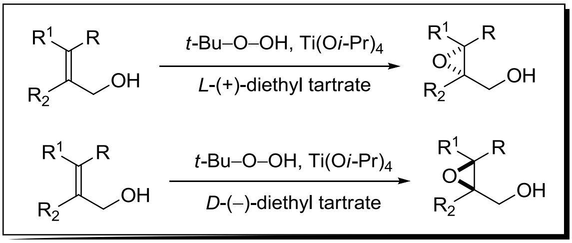


References

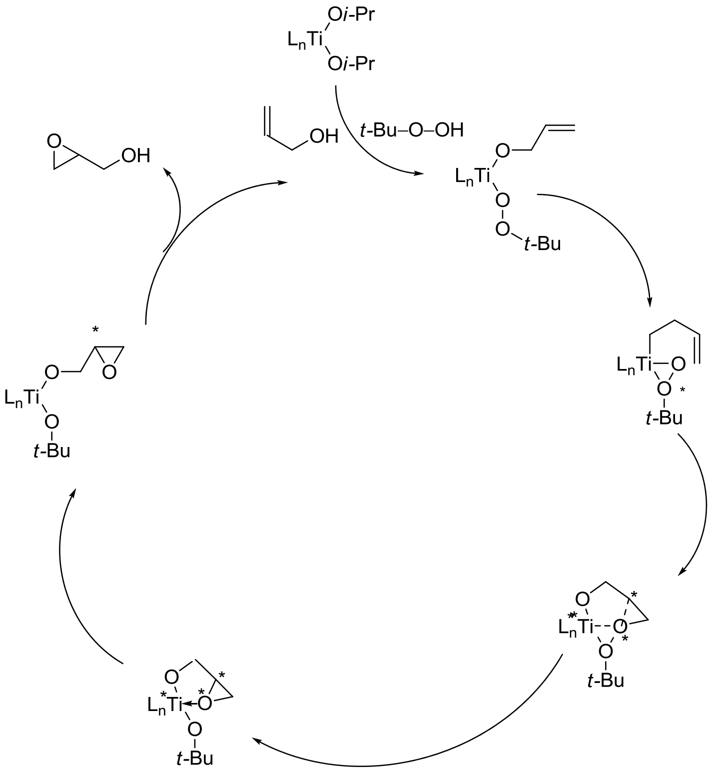
1. (a) Jacobsen, E. N.; Markó, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc*. **1988,** *110*, 1968–1970. (b) Wai, J. S. M.; Markó, I.; Svenden, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc*. **1989,** *111*, 1123–1125.
2. Kim, N.-S.; Choi, J.-R.; Cha, J. K. *J. Org. Chem*. **1993,** *58,* 7096–7699.
3. Kolb, H. C.; VanNiewenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994,** *94*, 2483–2547. (Review).
4. Rao, A. V. R.; Chakraborty, T. K.; Reddy, K. L.; Rao, A. S. *Tetrahedron Lett.* **1994,** *35*, 5043–5046.
5. Corey, E. J.; Noe, M. C. *J. Am. Chem. Soc*. **1996,** *118*, 319–329. (Mechanism).
6. DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. A. *J. Am. Chem. Soc*. **1997,** *119*, 9907–9908. (Mechanism).
7. Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002,** *41*, 2024–2032. (Review, Nobel Prize Address).
8. Zhang, Y.; O'Doherty, G. A. *Tetrahedron* **2005,** *61*, 6337–6351.
9. Chandrasekhar, S.; Reddy, N. R.; Rao, Y. S. *Tetrahedron* **2006,** *62*, 12098–12107.
10. Ferreira, F. C.; Branco, L. C.; Verma, K. K.; Crespo, J. G.; Afonso, C. A. M. *Tetrahedron: Asymmetry* **2007,** *18*, 1637–1641.
11. Ramon, R.; Alonso, M.; Riera, A. *Tetrahedron: Asymmetry* **2007,** *18*, 2797–2802.
12. Krishna, P. R.; Reddy, P. S. *Synlett* **2009,** 209–212.
13. Kamal, A.; Vangala, S. R. *Org. Biomol. Chem*. **2013,** *11*, 4442–4448.

Sharpless asymmetric epoxidation

Enantioselective epoxidation of allylic alcohols using *t*-butyl peroxide, titanium tetra-*iso*-propoxide, and optically pure diethyl tartrate.



The catalytic cycle:



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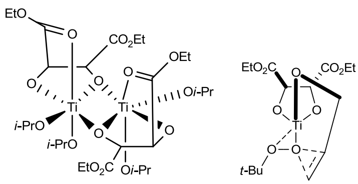
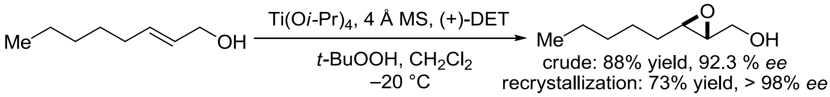
DOI 10.1007/978-3-319-03979-4_250, © Springer International Publishing Switzerland 2014

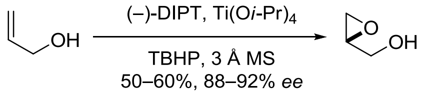
The putative active catalyst:



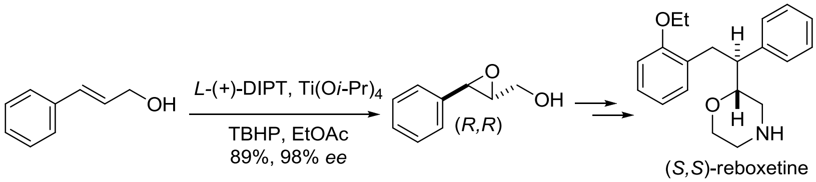
Example 1[3]



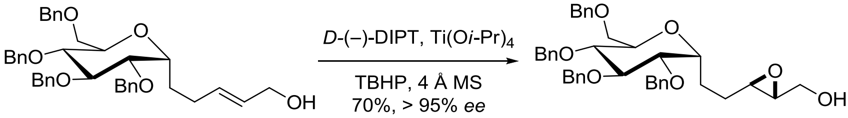
Example 2[3]



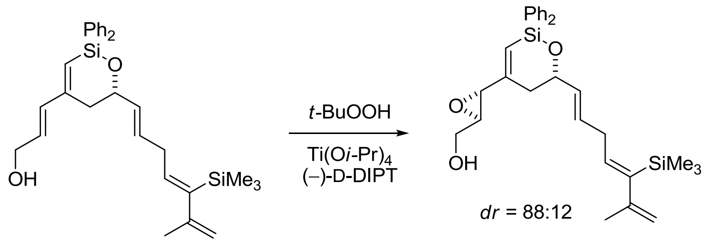
Example 3[11]



Example 4[12]



Example 5[14]

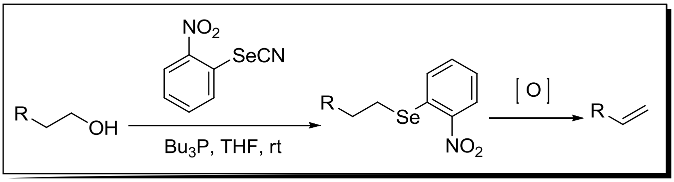


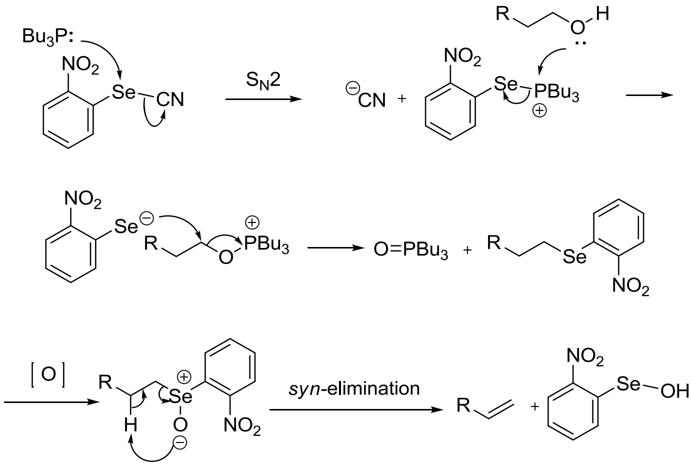
References

1. (a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc*. **1980,** *102*, 5974–5976. (b) Williams, I. D.; Pedersen, S. F.; Sharpless, K. B.; Lippard, S. J. *J. Am. Chem. Soc*. **1984,** *106*, 6430–6433. (c) Woodard, S. S.; Finn, M. G.; Sharpless, K. B. *J. Am. Chem. Soc*. **1991,** *113*, 106–113.
2. Pfenninger, A. *Synthesis* **1986,** 89–116. (Review).
3. Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc*. **1987,** *109*, 5765–5780.
4. Corey, E. J. *J. Org. Chem*. **1990,** *55*, 1693–1694. (Review).
5. Johnson, R. A.; Sharpless, K. B. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed,; Pergamon Press: New York, **1991**; Vol. 7, Chapter 3.2. (Review).
6. Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., ed,; VCH: New York, **1993**; Chapter 4.1, pp 103–158. (Review).
7. Schinzer, D. *Org. Synth. Highlights II* **1995,** 3. (Review).
8. Katsuki, T.; Martin, V. S. *Org. React.* **1996,** *48*, 1–299. (Review).
9. Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis;* 2nd ed., Ojima, I., ed.; Wiley-VCH: New York, **2000,** 231–285. (Review).
10. Palucki, M. *Sharpless–Katsuki Epoxidation*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** 50–62. (Review).
11. Henegar, K. E.; Cebula, M. *Org. Proc. Res. Dev.* **2007,** *11*, 354–358.
12. Pu, J.; Franck, R. W. *Tetrahedron* **2008,** *64*, 8618–8629.
13. Knight, D. W.; Morgan, I. R. *Tetrahedron Lett.* **2009,** *50*, 35–38.
14. Volchkov, I.; Lee, D. *J. Am. Chem. Soc*. **2013,** *135*, 5324–5327.

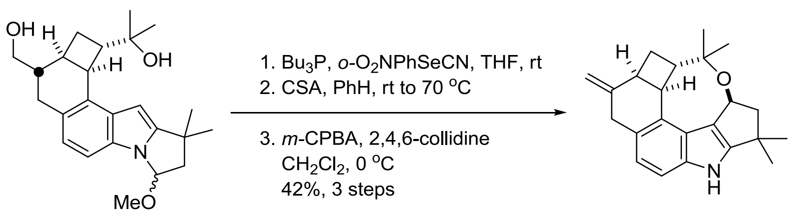
Sharpless olefin synthesis

Olefin synthesis from the *syn*-oxidative elimination of *o*-nitrophenyl selenides, which may be prepared using *o*-nitrophenyl selenocyanate and Bu_3P, among other methods.

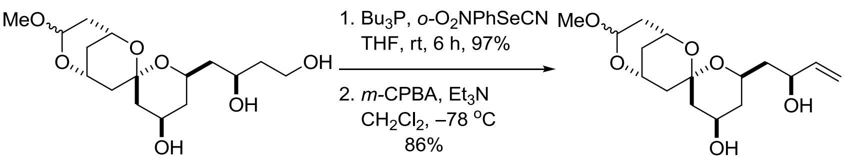




Example 1[3]



Example 2[6]



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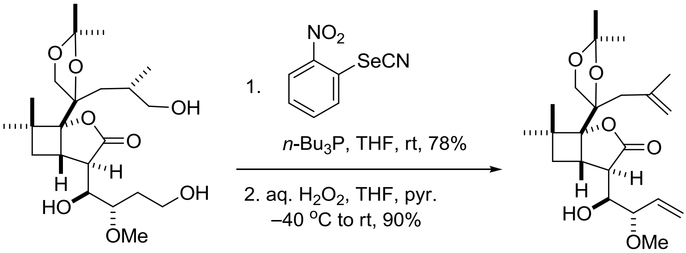
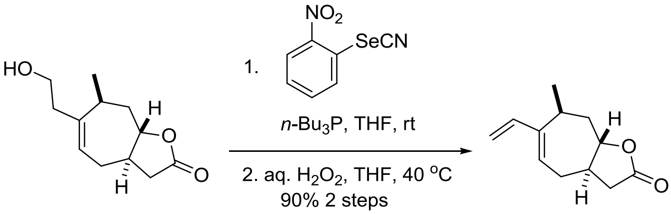
Example 3[9]



Example 4[10]

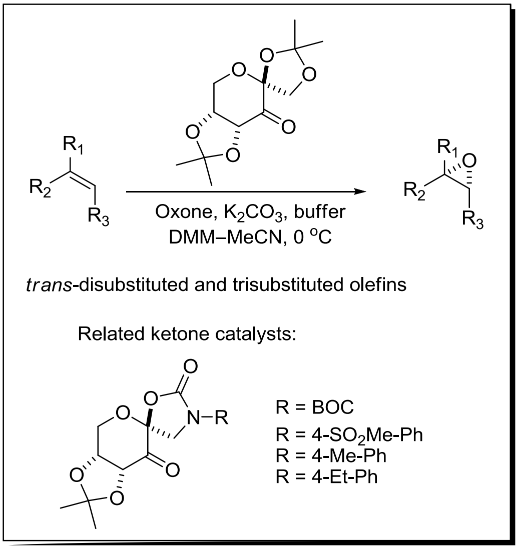


References

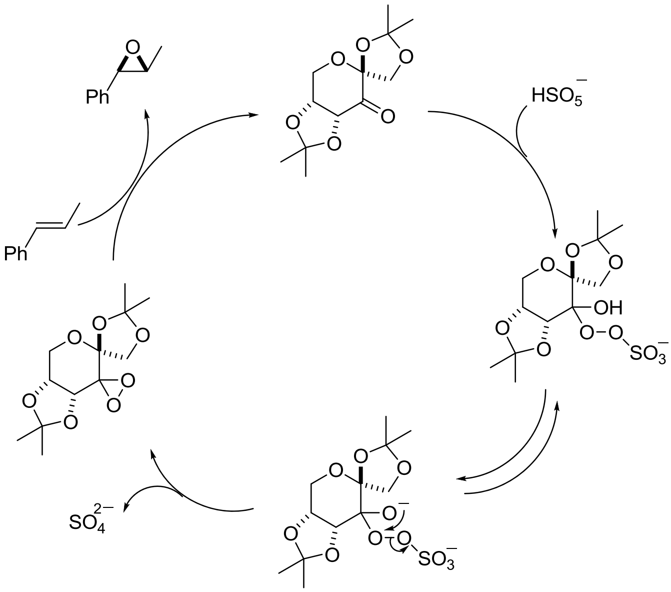
1. (a) Sharpless, K. B.; Young, M. Y.; Lauer, R. F. *Tetrahedron Lett.* **1973,** *22,* 1979–1982. (b) Sharpless, K. B.; Young, M. Y. *J. Org. Chem.* **1975,** *40*, 947–949.
2. (a) Grieco, P. A.; Miyashita, M. *J. Org. Chem.* **1974,** *39*, 120–122. (b) Grieco, P. A.; Miyashita, M. *Tetrahedron Lett.* **1974,** *21,* 1869–1871. (c) Grieco, P. A.; Masaki, Y.; Boxler, D. *J. Am. Chem. Soc*. **1977,** *97*, 1597–1599. (d) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976,** *41*, 1485–1486. (e) Grieco, P. A.; Yokoyama, Y. *J. Am. Chem. Soc*. **1977,** *99*, 5210–5219.
3. Smith, A. B., III; Haseltine, J. N.; Visnick, M. *Tetrahedron* **1989,** *45,* 2431–2449.
4. Reich, H. J.; Wollowitz, S. *Org. React.* **1993,** *44,* 1–296. (Review).
5. Hsu, D.-S.; Liao, C.-C. *Org. Lett.* **2003,** *5,* 4741–4743.
6. Meilert, K.; Pettit, G. R.; Vogel, P. *Helv. Chim. Acta* **2004,** *87,* 1493–1507.
7. Siebum, A. H. G.; Woo, W. S.; Raap, J.; Lugtenburg, J. *Eur. J. Org. Chem.* **2004,** 2905–2916.
8. Blay, G.; Cardona, L.; Collado, A. M.; Garcia, B.; Morcillo, V.; Pedro, J. R. *J. Org. Chem.* **2004,** *69,* 7294–7302. The authors observed the concurrent epoxidation of a tri-subsituted olefin, possibly by the *o*-nitrophenylselenic acid *via* an intramolecular process.
9. Paquette, L. A.; Dong, S.; Parker, G. D. *J. Org. Chem.* **2007,** *72*, 7135–7147.
10. Yokoe, H.; Yoshida, M.; Shishido, K. *Tetrahedron Lett*. **2008,** *49*, 3504–3506.
11. Debnar, T.; Wang, T.; Menche, D. *Org. Lett.* **2013,** *15,* 2774–2777.

Shi asymmetric epoxidation

An asymmetric epoxidation using a fructose-derived chiral ketone. It is an organocatalyst with Oxone typically used as the primary oxidant.



The catalytic cycle:



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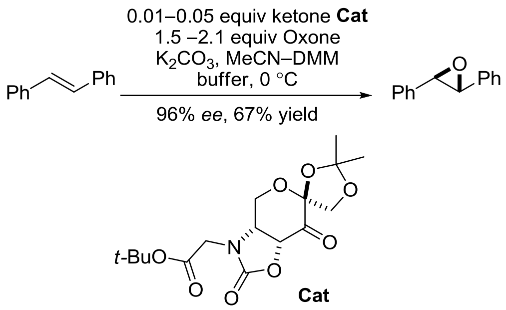
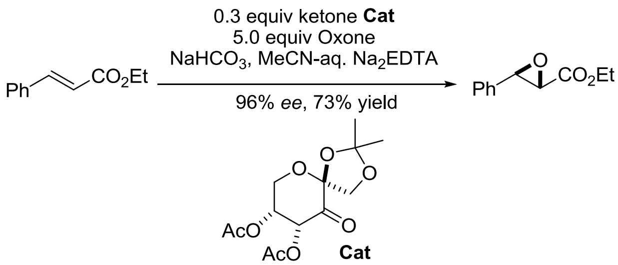
DOI 10.1007/978-3-319-03979-4_252,

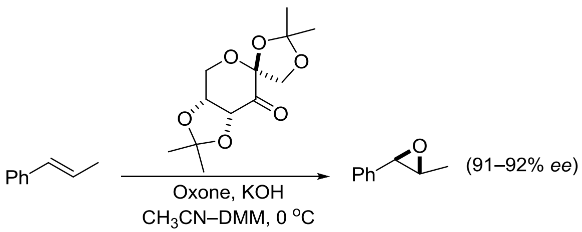
Example 1[6]



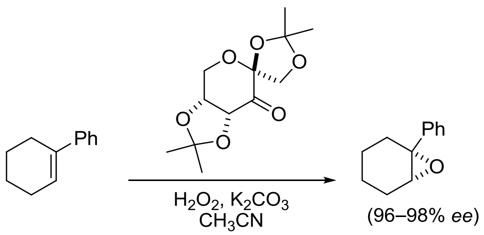
Example 2[7]



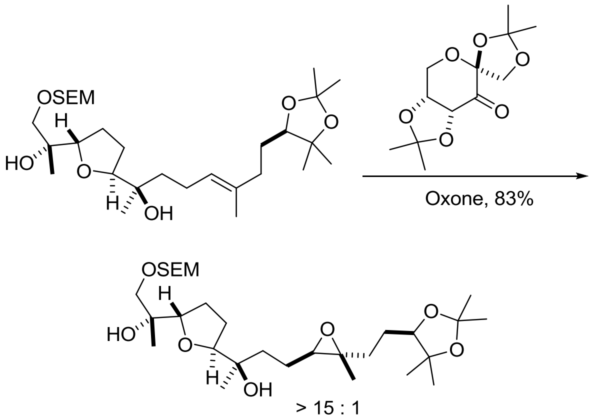
Example 3[8]



Example 4[8]



Example 5[9]

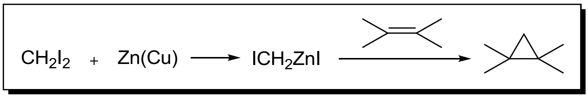


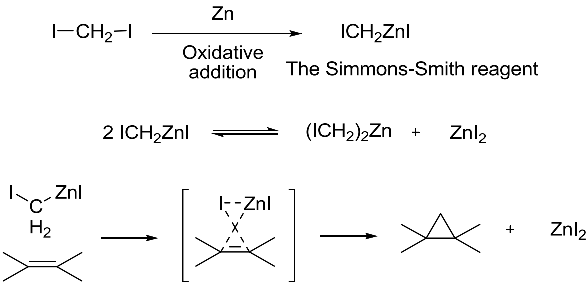
References

1. Wang, Z.-X.; Tu, Y.; Frohn, M.; Zhang, J.-R.; Shi, Y. *J. Am. Chem. Soc*. **1997,** *119*, 11224–11235.
2. Wang, Z.-X.; Shi, Y. *J. Org. Chem*. **1997,** *62*, 8622–8623.
3. Tu, Y.; Wang, Z.-X.; Frohn, M.; He, M.; Yu, H.; Tang, Y.; Shi, Y. *J. Org. Chem*. **1998,** *63*, 8475–8485.
4. Tian, H.; She, X.; Shu, L.; Yu, H.; Shi, Y. *J. Am. Chem. Soc*. **2000,** *122*, 11551–11552.
5. Katsuki, T. In *Catalytic Asymmetric Synthesis;* 2nd ed., Ojima, I., ed.; Wiley–VCH: New York, 2000, pp 287–325. (Review).
6. Tian, H.; She, X.; Shi, Y. *Org. Lett.* **2001,** *3*, 715–717.
7. Wu, X.-Y.; She, X.; Shi, Y. *J. Am. Chem. Soc.* **2002,** *124,* 8792–8783.
8. Wang, Z.-X.; Shu, L.; Frohn, M.; Tu, Y.; Shi, Y. *Org. Synth.* **2003,** *80,* 9–17*; Coll. Vol. 11,* **2003***,* 183–188.
9. Julien, C.; Axel, B.; Antoinette, C.; Wolf, D. W. *Org. Lett.* **2008,** *10*, 512–516.
10. Yang, B. V. *Shi Epoxidation*. In *Name Reactions in Heterocyclic Chemistry II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2011,** 21–39. (Review).
11. Kumar, V. P.; Chandrasekhar, S. *Org. Lett.* **2013,** *5*, 3610–3613.

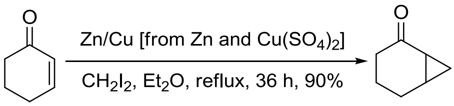
Simmons–Smith reaction

Cyclopropanation of olefins using CH_2I_2 and Zn(Cu).

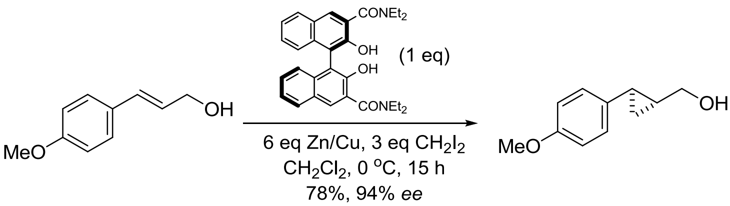




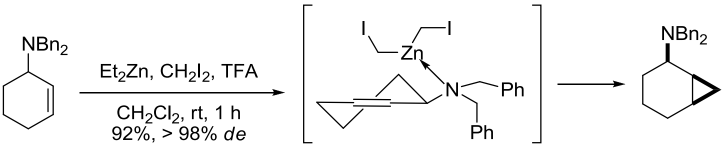
Example 1[2]



Example 2, An asymmetric version[3]



Example 3, Diastereoselective Simmons–Smith cyclopropanations of allylic amines and carbamates[9]



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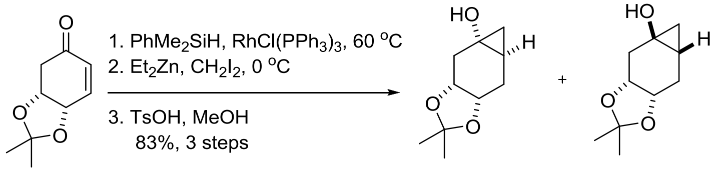
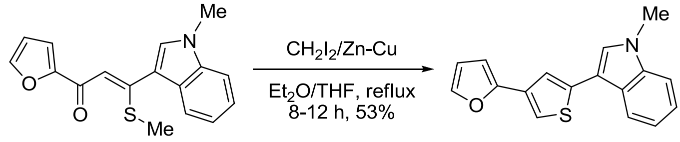
DOI 10.1007/978-3-319-03979-4_253, © Springer International Publishing Switzerland 2014

Example 4[10]



Example 5[12]

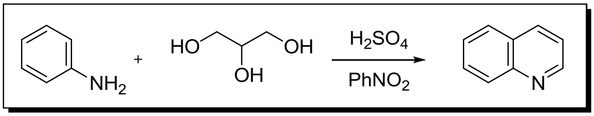


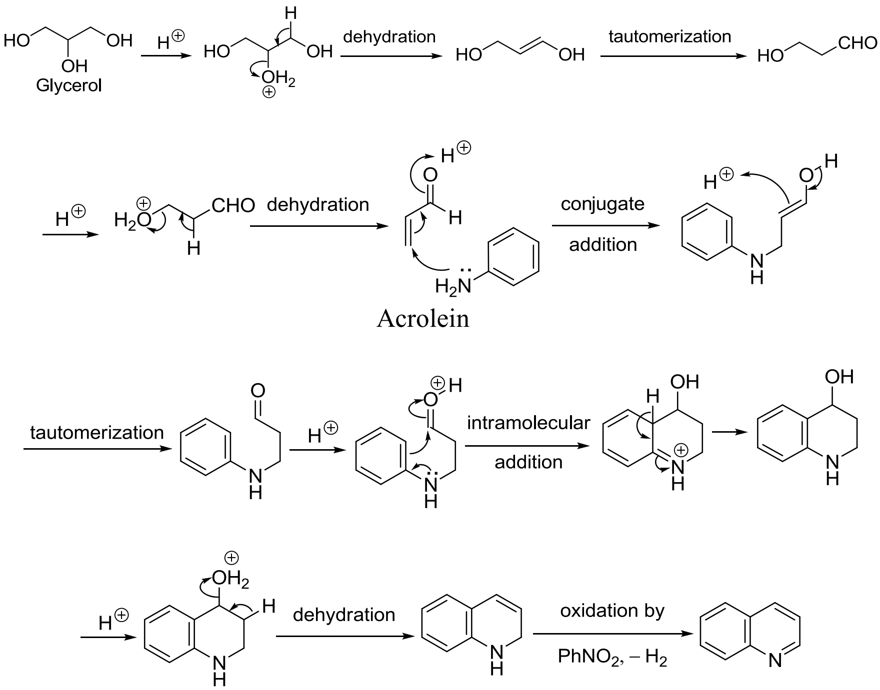
References

1. Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1958,** *80*, 5323–5324. Howard E. Simmons (1929–1997) was born in Norfolk, Virginia. He carried out his graduate studies at MIT under John D. Roberts and Arthur Cope. After obtaining his Ph.D. In 1954, he joined the Chemical Department of the DuPont Company, where he discovered the Simmons–Smith reaction with his colleague, R. D. Smith. Simmons rose to be the vice president of the Central Research at DuPont in 1979. His views on physical exercise were the same as those of Alexander Woollcot's: "If I think about exercise, I know if I wait long enough, the thought will go away."
2. Limasset, J.-C.; Amice, P.; Conia, J.-M. *Bull. Soc. Chim. Fr.* **1969,** 3981–3990.
3. Kitajima, H.; Ito, K.; Aoki, Y.; Katsuki, T. *Bull. Chem. Soc. Jpn.* **1997,** *70*, 207–217.
4. Nakamura, E.; Hirai, A.; Nakamura, M. *J. Am. Chem. Soc.* **1998,** *120*, 5844–5845.
5. Loeppky, R. N.; Elomari, S. *J. Org. Chem.* **2000,** *65*, 96–103.
6. Charette, A. B.; Beauchemin, A. *Org. React.* **2001,** *58*, 1–415. (Review).
7. Nakamura, M.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **2003,** *125*, 2341–2350.
8. Long, J.; Du, H.; Li, K.; Shi, Y. *Tetrahedron Lett.* **2005,** *46*, 2737–2740.
9. Davies, S. G.; Ling, K. B.; Roberts, P. M.; Russell, A. J.; Thomson, J. E. *Chem. Commun.* **2007,** 4029–4031.
10. Shan, M.; O'Doherty, G. A. *Synthesis* **2008,** 3171–3179.
11. Kim, H. Y.; Salvi, L.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2009,** *131*, 954–962.
12. Swaroop, T. R.; Roopashree, R.; Ila, H.; Rangappa, K. S. *Tetrahedron Lett.* **2013,** *54*, 147–150.

Skraup quinoline synthesis

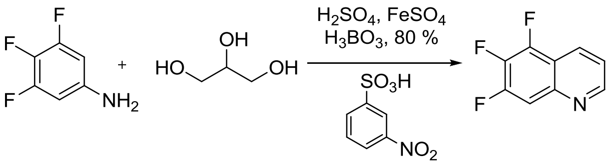
Quinoline from aniline, glycerol, sulfuric acid and oxidizing agent (e.g. $PhNO_2$).





For an alternative mechanism, see that of the Doebner–von Miller reaction.

Example 1[5]



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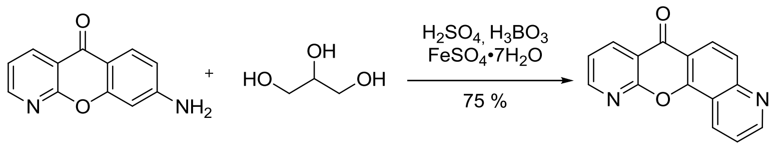
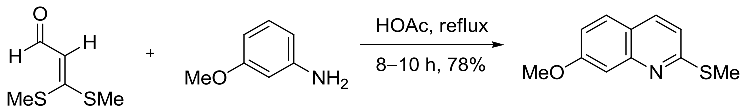
DOI 10.1007/978-3-319-03979-4_254, © Springer International Publishing Switzerland 2014

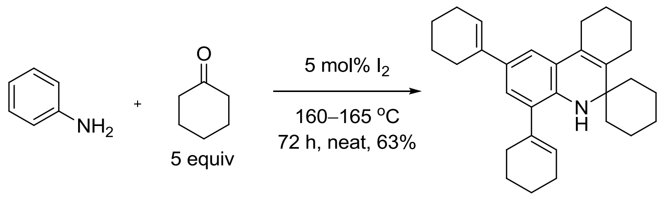
Example 2[6]



Example 3, A modified Skraup quinoline synthesis[8]



Example 4, A Skraup–Doebner–Von Miller quinoline synthesis[12]

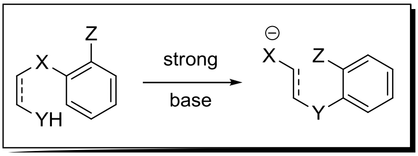


References

1. (a) Skraup, Z. H. *Monatsh. Chem.* **1880,** *1*, 316. Zdenko Hans Skraup (1850–1910) was born in Prague, Czechoslovakia. He apprenticed under Lieben at the University of Vienna. (b) Skraup, Z. H. *Ber.* **1880,** *13*, 2086.
2. Manske, R. H. F.; Kulka, M. *Org. React.* **1953,** *7*, 80–99. (Review).
3. Bergstrom, F. W. *Chem. Rev.* **1944,** *35,* 77–277. (Review).
4. Eisch, J. J.; Dluzniewski, T. *J. Org. Chem.* **1989,** *54,* 1269–1274.
5. Oleynik, I. I.; Shteingarts, V. D. *J. Fluorine Chem.* **1998,** *91*, 25–26.
6. Fujiwara, H.; Kitagawa, K. *Heterocycles* **2000,** *53*, 409–418.
7. Ranu, B. C.; Hajra, A.; Dey, S. S.; Jana, U. *Tetrahedron* **2003,** *59*, 813–819.
8. Panda, K.; Siddiqui, I.; Mahata, P. K.; Ila, H.; Junjappa, H. *Synlett* **2004,** 449–452.
9. Moore, A. *Skraup Doebner–von Miller Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 488–494. (Review).
10. Denmark, S. E.; Venkatraman, S. *J. Org. Chem.* **2006,** *71*, 1668–1676. Mechanistic study using ^{13}C-labelled α,β-unsaturated ketones.
11. Vora, J. J.; Vasava, S. B.; Patel, Asha D.; Parmar, K. C.; Chauhan, S. K.; Sharma, S. S. *E. J. Chem*. **2009,** *6*, 201–206.
12. Fotie, J.; Kemami Wangun, H. V.; Fronczek, F. R.; Massawe, N.; Bhattarai, B. T. Rhodus, J. L.; Singleton, T. A.; Bohle, D. S. *J. Org. Chem.* **2012,** *77*, 2784–2790.

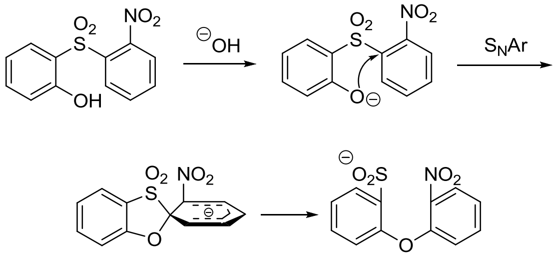
Smiles rearrangement

Intramolecular nucleophilic aromatic rearrangement. General scheme:



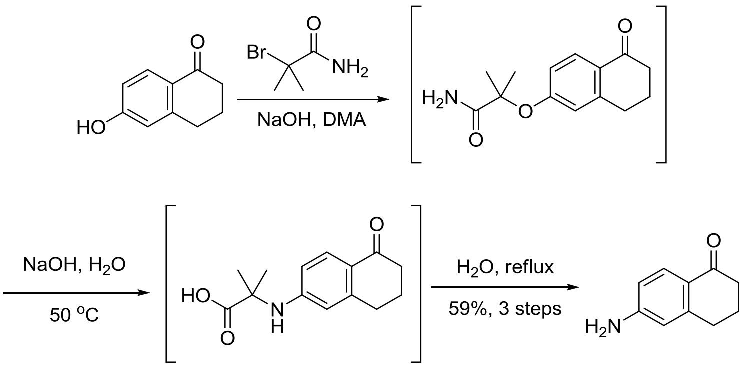
X = S, SO, SO_2, O, CO_2
YH = OH, NHR, SH, CH_2R, CONHR
Z = NO_2, SO_2R

Mechanism:

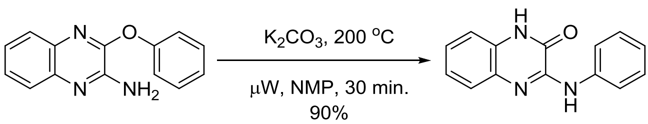


spirocyclic anion intermediate (Meisenheimer complex)

Example 1[7]



Example 2, Microwave Smiles rearrangement[9]



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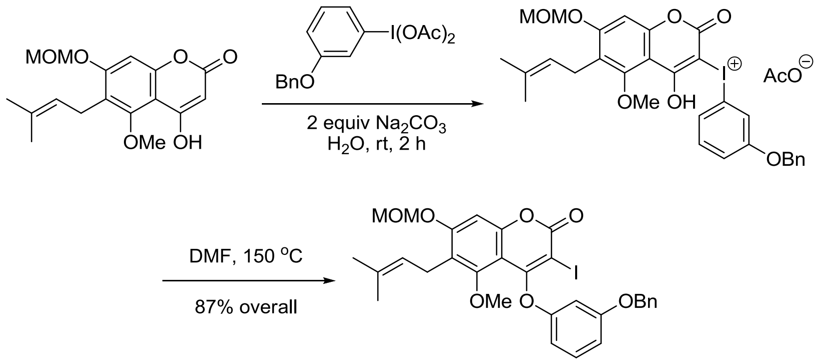
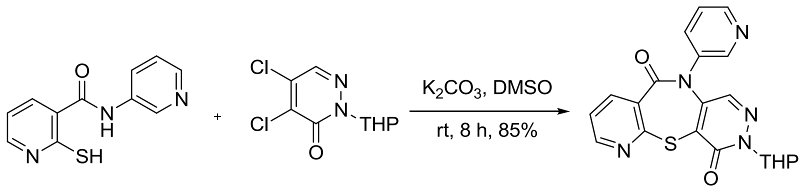
DOI 10.1007/978-3-319-03979-4_255, © Springer International Publishing Switzerland 2014

Example 3[10]



Example 4[11]

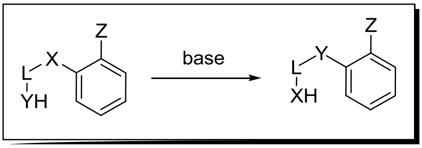


References

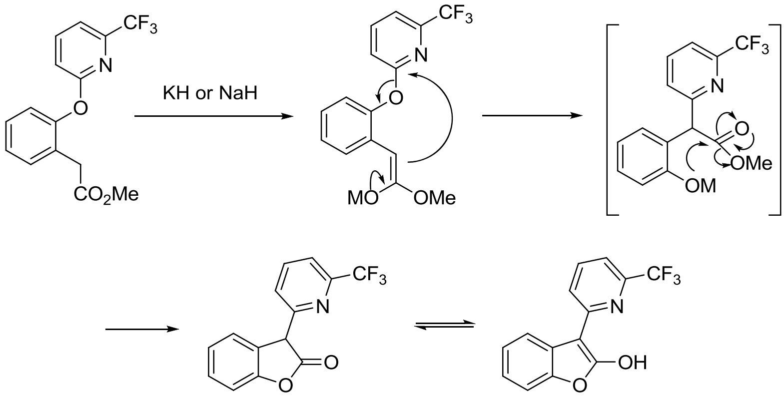
1. Evans, W. J.; Smiles, S. *J. Chem. Soc.* **1935,** 181–188. Samuel Smiles began his career at King's College London as an assistant professor. He later became professor and chair there. He was elected Fellow of the Royal Society (FRS) in 1918.
2. Truce, W. E.; Kreider, E. M.; Brand, W. W. *Org. React.* **1970,** *18*, 99–215. (Review).
3. Gerasimova, T. N.; Kolchina, E. F. *J. Fluorine Chem.* **1994,** *66*, 69–74. (Review).
4. Boschi, D.; Sorba, G.; Bertinaria, M.; Fruttero, R.; Calvino, R.; Gasco, A. *J. Chem. Soc., Perkin Trans. 1* **2001,** 1751–1757.
5. Hirota, T.; Tomita, K.-I.; Sasaki, K.; Okuda, K.; Yoshida, M.; Kashino, S. *Heterocycles* **2001,** *55*, 741–752.
6. Selvakumar, N.; Srinivas, D.; Azhagan, A. M. *Synthesis* **2002,** 2421–2425.
7. Mizuno, M.; Yamano, M. *Org. Lett.* **2005,** *7*, 3629–3631.
8. Bacque, E.; El Qacemi, M.; Zard, S. Z. *Org. Lett.* **2005,** *7*, 3817–3820.
9. Bi, C. F.; Aspnes, G. E.; Guzman-Perez, A.; Walker, D. P. *Tetrahedron Lett.* **2008,** *49*, 1832–1835.
10. Jin, Y. L.; Kim, S.; Kim, Y. S.; Kim, S.-A.; Kim, H. S. *Tetrahedron Lett.* **2008,** *49*, 6835–6837.
11. Niu, X.; Yang, B.; Li, Y.; Fang, S.; Huang, Z.; Xie, C.; Ma, C. *Org. Biomol. Chem.* **2013,** *11*, 4102–4108.

Truce–Smile rearrangement

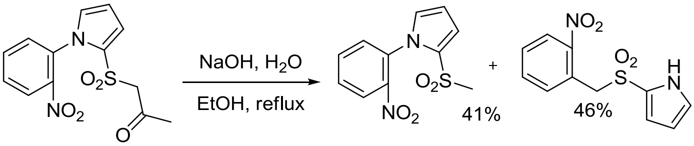
A variant of the Smiles rearrangement where Y is carbon:



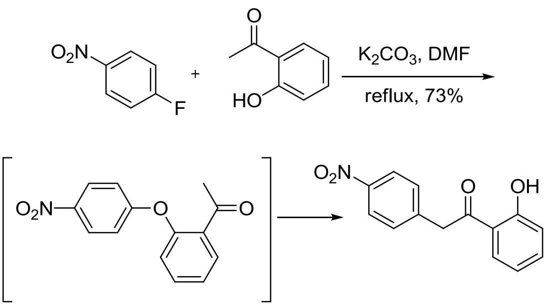
Example 1[6]



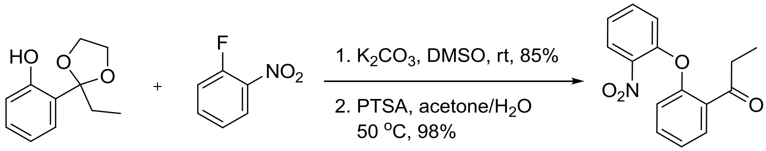
Example 2[7]

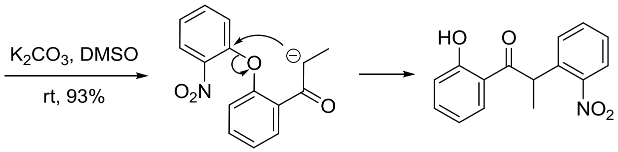


Example 3[8]



Example 4[10]



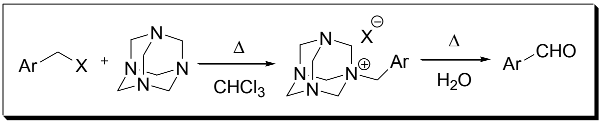


References

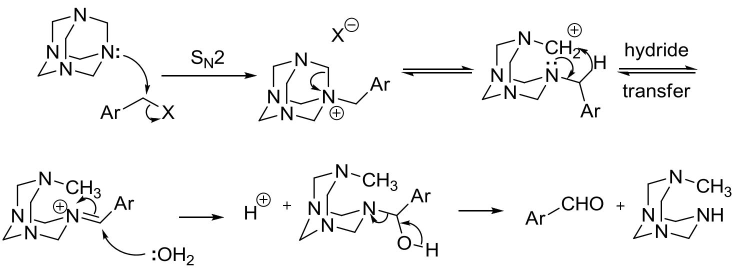
1. Truce, W. E.; Ray, W. J. Jr.; Norman, O. L.; Eickemeyer, D. B. *J. Am. Chem. Soc.* **1958,** *80*, 3625–3629. William E. Truce was a professor at Purdue University.
2. Truce, W. E.; Hampton, D. C. *J. Org. Chem.* **1963,** *28*, 2276–2279.
3. Bayne, D. W; Nicol, A. J.; Tennant, G. *J. Chem. Soc., Chem. Comm.* **1975,** *19*, 782–783.
4. Fukazawa, Y.; Kato, N.; Ito, S.; *Tetrahedron Lett.* **1982,** *23*, 437–438.
5. Hoffman, R. V.; Jankowski, B. C.; Carr, C. S.; Düsler, E. N *J. Org. Chem.* **1986,** *51*, 130–135.
6. Erickson, W. R.; McKennon, M. J. *Tetrahedron Lett.* **2000,** *41*, 4541–4544.
7. Kimbaris, A.; Cobb, J.; Tsakonas, G.; Varvounis, G. *Tetrahedron* **2004,** *60*, 8807–8815.
8. Mitchell, L. H.; Barvian, N. C. *Tetrahedron Lett.* **2004,** *45*, 5669–5672.
9. Snape, T. J. *Chem. Soc. Rev.* **2008,** *37*, 2452–2458. (Review).
10. Snape, T. J. *Synlett* **2008,** 2689–2691.

Sommelet reaction

Transformation of benzyl halides to the corresponding benzaldehydes with the aid of hexamethylenetetramine (HMTA). *Cf*. Delépine amine synthesis.

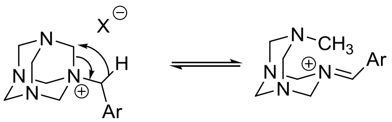


Hexamethylenetetramine (pungent rotten fish smell)

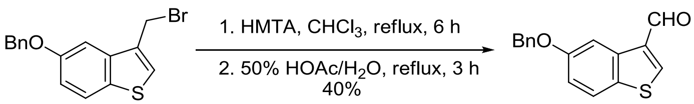


hemiaminal

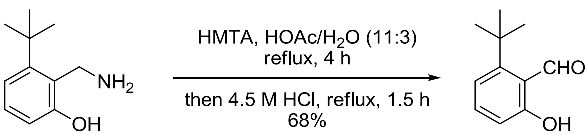
The hydride transfer and the ring-opening of hexamethylenetetramine may occur in a synchronized fashion:



Example 1[3]



Example 2[4]



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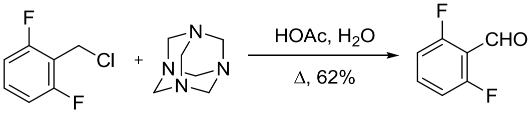
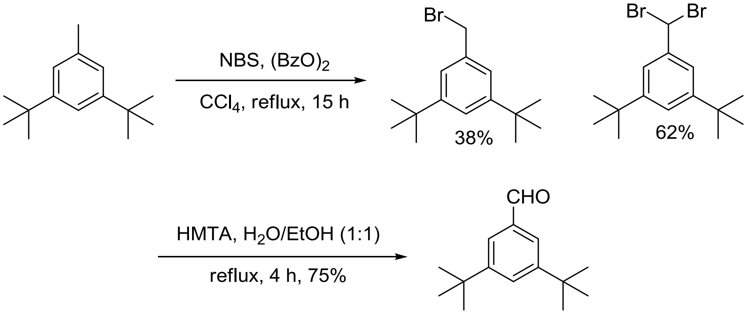
DOI 10.1007/978-3-319-03979-4_256, © Springer International Publishing Switzerland 2014

Example 3[7]



Example 4[8]

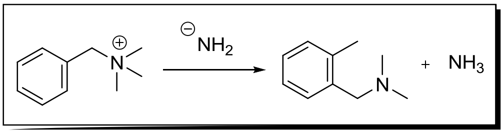


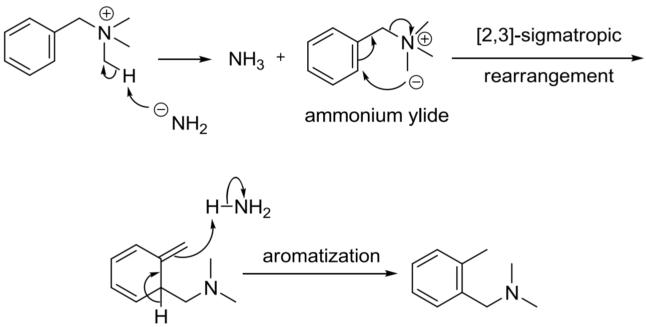
References

1. Sommelet, M. *Compt. Rend.* **1913,** *157*, 852–854. Marcel Sommelet (1877–1952) was born in Langes, France. He received his Ph.D. In 1906 at Paris where he joined the Faculté de Pharmacie after WWI and became the chair of organic chemistry in 1934.
2. Angyal, S. J. *Org. React*. **1954,** *8,* 197–217. (Review).
3. Campaigne, E.; Bosin, T.; Neiss, E. S. *J. Med. Chem*. **1967,** *10*, 270–271.
4. Stokker, G. E.; Schultz, E. M. *Synth. Commun*. **1982,** *12*, 847–853.
5. Armesto, D.; Horspool, W. M.; Martin, J. A. F.; Perez-Ossorio, R. *Tetrahedron Lett.* **1985,** *26*, 5217–5220.
6. Kilenyi, S. N., in *Encyclopedia of Reagents of Organic Synthesis*, ed. Paquette, L. A., Wiley: Hoboken, NJ, **1995,** *Vol. 3*, p. 2666. (Review).
7. Malykhin, E. V.; Shteingart, V. D. *J. Fluorine Chem*. **1998,** *91*, 19–20.
8. Karamé, I.; Jahjah, M.; Messaoudi, A.; Tommasino, M. L.; Lemaire, M. *Tetrahedron: Asymmetry* **2004,** *15*, 1569–1581.
9. Göker, H.; Boykin, D. W.; Yildiz, S. *Bioorg. Med. Chem*. **2005,** *13*, 1707–1714.
10. Li, J. J. *Sommelet Reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 689–695. (Review).

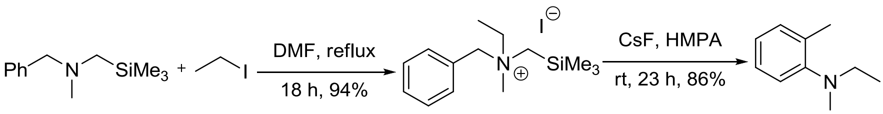
Sommelet–Hauser rearrangement

[2,3]-Wittig rearrangement of benzylic quaternary ammonium salts upon treatment with alkali metal amides *via* the ammonium ylide intermediates.

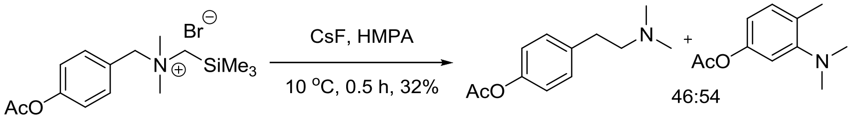




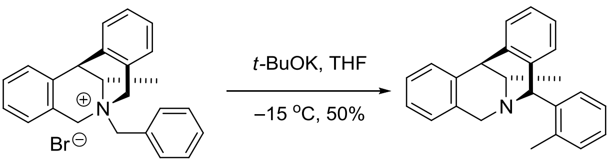
Example 1[3]



Example 2[4]



Example 3[8]



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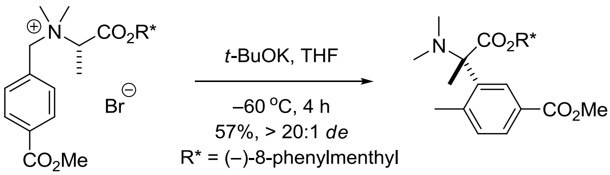
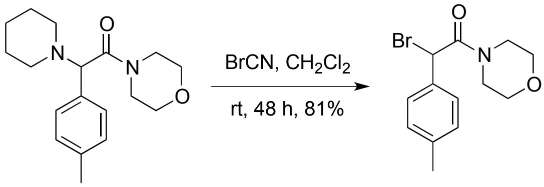
Example 4[10]



Example 5[12]

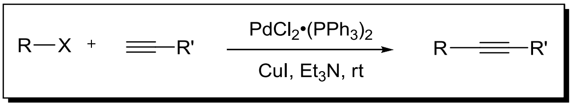


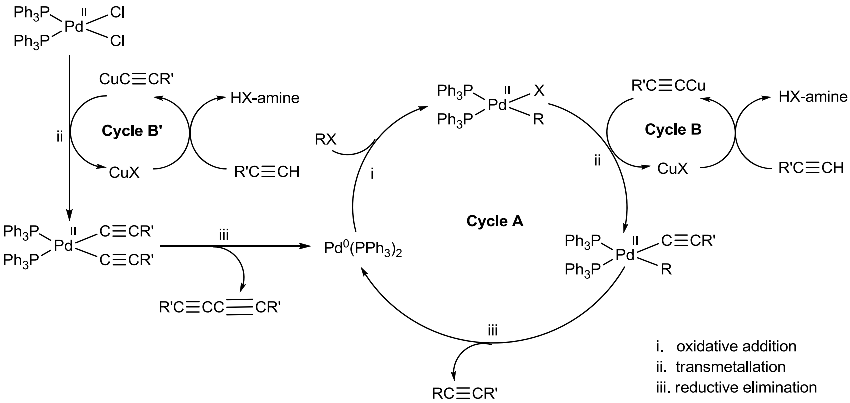
References

1. (a) Sommelet, M. *Compt. Rend.* **1937,** *205*, 56–58. (b) Kantor, S. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1951,** *73*, 4122–4131. Charles R. Hauser (1900–1970) was a professor at Duke University.
2. Shirai, N.; Sato, Y. *J. Org. Chem.* **1988,** *53,* 194–196.
3. Shirai, N.; Watanabe, Y.; Sato, Y. *J. Org. Chem*. **1990,** *55*, 2767–2770.
4. Tanaka, T.; Shirai, N.; Sugimori, J.; Sato, Y. *J. Org. Chem*. **1992,** *57*, 5034–5036.
5. Klunder, J. M. *J. Heterocycl. Chem*. **1995,** *32*, 1687–1691.
6. Maeda, Y.; Sato, Y. *J. Org. Chem*. **1996,** *61*, 5188–5190.
7. Endo, Y.; Uchida, T.; Shudo, K. *Tetrahedron Lett*. **1997,** *38*, 2113–2116.
8. Hanessian, S.; Talbot, C.; Saravanan, P. *Synthesis* **2006,** 723–734.
9. Liao, M.; Peng, L.; Wang, J. *Org. Lett*. **2008,** *10*, 693–696.
10. Tayama, E.; Orihara, K.; Kimura, H. *Org. Biomol. Chem*. **2008,** *6*, 3673–3680.
11. Zografos, A. L. In *Name Reactions in Heterocyclic Chemistry-II*, Li, J. J., Ed.; Wiley: Hoboken, NJ, 2011, pp 197–206. (Review).
12. Tayama, Eiji; Sato, Ryota; Takedachi, Keisuke; Iwamoto, Hajime; Hasegawa, Eietsu *Tetrahedron* **2012,** *68*, 4710–4718.

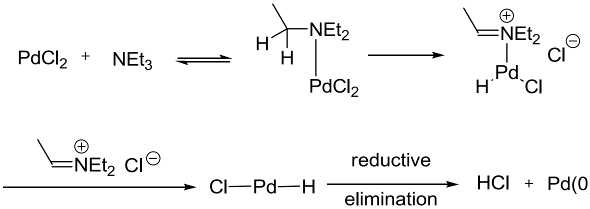
Sonogashira reaction

Pd/Cu-catalyzed cross-coupling of organohalides with terminal alkynes. *Cf.* Cadiot–Chodkiewicz coupling and Castro−Stephens reaction. The Castro–Stephens coupling uses stoichiometric copper, whereas the Sonogashira variant uses catalytic palladium and copper.

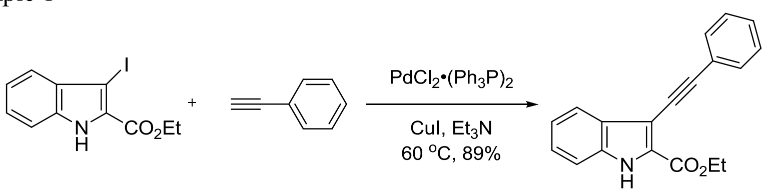




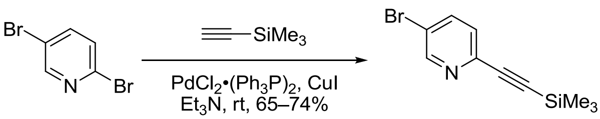
Note that Et_3N may reduce Pd(II) to Pd(0) as well, where Et_3N is oxidized to the iminium ion at the same time:



Example 1[2]



Example 2[3]



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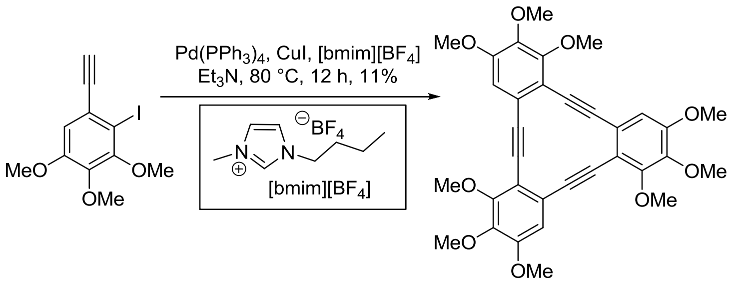
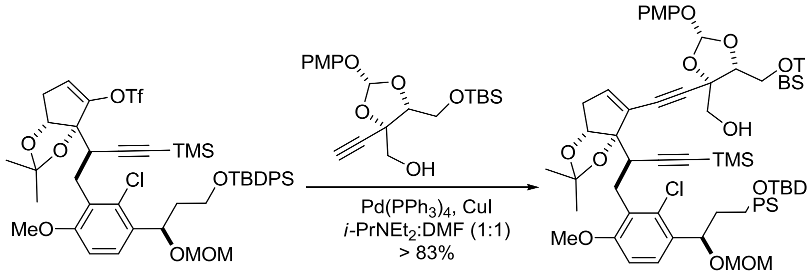
Example 3[8]



Example 4[9]

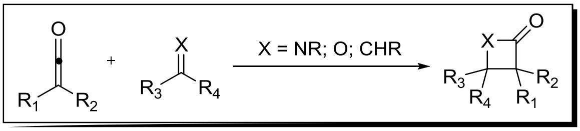


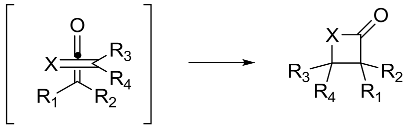
References

1. (a) Sonogashira K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975,** *50,* 4467–4470. Kenkichi Sonogashira was a professor at Fukui University. Richard Heck also discovered the same transformation using palladium but without the use of copper: *J. Organomet. Chem.* **1975,** *93*, 259–263.
2. Sakamoto, T.; Nagano, T.; Kondo, Y.; Yamanaka, H. *Chem. Pharm. Bull.* **1988,** *36*, 2248–2252.
3. Ernst, A.; Gobbi, L.; Vasella, A. *Tetrahedron Lett.* **1996,** *37*, 7959–7962.
4. Hundermark, T.; Littke, A.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000,** *2*, 1729–1731.
5. Batey, R. A.; Shen, M.; Lough, A. J. *Org. Lett.* **2002,** *4*, 1411–1414.
6. Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; de Meijere, A., Eds.; Wiley-VCH: Weinheim, **2004**; *Vol. 1*, 319. (Review).
7. Lemhadri, M.; Doucet, H.; Santelli, M. *Tetrahedron* **2005,** *61*, 9839–9847.
8. Li, Y.; Zhang, J.; Wang, W.; Miao, Q.; She, X.; Pan, X. *J. Org. Chem.* **2005,** *70*, 3285–3287.
9. Komano, K.; Shimamura, S.; Inoue, M.; Hirama, M. *J. Am. Chem. Soc.* **2007,** *129*, 14184–11186.
10. Nakatsuji, H.; Ueno, K.; Misaki, T.; Tanabe, Y. *Org. Lett.* **2008,** *10*, 2131–2134.
11. Gray, D. L. *Sonogashira Reaction*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 100–133. (Review).
12. Shigeta, M.; Watanabe, J.; Konishi, G.-i. *Tetrahedron Lett.* **2013,** *54*, 1761–1764.

Staudinger ketene cycloaddition

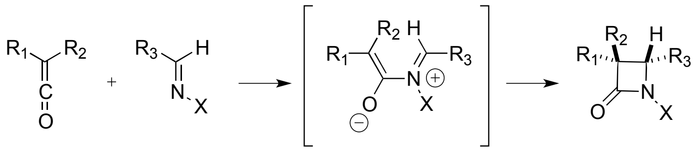
Also known as the Staudinger reaction. [2 + 2]-Cycloaddition of ketene and imine to form β-lactams. Other coupling partners for ketenes include: olefin to give cyclobutanone and carbonyl to give β-lactone.



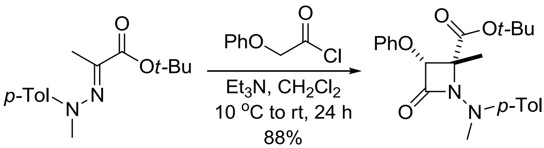


puckered transition state

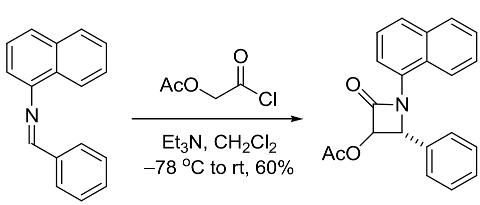
When X = N:



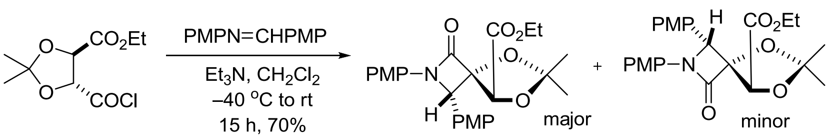
Example 1[6]



Example 2[7]



Example 3[9]



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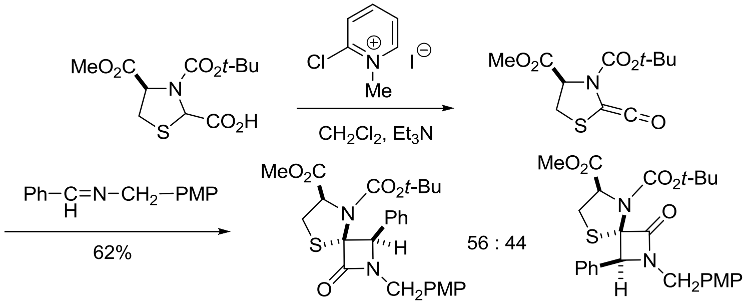
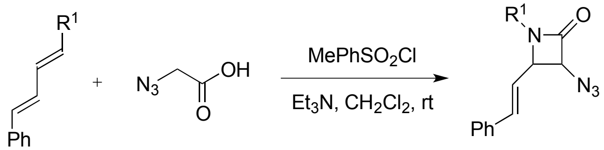
DOI 10.1007/978-3-319-03979-4_259, © Springer International Publishing Switzerland 2014

Example 4[10]



Example 5[11]

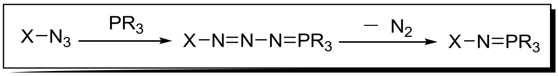


References

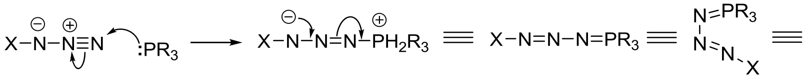
1. Staudinger, H. *Ber.* **1907,** *40*, 1145−1146. Hermann Staudinger (Germany, 1881−1965) won the Nobel Prize in Chemistry in 1953 for his discoveries in the area of macromolecular chemistry.
2. Cooper, R. D. G.; Daugherty, B. W.; Boyd, D. B. *Pure Appl. Chem.* **1987,** *59*, 485−492. (Review).
3. Snider, B. B. *Chem. Rev.* **1988,** *88,* 793−811. (Review).
4. Hyatt, J. A.; Raynolds, P. W. *Org. React.* **1994,** *45,* 159−646. (Review).
5. Orr, R. K.; Calter, M. A. *Tetrahedron* **2003,** *59,* 3545−3565. (Review).
6. Bianchi, L.; Dell'Erba, C.; Maccagno, M.; Mugnoli, A.; Novi, M.; Petrillo, G.; Sancassan, F.; Tavani, C. *Tetrahedron* **2003,** *59,* 10195−10201.
7. Banik, I.; Becker, F. F.; Banik, B. K. *J. Med. Chem.* **2003,** *46,* 12−15.
8. Banik, B. K.; Banik, I.; Becker, F. F. *Bioorg. Med. Chem. Lett.* **2005,** *13*, 3611−3622.
9. Chincholkar, P. M.; Puranik, V. G.; Rakeeb, A.; Deshmukh, A. S. *Synlett* **2007,** *14,* 2242−2246.
10. Cremonesi, G.; Dalla Croce, P.; Fontana, F.; La Rosa, C. *Tetrahedron: Asymmetry* **2008,** *19,* 554–561.
11. Raj, R.; Singh, P.; Haberkern, N. T.; Faucher, R. M.; Patel, N.; Land, K. M.; Kumar, V. *Eur. J. Med. Chem*. **2013,** *63,* 897–906.
12. Tuba, R. *Org. Biomol. Chem*. **2013,** *11,* 5976–5988. (Review).

Staudinger reduction

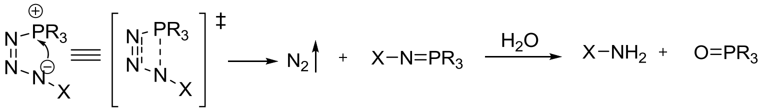
Phosphazo compounds (e.g., iminophosphoranes) from the reduction of organic azides using tertiary phosphine (e.g., Ph_3P). Hydrolysis then provides the corresponding amines.



phosphazide

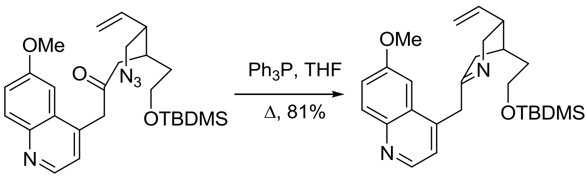


phosphazide

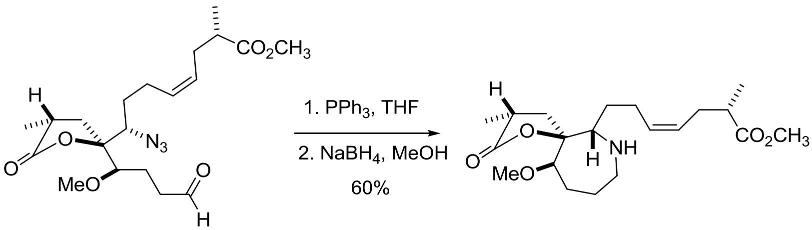


4-membered ring transition state

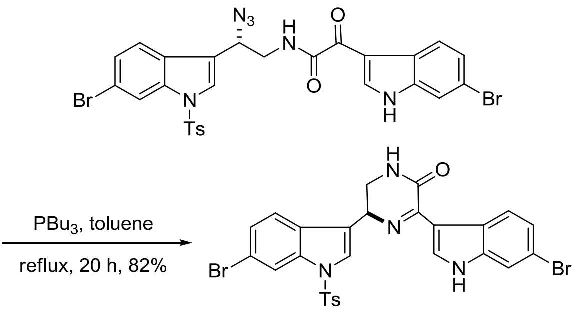
Example 1[2]



Example 2[3]



Example 3[4]



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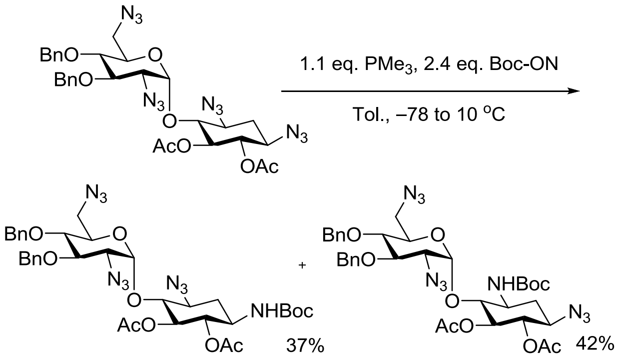
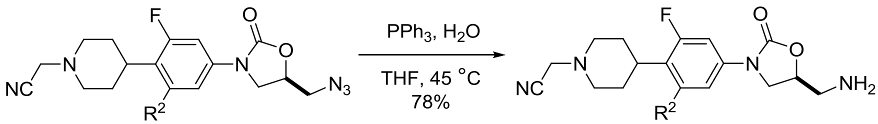
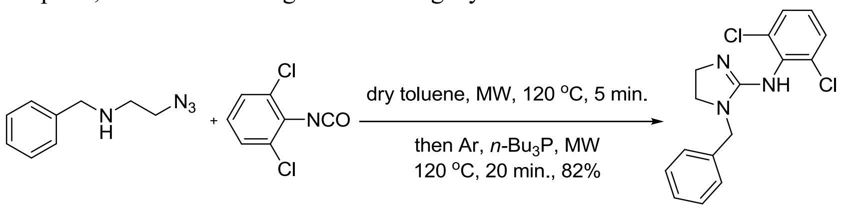
Example 4[8]



Example 5[9]



Example 6, Tandem Staudinger/Aza-Wittig Cyclization[11]

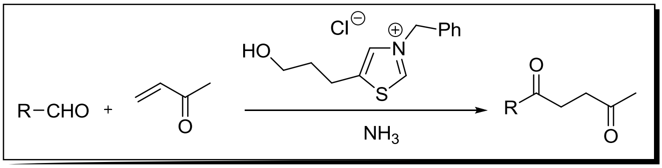


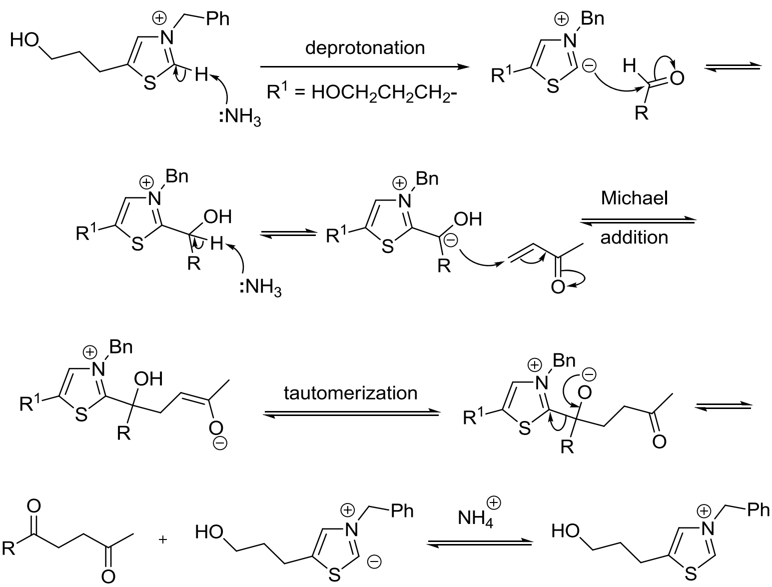
References

1. Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919,** *2*, 635–646.
2. Stork, G.; Niu, D.; Fujimoto, R. A.; Koft, E. R.; Bakovec, J. M.; Tata, J. R.; Dake, G. R. *J. Am. Chem. Soc*. **2001,** *123,* 3239–3242.
3. Williams, D. R.; Fromhold, M. G.; Earley, J. D. *Org. Lett.* **2001,** *3*, 2721–2722.
4. Jiang, B.; Yang, C.-G.; Wang, J. *J. Org. Chem*. **2002,** *67*, 1369–1371.
5. Venturini, A.; Gonzalez, J. *J. Org. Chem.* **2002,** *67,* 9089–9092.
6. Chen, J.; Forsyth, C. J. *Org. Lett.* **2003,** *5,* 1281–1283.
7. Fresneda, P. M.; Castaneda, M.; Sanz, M. A.; Molina, P. *Tetrahedron Lett*. **2004,** *45,* 1655–1657.
8. Li, J.; Chen, H.-N.; Chang, H.; Wang, J.; Chang, C.-W. T. *Org. Lett.* **2005,** *7,* 3061–3064.
9. Takhi, M.; Murugan, C.; Munikumar, M.; Bhaskarreddy, K. M.; Singh, G.; Sreenivas, K.; Sitaramkumar, M.; Selvakumar, N.; Das, J.; Trehan, S.; Iqbal, J. *Bioorg. Med. Chem. Lett.* **2006,** *16*, 2391–2395.
10. Iula, D. M. *Staudinger Reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 129–151. (Review).
11. Kumar, R.; Ermolat'ev, D. S.;Van der Eycken, E. V. *J. Org. Chem.* **2013,** *78*, 5737–5743.

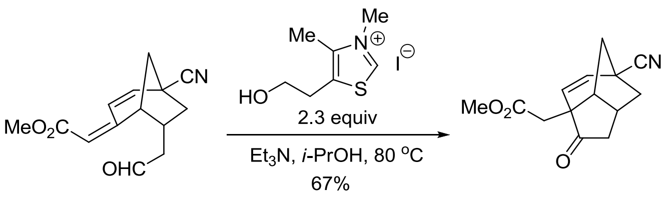
Stetter reaction

1,4-Dicarbonyl derivatives from aldehydes and α,β-unsaturated ketones and esters. The thiazolium catalyst serves as a safe surrogate for ⁻CN. Also known as the Michael–Stetter reaction. *Cf.* Benzoin condensation.





Example 1, Intramolecular Stetter reaction[2]



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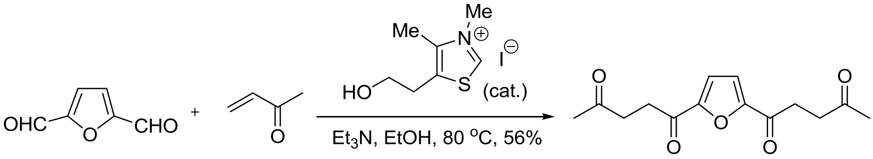
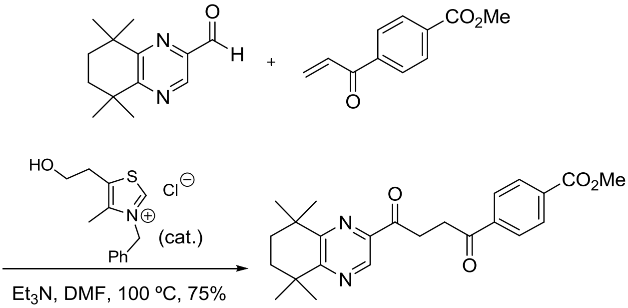
DOI 10.1007/978-3-319-03979-4_261, © Springer International Publishing Switzerland 2014

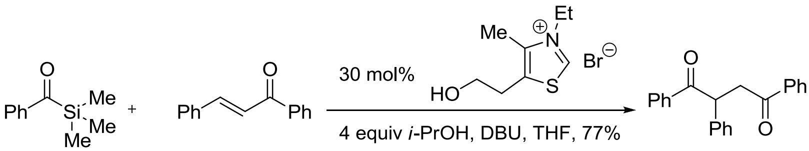
Example 2[3]



Example 3[5]



Example 4, Sila-Stetter reaction[9]

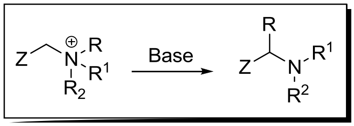


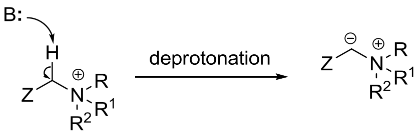
References

1. (a) Stetter, H.; Schreckenberg, H. *Angew. Chem.* **1973,** *85*, 89. Hermann Stetter (1917−1993), born in Bonn, Germany, was a chemist at Technische Hochschule Aachen in West Germany. (b) Stetter, H. *Angew. Chem.* **1976,** *88*, 695−704. (Review). (c) Stetter, H.; Kuhlmann, H.; Haese, W. *Org. Synth.* **1987,** *65*, 26.
2. Trost, B. M.; Shuey, C. D.; DiNinno, F., Jr.; McElvain, S. S. *J. Am. Chem. Soc.* **1979,** *101*, 1284−1285.
3. El-Haji, T.; Martin, J. C.; Descotes, G. *J. Heterocycl. Chem.* **1983,** *20*, 233−235.
4. Harrington, P. E.; Tius, M. A. *Org. Lett.* **1999,** *1*, 649−651.
5. Kikuchi, K.; Hibi, S.; Yoshimura, H.; Tokuhara, N.; Tai, K.; Hida, T.; Yamauchi, T.; Nagai, M. *J. Med. Chem.* **2000,** *43*, 409−419.
6. Kobayashi, N.; Kaku, Y.; Higurashi, K. *Bioorg. Med. Chem. Lett.* **2002,** *12*, 1747−1750.
7. Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2005,** *127*, 6284−6289.
8. Reynolds, N. T.; Rovis, T. *Tetrahedron* **2005,** *61*, 6368−6378.
9. Mattson, A. E.; Bharadwaj, A. R.; Zuhl, A. M.; Scheidt, K. A. *J. Org. Chem.* **2006,** *71*, 5715−5724.
10. Cee, V. J. *Stetter Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 576−587. (Review).
11. Zhang, J.; Xing, C.; Tiwari, B.; Chi, Y. R. *J. Am. Chem. Soc.* **2013,** *135*, 8113−8116.

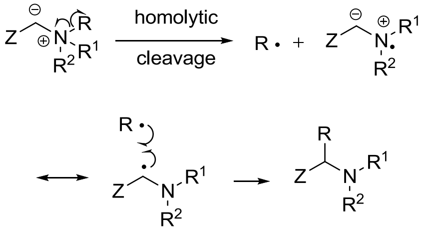
Stevens rearrangement

A quaternary ammonium salt containing an electron-withdrawing group Z on one of the carbons attached to the nitrogen is treated with a strong base to give a rearranged tertiary amine.

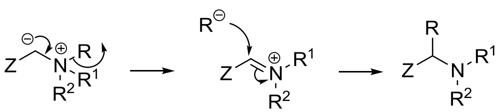




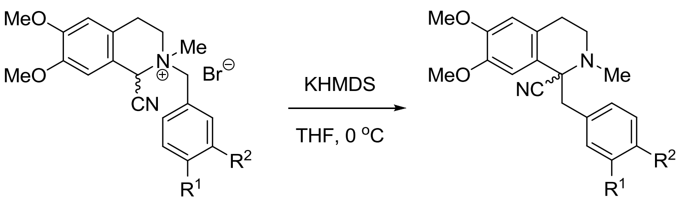
The contemporary radical mechanism:



The original ionic mechanism:



Example 1, Stevens Rearrangement/Reduction Sequence[10]



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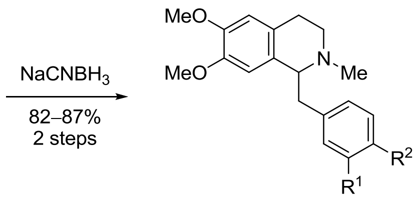
DOI 10.1007/978-3-319-03979-4_262, © Springer International Publishing Switzerland 2014

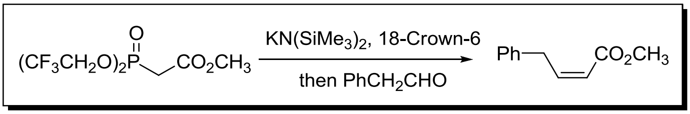


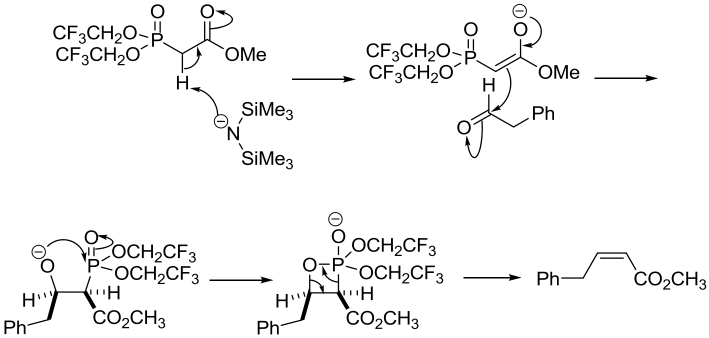
References

1. Stevens, T. S.; Creighton, E. M.; Gordon, A. B.; MacNicol, M. *J. Chem. Soc.* **1928,** 3193–3197.
2. Schöllkopf, U.; Ludwig, U.; Ostermann, G.; Patsch, M. *Tetrahedron Lett.* **1969,** *10,* 3415–3418.
3. Pine, S. H.; Catto, B. A.; Yamagishi, F. G. *J. Org. Chem.* **1970,** *35*, 3663–3665. (Mechanism).
4. Doyle, M. P.; Ene, D. G.; Forbes, D. C.; Tedrow, J. S. *Tetrahedron Lett*. **1997,** *38*, 4367–4370.
5. Makita, K.; Koketsu, J.; Ando, F.; Ninomiya, Y.; Koga, N. *J. Am. Chem. Soc*. **1998,** *120*, 5764–5770.
6. Feldman, K. S.; Wrobleski, M. L. *J. Org. Chem*. **2000,** *65*, 8659-8668.
7. Kitagaki, S.; Yanamoto, Y.; Tsutsui, H.; Anada, M.; Nakajima, M.; Hashimoto, S. *Tetrahedron Lett*. **2001,** *42*, 6361–6364.
8. Knapp, S.; Morriello, G. J.; Doss, G. A. *Tetrahedron Lett*. **2002,** *43*, 5797–5800.
9. Hanessian, S.; Parthasarathy, S.; Mauduit, M.; Payza, K. *J. Med. Chem*. **2003,** *46*, 34–38.
10. Pacheco, J. C. O.; Lahm, G.; Opatz, T. *J. Org. Chem*. **2013,** *78*, 4985–4992.

Still–Gennari phosphonate reaction

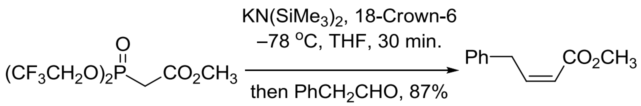
A variant of the Horner–Emmons reaction using bis(trifluoroethyl)phosphonate to give *Z*-olefins.



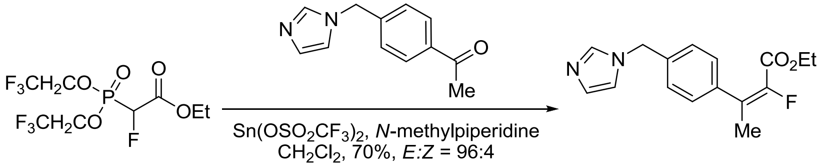


erythro isomer, kinetic adduct

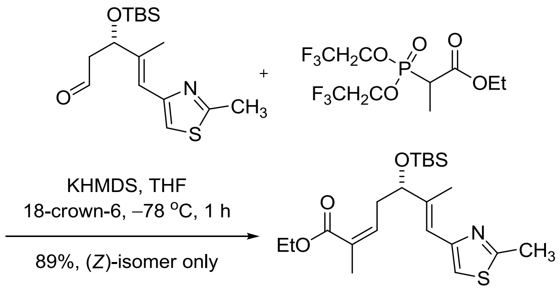
Example 1[2]



Example 2[3]



Example 3[4]



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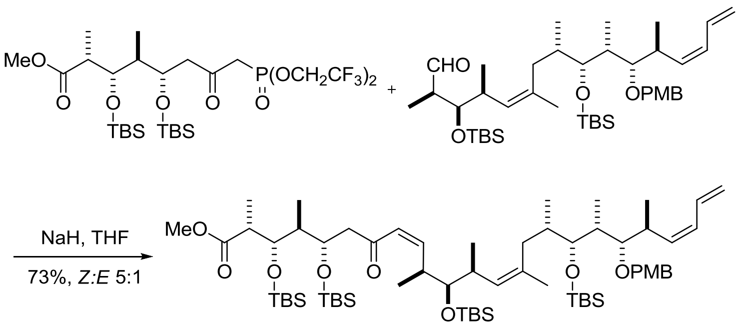
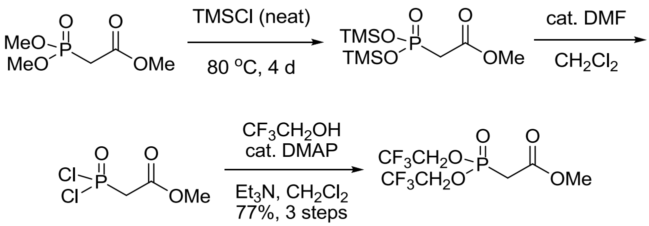
DOI 10.1007/978-3-319-03979-4_263, © Springer International Publishing Switzerland 2014

Example 4[9]



Example 5, An expedient access to Still–Gennari phosphonates[11]

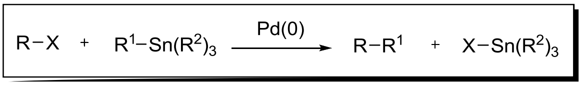


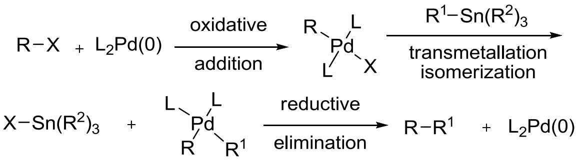
References

1. Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983,** *24,* 4405–4408. W. Clark Still (1946–) was born in Augusta, Georgia. He was a professor at Columbia University.
2. Nicolaou, K. C.; Nadin, A.; Leresche, J. E.; LaGreca, S.; Tsuri, T.; Yue, E. W.; Yang, Z. *Chem. Eur. J.* **1995,** *1*, 467–494.
3. Sano, S. Yokoyama, K.; Shiro, M.; Nagao, Y. *Chem. Pharm. Bull.* **2002,** *50*, 706–709.
4. Mulzer, J.; Mantoulidis, A.; Öhler, E. *Tetrahedron Lett.* **1998,** *39*, 8633–8636.
5. Paterson, I.; Florence, G. J.; Gerlach, K.; Scott, J. P.; Sereinig, N. *J. Am. Chem. Soc.* **2001,** *123*, 9535–9544.
6. Mulzer, J.; Ohler, E. *Angew. Chem. Int. Ed.* **2001,** *40*, 3842–3846.
7. Beaudry, C. M.; Trauner, D. *Org. Lett.* **2002,** *4*, 2221–2224.
8. Dakin, L. A.; Langille, N. F.; Panek, J. S. *J. Org. Chem.* **2002,** *67,* 6812–6815.
9. Paterson, I.; Lyothier, I. *J. Org. Chem.* **2005,** *70,* 5494–5507.
10. Rong, F. *Horner–Wadsworth–Emmons reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 420–466. (Review).
11. Messik, F.; Oberthür, M. *Synthesis* **2013,** *45*, 167–170.

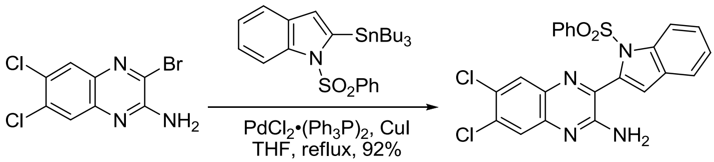
Stille coupling

Palladium-catalyzed cross-coupling reaction of organostannanes with organic halides, triflates, *etc*. For the catalytic cycle, see Kumada coupling.

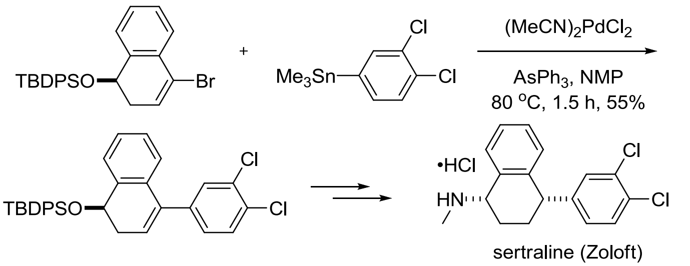




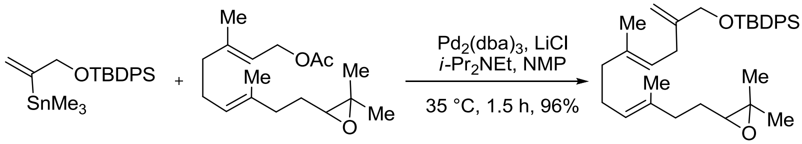
Example 1[4]



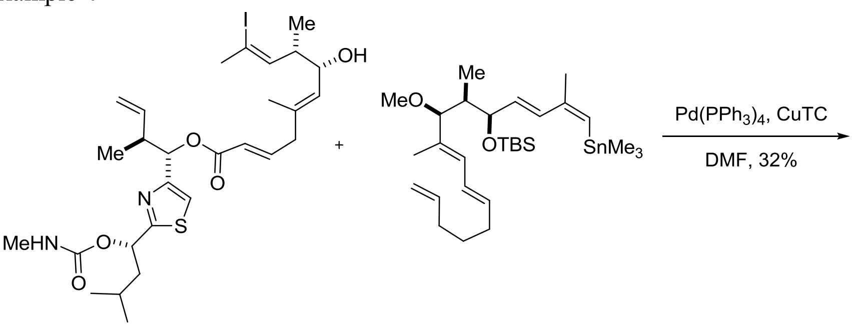
Example 2[5]



Example 3, π-Allyl Stille coupling[8]



Example 4[9]



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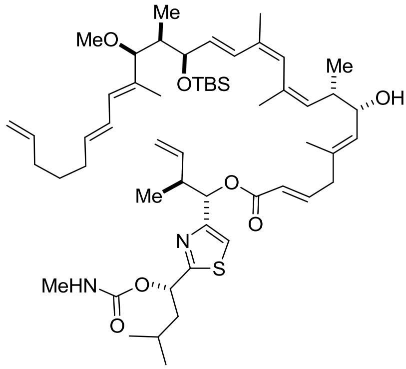
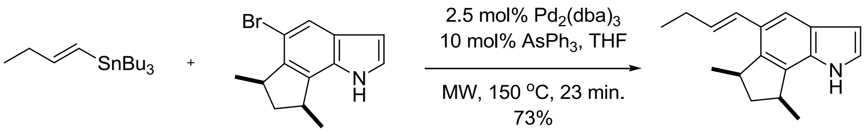


Example 5[11]

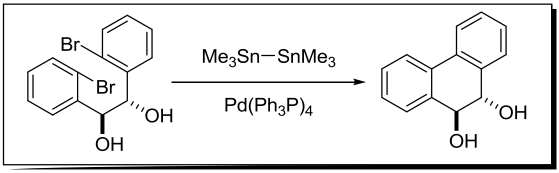


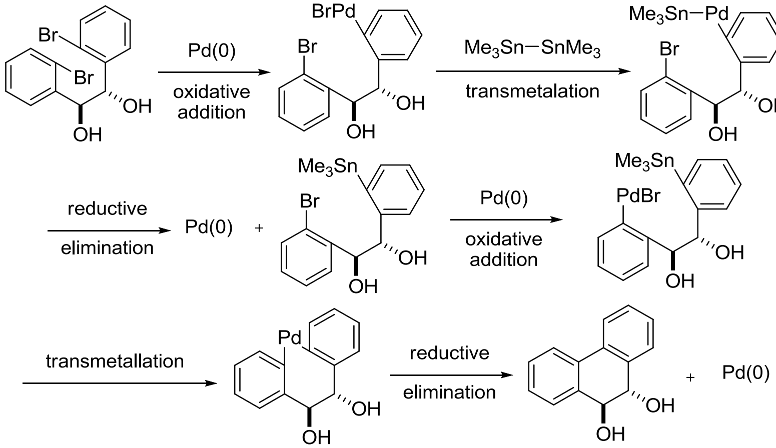
References

1. (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978,** *100*, 3636−3638. John Kenneth Stille (1930−1989) was born in Tucson, Arizona. He developed the reaction bearing his name at Colorado State University. At the height of his career, Stille unfortunately died of an airplane accident returning from an ACS meeting. (b) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979,** *101*, 4992−4998. (c) Stille, J. K. *Angew. Chem. Int. Ed.* **1986,** *25*, 508−524.
2. Farina, V.; Krishnamurphy, V.; Scott, W. J. *Org. React.* **1997,** *50*, 1−652. (Review).
3. Duncton, M. A. J.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1999,** 1235−1249. (Review on the intramolecular Stille reaction).
4. Li, J. J.; Yue, W. S. *Tetrahedron Lett.* **1999,** *40*, 4507−4510.
5. Lautens, M.; Rovis, T. *Tetrahedron*, **1999,** *55*, 8967−8976.
6. Mitchell, T. N. *Organotin Reagents in Cross-Coupling Reactions*. In *Metal-Catalyzed Cross-Coupling Reactions* (2nd edn.) De Meijere, A.; Diederich, F. eds., **2004,** 1, 125−161. Wiley-VCH: Weinheim, Germany. (Review).
7. Schröter, S.; Stock, C.; Bach, T. *Tetrahedron* **2005,** *61,* 2245−2267. (Review).
8. Snyder, S. A.; Corey, E. J. *J. Am. Chem. Soc.* **2006,** *128*, 740−742.
9. Roethle, P. A.; Chen, I. T.; Trauner, D. *J. Am. Chem. Soc.* **2007,** *129,* 8960−8961.
10. Mascitti, V. *Stille Coupling*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 133−162. (Review).
11. Chandrasoma, N.; Brown, N.; Brassfield, A.; Nerurkar, A.; Suarez, S.; Buszek, K. R. *Tetrahedron Lett.* **2013,** *54,* 913−917.

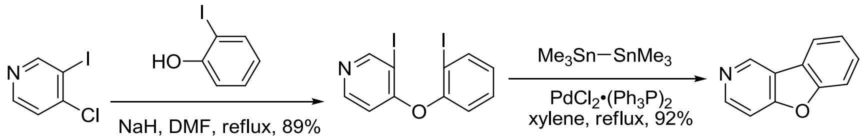
Stille–Kelly reaction

Palladium-catalyzed intramolecular cross-coupling reaction of bis-aryl halides using ditin reagents.





Example 1[6]



References

1. Kelly, T. R.; Li, Q.; Bhushan, V. *Tetrahedron Lett.* **1990,** *31*, 161–164. T. Ross Kelly is a professor at Boston College.
2. Grigg, R.; Teasdale, A.; Sridharan, V. *Tetrahedron Lett.* **1991,** *32*, 3859–3862.
3. Iyoda, M.; Miura, M.; Sasaki, S.; Kabir, S. M. H.; Kuwatani, Y.; Yoshida, M. *Heterocycles* **1997,** *38*, 4581–4582.
4. Fukuyama, Y.; Yaso, H.; Nakamura, K.; Kodama, M. *Tetrahedron Lett.* **1999,** *40*, 105–108.
5. Iwaki, T.; Yasuhara, A.; Sakamoto, T. *J. Chem. Soc., Perkin Trans. 1* **1999,** 1505–1510.
6. Yue, W. S.; Li, J. J. *Org. Lett.* **2002,** *4,* 2201–2203.
7. Olivera, R.; SanMartin, R.; Tellitu, I.; Dominguez, E. *Tetrahedron* **2002,** *58,* 3021–3037.
8. Mascitti, V. *Stille Coupling*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 133–162. (Review).

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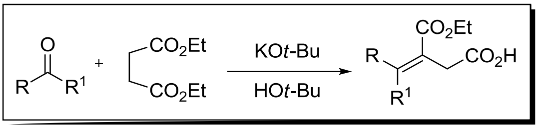
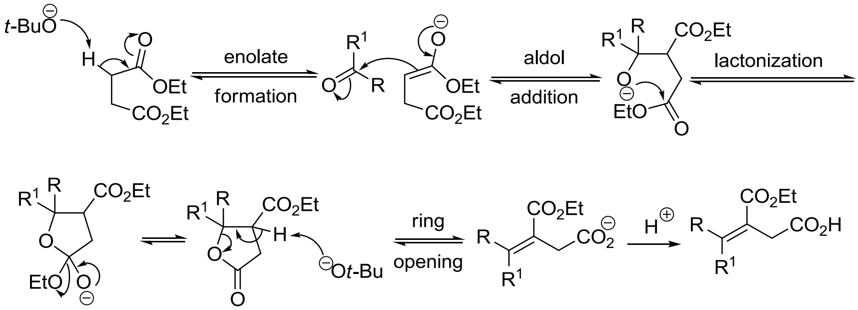
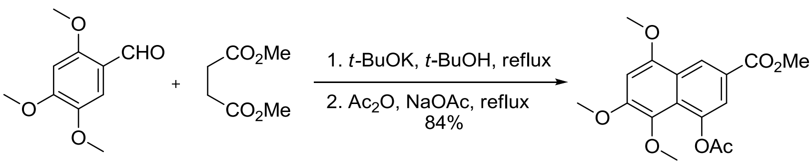
Stobbe condensation

Condensation of diethyl succinate and its derivatives with carbonyl compounds in the presence of bases.

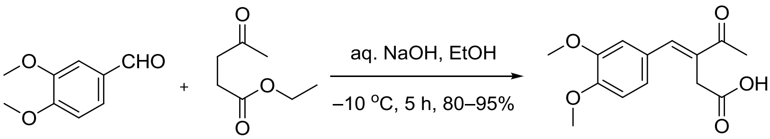




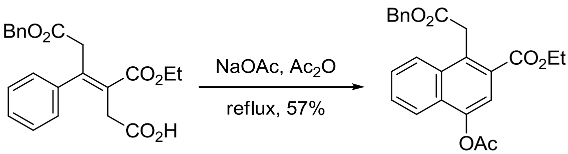
Example 1, Stobbe condensation and cyclization[5]



Example 2[6]



Example 3, Cyclization of the Stobbe product[7]



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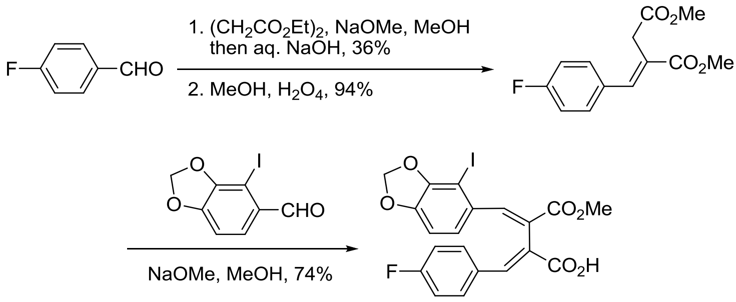
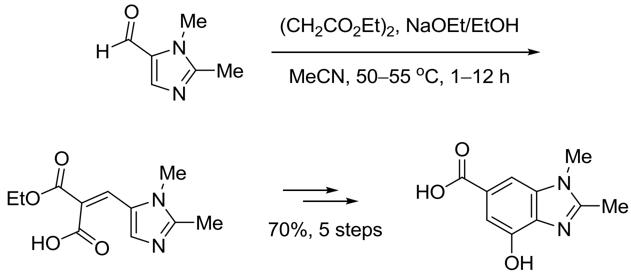
DOI 10.1007/978-3-319-03979-4_266,

Example 4, Two sequential Stobbe condensations[9]



Example 5[11]

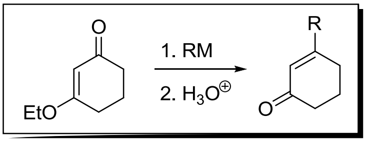


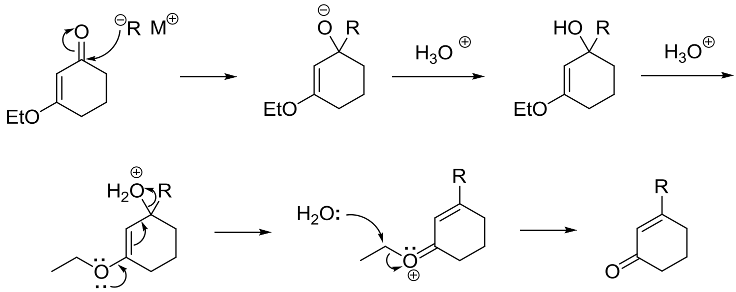
References

1. Stobbe, H. *Ber.* **1893,** *26*, 2312. Hans Stobbe (1860–1938) was born in Tiehenhof, Germany. He earned his Ph.D. In 1889 at the University of Leipzig where he became a professor in 1894.
2. Zerrer, R.; Simchen, G. *Synthesis* **1992,** 922–924.
3. Yvon, B. L.; Datta, P. K.; Le, T. N.; Charlton, J. L. *Synthesis* **2001,** 1556–1560.
4. Liu, J.; Brooks, N. R. *Org. Lett.* **2002,** *4*, 3521–3524.
5. Giles, R. G. F.; Green, I. R.; van Eeden, N. *Eur. J. Org. Chem.* **2004,** 4416–4423.
6. Mahajan, V. A.; Shinde, P. D.; Borate, H. B.; Wakharkar, R. D. *Tetrahedron Lett.* **2005,** *46*, 1009–1012.
7. Sato, A.; Scott, A.; Asao, T.; Lee, M. *J. Org. Chem.* **2006,** *71*, 4692–4695.
8. Kapferer, T.; Brückner, R. *Eur. J. Org. Chem.* **2006,** 2119–2133.
9. Mizufune, H.; Nakamura, M.; Mitsudera, H. *Tetrahedron* **2006,** *62*, 8539–8549.
10. Lowell, A. N.; Fennie, M. W.; Kozlowski, M. C. *J. Org. Chem.* **2008,** *73*, 1911–1918.
11. Webel, M.; Palmer, A. M.; Scheufler, C.; Haag, D.; Muller, B. *Org. Process Res. Dev.* **2010,** *14,* 142–151.
12. Kodet, J. G.; Wiemer, D. F. *J. Org. Chem.* **2013,** *78*, 9291–9302.

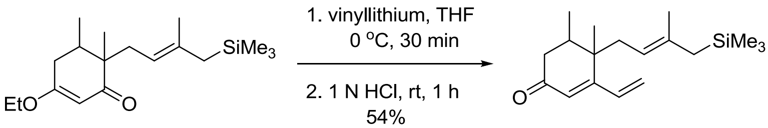
Stork–Danheiser transposition

Treatment of alkoxy-enone (vinylogous ester) with an organometallic (Grignard reagent or organolithium) was followed by treatment with acid to afford another enone where the ketone locates at the enole ther position of the starting material.

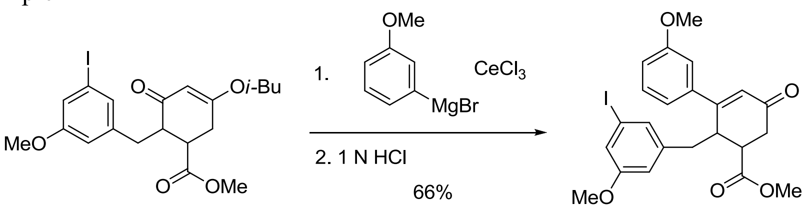




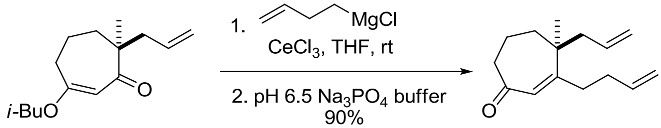
Example 1[2]



Example 2[6]



Example 3[7]



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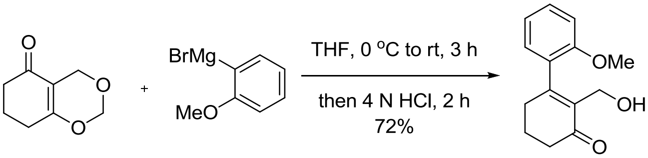
DOI 10.1007/978-3-319-03979-4_267,

Example 4[9]

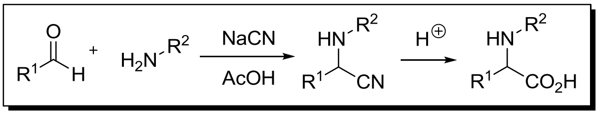


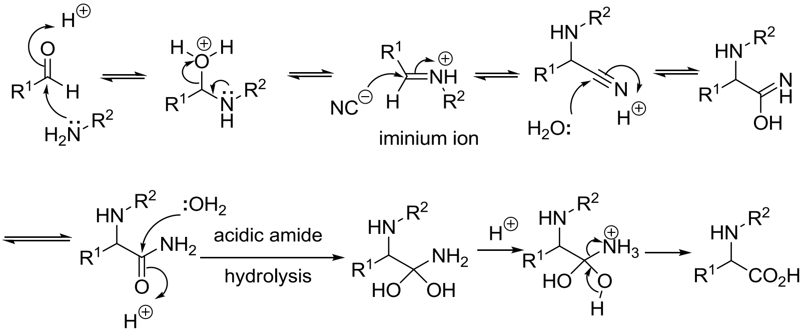
References

1. Stork, G.; Danheiser, R. L. *J. Org. Chem.* **1973,** *38*, 1775.
2. Majetich, G.; Behnke, M.; Hull, K. *J. Org. Chem.* **1985,** *50*, 3615–3618.
3. Kende, A. S.; Fludzinski, P. *Org. Synth*. **1986,** *64*.
4. Liepa, A. J.; Wilkie, J. S.; Winkler, D. A.; Winzenberg, K. N. *Aust. J. Chem.* **1992,** *45*, 759–767.
5. For asymmetric Stork–Danheiser alkylation, see Dudley, G. B.; Takaki, K. S.; Cha, D. D.; Danheiser, R. L. *Org. Lett.* **2000,** *21*, 3407–3410.
6. Grundl, M. A.; Trauner, D. *Org. Lett.* **2006,** *8*, 23–25.
7. Bennett, N. B.; Hong, A. Y.; Harned, A. M.; Stoltz, B. M. *Org. Biomol. Chem.* **2012,** *10*, 56–59.
8. Majetich, G.; Grove, J. L. *Heterocycles* **2012,** *84*, 963–982.
9. Kakde, B. N.; Bhunia, S.; Bisai, A. *Tetrahedron Lett*. **2013,** *54*, 1436–1439.

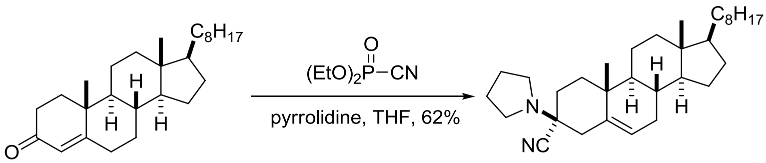
Strecker amino acid synthesis

Sodium cyanide-promoted condensation of aldehyde, or ketone, with an amine to afford α-amino nitrile, which may be hydrolyzed to an α-amino acid.

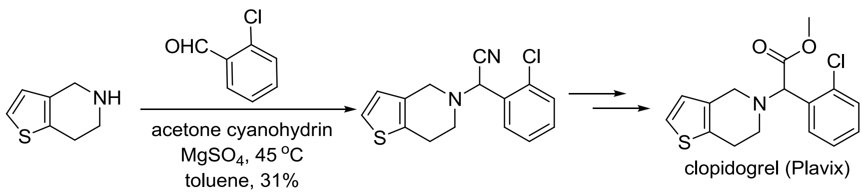




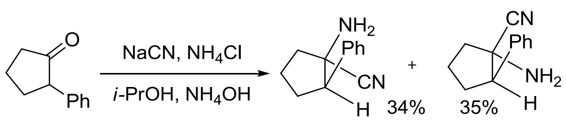
Example 1, Soluble cyanide source[2]



Example 2[3]



Example 3[8]



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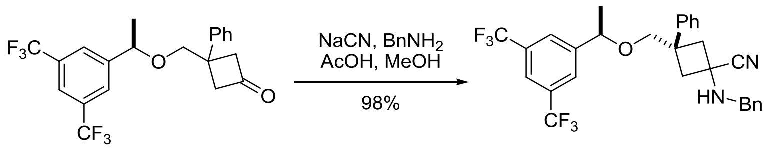
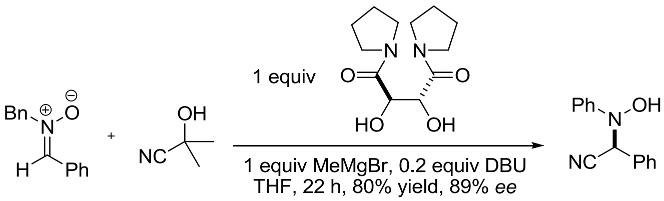
DOI 10.1007/978-3-319-03979-4_268, © Springer International Publishing Switzerland 2014

Example 4[9]



Example 5, Asymmetric Strecker-Type Reaction of Nitrones[11]

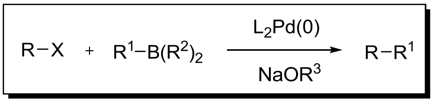


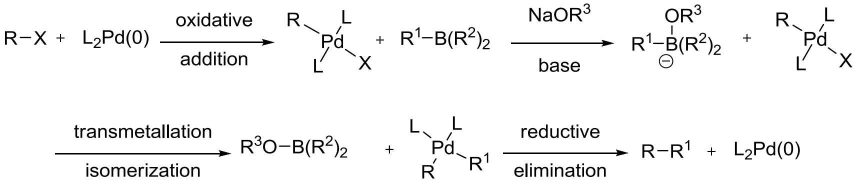
References

1. Strecker, A. *Ann.* **1850,** *75*, 27–45. Adolph Strecker devised this reaction over 160 years ago. In his paper he described: "The larger crystals of alanine are mother-of-pearl-shiny, hard and crunch between the teeth."
2. Harusawa, S.; Hamada, Y.; Shioiri, T. *Tetrahedron Lett*. **1979,** *20,* 4663–4666.
3. Burgos, A.; Herbert, J. M.; Simpson, I. *J. Labelled. Compd. Radiopharm.* **2000,** *43*, 891–898.
4. Ishitani, H.; Komiyama, S.; Hasegawa, Y.; Kobayashi, S. *J. Am. Chem. Soc.* **2000,** *122*, 762–766.
5. Yet, L. *Recent Developments in Catalytic Asymmetric Strecker-Type Reactions,* in *Organic Synthesis Highlights V,* Schmalz, H.-G.; Wirth, T. eds.; Wiley–VCH: Weinheim, Germany, **2003,** pp 187–193. (Review).
6. Meyer, U.; Breitling, E.; Bisel, P.; Frahm, A. W. *Tetrahedron: Asymmetry* **2004,** *15*, 2029–2037.
7. Huang, J.; Corey, E. J. *Org. Lett.* **2004,** *6*, 5027–5029.
8. Cativiela, C.; Lasa, M.; Lopez, P. *Tetrahedron: Asymmetry* **2005,** *16*, 2613–2523.
9. Wrobleski, M. L.; Reichard, G. A.; Paliwal, S.; Shah, S.; Tsui, H.-C.; Duffy, R. A.; Lachowicz, J. E.; Morgan, C. A.; Varty, G. B.; Shih, N.-Y. *Bioorg. Med. Chem. Lett.* **2006,** *16*, 3859–3863.
10. Galatsis, P. *Strecker Amino Acid Synthesis*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 477–499. (Review).
11. Belokon, Y. N.; Hunt, J.; North, M. *Tetrahedron: Asymmetry* **2008,** *19*, 2804–2815.
12. Sakai, T.; Soeta, T.; Endo, K.; Fujinami, S.; Ukaji, Y. *Org. Lett.* **2013,** *15*, 2422–2425.

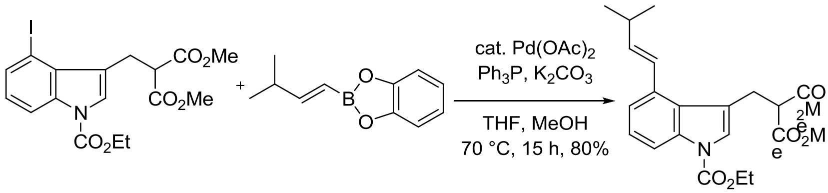
Suzuki–Miyaura coupling

Palladium-catalyzed cross-coupling reaction of organoboranes with organic halides, triflates, *etc*. In the presence of a base (transmetallation is reluctant to occur without the activating effect of a base). For the catalytic cycle, see Kumada coupling.

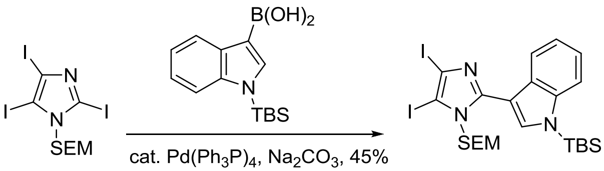




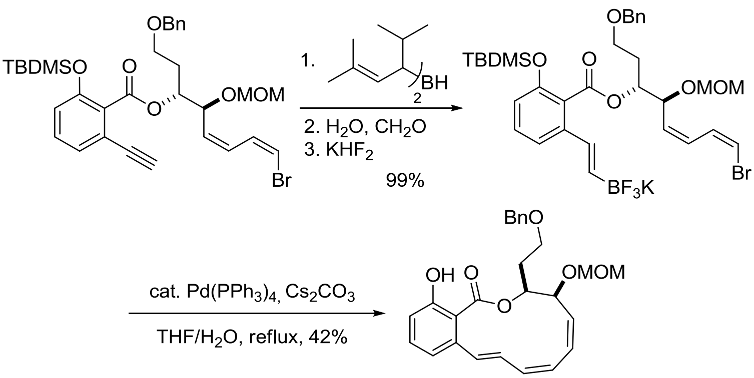
Example 1[2]



Example 2[4]



Example 3, Intramolecular Suzuki–Miyaura coupling[8]



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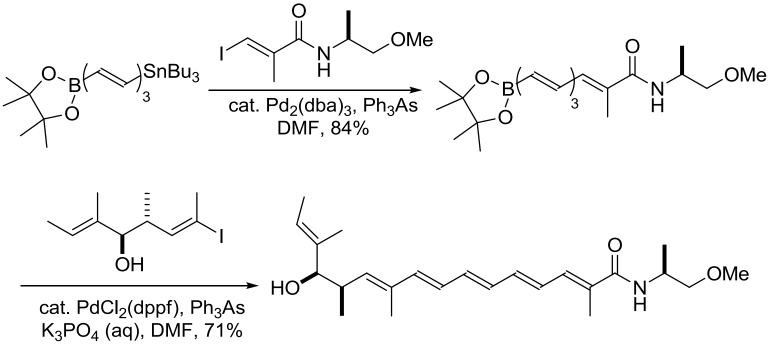
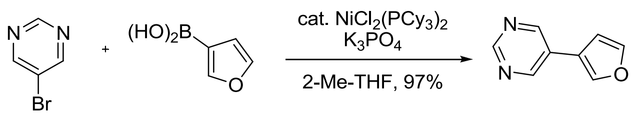
DOI 10.1007/978-3-319-03979-4_269, © Springer International Publishing Switzerland 2014

Example 4[9]



Example 5, Nickel-catalyzed Suzuki-Miyaura coupling in green solvents[12]

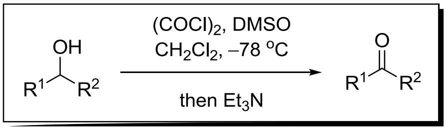


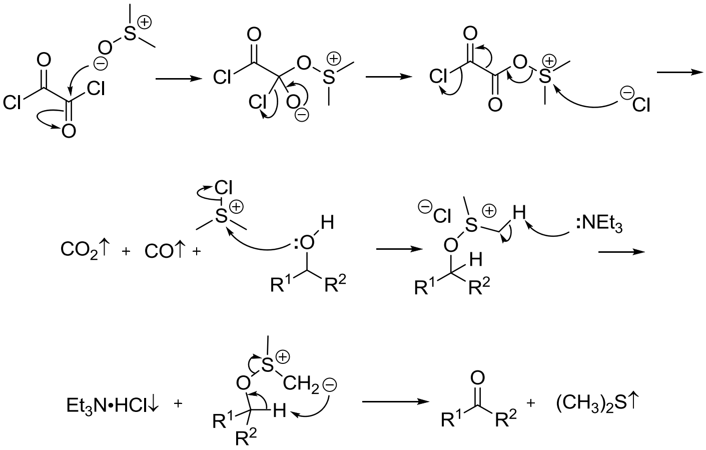
References

1. (a) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979,** *36*, 3437–3440. (b) Miyaura, N.; Suzuki, A. *Chem. Commun.* **1979,** 866–867. Akira Suzuki won Nobel Prize in 2010 along with Richard F. Heck and Ei-ichi Negishi "for palladium-catalyzed cross couplings in organic synthesis".
2. Tidwell, J. H.; Peat, A. J.; Buchwald, S. L. *J. Org. Chem.* **1994,** *59*, 7164–7168.
3. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995,** *95*, 2457–2483. (Review).
4. (a) Kawasaki, I.; Katsuma, H.; Nakayama, Y.; Yamashita, M.; Ohta, S. *Heterocycles* **1998,** *48,* 1887–1901. (b) Kawaski, I.; Yamashita, M.; Ohta, S. *Chem. Pharm. Bull.* **1996,** *44,* 1831–1839.
5. Suzuki, A. In *Metal-catalyzed Cross-coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley–VCH: Weinhein, Germany, **1998,** 49–97. (Review).
6. Stanforth, S. P. *Tetrahedron* **1998,** *54*, 263–303. (Review).
7. Zapf, A. *Coupling of Aryl and Alkyl Halides with Organoboron Reagents (Suzuki Reaction)*. In *Transition Metals for Organic Synthesis* (2nd edn.); Beller, M.; Bolm, C. eds., **2004,** 1, 211–229. Wiley–VCH: Weinheim, Germany. (Review).
8. Molander, G. A.; Dehmel, F. *J. Am. Chem. Soc.* **2004,** *126*, 10313–10318.
9. Coleman, R. S.; Lu, X.; Modolo, I. *J. Am. Chem. Soc.* **2007,** *129*, 3826–3827.
10. Wolfe, J. P.; Nakhla, J. S. *Suzuki Coupling*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 163–184. (Review).
11. Weimar, M.; Fuchter, M. J. *Org. Biomol. Chem.* **2013,** *11*, 31–34.
12. Ramgren, S.; Hie, L.; Ye, Y.; Garg, N. K. *Org. Lett.* **2013,** *15*, 3950–3953.

Swern oxidation

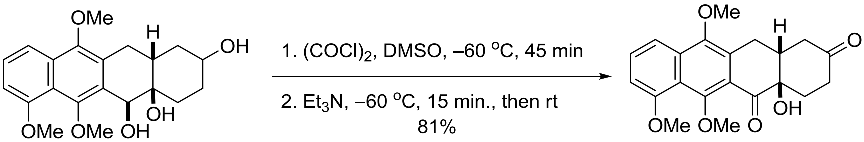
Oxidation of alcohols to the corresponding carbonyl compounds using $(COCl)_2$, DMSO, and quenching with Et_3N.



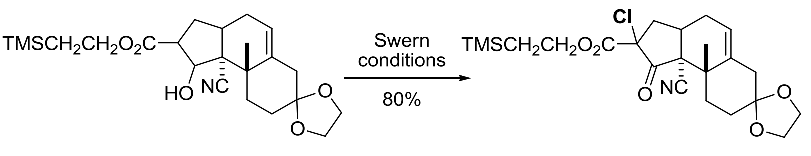


sulfur ylide

Example 1[2]



Example 2[3]



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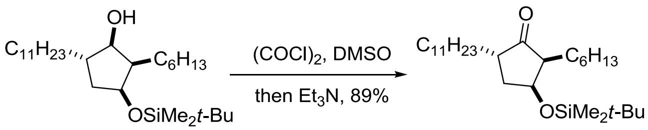
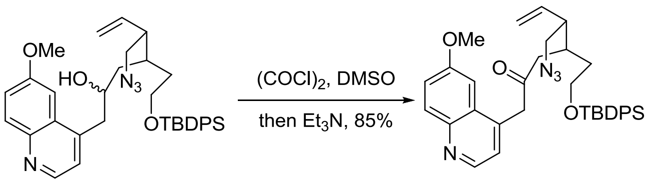
DOI 10.1007/978-3-319-03979-4_270, © Springer International Publishing Switzerland 2014

Example 3[5]



Example 4[7]

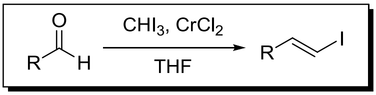


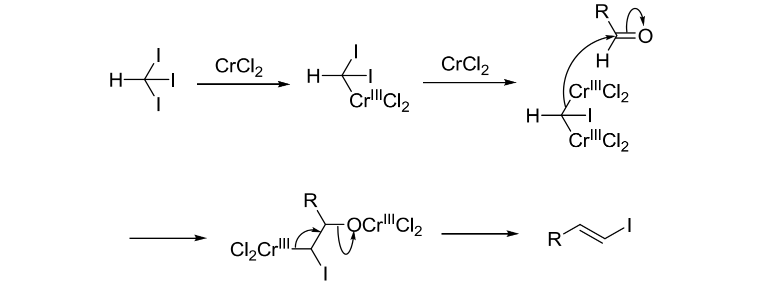
References

1. (a) Huang, S. L.; Omura, K.; Swern, D. *J. Org. Chem.* **1976,** *41*, 3329–3331. (b) Huang, S. L.; Omura, K.; Swern, D. *Synthesis* **1978,** *4*, 297–299. (c) Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978,** *43*, 2480–2482. Daniel Swern was a professor at Temple University.
2. Ghera, E.; Ben-David, Y. *J. Org. Chem*. **1988,** *53*, 2972–2979.
3. Smith, A. B., III; Leenay, T. L.; Liu, H. J.; Nelson, L. A. K.; Ball, R. G. *Tetrahedron Lett*. **1988,** *29*, 49–52.
4. Tidwell, T. T. *Org. React.* **1990,** *39*, 297–572. (Review).
5. Chadka, N. K.; Batcho, A. D.; Tang P. C.; Courtney, L. F.; Cook C. M.; Wovliulich, P. M.; Usković, M. R. *J. Org. Chem*. **1991,** *56*, 4714–4718.
6. Harris, J. M.; Liu, Y.; Chai, S.; Andrews, M. D.; Vederas, J. C. *J. Org. Chem*. **1998,** *63*, 2407–2409. (Odorless protocols).
7. Stork, G.; Niu, D.; Fujimoto, R. A.; Koft, E. R.; Bakovec, J. M.; Tata, J. R.; Dake, G. R. *J. Am. Chem. Soc*. **2001,** *123,* 3239–3242.
8. Nishide, K.; Ohsugi, S.-i.; Fudesaka, M.; Kodama, S.; Node, M. *Tetrahedron Lett.* **2002,** *43*, 5177–5179. (Another odorless protocols).
9. Ahmad, N. M. *Swern Oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 291–308. (Review).
10. Lopez-Alvarado, P; Steinhoff, J; Miranda, S; Avendano, C; Menendez, J. C. *Tetrahedron* **2009,** *65*, 1660–1672.
11. Zanatta, N.; Aquino, E. da C.; da Silva, F. M.; Bonacorso, H. G.; Martins, M. A. P. *Synthesis* **2012,** *44*, 3477–3482.

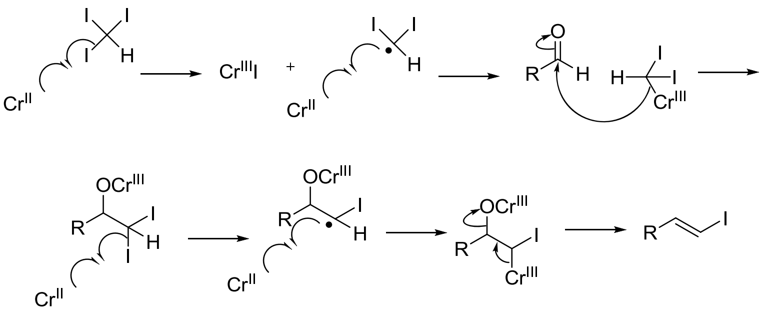
Takai reaction

Stereoselective conversion of an aldehyde to the corresponding *E*-vinyl iodide using CHI_3 and $CrCl_2$.

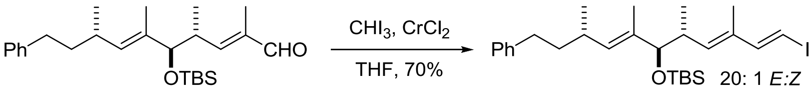




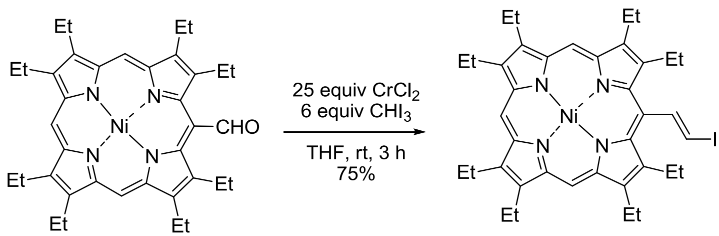
A radical mechanism was recently proposed[10]



Example 1[2]



Example 2[3]



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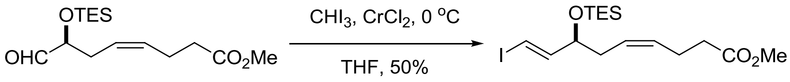
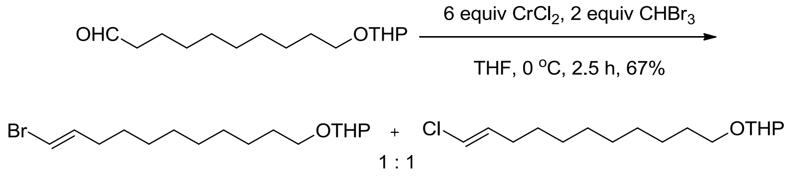
DOI 10.1007/978-3-319-03979-4_271,

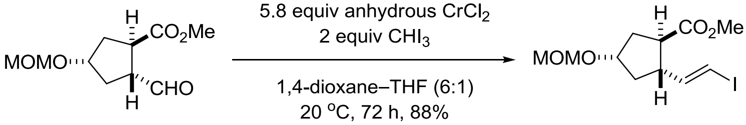
Example 3[4]



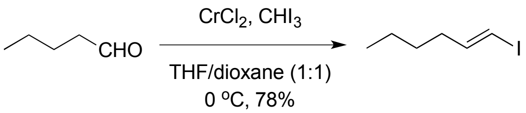
Example 4, A Br/Cl variant[9]



Example 5[10]



Example 5[10]

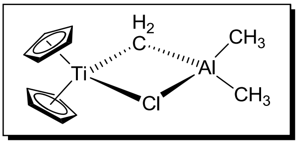


References

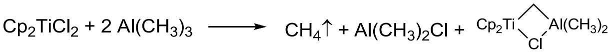
1. Takai, K.; Nitta, Utimoto, K. *J. Am. Chem. Soc*. **1986,** *108*, 7408–7410. Kazuhiko Takai was a professor at Kyoto University.
2. Andrus, M. B.; Lepore, S. D.; Turner, T. M. *J. Am. Chem. Soc*. **1997,** *119*, 12159–12169.
3. Arnold, D. P.; Hartnell, R. D. *Tetrahedron* **2001,** *57*, 1335–1345.
4. Rodriguez, A. R.; Spur, B. W. *Tetrahedron Lett.* **2004,** *45*, 8717–8724.
5. Dineen, T. A.; Roush, W. R. *Org. Lett.* **2004,** *6*, 2043–2046.
6. Lipomi, D. J.; Langille, N. F.; Panek, J. S. *Org. Lett.* **2004,** *6*, 3533–3536.
7. Paterson, I.; Mackay, A. C. *Synlett* **2004,** 1359–1362.
8. Concellón, J. M.; Bernad, P. L.; Méjica, C. *Tetrahedron Lett.* **2005,** *46*, 569–571.
9. Gung, B. W.; Gibeau, C.; Jones, A. *Tetrahedron: Asymmetry* **2005,** *16*, 3107–3114.
10. Legrand, F.; Archambaud, S.; Collet, S.; Aphecetche-Julienne, K.; Guingant, A.; Evain, M. *Synlett* **2008,** 389–393.
11. Saikia, B.; Joymati Devi, T.; Barua, N. C. *Org. Biomol. Chem*. **2013,** *11*, 905–913.

Tebbe reagent

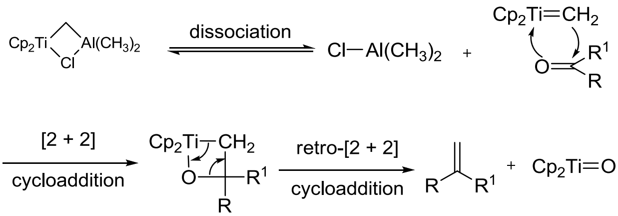
The Tebbe reagent, μ-chlorobis(cyclopentadienyl)(dimethylaluminium)-μ-methylenetitanium, transforms a carbonyl compound to the corresponding *exo*-olefin.



Preparation:[2,6]



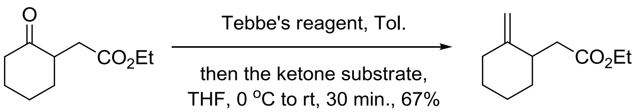
Mechanism:[3]



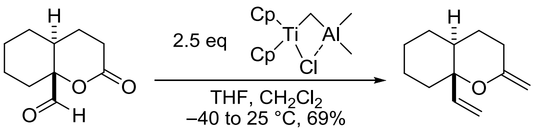
oxatitanacyclobutane

formation of the strong Ti=O bond is the driving force.

Example 1, Ketone[2]



Example 2, Double Tebbe[4]



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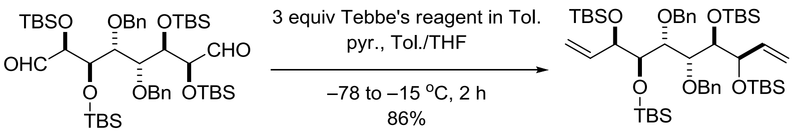
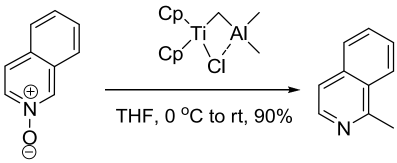
DOI 10.1007/978-3-319-03979-4_272, © Springer International Publishing Switzerland 2014

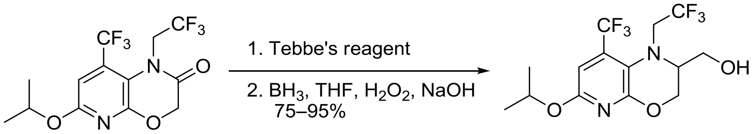
Example 3, Double Tebbe[5]



Example 4, *N*-Oxide[6]



Example 5, Amide[11]

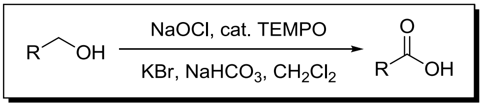


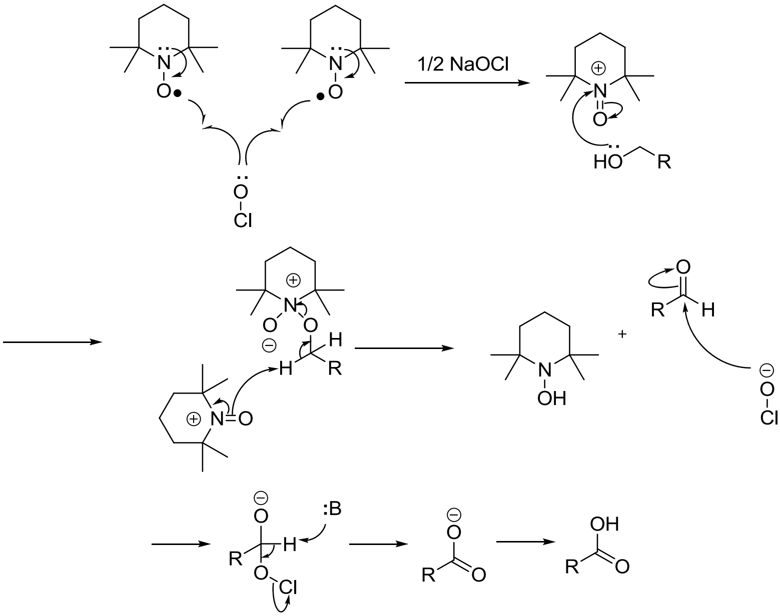
References

1. Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978,** *100*, 3611–3613. Fred Tebbe worked at DuPont Central Research.
2. Pine, S. H.; Pettit, R. J.; Geib, G. D.; Cruz, S. G.; Gallego, C. H.; Tijerina, T.; Pine, R. D. *J. Org. Chem.* **1985,** *50*, 1212–1216.
3. Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985,** *50*, 2386–2387.
4. Philippo, C. M. G.; Vo, N. H.; Paquette, L. A. *J. Am. Chem. Soc*. **1991,** *113*, 2762–2764.
5. Ikemoto, N.; Schreiber, L. S. *J. Am. Chem. Soc*. **1992,** *114*, 2524–2536.
6. Pine, S. H. *Org. React.* **1993,** *43*, 1–98. (Review).
7. Nicolaou, K. C.; Koumbis, A. E.; Snyder, S. A.; Simonsen, K. B. *Angew. Chem. Int. Ed.* **2000,** *39*, 2529–2533.
8. Straus, D. A. *Encyclopedia of Reagents for Organic Synthesis;* Wiley & Sons, **2000**. (Review).
9. Payack, J. F.; Hughes, D. L.; Cai, D.; Cottrell, I. F.; Verhoeven, T. R. *Org. Syn.*, *Coll. Vol. 10*, **2004,** p 355.
10. Beadham, I.; Micklefield, J. *Curr. Org. Synth.* **2005,** *2*, 231–250. (Review).
11. Long, Y. O.; Higuchi, R. I.; Caferro, T.s R.; Lau, T. L. S.; Wu, M.; Cummings, M. L.; Martinborough, E. A.; Marschke, K. B.; Chang, W. Y.; Lopez, F. J.; Karanewsky, D. S.; Zhi, L. *Bioorg. Med. Chem. Lett.* **2008,** *18*, 2967–2971.
12. Zhang, J. *Tebbe reagent*. In *Name Reactions for Homolotions-Part I*; Li, J. J., Corey, E. J., Eds., Wiley: Hoboken, NJ, **2009,** pp 319–333. (Review).
13. Yamashita, S.; Suda, N.; Hayashi, Y.; Hirama, M. *Tetrahedron Lett.* **2013,** *54*, 1389–1391.

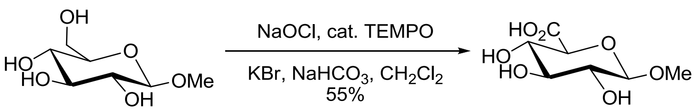
TEMPO oxidation

TEMPO = **Te**tra**m**ethyl **p**entahydropyridine **o**xide. 2,2,6,6-Tetramethylpiperi-dinyloxy is a stable nitroxyl radical, which serves in oxidations as catalyst.

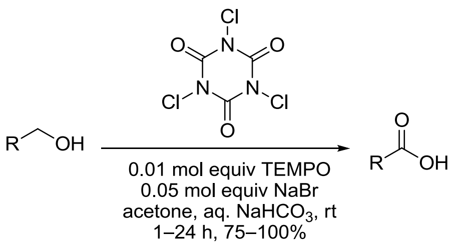




Example 1[4]



Example 2, Trichloroisocyanuric/TEMPO oxidation[5]



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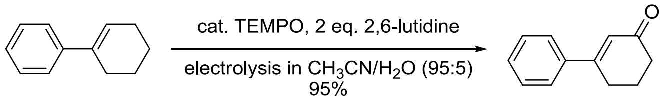
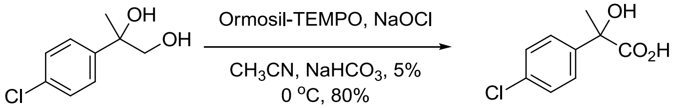
Example 3[8]

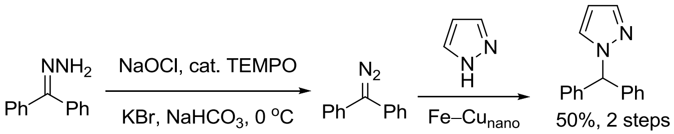


Example 4[10]

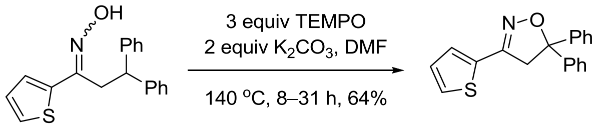


"Ormosil-TEMPO" is a sol-gel hydrophobized nanostructured silica matrix doped with TEMPO

Example 5[12]



Example 6, TEMPO-mediated aliphatic C–H oxidation with oximes[13]

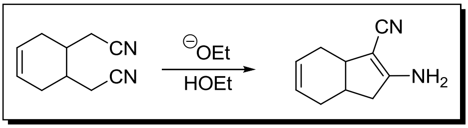


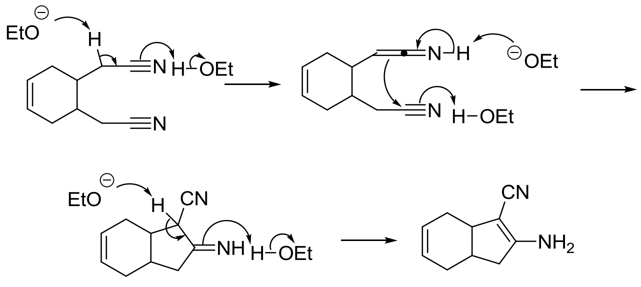
References

1. Garapon, J.; Sillion, B.; Bonnier, J. M. *Tetrahedron Lett.* **1970,** *11,* 4905–4908.
2. de Nooy, A. E.; Besemer, A. C.; van Bekkum, H. *Synthesis* **1996,** 1153–1174. (Review).
3. Rychnovsky, S. D.; Vaidyanathan, R. *J. Org. Chem*. **1999,** *64*, 310–312.
4. Fabbrini, M.; Galli, C.; Gentili, P.; Macchitella, D. *Tetrahedron Lett.* **2001,** *42*, 7551–7553.
5. De Luca, L.; Giacomelli, G.; Masala, S.; Porcheddu, A. *J. Org. Chem*. **2003,** *45*, 4999–5001.
6. Ciriminna, R.; Pagliaro, M. *Tetrahedron Lett.* **2004,** *45*, 6381–6383.
7. Tashino, Y.; Togo, H. *Synlett* **2004,** 2010–2012.
8. Breton, T.; Liaigre, D.; Belgsir, E. M. *Tetrahedron Lett.* **2005,** *46*, 2487–2490.
9. Chauvin, A.-L.; Nepogodiev, S. A.; Field, R. A. *J. Org. Chem*. **2005,** *47*, 960–966.
10. Gancitano, P.; Ciriminna, R.; Testa, M. L.; Fidalgo, A.; Ilharco, L. M.; Pagliaro, M. *Org. Biomol. Chem*. **2005,** *3,* 2389–2392.
11. Zhang, M.; Chen, C.; Ma, W.; Zhao, J. *Angew. Chem. Int. Ed.* **2008,** *47*, 9730–9733.
12. Perusquía-Hernández, C.; Lara-Issasi, G. R.; Frontana-Uribe, B. A.; Cuevas-Yañez, E. *Tetrahedron Lett.* **2013,** *54*, 3302–3305.
13. Zhu, X.; Wang, Y.-F.; Ren, W.; Zhang, F.-L.; Chiba, S. *Org. Lett.* **2013,** *15*, 3214–3217.

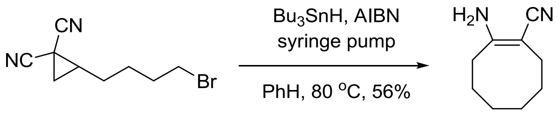
Thorpe–Ziegler reaction

The intramolecular version of the Thorpe reaction, which is base-catalyzed self-condensation of nitriles to yield imines that tautomerize to enamine.

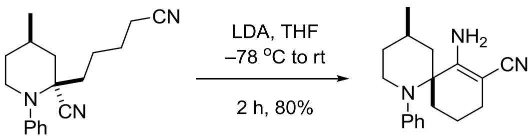




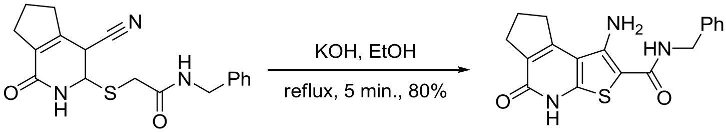
Example 1, A radical-mediated Thorpe–Ziegler reaction[2]



Example 2[5]



Example 3[8]



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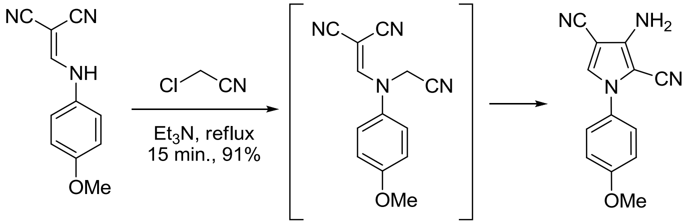
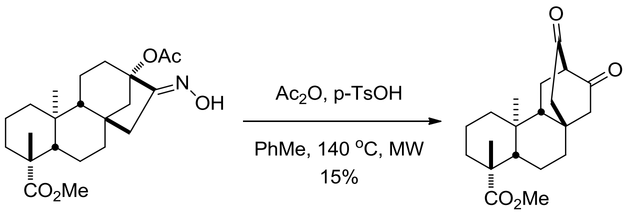
Example 4[9]



Example 5[11]

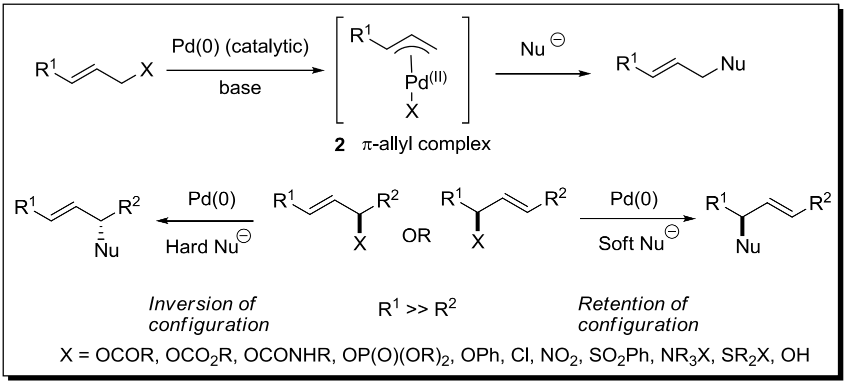


References

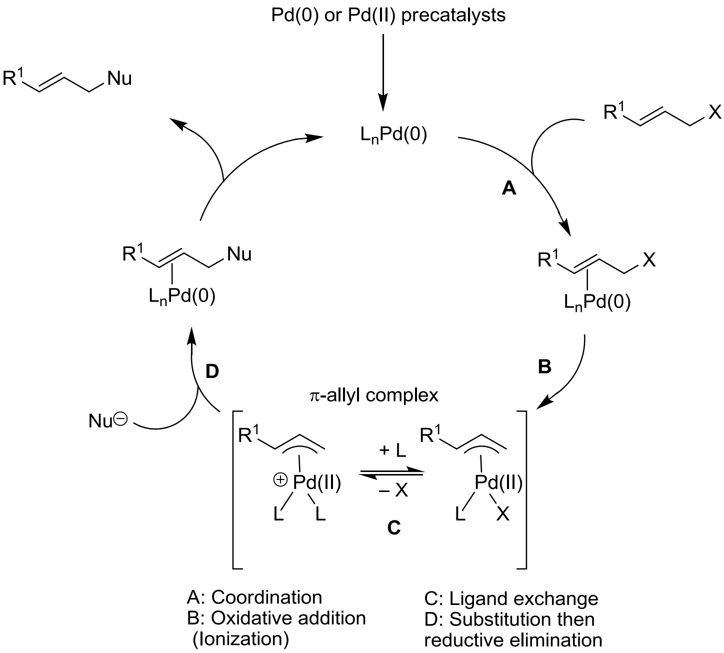
1. (a) Baron, H.; Remfry, F. G. P.; Thorpe, Y. F. *J. Chem. Soc.* **1904,** *85*, 1726–1761. (b) Ziegler, K. *et al. Ann.* **1933,** *504,* 94–130. Karl Ziegler (1898–1973), born in Helsa, Germany, received his Ph.D. In 1920 from von Auwers at the University of Marburg. He became the director of the Max-Planck-Institut für Kohlenforschung at Mülheim/Ruhr in 1943. He shared the Nobel Prize in Chemistry in 1963 with Giulio Natta (1903–1979) for their work in polymer chemistry. The Ziegler–Natta catalyst is widely used in polymerization.
2. Curran, D. P.; Liu, W. *Synlett* **1999,** 117–119.
3. Dansou, B.; Pichon, C.; Dhal, R.; Brown, E.; Mille, S. *Eur. J. Org. Chem*. **2000,** 1527–1531.
4. Keller, L.; Dumas, F.; Pizzonero, M.; d'Angelo, J.; Morgant, G.; Nguyen-Huy, D. *Tetrahedron Lett*. **2002,** *43,* 3225–3228.
5. Malassene, R.; Toupet, L.; Hurvois, J.-P.; Moinet, C. *Synlett* **2002,** 895–898.
6. Satoh, T.; Wakasugi, D. *Tetrahedron Lett.* **2003,** *44,* 7517–7520.
7. Wakasugi, D.; Satoh, T. *Tetrahedron* **2005,** *61,* 1245–1256.
8. Dotsenko, V. V.; Krivokolysko, S. G.; Litvinov, V. P. *Monatsh. Chem*. **2008,** *139,* 271–275.
9. Salaheldin, A. M.; Oliveira-Campos, A. M. F.; Rodrigues, L. M. *ARKIVOC* **2008,** 180–190.
10. Miszke, A.; Foks, H.; Brozewicz, K.; Kedzia, A.; Kwapisz, E.; Zwolska, Z. *Heterocycles* **2008,** *75,* 2723–2734.
11. Hutt, O. E.; Doan, T. L.; Georg, G. I. *Org. Lett.* **2013,** *15,* 1602–1605.

Tsuji–Trost reaction

The Tsuji–Trost reaction is the palladium-catalyzed substitution of allylic leaving groups by carbon nucleophiles. These reactions proceed via π-allylpalladium intermediates.



The catalytic cycle:



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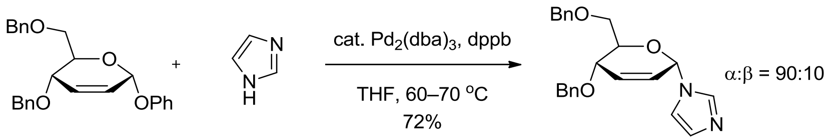
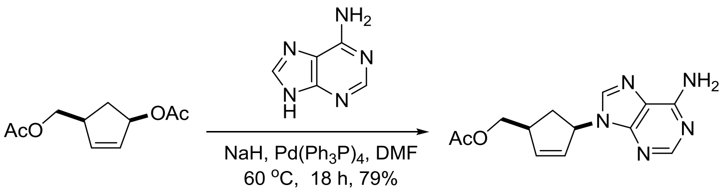
DOI 10.1007/978-3-319-03979-4_275, © Springer International Publishing Switzerland 2014

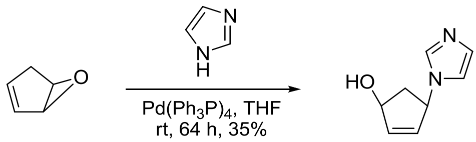
Example 1, Allylic ether[3]



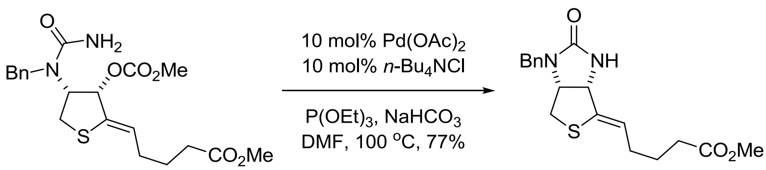
Example 2, Allylic acetate[3]



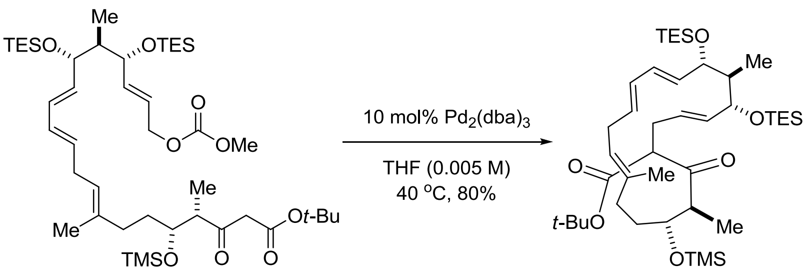
Example 3, Allylic epoxide[5]



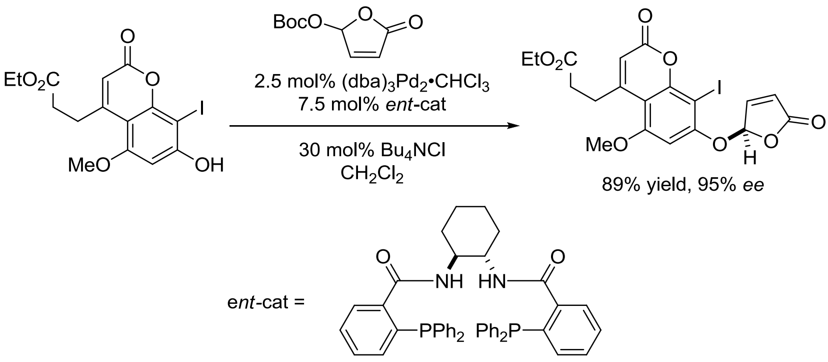
Example 4, Intramolecular Tsuji–Trost reaction[6]



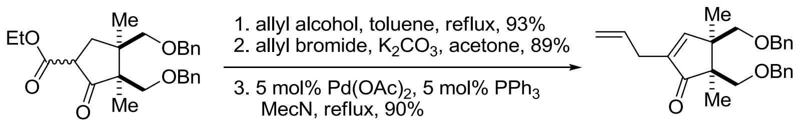
Example 5, Intramolecular Tsuji–Trost reaction[7]



Example 6, Asymmetric Tsuji–Trost reaction[8]



Example 7, Tsuji–Trost decarboxylation–dehydrogenation sequence[12]

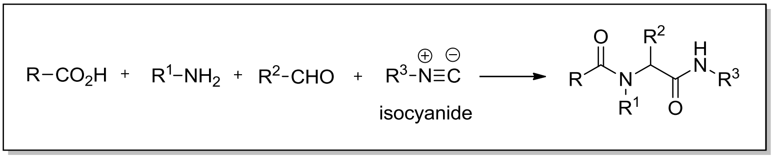


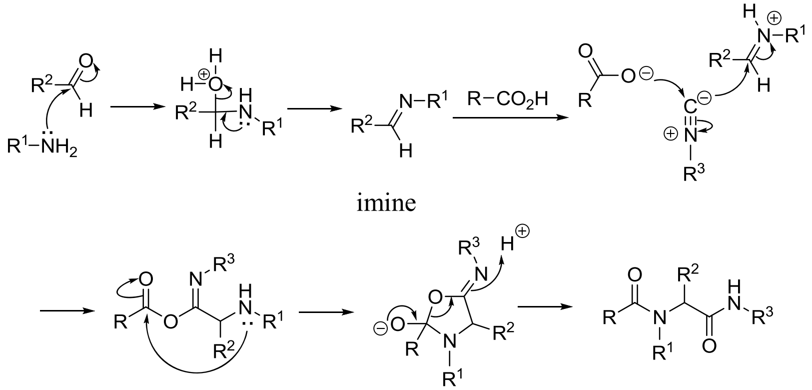
References

1. (a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965,** *6,* 4387–4388. (b) Tsuji, J. *Acc. Chem. Res.* **1969,** *2*, 144–152. (Review). Jiro Tsuji (1927–), now retired, worked at the Toyo Rayon Company in Japan.
2. Godleski, S. A. In *Comprehensive Organic Synthesis;* Trost, B. M.; Fleming, I., eds.; *Vol. 4*. Chapter 3.3. Pergamon: Oxford, 1991. (Review).
3. Bolitt, V.; Chaguir, B.; Sinou, D. *Tetrahedron Lett.* **1992,** *33,* 2481–2484.
4. Moreno-Mañas, M.; Pleixats, R. In *Advances in Heterocyclic Chemistry;* Katritzky, A. R., ed.; Academic Press: San Diego, **1996,** *66*, 73. (Review).
5. Arnau, N.; Cortes, J.; Moreno-Mañas, M.; Pleixats, R.; Villarroya, M. *J. Heterocycl. Chem.* **1997,** *34*, 233–239.
6. Seki, M.; Mori, Y.; Hatsuda, M.; Yamada, S. *J. Org. Chem.* **2002,** *67*, 5527–5536.
7. Vanderwal, C. D.; Vosburg, D. A.; Weiler, S.; Sorenson, E. J. *J. Am. Chem. Soc.* **2003,** *125*, 5393–5407.
8. Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc*. **2003,** *125*, 3090–3100.
9. Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc*. **2004,** *126,* 15044–15045.
10. Fuchter, M. J. *Tsuji–Trost Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 185–211. (Review).
11. Shi, L.; Meyer, K.; Greaney, M. F. *Angew. Chem. Int. Ed.* **2010,** *49*, 9250–9253.
12. Brehm, E.; Breinbauer, R. *Org. Biomol. Chem.* **2013,** *11*, 4750–4756.

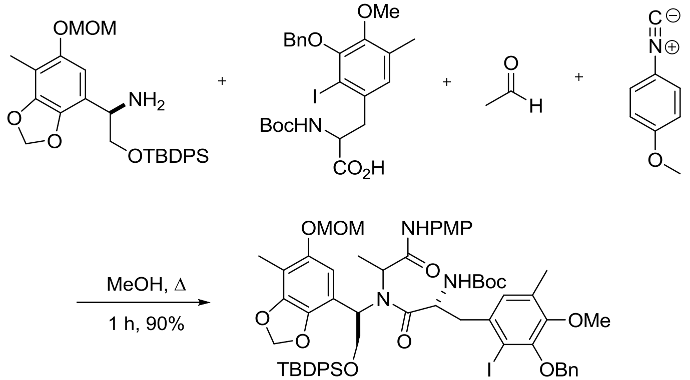
Ugi reaction

Four-component condensation (4CC) of carboxylic acids, *C*-isocyanides, amines, and carbonyl compounds to afford diamides. Also known as four-component reaction (4CR). *Cf.* Passerini reaction.

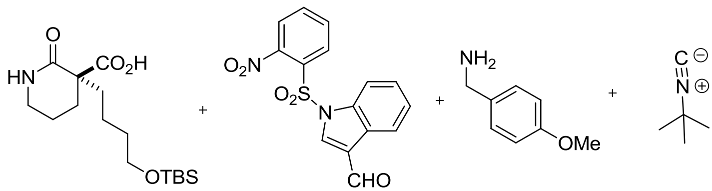




Example 1[2]



Example 2[5]



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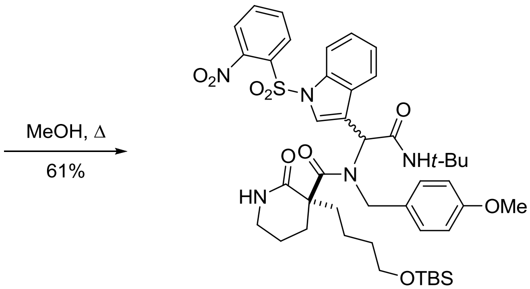
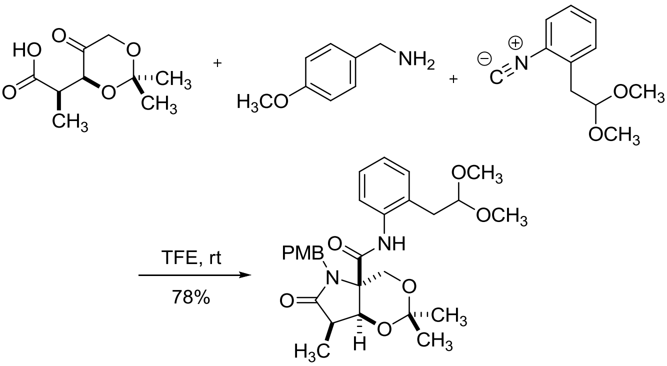
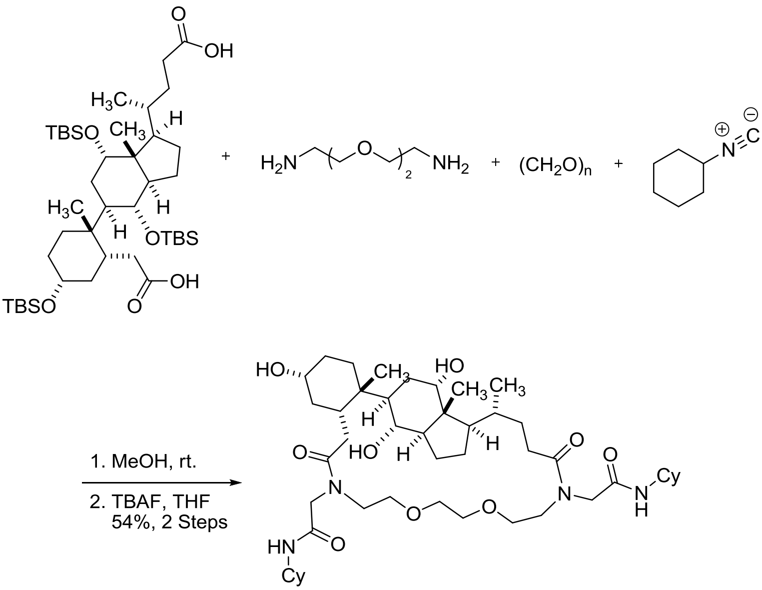


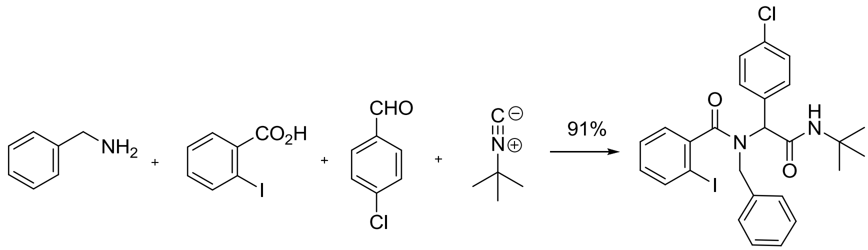
Example 3[7]



Example 4[8]



Example 5[11]

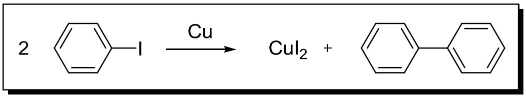


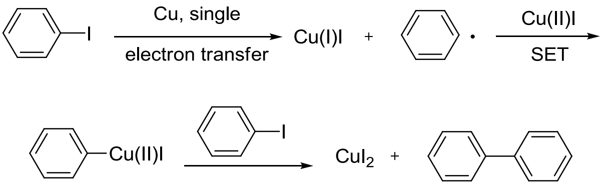
References

1. (a) Ugi, I. *Angew. Chem. Int. Ed.* **1962,** *1*, 8–21.; (b) Ugi, I.; Offermann, K.; Herlinger, H.; Marquarding, D. *Liebigs Ann. Chem.* **1967,** *709*, 1–10.; (c) Ugi, I.; Kaufhold, G. *Ann.* **1967,** *709*, 11–28; (d) Ugi, I.; Lohberger, S.; Karl, R. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, **1991,** *Vol. 2*, 1083. (Review); (e) Dömling, A.; Ugi, I. *Angew. Chem. Int. Ed.* **2000,** *39*, 3168. (Review); (f) Ugi, I. *Pure Appl. Chem.* **2001,** *73*, 187–191. (Review). Ivar Karl Ugi (1930–2005) earned his Ph.D. under the guidance of Prof. Rolf Huisgen. Since 1962, he worked at Bayer AG, rising through the ranks to director. But he left Bayer in 1969 to pursue his indendent academic career at the University of Southern California (USC). In 1973, he moved to the Technische Universität München, where stayed until his retirement in 1999. Ugi was one of the pioneers in multi-component recations (MCRs).
2. Endo, A.; Yanagisawa, A.; Abe, M.; Tohma, S.; Kan, T.; Fukuyama, T. *J. Am. Chem. Soc*. **2002,** *124,* 6552–6554.
3. Hebach, C.; Kazmaier, U. *Chem. Commun*. **2003,** 596–597.
4. *Multicomponent Reactions* J. Zhu, H. Bienaymé, Eds.; Wiley-VCH, Weinheim, **2005**.
5. Oguri, H.; Schreiber, S. L. *Org. Lett.* **2005,** *7*, 47–50.
6. Dömling, A. *Chem. Rev.* **2006,** *106*, 17–89.
7. Gilley, C. B.; Buller, M. J.; Kobayashi, Y. *Org. Lett.* **2007,** *9*, 3631–3634.
8. Rivera, D. G.; Pando, O.; Bosch, R.; Wessjohann, L. A. *J. Org. Chem.* **2008,** *73*, 6229–6238.
9. Bonger, K. M.; Wennekes, T.; Filippov, D. V.; Lodder, G.; van der Marel, G. A.; Overkleeft, H. S. *Eur. J. Org. Chem.* **2008,** 3678–3688.
10. Williams, D. R.; Walsh, M. J. *Ugi Reaction*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 786–805. (Review).
11. Tyagi, V.; Shahnawaz Khan, S.; Chauhan, P. M. S. *Tetrahedron Lett.* **2013,** *54*, 1279–1284.

Ullmann coupling

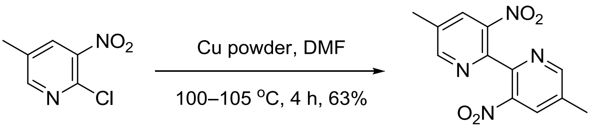
Homocoupling of aryl iodides in the presence of Cu or Ni or Pd to afford biaryls.



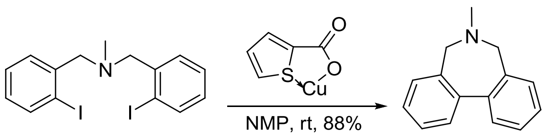


The overall transformation of PhI to PhCuI is an oxidative addition process.

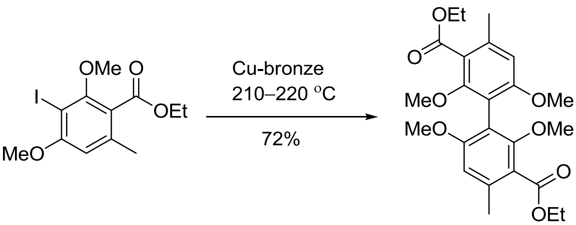
Example 1[3]



Example 2, CuTC-catalyzed Ullmann coupling (CuTC, Copper(I)-thiophene-2-carboxylate)[4]



Example 3[5]



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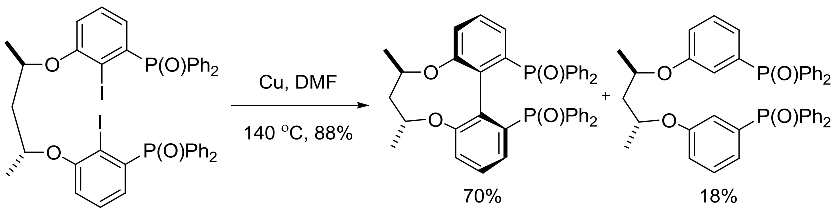
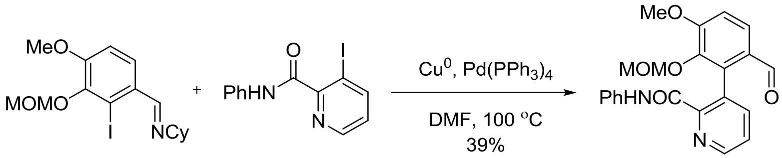
DOI 10.1007/978-3-319-03979-4_277, © Springer International Publishing Switzerland 2014

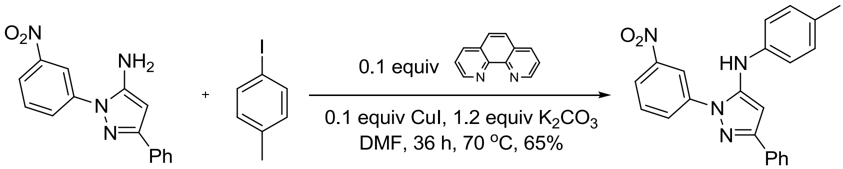
Example 4[8]



Example 5[9]



Example 6[11]

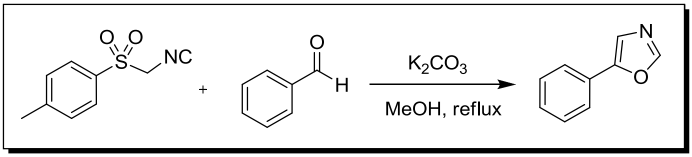


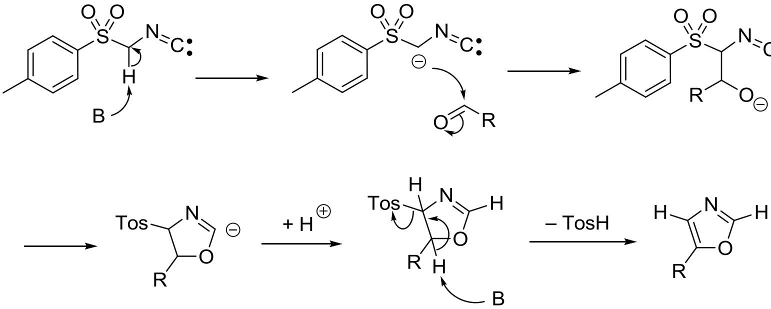
References

1. (a) Ullmann, F.; Bielecki, J. *Ber.* **1901,** *34,* 2174–2185. Fritz Ullmann (1875–1939), born in Fürth, Bavaria, studied under Graebe at Geneva. He taught at the Technische Hochschule in Berlin and the University of Geneva. (b) Ullmann, F. *Ann.* **1904,** *332,* 38–81.
2. Fanta, P. E. *Synthesis* **1974,** 9–21. (Review).
3. Kaczmarek, L.; Nowak, B.; Zukowski, J.; Borowicz, P.; Sepiol, J.; Grabowska, A. *J. Mol. Struct.* **1991,** *248,* 189–200.
4. Zhang, S.; Zhang, D.; Liebskind, L. S. *J. Org. Chem.* **1997,** *62,* 2312–2313.
5. Hauser, F. M.; Gauuan, P. J. F. *Org. Lett.* **1999,** *1*, 671–672.
6. Buck, E.; Song, Z. J.; Tschaen, D.; Dormer, P. G.; Volante, R. P.; Reider, P. J. *Org. Lett.* **2002,** *4*, 1623–1626.
7. Nelson, T. D.; Crouch, R. D. *Org. React.* **2004,** *63,* 265–556. (Review).
8. Qui, L.; Kwong, F. Y.; Wu, J.; Wai, H. L.; Chan, S.; Yu, W.-Y.; Li, Y.-M.; Guo, R.; Zhou, Z.; Chan, A. S. C. *J Am. Chem. Soc.* **2006,** *128*, 5955–5965.
9. Markey, M. D.; Fu, Y.; Kelly, T. R. *Org. Lett.* **2007,** *9*, 3255–3257.
10. Ahmad, N. M. *Ullman Coupling*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, 2009; pp 255–267. (Review).
11. Chang, E. C.; Chen, C.-Y.; Wang, L.-Y.; Huang, Y.-Y.; Yeh, M.-Y.; Wong, F. F. *Tetrahedron* **2013,** *69*, 570–576.

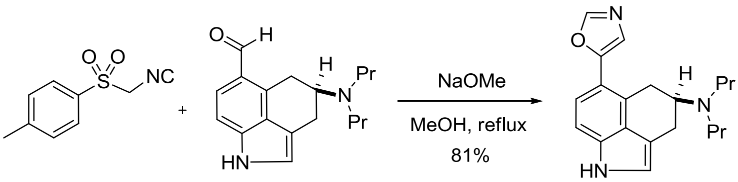
van Leusen oxazole synthesis

Formation of 5-substituted oxazoles through the reaction of *p*-tolylsulfonylmethyl isocyanide (TosMIC, also known as the van Leusen reagent) with aldehydes in protic solvents at refluxing temperatures.





Example 1[3]



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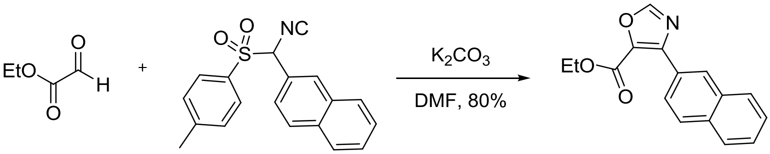
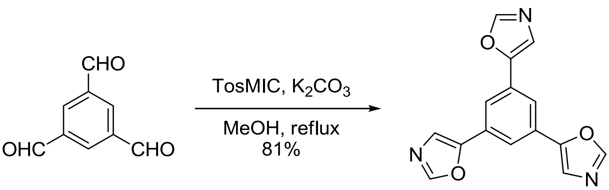


Example 3[9]



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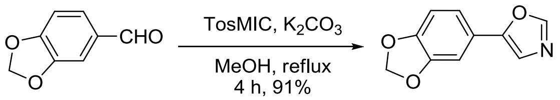
Example 4[10]

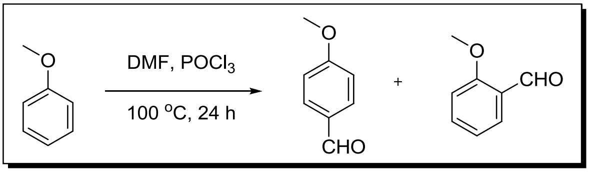


References

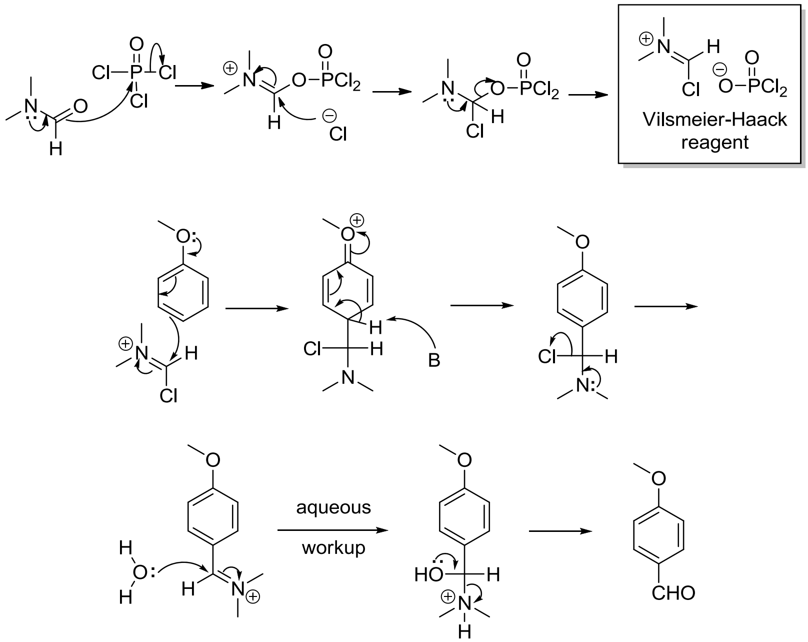
1. (a) van Leusen, A. M.; Hoogenboom, B. E.; Siderius, H. *Tetrahedron Lett.* **1972,** *13,* 2369–2381. (b) Possel, O.; van Leusen, A. M. *Heterocycles* **1977,** *7*, 77–80. (c) Saikachi, H.; Kitagawa, T.; Sasaki, H.; van Leusen, A. M. *Chem. Pharm. Bull.* **1979,** *27*, 793–796. (d) van Nispen, S. P. J. M.; Mensink, C.; van Leusen, A. M. *Tetrahedron Lett.* **1980,** *21*, 3723–3726. Van Leusen was a professor at The University Zernikelaan Groningen, The Netherlands.
2. van Leusen, A. M.; van Leusen, D. In *Encyclopedia of Reagents of Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, **1995**; *Vol. 7*, 4973–4979. (Review).
3. Anderson, B. A.; Becke, L. M.; Booher, R. N.; Flaugh, M. E.; Harn, N. K.; Kress, T. J.; Varie, D. L.; Wepsiec, J. P. *J. Org. Chem.* **1997,** *62*, 8634–8639.
4. Kulkarni, B. A.; Ganesan, A. *Tetrahedron Lett.* **1999,** *40*, 5633–5636.
5. Sisko, J.; Kassick, A. J.; Mellinger, M.; Filan, J. J.; Allen, A.; Olsen, M. A. *J. Org. Chem.* **2000,** *65*, 1516–1524.
6. Barrett, A. G. M.; Cramp, S. M.; Hennessy, A. J.; Procopiou, P. A.; Roberts, R. S. *Org. Lett.* **2001,** *3*, 271–273.
7. Herr, R. J.; Fairfax, D. J., Meckler, H.; Wilson, J. D. *Org. Process Res. Dev.* **2002,** *6*, 677–681.
8. Brooks, D. A. *van Leusen Oxazole Synthesis*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 254–259. (Review).
9. Kotha, S.; Shah, V. R. *Synthesis* **2007,** 3653–3658.
10. Besselièvre, F.; Mahuteau-Betzer, F.; Grierson, D. S.; Piguel, S. *J. Org. Chem.* **2008,** *73*, 3278–3280.
11. Wu, B.; Wen, J.; Zhang, J.; Li, J.; Xiang, Y.-Z.; Yu, X.-Q. *Synlett* **2009,** 500–504.

Vilsmeier–Haack reaction

The Vilsmeier–Haack reagent, a chloroiminium salt, is a weak electrophile. Therefore, the Vilsmeier–Haack reaction works better with electron-rich carbocycles and heterocycles.



34% 4%



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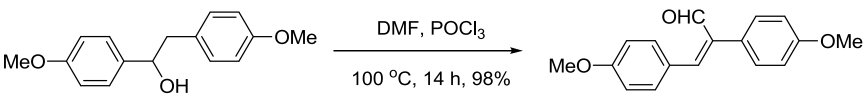

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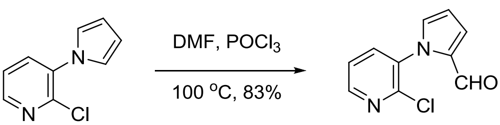

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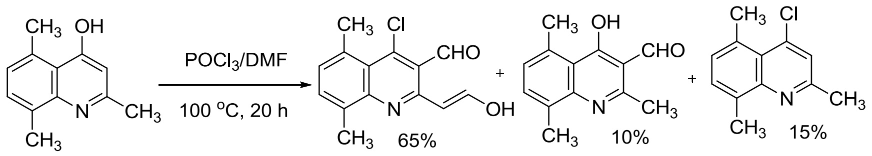
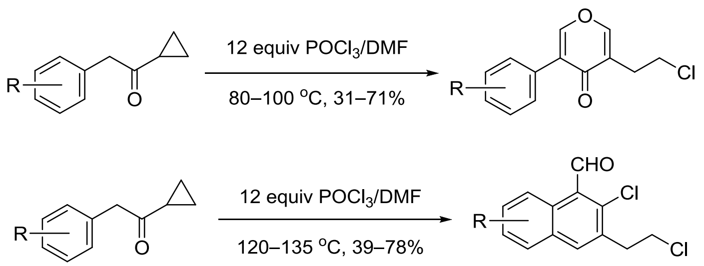
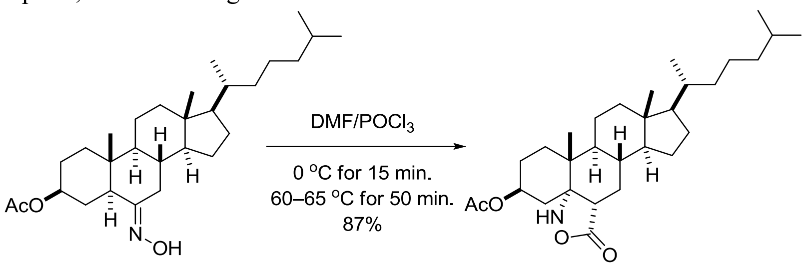
Example 3[9]



Example 4, Reaction outcomes differ as temperature differs[10]



Example 5, An interesting mechanism[11]

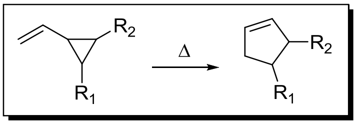


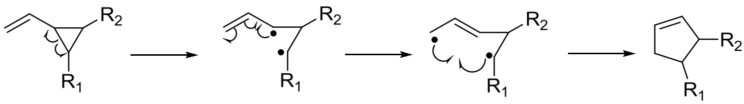
References

1. Vilsmeier, A.; Haack, A. *Ber.* **1927,** *60*, 119–122. German chemists Anton Vilsmeier and Albrecht Haack discovered this recation in 1927.
2. Reddy, M. P.; Rao, G. S. K. *J. Chem. Soc., Perkin Trans. 1* **1981,** 2662–2665.
3. Lancelot, J.-C.; Ladureé, D.; Robba, M. *Chem. Pharm. Bull.* **1985,** *33*, 3122–3128.
4. Marson, C. M.; Giles, P. R. *Synthesis Using Vilsmeier Reagents* CRC Press, **1994**. (Book).
5. Seybold, G. *J. Prakt. Chem.* **1996,** *338,* 392–396 (Review).
6. Jones, G.; Stanforth, S. P. *Org. React.* **1997,** *49*, 1–330. (Review).
7. Jones, G.; Stanforth, S. P. *Org. React.* **2000,** *56*, 355–659. (Review).
8. Tasneem, *Synlett* **2003,** 138–139. (Review of the Vilsmeier–Haack reagent).
9. Nandhakumar, R.; Suresh, T.; Jude, A. L. C.; Kannan, V. R.; Mohan, P. S. *Eur. J. Med. Chem.* **2007,** *42*, 1128–1136.
10. Tang, X.-Y.; Shi, M. *J. Org. Chem.* **2008,** *73*, 8317–8320.
11. Shamsuzzaman, Hena Khanam, H.; Mashrai, A.; Siddiqui, N. *Tetrahedron Lett.* **2013,** *54,* 874–877.

Vinylcyclopropane–cyclopentene rearrangement

Transformation of vinylcyclopropane to cyclopentene *via* a diradical intermediate.





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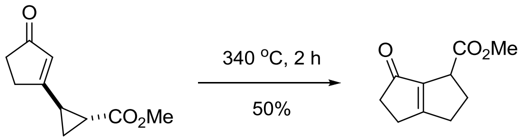

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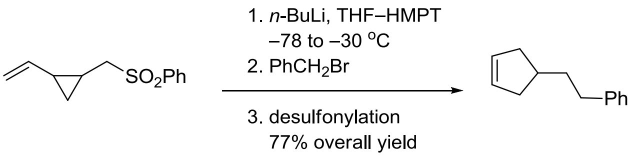

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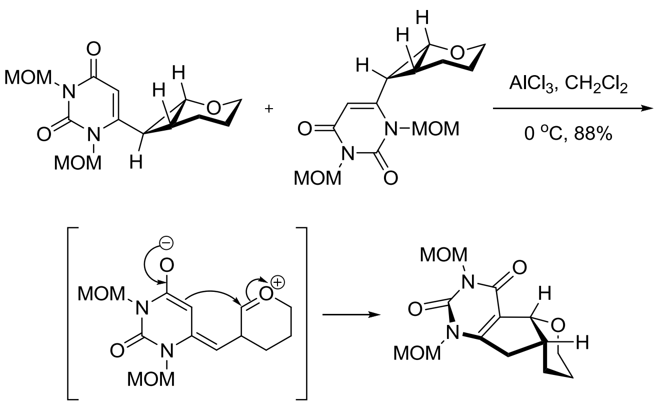

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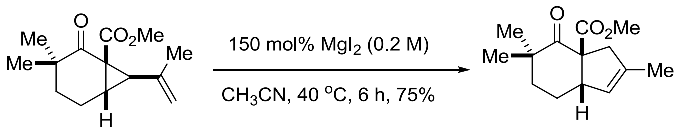
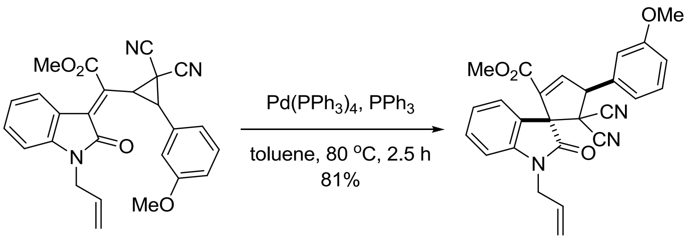
Example 4[10]



Example 5[11]

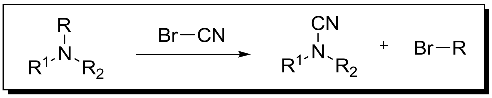


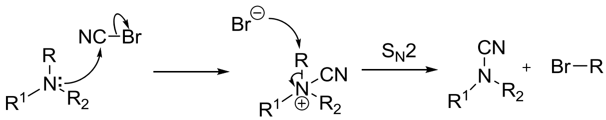
References

1. Brule, D.; Chalchat, J. C.; Garry, R. P.; Lacroix, B.; Michet, A.; Vessier, R. *Bull. Soc. Chim. Fr.* **1981,** *1–2,* 57–64.
2. Danheiser, R. L.; Bronson, J. J.; Okano, K. *J. Am. Chem. Soc*. **1985,** *107,* 4579–4581.
3. Hudlický, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985,** *33*, 247–335. (Review).
4. Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988,** *17*, 229–267. (Review).
5. Sonawane, H. R.; Bellur, N. S.; Kulkarni, D. G.; Ahuja, J. R. *Synlett* **1993,** 875–884. (Review).
6. Hiroi, K.; Arinaga, Y. *Tetrahedron Lett.* **1994,** *35*, 153–156.
7. Baldwin, J. E. *Chem. Rev.* **2003,** *103*, 1197–1212. (Review).
8. Wang, S. C.; Tantillo, D. J. *J. Organomet. Chem.* **2006,** *691*, 4386–4392.
9. Zhang, F.; Kulesza, A.; Rani, S.; Bernet, B.; Vasella, A. *Helv. Chim. Acta* **2008,** *91*, 1201–1218.
10. Coscia, R. W.; Lambert, T. H. *J. Am. Chem. Soc*. **2009,** *131*, 2496–2498.
11. Lingam, K. A. P.; Shanmugam, P. *Tetrahedron Lett.* **2013,** *32*, 4202–4206.

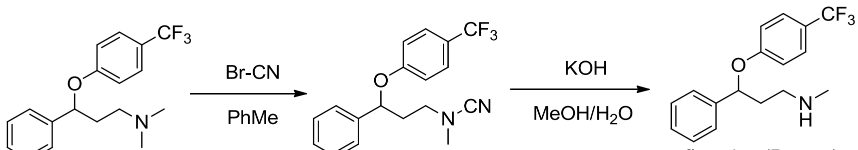
von Braun reaction

Different from the von Braun degradation reaction (amide to nitrile), the von Braun reaction refers to the treatment of tertiary amines with cyanogen bromide, resulting in a substituted cyanamide.



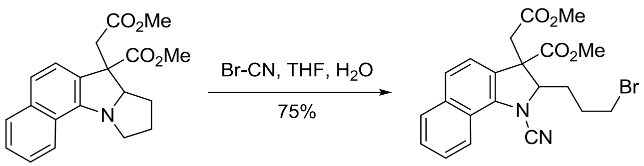


Example 1[4]



floxetine (Prozac)

Example 2[5]



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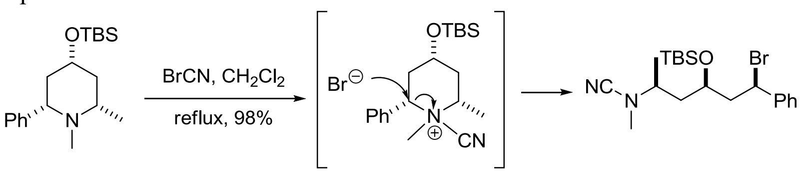

References

1. von Braun, J. *Ber.* **1907,** *40*, 3914–3933. Julius von Braun (1875–1940), born in Warsaw, Poland, was a Professor of Chemistry at Frankfurt.
2. Hageman, H. A. *Org. React.* **1953,** *7*, 198–262. (Review).
3. Fodor, G.; Nagubandi, S. *Tetrahedron* **1980,** *36*, 1279–1300. (Review).
4. Mody, S. B.; Mehta, B. P.; Udani, K. L.; Patel, M. V.; Mahajan, Rajendra N.. Indian Patent IN177159 (1996).
5. McLean, S.; Reynolds, W. F.; Zhu, X. *Can. J. Chem.* **1987,** *65*, 200–204.
6. Chambert, S.; Thomasson, F.; Décout, J.-L. *J. Org. Chem.* **2002,** *67*, 1898–1904.
7. Hatsuda, M.; Seki, M. *Tetrahedron* **2005,** *61*, 9908–9917.
8. Thavaneswaran, S.; McCamley, K.; Scammells, P. J. *Nat. Prod. Commun.* **2006,** *1*, 885–897. (Review).
9. McCall, W. S.; Abad Grillo, T.; Comins, D. L. *Org. Lett.* **2008,** *10*, 3255–3257.
10. Tayama, E.; Sato, R.; Ito, M.; Iwamoto, H.; Hasegawa, E. *Heterocycles* **2013,** *87*, 381–388.

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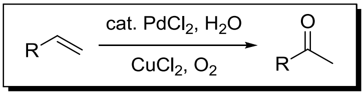
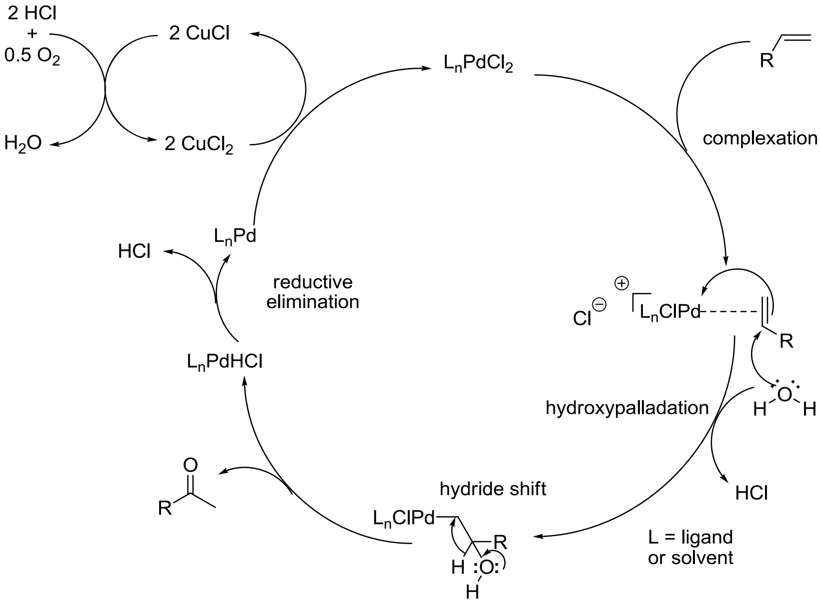
DOI 10.1007/978-3-319-03979-4_281,

Wacker oxidation

Palladium-catalyzed oxidation of olefins to ketones, and aldehydes in certain cases.





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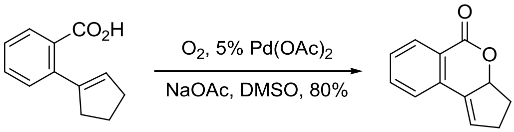

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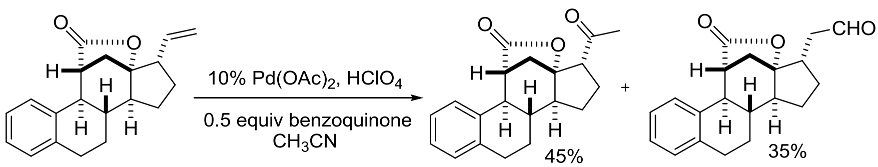

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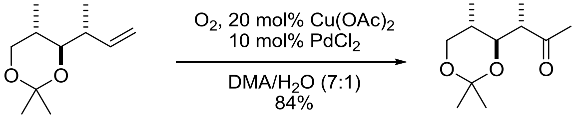

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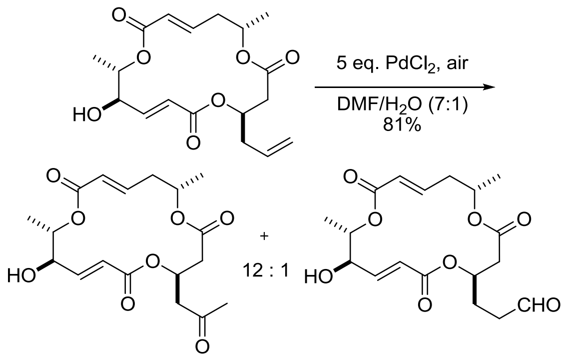
Example 4[10]



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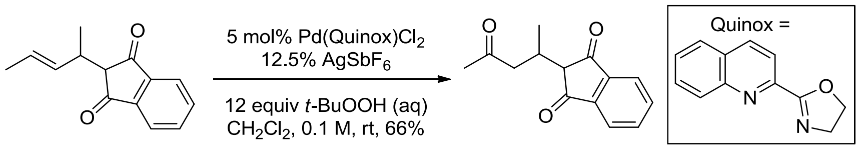
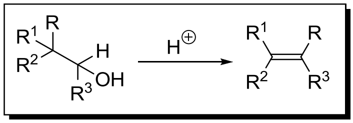


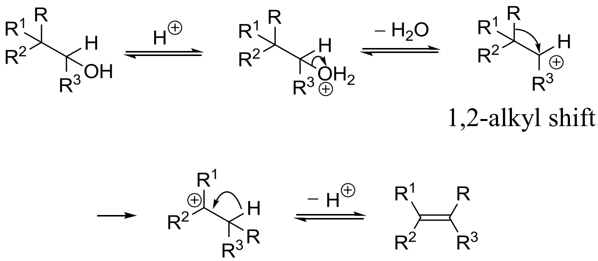
References

1. Smidt, J.; Sieber, R. *Angew. Chem. Int. Ed.* **1962,** *1*, 80–88. Wacker is not a person, but a place in Germany where Wacker Chemie developed this process. Since Hoechst AG later refined the reaction, this is sometimes called Hoechst–Wacker process.
2. Tsuji, J. *Synthesis* **1984,** 369–384. (Review).
3. Hegedus, L. S. In *Comp. Org. Syn.* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 4*, 552. (Review).
4. Tsuji, J. In *Comp. Org. Syn.* Trost, B. M.; Fleming, I., Eds.; Pergamon, **1991,** *Vol. 7*, 449. (Review).
5. Larock, R. C.; Hightower, T. R. *J. Org. Chem.* **1993,** *58*, 5298–5300.
6. Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecule* **1994,** University Science Books: Mill Valley, CA, pp 199–208. (Review).
7. Pellissier, H.; Michellys, P.-Y.; Santelli, M. *Tetrahedron* **1997,** *53,* 10733–10742.
8. Feringa, B. L. *Wacker oxidation*. In *Transition Met. Org. Synth*. Beller, M.; Bolm, C., eds.; Wiley–VCH: Weinheim, Germany. **1998,** *2*, 307–315. (Review).
9. Smith, A. B.; Friestad, G. K.; Barbosa, J.; Bertounesque, E.; Hull, K. G.; Iwashima, M.; Qiu, Y.; Salvatore, B. A.; Spoors, P. G.; Duan, J. J.-W. *J. Am. Chem. Soc.* **1999,** *121*, 10468–10477.
10. Kobayashi, Y.; Wang, Y.-G. *Tetrahedron Lett.* **2002,** *43,* 4381–4384.
11. Hintermann, L. *Wacker-type Oxidations* in *Transition Met. Org. Synth. (2nd edn.)* Beller, M.; Bolm, C., eds., Wiley–VCH: Weinheim, Germany. **2004,** *2*, pp 379–388. (Review).
12. Li, J. J. *Wacker–Tsuji oxidation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 309–326. (Review).
13. Okamoto, M.; Taniguchi, Y. *J. Cat.* **2009,** *261,* 195–200.
14. DeLuca, R. J.; Edwards, J. L.; Steffens, L. D.; Michel, B. W.; Qiao, X.; Zhu, C.; Cook, S. P.; Sigman, M. S. *J. Org. Chem.* **2013,** *78,* 1682–1686.

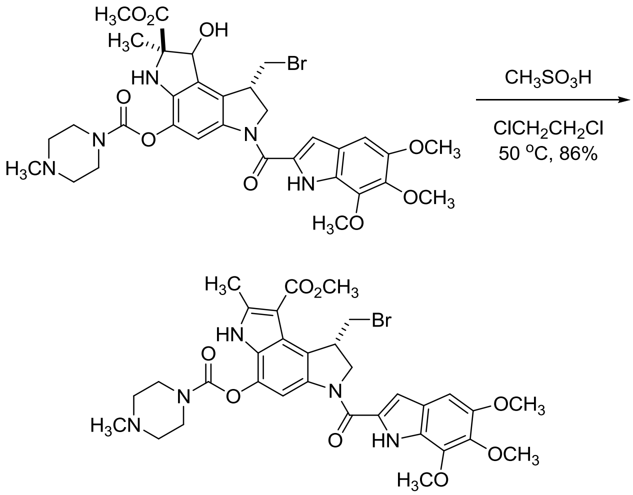
Wagner–Meerwein rearrangement

Acid-catalyzed alkyl group migration of alcohols to give more substituted olefins.





Example 1[3]



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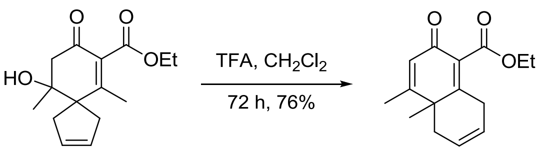

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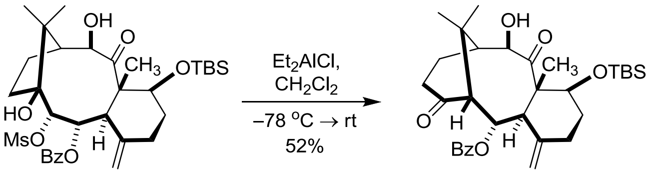
DOI 10.1007/978-3-319-03979-4_283,

Example 3[7]



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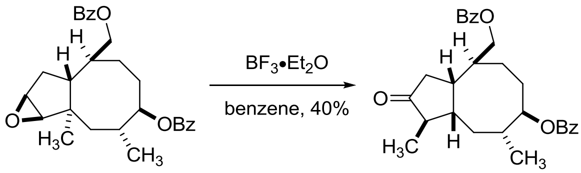
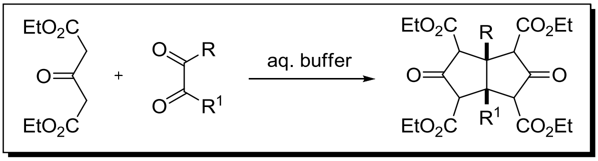


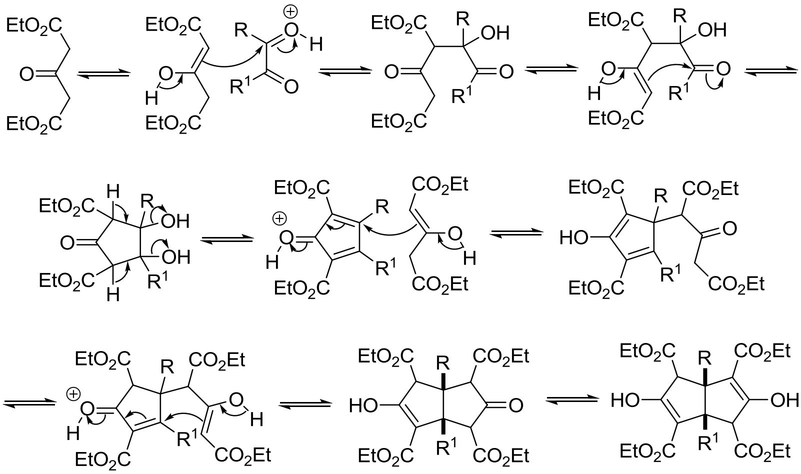
References

1. Wagner, G. *J. Russ. Phys. Chem. Soc.* **1899,** *31,* 690. Wagner first observed this rearrangement in 1899 and German chemist Hans Meerwein unveiled the mechanism in 1914.
2. Hogeveen, H.; Van Kruchten, E. M. G. A. *Top. Curr. Chem.* **1979,** *80,* 89–124. (Review).
3. Kinugawa, M.; Nagamura, S.; Sakaguchi, A.; Masuda, Y.; Saito, H.; Ogasa, T.; Kasai, M. *Org. Proc. Res. Dev.* **1998,** *2*, 344–350.
4. Trost, B. M.; Yasukata, T. *J. Am. Chem. Soc.* **2001,** *123,* 7162–7163.
5. Guizzardi, B.; Mella, M.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2003,** *68*, 1067–1074.
6. Bose, G.; Ullah, E.; Langer, P. *Chem. Eur. J.* **2004,** *10*, 6015–6028.
7. Guo, X.; Paquette, L. A. *J. Org. Chem.* **2005,** *70*, 315–320.
8. Li, W.-D. Z.; Yang, Y.-R. *Org. Lett.* **2005,** *7*, 3107–3110.
9. Michalak, K.; Michalak, M.; Wicha, J. *Molecules* **2005,** *10*, 1084–1100.
10. Mullins, R. J.; Grote, A. L. *Wagner–Meerwein Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 373–394. (Review).
11. Ghorpade, S.; Su, M.-D.; Liu, R.-S. *Angew. Chem. Int. Ed.* **2013,** *52*, 4229–4234.

Weiss–Cook condensation

Synthesis of *cis*-bicyclo[3.3.0]octane-3,7-dione. The product is frequently decarboxylated.





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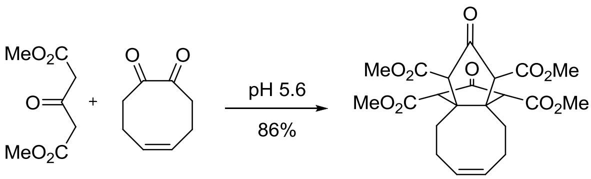

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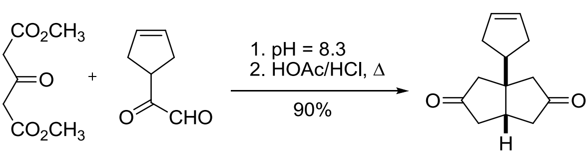

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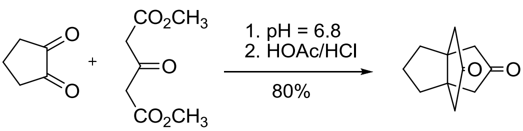

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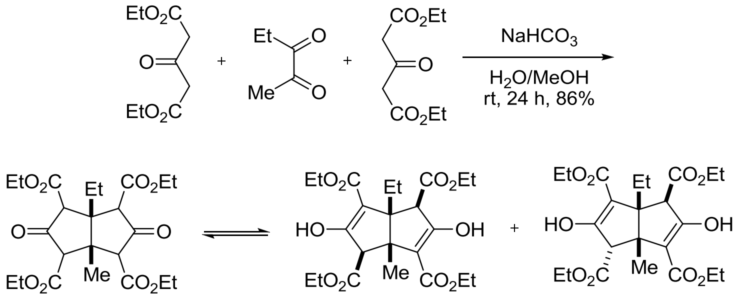
Example 4[9]

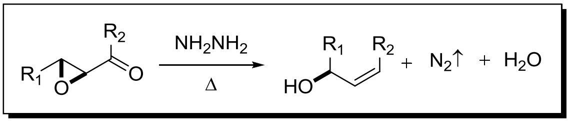


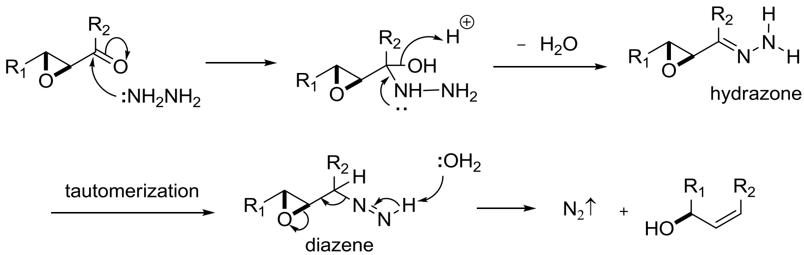
References

1. Weiss, U.; Edwards, J. M. *Tetrahedron Lett*. **1968,** *9*, 4885–4887. Weiss was a scientist at the National Institutte of Health in Bethesda, Maryland.
2. Bertz, S. H.; Cook, J. M.; Gawish, A.; Weiss, U. *Orga. Synth*. **1986,** *64*, 27–38. James M. Cook is a professor at University of Wisconsin, Milwaukee.
3. Kubiak, G.; Fu, X.; Gupta, A. K.; Cook, J. M. *Tetrahedron Lett*. **1990,** *31*, 4285–4288.
4. Wrobel, J.; Takahashi, K.; Honkan, V.; Lannoye, G.; Bertz, S. H.; Cook, J. M. *J. Org Chem*. **1983,** *48*, 139–141.
5. Gupta, A. K.; Fu, X.; Snyder, J. P.; Cook, J. M. *Tetrahedron* **1991,** *47*, 3665–3710.
6. Paquette, L. A.; Kesselmayer, M. A.; Underiner, G. E.; House, S. D.; Rogers, R. D.; Meerholz, K.; Heinze, J. *J. Am. Chem. Soc.* **1992,** *114*, 2644–2652.
7. Fu, X.; Cook, J. M. *Aldrichimica Acta* **1992,** *25*, 43–54. (Review).
8. Fu, X.; Kubiak, G.; Zhang, W.; Han, W.; Gupta, A. K.; Cook, J. M. *Tetrahedron* **1993,** *49*, 1511–1518.
9. Williams, R. V.; Gadgil, V. R.; Vij, As.; Cook, J. M.; Kubiak, G.; Huang, Q. *J. Chem. Soc., Perkin Trans. 1* **1997,** 1425–1428.
10. van Ornum, S. G.; Li, J.; Kubiak, G. G.; Cook, J. M. *J. Chem. Soc., Perkin Trans. 1* **1997,** 3471–3478.
11. Galatsis, P. *Weiss–Cook Reaction*, In Name Reactions for Carbocyclic Ring Formations, Li, J. J., Ed.; Wiley: Hoboken, NJ, 2010, pp 181–196. (Review).

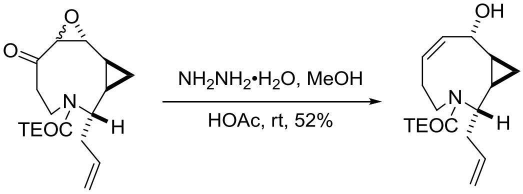
Wharton reaction

Reduction of α,β-epoxy ketones by hydrazine to allylic alcohols.

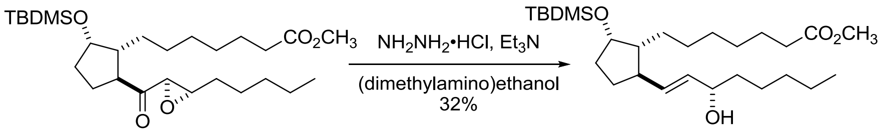




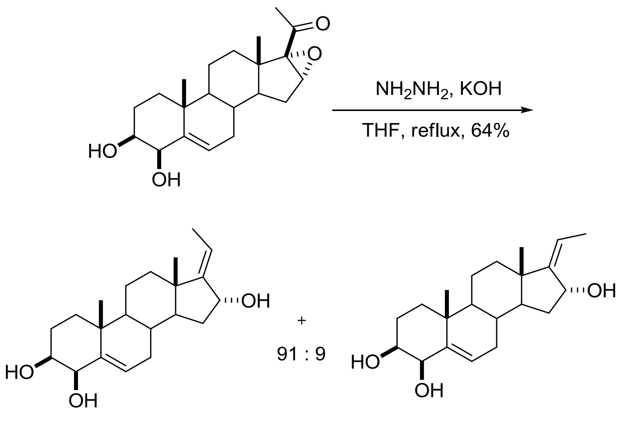
Example 1[5]



Example 2[6]



Example 3[7]



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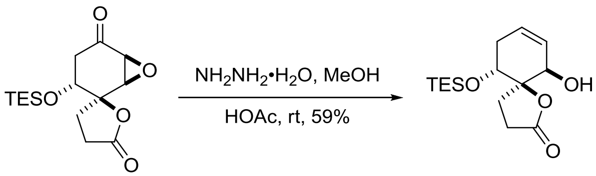
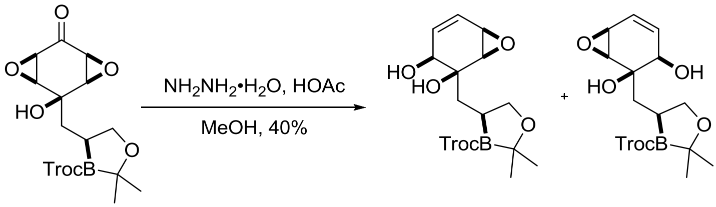
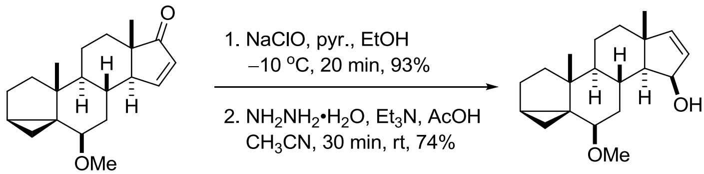
Example 4[8]



Example 5[10]



Example 6[11]

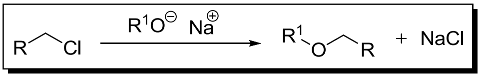


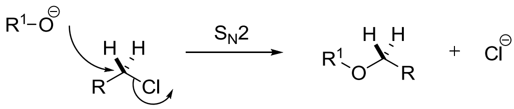
References

1. (a) Wharton, P. S.; Bohlen, D. H. *J. Org. Chem*. **1961,** *26*, 3615–3616. (b) Wharton, P. S. *J. Org. Chem*. **1961,** *26*, 4781–4782. Peter S. Wharton earned his Ph.D. at Yale University under the tutelage of Harry H. Wasserman and began his independent academia career at University of Wisconsin at Madison. This was his first paper out of graduate school!
2. Caine, D. *Org. Prep. Proced. Int.* **1988,** *20*, 1–51. (Review).
3. Dupuy, C.; Luche, J. L. *Tetrahedron* **1989,** *45*, 3437–3444. (Review).
4. Thomas, A. F.; Di Giorgio, R.; Guntern, O. *Helv. Chim. Acta* **1989,** *72*, 767–773.
5. Kim, G.; Chu-Moyer, M. Y.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1990,** *112*, 2003–2004.
6. Yamada, K.-i.; Arai, T.; Sasai, H.; Shibasaki, M. *J. Org. Chem*. **1998,** *63*, 3666–3672.
7. Di Filippo, M.; Fezza, F.; Izzo, I.; De Riccardis, F.; Sodano, G. *Eur. J. Org. Chem*. **2000,** 3247–3249.
8. Takagi, R.; Tojo, K.; Iwata, M.; Ohkata, K. *Org. Biomol. Chem*. **2005,** *3,* 2031–2036.
9. Li, J. J. *Wharton Reaction*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 152–158. (Review).
10. Hoye, T. R.; Jeffrey, C. S.; Nelson, D. P. *Org. Lett.* **2010,** *12*, 52–55.
11. Isaka, N.; Tamiya, M.; Hasegawa, A.; Ishiguro, M. *Eur. J. Org. Chem*. **2012,** 665–668.

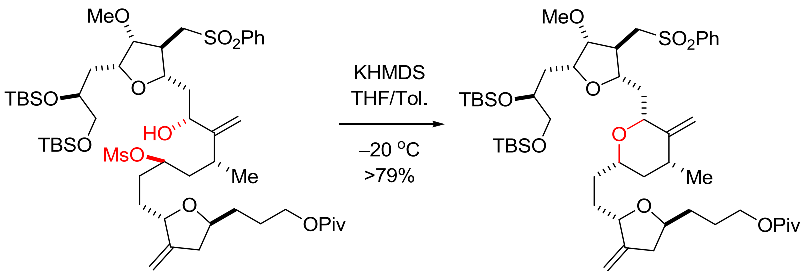
Williamson ether synthesis

Ether from the alkylation of alkoxides by alkyl halides. In order for reaction to go smoothly, the alkyl halides are preferred to be primary. Secondary halides work as well sometimes, but tertiary halides do not work at all because E_2 elimination will be the predominant reaction pathway.





Example 1, Cyclic etherification[9]



References

1. Williamson, A. W. *J. Chem. Soc.* **1852,** *4,* 229–239. Alexander William Williamson (1824–1904) discovered this reaction in 1850 at University College, London.
2. Dermer, O. C. *Chem. Rev.* **1934,** *14,* 385–430. (Review).
3. Freedman, H. H.; Dubois, R. A. *Tetrahedron Lett*. **1975,** *16*, 3251–3254.
4. Jursic, B. *Tetrahedron* **1988,** *44*, 6677–6680.
5. Tan, S. N.; Dryfe, R. A.; Girault, H. H. *Helv. Chim. Acta* **1994,** *77*, 231–242.
6. Silva, A. L.; Quiroz, B.; Maldonado, L. A. *Tetrahedron Lett*. **1998,** *39*, 2055–2058.
7. Peng, Y.; Song, G. *Green Chem.* **2002,** *4,* 349–351.
8. Stabile, R. G.; Dicks, A. P. *J. Chem. Educ.* **2003,** *80,* 313–315.
9. Austad, B. C.; Benayoud, F.; Calkins, T. L.; et al. *Synlett* **2013,** *17*, 327–332.

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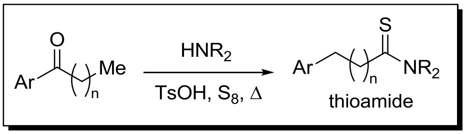
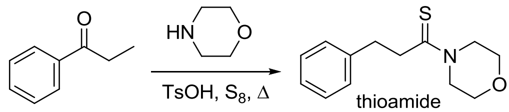
DOI 10.1007/978-3-319-03979-4_286,

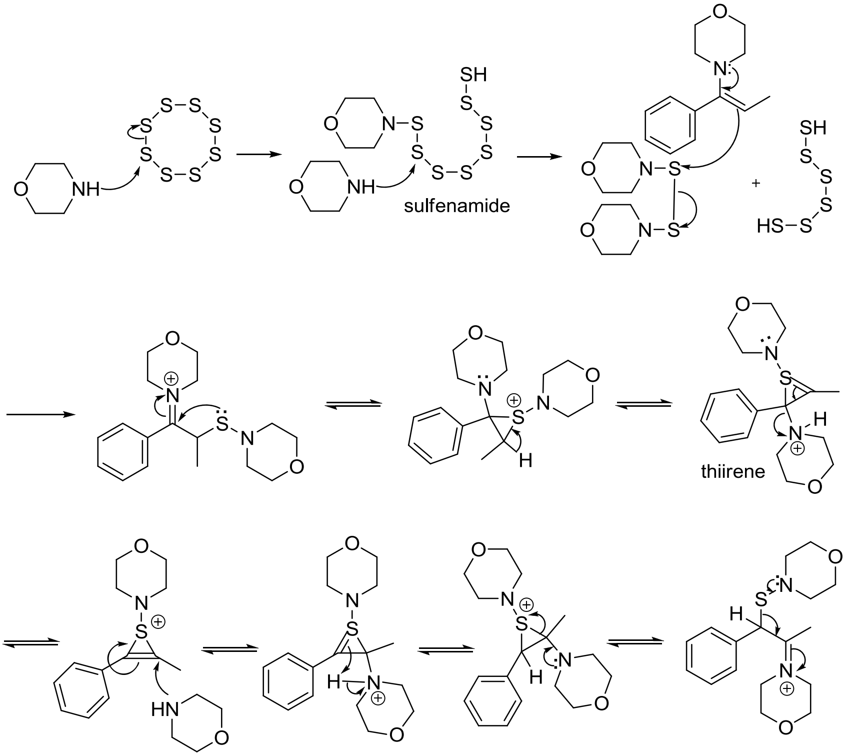
Willgerodt–Kindler reaction

Conversion of a ketone to thioamide, with functional group migration.



In Carmack's mechanism,[2] the most unusual movement of a carbonyl group from methylene carbon to methylene carbon was proposed to go through an intricate pathway *via* a highly reactive intermediate with a sulfur-containing heterocyclic ring. The sulfenamide serves as the isomerization catalyst. e.g.:





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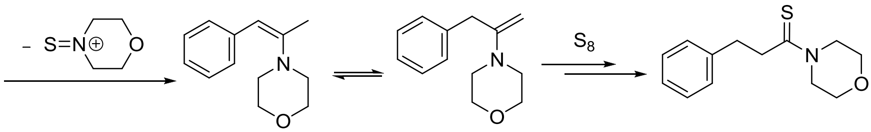
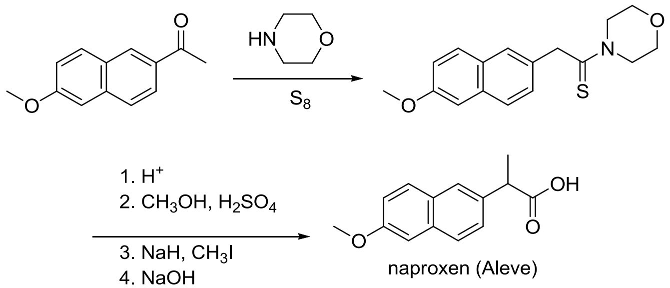
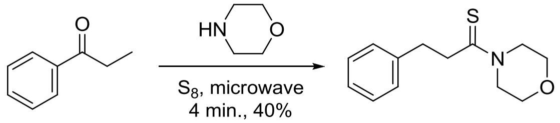
DOI 10.1007/978-3-319-03979-4_287, © Springer International Publishing Switzerland 2014



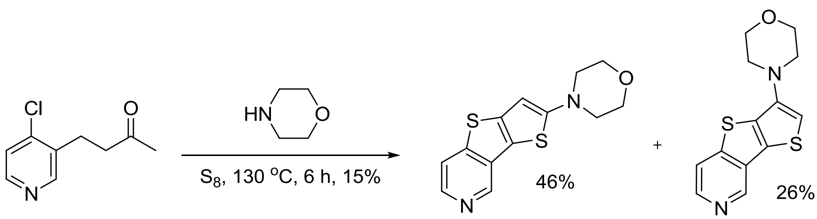
Example 1, The Willgerodt–Kindler reaction was a key operation in the initial synthesis of racemic naproxen (Aleve):[3]



Example 2[5]



Example 3, A domino annulation reaction under Willgerodt–Kindler conditions:[10]



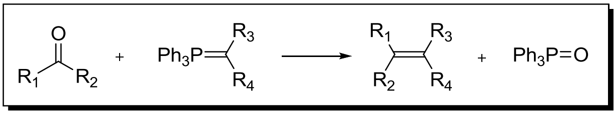
References

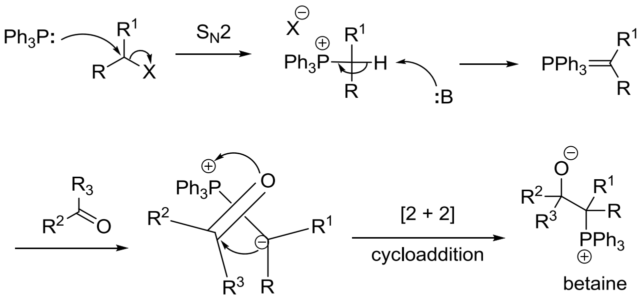
1. (a) Willgerodt, C. *Ber.* **1887,** *20*, 2467–2470. Conrad Willgerodt (1841–1930), born in Harlingerode, Germany, was a son of a farmer. He worked to accumulate enough money to support his study toward his doctorate, which he received from Claus. He became a professor at Freiburg, where he taught for 37 years. (b) Kindler, K. *Arch. Pharm.* **1927,** *265,* 389–415.
2. Carmack, M.; Spielman, M. A. *Org. React.* **1946,** *3,* 83–107. (Review).
3. Harrison, I. T.; Lewis, B.; Nelson, P.; Rooks, W.; Roskowski, A.; Tomolonis, A.; Fried, J. H. *J. Med. Chem.* **1970,** *13,* 203–205.
4. Carmack, M. *J. Heterocycl. Chem.* **1989,** *26,* 1319–1323.

5. Nooshabadi, M.; Aghapoor, K.; Darabi, H. R.; Mojtahedi, M. M. *Tetrahedron Lett.* **1999,** *40*, 7549–7552.
6. Alam, M. M.; Adapa, S. R. *Synth. Commun.* **2003,** *33,* 59–63.
7. Reza Darabi, H.; Aghapoor, K.; Tajbakhsh, M. *Tetrahedron Lett.* **2004,** *45*, 4167–4169.
8. Purrello, G. *Heterocycles* **2005,** *65*, 411–449. (Review).
9. Okamoto, K.; Yamamoto, T.; Kanbara, T. *Synlett* **2007,** 2687–2690.
10. Kadzimirsz, D.; Kramer, D.; Sripanom, L.; Oppel, I. M.; Rodziewicz, P.; Doltsinis, N. L.; Dyker, G. *J. Org. Chem*. **2008,** *73*, 4644–4649.
11. Eftekhari-Sis, B.; Khajeh, S. V.i; Büyükgüngör, O. *Synlett* **2013,** *24*, 977–980.

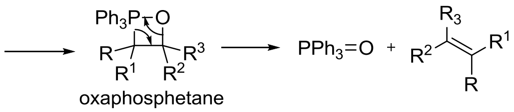
Wittig reaction

Olefination of carbonyls using phosphorus ylides, typically the *Z*-olefin is obtained.

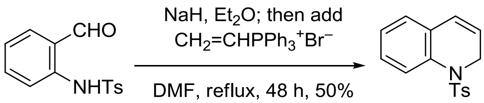




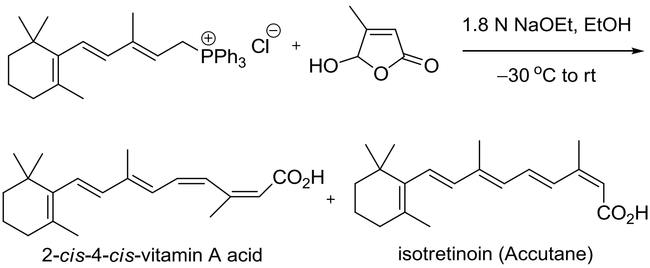
The "puckered" transition state, irreversible and concerted



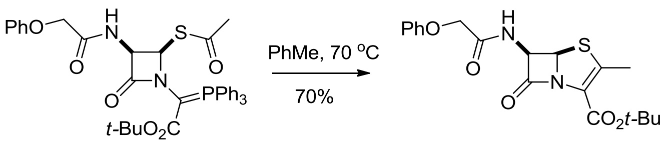
Example 1[3]



Example 2[4]



Example 3[5]



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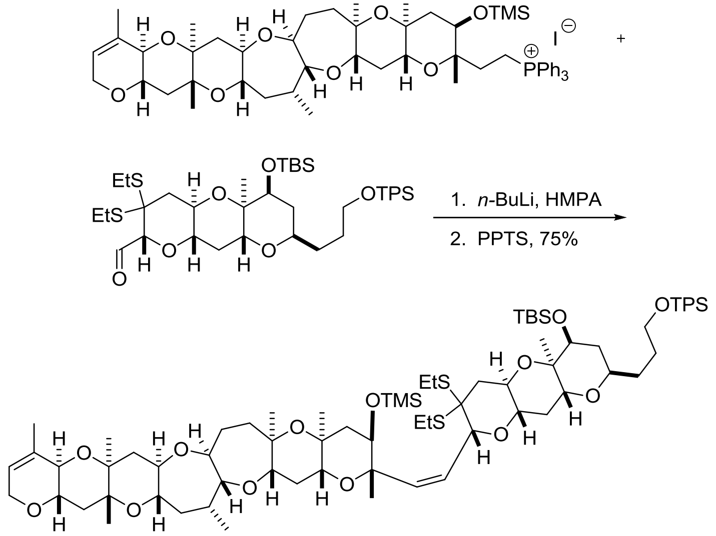
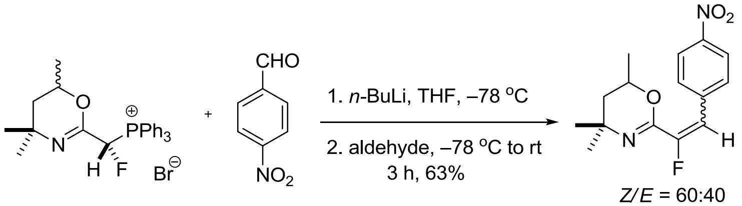
DOI 10.1007/978-3-319-03979-4_288, © Springer International Publishing Switzerland 2014

Example 4[9]



Example 5[11]

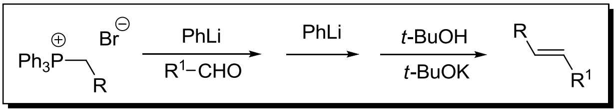


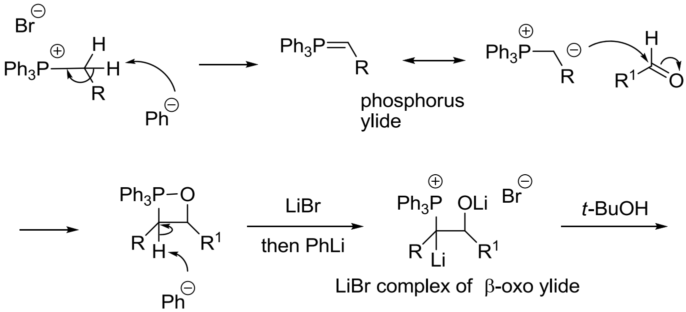
References

1. Wittig, G.; Schöllkopf, U. *Ber.* **1954,** *87*, 1318–1330. Georg Wittig (Germany, 1897–1987), born in Berlin, Germany, received his Ph.D. from K. von Auwers. He shared the Nobel Prize in Chemistry in 1981 with Herbert C. Brown (USA, 1912–2004) for their development of organic boron and phosphorous compounds.
2. Maercker, A. *Org. React.* **1965,** *14,* 270–490. (Review).
3. Schweizer, E. E.; Smucker, L. D. *J. Org. Chem.* **1966,** *31*, 3146–3149.
4. Garbers, C. F.; Schneider, D. F.; van der Merwe, J. P. *J. Chem. Soc. (C)* **1968,** 1982–1983.
5. Ernest, I.; Gosteli, J.; Greengrass, C. W.; Holick, W.; Jackman, D. E.; Pfaendler, H. R.; Woodward, R. B. *J. Am. Chem. Soc.* **1978,** *100*, 8214–8222.
6. Murphy, P. J.; Brennan, J. *Chem. Soc. Rev.* **1988,** *17,* 1–30. (Review).
7. Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1988,** *89,* 863–927. (Review).
8. Vedejs, E.; Peterson, M. J. *Top. Stereochem.* **1994,** *21,* 1–157. (Review).
9. Nicolaou, K. C. *Angew. Chem. Int. Ed.* **1996,** *35*, 589–607.
10. Rong, F. *Wittig reaction* in. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 588–612. (Review).
11. Kajjout, M.; Smietana, M.; Leroy, J.; Rolando, C. *Tetrahedron Lett.* **2013,** *38*, 1658–1660.

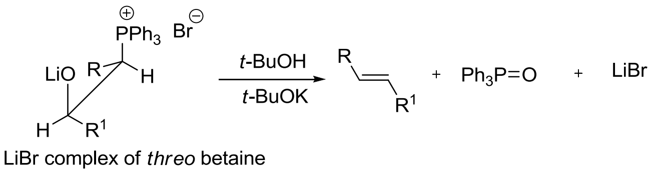
Schlosser modification of the Wittig reaction

Also known as the Wittig–Schlosser reaction. The normal Wittig reaction of nonstabilized ylides with aldehydes gives *Z*-olefins. The Schlosser modification of the Wittig reaction of nonstabilized ylides furnishes *E*-olefins instead.

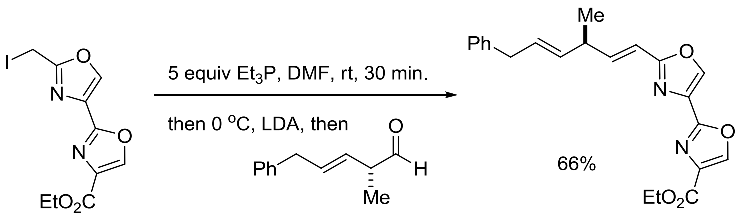




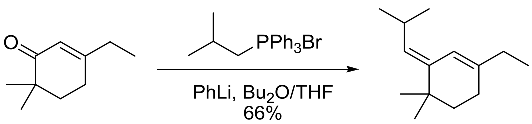
These conditions allow for the *erythreo* betaine to interconvert to the *threo* betaine



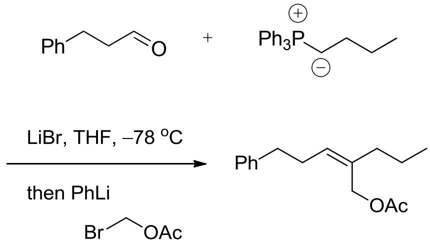
Example 1[6]



Example 2[10]



Example 3[11]

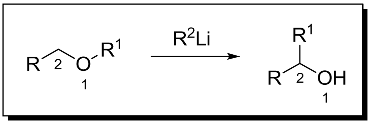


References

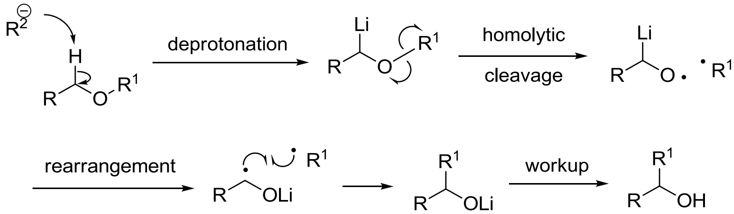
1. (a) Schlosser, M.; Christmann, K. F. *Angew. Chem. Int. Ed.* **1966,** *5*, 126. (b) Schlosser, M.; Christmann, K. F. *Ann.* **1967,** *708*, 1–35. (c) Schlosser, M.; Christmann, K. F.; Piskala, A.; Coffinet, D. *Synthesis* **1971,** 29–31. Born in Ludwigshafen on Rhine (Germany), Manfred Schlosser earned his Ph.D. in 1960 under Georg Wittig. He intiailly worked at at the German Cancer Research Center and moved to France to be a professor at the University of Lausanne. Schlosser retired in 2004.
2. van Tamelen, E. E.; Leiden, T. M. *J. Am. Chem. Soc.* **1982,** *104*, 2061–2062.
3. Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* **1991,** *113*, 4595–606.
4. Sarkar, T. K.; Ghosh, S. K.; Rao, P. S.; Satapathi, T. K.; Mamdapur, V. R. *Tetrahedron* **1992,** *48,* 6897–6908.
5. Deagostino, A.; Prandi, C.; Tonachini, G.; Venturello, P. *Trends Org. Chem.* **1995,** *5*, 103–113. (Review).
6. Celatka, C. A.; Liu, P.; Panek, J. S. *Tetrahedron Lett.* **1997,** *38*, 5449–5452.
7. Panek, J. S.; Liu, P. *J. Am. Chem. Soc.* **2000,** *122* 11090–11097.
8. Duffield, J. J.; Pettit, G. R. *J. Nat. Prod.* **2001,** *64*, 472–479.
9. Kraft, P.; Popaj, K. *Eur. J. Org. Chem.* **2004,** 4995–5002.
10. Kraft, P.; Popaj, K. *Eur. J. Org. Chem.* **2008,** 4806–4814.
11. Hodgson, D. M.; Arif, T. *Org. Lett.* **2010,** *12*, 4204–4207.
12. Mikula, H.; Hametner, C.; Froehlich, J. *Synth. Commun.* **2013,** *43*, 1939–1946.

[1,2]-Wittig rearrangement

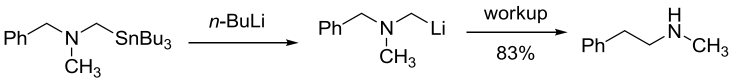
Treatment of ethers with bases such as alkyl lithium results in alcohols.



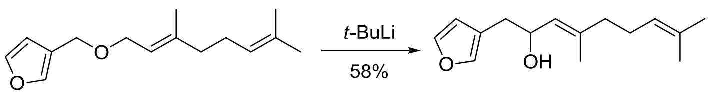
The [1,2]-Wittig rearrangement is believed to proceed via a radical mechanism:



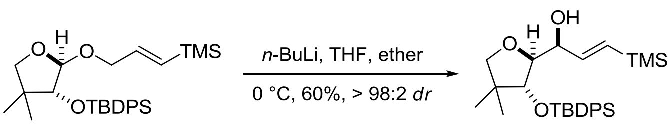
Example 1, Aza [1,2]-Wittig rearrangement[2]



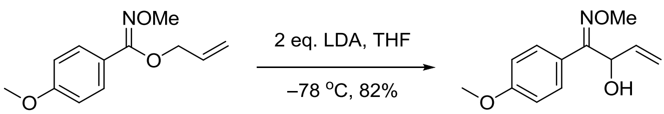
Example 2[3]



Example 3[4]



Example 4[6]



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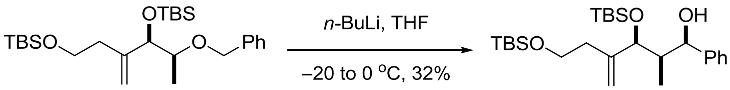
DOI 10.1007/978-3-319-03979-4_289,

Example 5[8]



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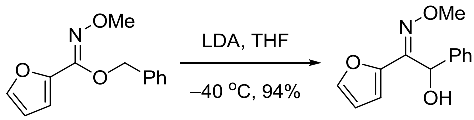
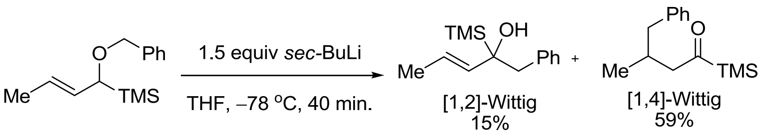


Example 7[11]

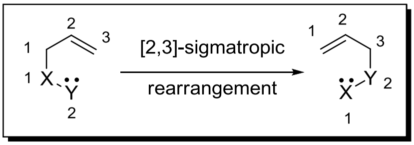


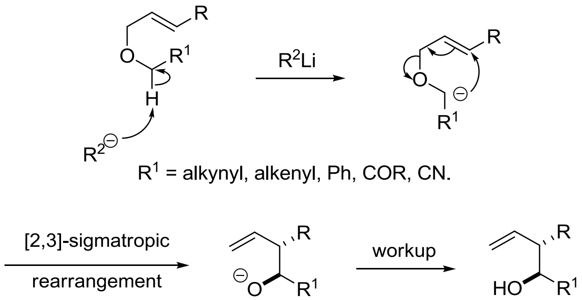
References

1 Wittig, G.; Löhmann, L. *Ann.* **1942,** *550*, 260–268.
2 Peterson, D. J.; Ward, J. F. *J. Organomet. Chem.* **1974,** *66*, 209–217.
3 Tsubuki, M.; Okita, H.; Honda, T. *J. Chem. Soc., Chem. Commun.* **1995,** 2135–2136.
4 Tomooka, K.; Yamamoto, H.; Nakai, T. *J. Am. Chem. Soc.* **1996,** *118*, 3317–3318.
5 Maleczka, R. E., Jr.; Geng, F. *J. Am. Chem. Soc*. **1998,** *120*, 8551–8552.
6 Miyata, O.; Asai, H.; Naito, T. *Synlett* **1999,** 1915–1916.
7 Katritzky, A. R.; Fang, Y. *Heterocycles* **2000,** *53*, 1783–1788.
8 Tomooka, K.; Kikuchi, M.; Igawa, K.; Suzuki, M.; Keong, P.-H.; Nakai, T. *Angew. Chem. Int. Ed.* **2000,** *39*, 4502–4505.
9 Miyata, O.; Asai, H.; Naito, T. *Chem. Pharm. Bull.* **2005,** *53*, 355–360.
10 Wolfe, J. P.; Guthrie, N. J. *[1,2]-Wittig Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 226–240. (Review).
11 Onyeozili, E. N.; Mori-Quiroz, L. M.; Maleczka, R. E., Jr. *Tetrahedron* **2013,** *69*, 849–860.

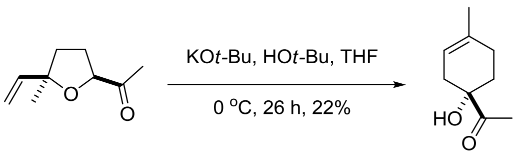
[2,3]-Wittig rearrangement

Transformation of allyl ethers into homoallylic alcohols by treatment with base. Also known as the Still–Wittig rearrangement. *Cf.* Sommelet–Hauser rearrangement.

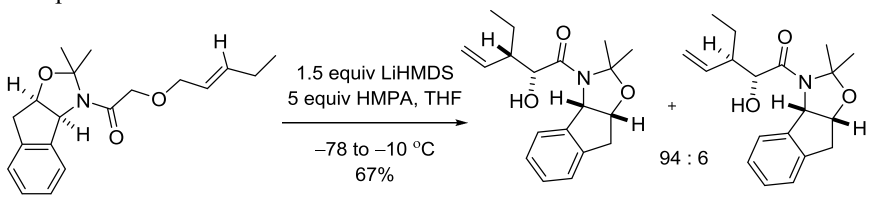




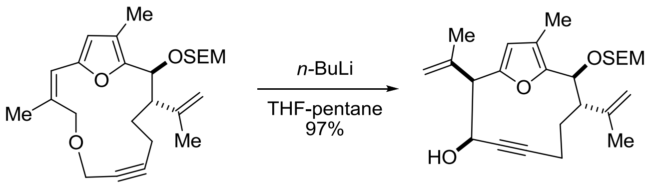
Example 1[3]



Example 2[5]



Example 3[6]



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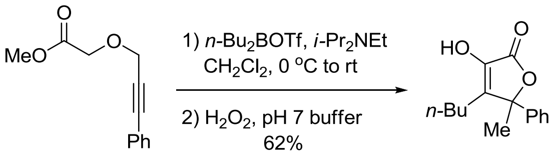
Example 4, Tandem Wittig rearrangement/alkylative cyclization reactions[6]

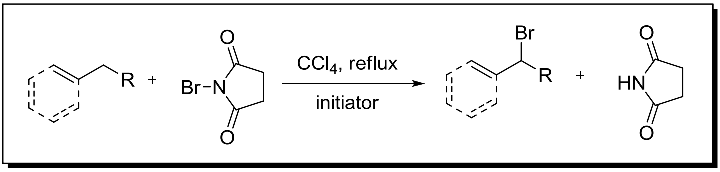


References

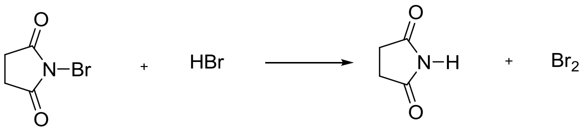
1. Cast, J.; Stevens, T. S.; Holmes, J. *J. Chem. Soc.* **1960,** 3521–3527.
2. Thomas, A. F.; Dubini, R. *Helv. Chim. Acta* **1974,** *57*, 2084–2087.
3. Nakai, T.; Mikami, K.; Taya, S.; Kimura, Y.; Mimura, T. *Tetrahedron Lett.* **1981,** *22*, 69–72.
4. Nakai, T.; Mikami, K. *Org. React.* **1994,** *46*, 105–209. (Review).
5. Kress, M. H.; Yang, C.; Yasuda, N.; Grabowski, E. J. J. *Tetrahedron Lett*. **1997,** *38*, 2633–2636.
6. Marshall, J. A.; Liao, J. *J. Org. Chem*. **1998,** *63*, 5962–5970.
7. Maleczka, R. E., Jr.; Geng, F. *Org. Lett*. **1999,** *1*, 1111–1113.
8. Tsubuki, M.; Kamata, T.; Nakatani, M.; Yamazaki, K.; Matsui, T.; Honda, T. *Tetrahedron: Asymmetry* **2000,** *11*, 4725–4736.
9. Schaudt, M.; Blechert, S. *J. Org. Chem.* **2003,** *68*, 2913–2920.
10. Ahmad, N. M. *[2,3]-Wittig Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, 2009, pp 241–256. (Review).
11. Everett, R. K.; Wolfe, J. P. *Org. Lett*. **2013,** *15*, 2926–2929.

Wohl–Ziegler reaction

The Wohl–Ziegler reaction is the reaction of an allylic or benzylic substrate with *N*-bromosuccinimide (NBS) under radical initiating conditions to provide the corresponding allylic or benzylic bromide. Conditions used to promote the radical reaction are typically radical initiators, light and/or heat; carbon tetrachloride (CCl_4) is typically utilized as the solvent.

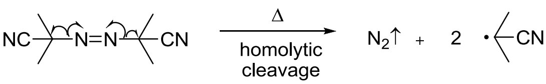


N-Bromosuccinimide (NBS) contains a small amount of HBr from the reaction between NBS and moisture. The minute amount of HBr, in turn, reacts with NBS to provide a low, constant concentration of Br_2. Moreover, NBS reacts with the HBr by-product to produce Br_2 and to prevent HBr addition across the double bond.

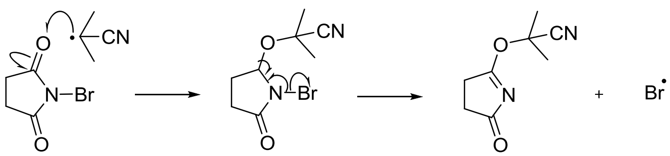


N-bromosuccinimide (NBS) succinimide

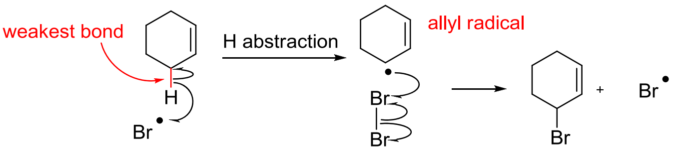
Initiation:



2,2′-azobisisobutyronitrile (AIBN)

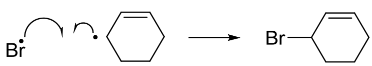


Propagation:



The bromine radical is now available for the next cycle of the radical chain reaction.

Termination:



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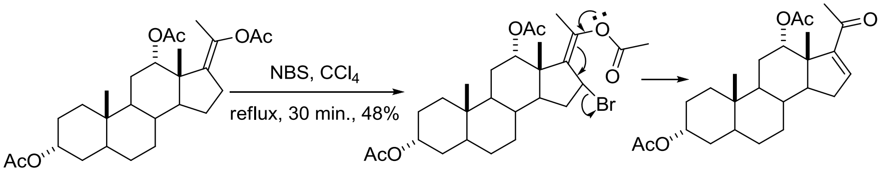
Example 1[3]



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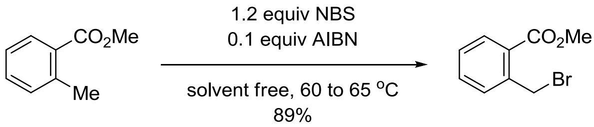
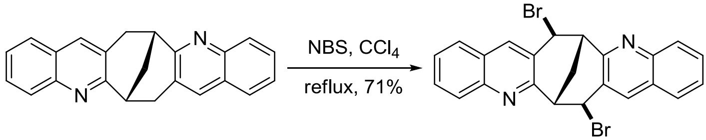
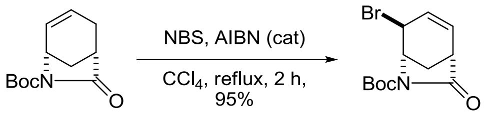


Example 3[8]



Example 4[9]

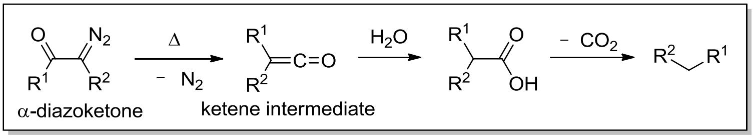


References

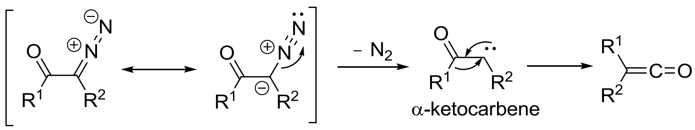
1. Wohl, A. *Ber.* **1919,** *52*, 51–63. Alfred Wohl (1863–1939), born in Graudenz, Germany, received his Ph.D. from A. W. Hofmann. In 1904, he was appointed Professor of Chemistry at the Technische Hochschule in Danzig.
2. Ziegler, K.; Spath, A.; Schaaf, E.; Schumann, W.; Winkelmann, E. *Ann.* **1942,** *551*, 80–119. Karl Ziegler (1898–1973), born in Helsa, Germany, received Ph.D. in 1920 from von Auwers at the University of Marburg. He became the director of the Max-Planck-Institut für Kohlenforschung at Mülheim/Ruhr in 1943 and stayed there until 1969. He shared the Nobel Prize in Chemistry in 1963 with Giulio Natta (1903–1979) for their work in polymer chemistry. The Ziegler–Natta catalyst is widely used in polymerization.
3. Djerassi, C.; Scholz, C. R. *J. Org. Chem.* **1949,** *14*, 660–663.
4. Allen, J. G.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2001,** *123*, 351–352.
5. Detterbeck, R.; Hesse, M. *Tetrahedron Lett.* **2002,** *43*, 4609–4612.
6. Stevens, C. V.; Van Heecke, G.; Barbero, C.; Patora, K.; De Kimpe, N.; Verhe, R. *Synlett* **2002,** 1089–1092.
7. Togo, H.; Hirai, T. *Synlett* **2003,** 702–704.
8. Marjo, C. E.; Bishop, R.; Craig, D. C.; Scudder, M. L. *Mendeleev Commun.* **2004,** 278–279.
9. Yeung, Y.-Y.; Hong, S.; Corey, E. J. *J. Am. Chem. Soc.* **2006,** *128*, 6310–6311.
10. Curran, T. T. *Wohl–Ziegler reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 661–674. (Review).
11. Tsuchiya, D.; Kawagoe, Y.; Moriyama, K.; Togo, H. *Org. Lett.* **2013,** *15*, 4194–4197.

Wolff rearrangement

Conversion of an α-diazoketone into a ketene.

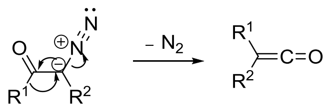


Step-wise mechanism:



Treatment of the ketene with water would give the corresponding homologated carboxylic acid.

Concerted mechanism:



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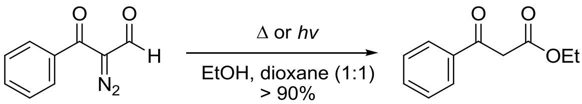
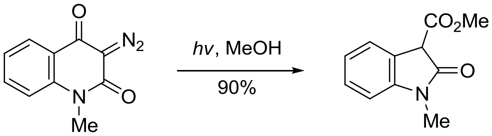


Example 2[3]



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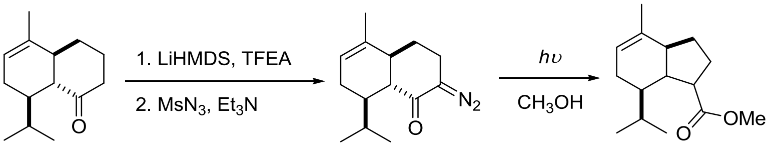

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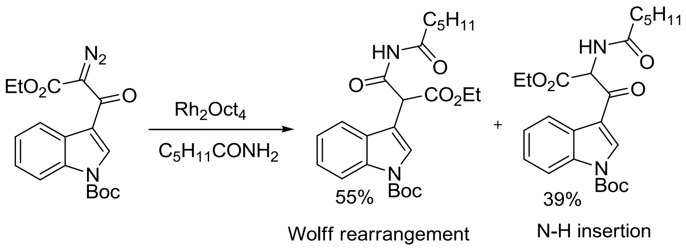
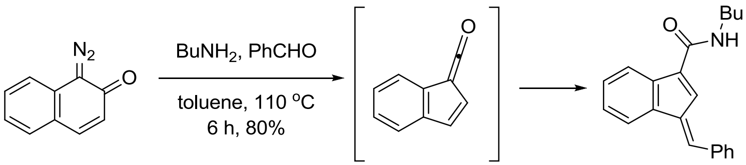
Example 4[9]



Example 5[11]

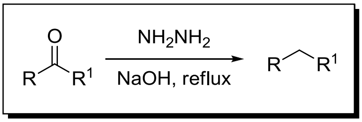


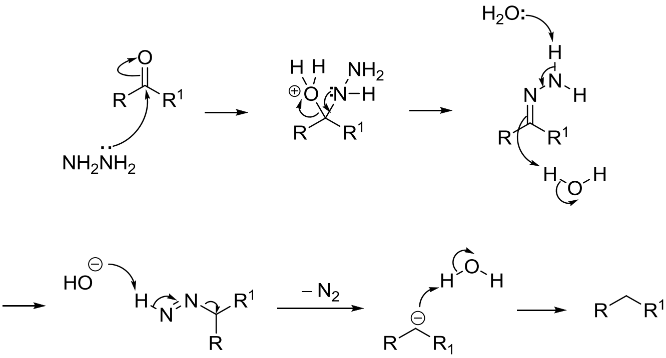
References

1. Wolff, L. *Ann.* **1912,** *394*, 23–108. Johann Ludwig Wolff (1857–1919) earned his doctorate in 1882 under Fittig at Strasbourg, where he later became an instructor. In 1891, Wolff joined the faculty of Jena, where he collaborated with Knorr for 27 years.
2. Zeller, K.-P.; Meier, H.; Müller, E. *Tetrahedron* **1972,** *28,* 5831–5838.
3. Kappe, C.; Fäber, G.; Wentrup, C.; Kappe, T. *Ber.* **1993,** *126,* 2357–2360.
4. Taber, D. F.; Kong, S.; Malcolm, S. C. *J. Org. Chem.* **1998,** *63*, 7953–7956.
5. Yang, H.; Foster, K.; Stephenson, C. R. J.; Brown, W.; Roberts, E. *Org. Lett.* **2000,** *2,* 2177–2179.
6. Kirmse, W. "100 years of the Wolff Rearrangement" *Eur. J. Org. Chem.* **2002,** 2193–2256. (Review).
7. Julian, R. R.; May, J. A.; Stoltz, B. M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **2003,** *125*, 4478–4486.
8. Zeller, K.-P.; Blocher, A.; Haiss, P. *Mini-Reviews Org. Chem.* **2004,** *1*, 291–308. (Review).
9. Davies, J. R.; Kane, P. D.; Moody, C. J.; Slawin, A. M. Z. *J. Org. Chem.* **2005,** *70,* 5840–5851.
10. Kumar, R. R.; Balasubramanian, M. *Wolff Rearrangement*. In *Name Reactions for Homologations-Part II*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009,** pp 257–273. (Review).
11. Somai Magar, K. B.; Lee, Y. R. *Org. Lett.* **2013,** *15,* 4288–4291.

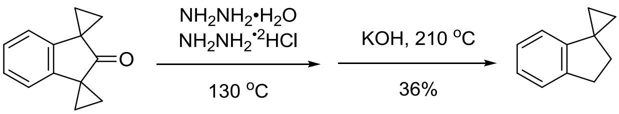
Wolff–Kishner reduction

Carbonyl reduction to methylene using basic hydrazine.

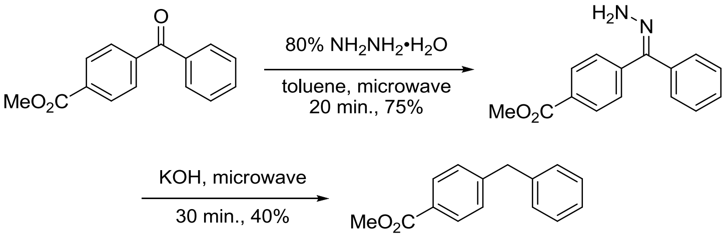




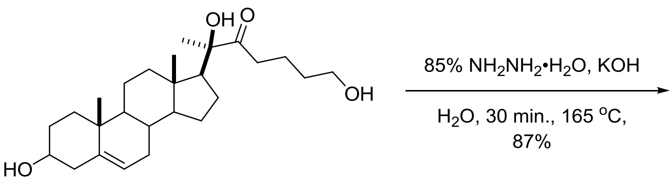
Example 1, The Huang Minlon modification, with loss of ethylene[5]



Example 2[7]



Example 3[8]



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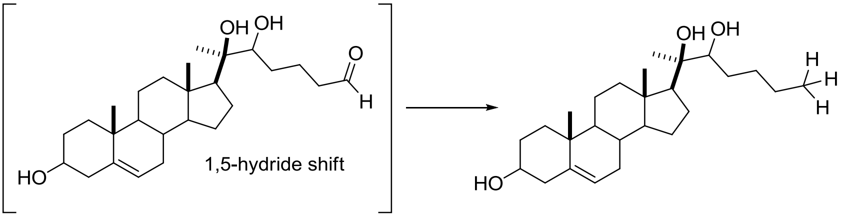
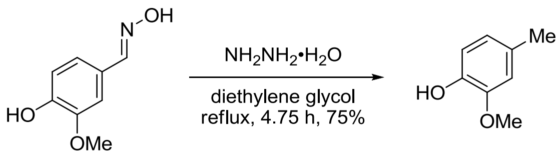
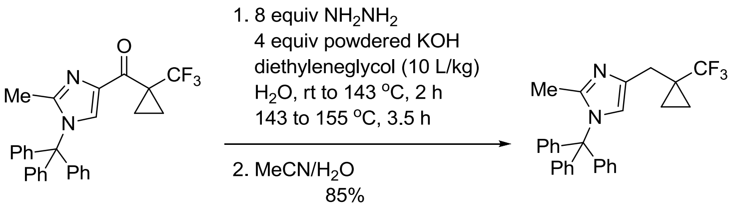


Example 4, Huang Minlon modification[10]



Example 3[13]

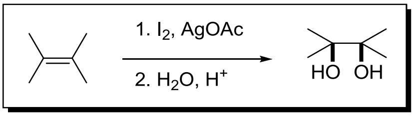


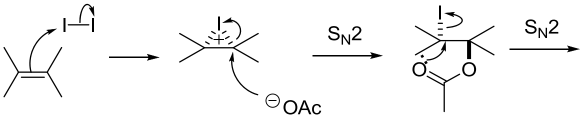
References

1. (a) Kishner, N. *J. Russ. Phys. Chem. Soc.* **1911,** *43,* 582–595. Nicolai Kishner was a Russian chemist. (b) Wolff, L. *Ann.* **1912,** *394*, 86. (c) Huang, Minlon *J. Am. Chem. Soc.* **1946,** *68*, 2487–2488. (d) Huang, Minlon *J. Am. Chem. Soc.* **1949,** *71*, 3301–3303. (The Huang Minlon modification).
2. Todd, D. *Org. React.* **1948,** *4*, 378–422. (Review).
3. Cram, D. J.; Sahyun, M. R. V.; Knox, G. R. *J. Am. Chem. Soc.* **1962,** *84*, 1734–1735.
4. Murray, R. K., Jr.; Babiak, K. A. *J. Org. Chem.* **1973,** *38*, 2556–2557.
5. Lemieux, R. P.; Beak, P. *Tetrahedron Lett.* **1989,** *30*, 1353–1356.
6. Taber, D. F.; Stachel, S. J. *Tetrahedron Lett.* **1992,** *33*, 903–906.
7. Gadhwal, S.; Baruah, M.; Sandhu, J. S. *Synlett* **1999,** 1573–1592.
8. Szendi, Z.; Forgó, P.; Tasi, G.; Böcskei, Z.; Nyerges, L.; Sweet, F. *Steroids* **2002,** *67*, 31–38.
9. Bashore, C. G.; Samardjiev, I. J.; Bordner, J.; Coe, J. W. *J. Am. Chem. Soc.* **2003,** *125*, 3268–3272.
10. Pasha, M. A. *Synth. Commun.* **2006,** *36*, 2183–2187.
11. Song, Y.-H.; Seo, J. *J. Heterocycl. Chem.* **2007,** *44*, 1439–1443.
12. Shibahara, M.; Watanabe, M.; Aso, K.; Shinmyozu, T. *Synthesis* **2008,** 3749–3754.
13. Kuethe, J. T.; Childers, K. G.; Peng, Z.; Journet, M.; Humphrey, G. R.; Vickery, T.; Bachert, D.; Lam, T. T. *Org. Process Res. Dev.* **2009,** *13*, 576–580.

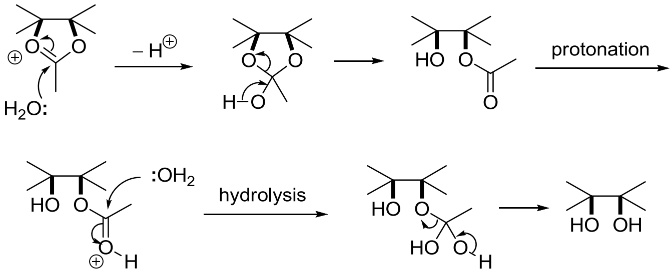
Woodward *cis*-dihydroxylation

Cf. Prévost *trans*-dihydroxylation.

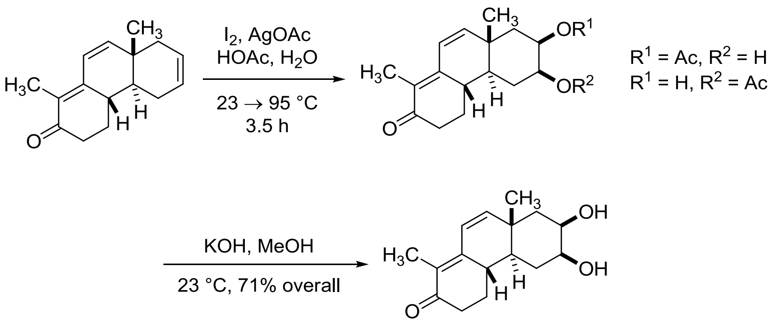




cyclic iodonium ion intermediate neighboring group assistance



Example 1[1]



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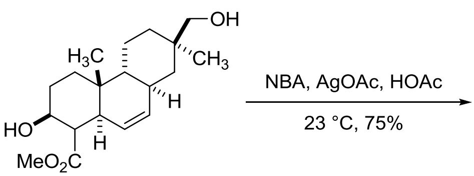

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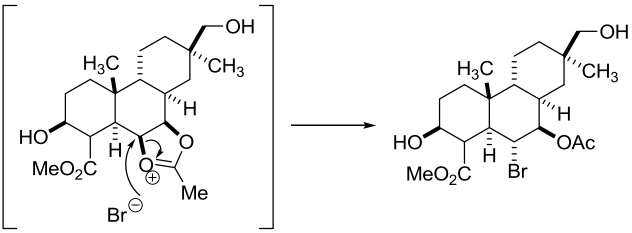
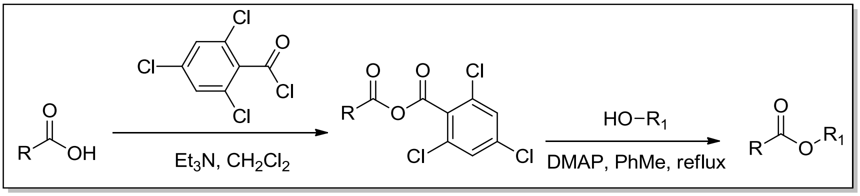


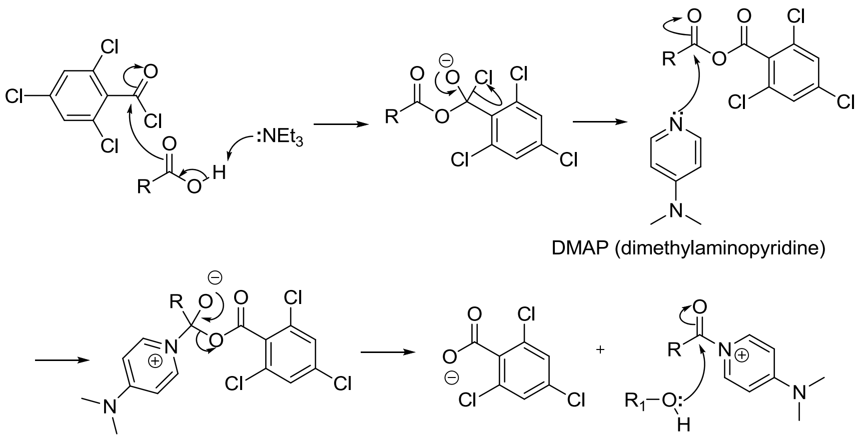
References

1. Woodward, R. B.; Brutcher, F. V., Jr. *J. Am. Chem. Soc.* **1958,** *80*, 209–211. Robert Burns Woodward (USA, 1917–1979) won the Nobel Prize in Chemistry in 1953 for his synthesis of natural products.
2. Kirschning, A.; Plumeier, C.; Rose, L. *Chem. Commun.* **1998,** 33–34.
3. Monenschein, H.; Sourkouni-Argirusi, G.; Schubothe, K. M.; O'Hare, T.; Kirschning, A. *Org. Lett.* **1999,** *1*, 2101–2104.
4. Kirschning, A.; Jesberger, M.; Monenschein, H. *Tetrahedron Lett.* **1999,** *40*, 8999–9002.
5. Muraki, T.; Yokoyama, M.; Togo, H. *J. Org. Chem.* **2000,** *65*, 4679–4684.
6. Germain, J.; Deslongchamps, P. *J. Org. Chem.* **2002,** *67*, 5269–5278.
7. Myint, Y. Y.; Pasha, M. A. *J. Chem. Res.* **2004,** 333–335.
8. Emmanuvel, L.; Shaikh, T. M. A.; Sudalai, A. *Org. Lett.* **2005,** *7*, 5071–5074.
9. Mergott, D. J. *Woodward* cis-*dihydroxylation*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 327–332. (Review).
10. Burlingham, B. T.; Rettig, J. C. *J. Chem. Ed.* **2008,** *85*, 959–961.

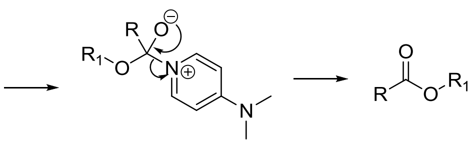
Yamaguchi esterification

Esterification using 2,4,6-trichlorobenzoyl chloride (the Yamaguchi reagent).

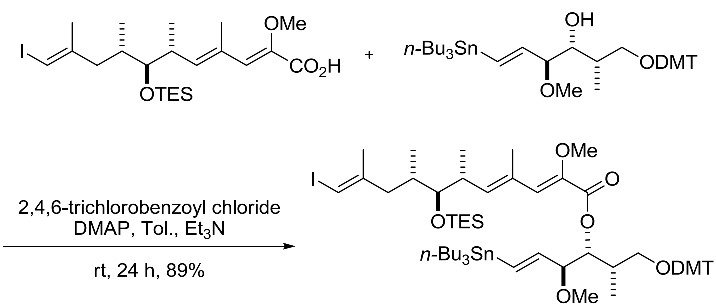




Steric hindrance of the chloro substituents blocks attack of the other carbonyl of the mixed anhydride intermediate.



Example 1, Intermolecular coupling[5]



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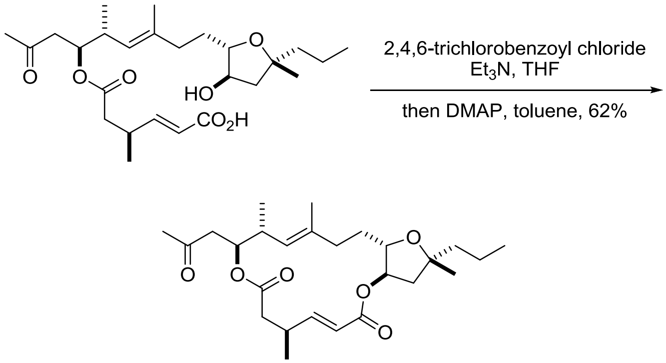
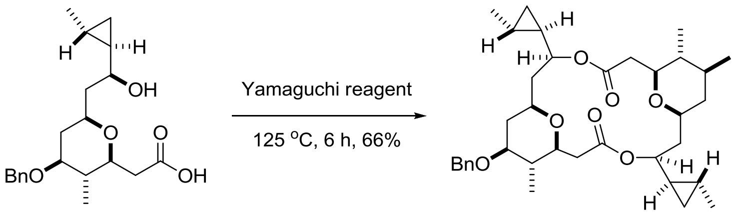
DOI 10.1007/978-3-319-03979-4_295,

Example 2, Intramolecular coupling[7]



Example 3, Dimerization[8]

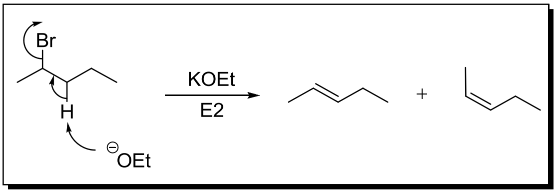


References

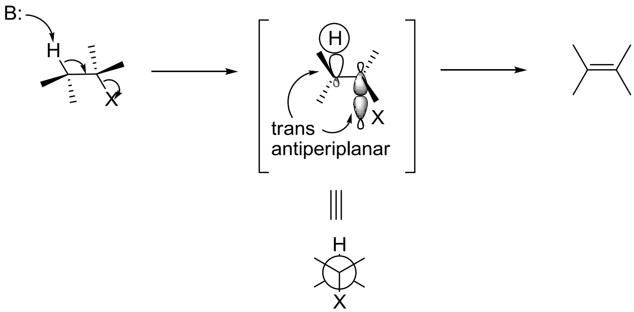
1. (a) Inanaga, J.; Hirata, K.; Saeki, H.; Katsuki, T.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1979,** *52*, 1989–1993. (b) Kawanami, Y.; Dainobu, Y.; Inanaga, J.; Katsuki, T.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1981,** *54*, 943–944. Masaru Yamaguchi was a professor at the Kyushu University.
2. Richardson, T. I.; Rychnovsky, S. D. *Tetrahedron* **1999,** *55*, 8977–8996.
3. Paterson, I.; Chen, D. Y.-K.; Aceña, J. L.; Franklin, A. S. *Org. Lett.* **2000,** *2*, 1513–1516.
4. Hamelin, O.; Wang, Y.; Deprés, J.-P.; Greene, A. E. *Angew. Chem. Int. Ed.* **2000,** *39*, 4314–4316.
5. Quéron, E.; Lett, R. *Tetrahedron Lett.* **2004,** *45*, 4533–4537.
6. Mlynarski, J.; Ruiz-Caro, J.; Fürstner, A. *Chem., Eur. J.* **2004,** *10*, 2214–2222.
7. Lepage, O.; Kattnig, E.; Fürstner, A. *J. Am. Chem. Soc.* **2004,** *126*, 15970–15971.
8. Smith, A. B. III.; Simov, V. *Org. Lett.* **2006,** *8*, 3315–3318.
9. Ahmad, N. M. *Yamaguchi esterification*. In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 545–550. (Review).
10. Wender, P. A.; Verma, V. A. *Org. Lett.* **2008,** *10*, 3331–3334.
11. Carrick, J. D.; Jennings, M. P. *Org. Lett.* **2009,** *11*, 769–772.
12. Lu, L.; Zhang, W.; Sangkil Nam, S.; Horne, D. A.; Jove, R.; Carter, R. G. *J. Org. Chem.* **2013,** *78*, 2213–2247

Zaitsev's elimination rule

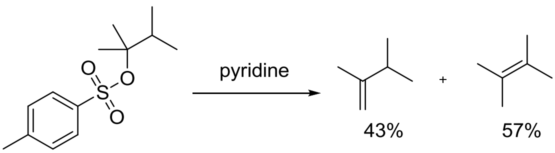
E_2 thermodynamic elimination gives the more substituted olefin as the major product because it is more stable.



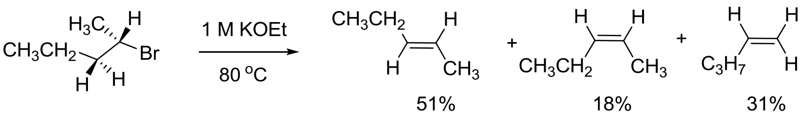
major minor



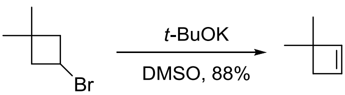
Example 1[2]



Example 2[3]



Example 3[5]



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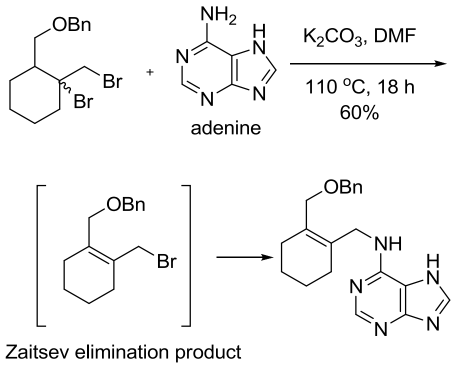
Example 4[8]

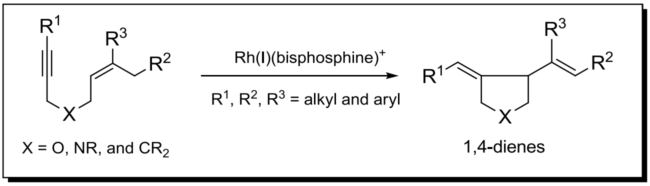


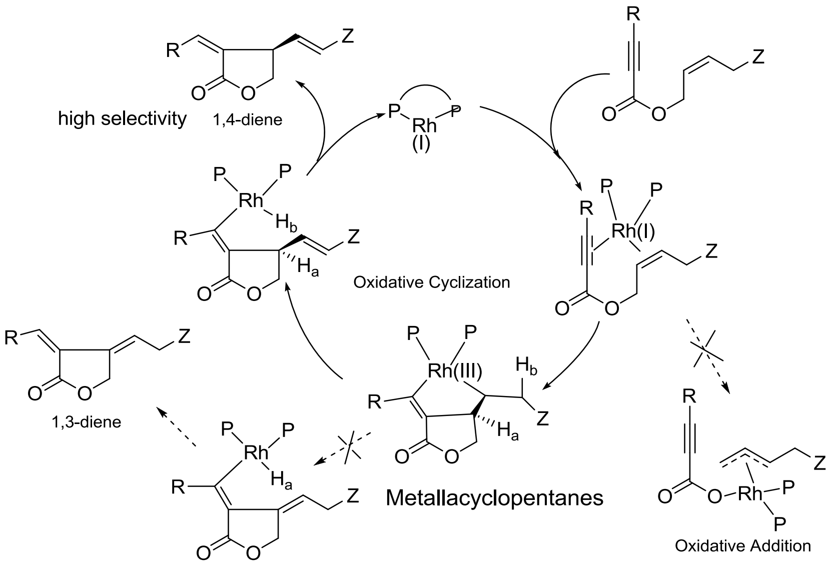
References

1. Aleksandr Mikhailovich Zaitsev (sometimes spelled as Saytseff, 1841–1910), like Markovnikov, was also a protégé of Aleksandr Mikhailovich Butlerov (1828–1882). But unlike Markovnikov's lack of tact and inability to compromise with administrators, Zaitsev was a skilled politician. He held the position of chair at Kazan' University for over four decades and educated a generation of organic chemistry.
2. Brown, H. C.; Wheeler, O. H. *J. Am. Chem. Soc.* **1956,** *78*, 2199–2210.
3. Chamberlin, A. R.; Bond, F. T. *Synthesis* **1979**, 44–45.
4. Elrod, D. W.; Maggiora, G. M.; Trenary, R. G. *Tetrahedron Comput. Methodol.* **1990,** *3*, 163–174.
5. Larsen, N. W.; Pedersen, T. *J. Mol. Spectrosc.* **1994**, *166*, 372–382.
6. Reinecke, M. G.; Smith, W. B. *J. Chem. Educ.* **1995,** *72*, 541.
7. Guan, H.-P.; Ksebati, M. B.; Kern, E. R.; Zemlicka, J. *J. Org. Chem.* **2000,** *65*, 5177–5184.
8. Guan, H.-P.; Ksebati, M. B.; Kern, E. R.; Zemlicka, J. *J. Org. Chem.* **2000,** *65,* 5177-5184.
9. Hagen, T. J. *Zaitsev Elimination,* In *Name Reactions for Functional Group Transformations*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2007,** pp 414–421. (Review).
10. Ramos, D. R.; Castillo, R.; Canle L., M.; Garcia, M. V.; Andres, J.; Santaballa, J. A. *Org. Biomol. Chem.* **2009,** *7*, 1807–1814. (Mechanism).

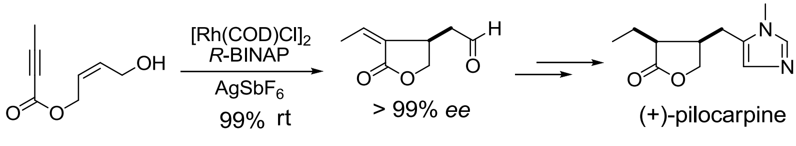
Zhang enyne cycloisomerization

Enynes are cycloisomerized regio- and enantio-selectively with a Rh complex with phosphine ligands.

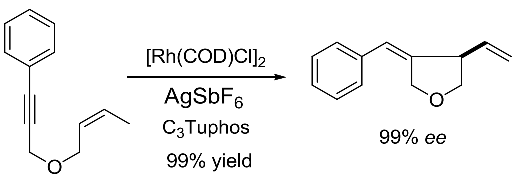




Example 1[3]



Example 2[4]



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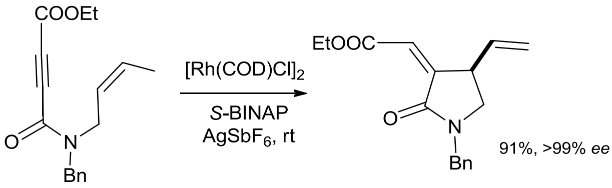
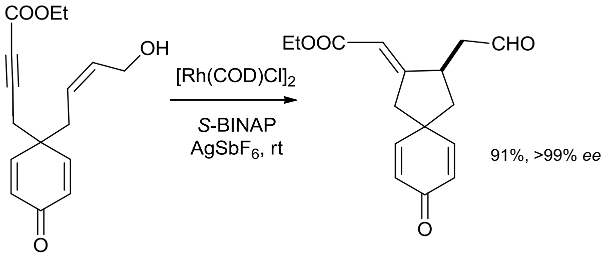
DOI 10.1007/978-3-319-03979-4_297, © Springer International Publishing Switzerland 2014

Example 3[5]



Example 4[11]

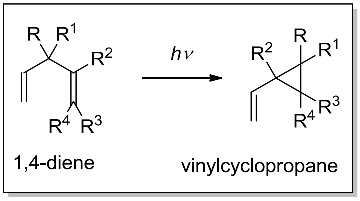


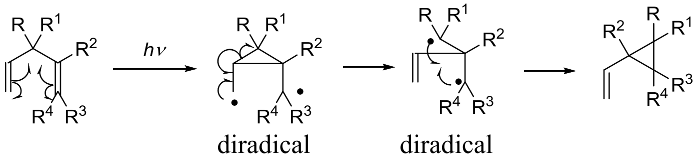
References

1. Cao, P.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2000,** *122*, 6490–6491. Born in 1961, Xumu Zhang studied as an undergraduate in Wuhan University, China. He earned his Ph.D. in 1992 at Stanford under James P. Collman. He began his independent academic career at Pennsyvania State University (1994–2006). Since 2007, he is a distinguished Professor of Chemistry at Rutgers, the State University of New Jersey. In addition to the Zhang enyne cyclization, his has worked in asymmetric hydrogenation, asymmetric hydroformylation and linear selective hydroformylation for pratical synthetic methods. The chiral ligand toolbox developed by Zhang's group includes TangPhos, DuanPhos, Binapine, ZhangPhos, TunePhos, f-binaphane, and YanPhos. His group and industrial partners applied his asymmetric hydrogenation methodologies and completed innovative synthesis of many chiral pharmaceutical intermediates.
2. Cao, P.; Zhang, X. *Angew. Chem. Int. Ed.* **2000,** *39*, 4104–4106.
3. Lei, A.; He, M., Zhang, X. *J. Am. Chem. Soc.* **2002,** *124*, 8198–8199.
4. Lei, A.; He, M.; Wu, S.; Zhang, X. *Angew. Chem. Int. Ed.* **2002,** *41*, 3457–3460.
5. Lei, A.; Waldkirch, J. P.; He, M.; Wu, S.; Zhang, X. *Angew. Chem. Int. Ed.* **2002,** *41*, 4526–4529.
6. Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2003,** *125*, 11472–11473**.**
7. Tong, X.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2003,** *125*, 6370–6371.
8. Tong, X.; Li, D.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2004,** *126*, 7601–7607.
9. He, M.; Lei, A.; Zhang, X. *Tetrahedron Lett.* **2005,** *46*, 1823–1826
10. Nicolaou, K. C.; Li, A.; Edmonds, D. J. *Angew. Chem. Int. Ed.* **2006,** *45*, 7086–7088.
11. Nicolaou, K. C.; Li, A.; Edmonds, D. J. *Angew. Chem. Int. Ed.* **2007,** *46*, 3942–3945.
12. Nicolaou, K. C.; et al. *Angew. Chem. Int. Ed.* **2007,** *46*, 6293–6295.
13. Nishimura, T.; Kawamoto, T.; Nagaosa, M.; Kumamoto, H.; Hayashi, T. *Angew. Chem. Int. Ed.* **2010,** *49*, 1638–1641.
14. Corkum, E. G.; Hass, M. J.; Sullivan, A. D.; Bergens, S. H. *Org. Lett.* **2011,** 13, 3522–3525.
15. Jackowski, O.; Wang, J.; Xie, X.; Ayad, T.; et al. *Org. Lett.* **2012,** *14*, 4006–4009.

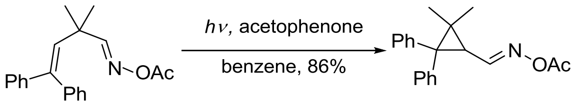
Zimmerman rearrangement

Conversion of 1,4-dienes to vinylcyclopropanes under photolysis. Also known as the **Di-π-methane rearrangement**.

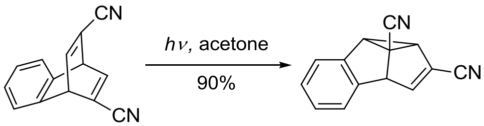




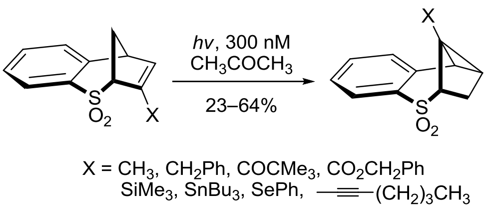
Example 1, Aza-π-methane rearrangement[2]



Example 2[4]



Example 3[8]



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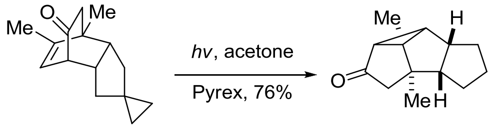
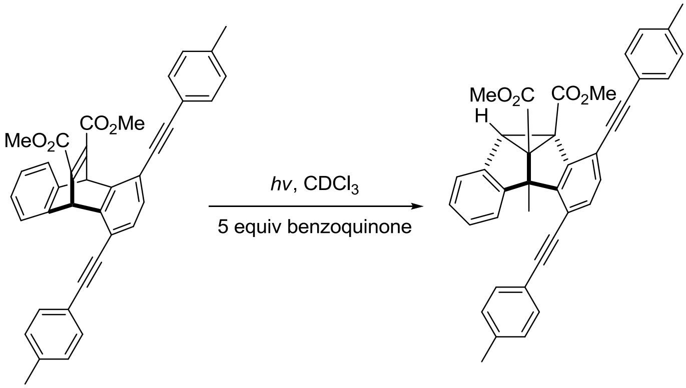
DOI 10.1007/978-3-319-03979-4_298, © Springer International Publishing Switzerland 2014

Example 4, Oxa-π-methane rearrangement[9]



Example 4, Oxa-π-methane rearrangement[10]

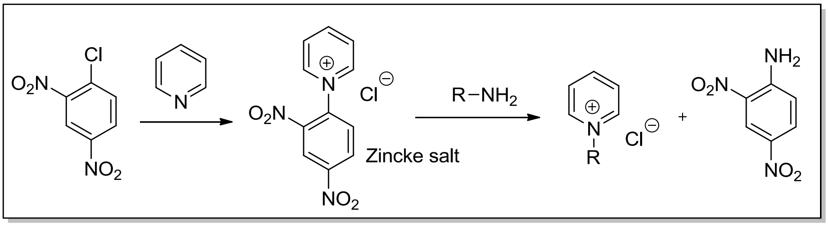


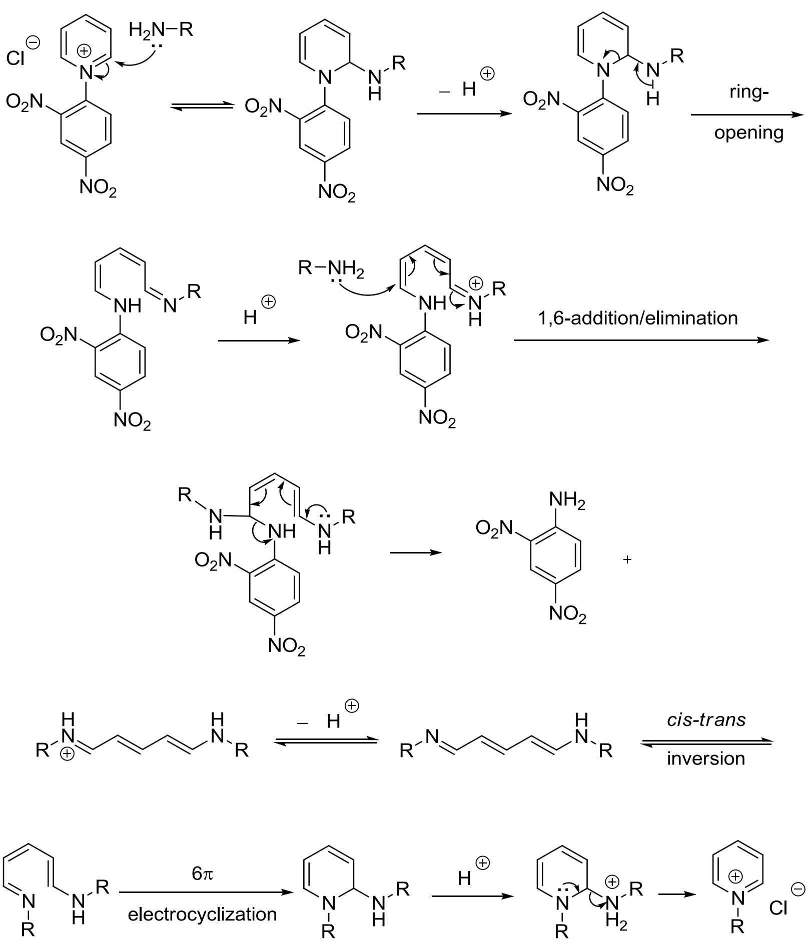
References

1. (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc*. **1966,** *88*, 183–184. Howard E. Zimmerman (1926–2012) was a professor at the University of Wisconsin at Madison. He is also known for the Traxler–Zimmerman trasition state for the asymmetric synthesis. (b) Zimmerman, H. E.; Armesto, D. *Chem. Rev*. **1996,** *96*, 3065–3112. (Review). (c) Zimmerman, H. E.; Církva, V. *Org. Lett*. **2000,** *2*, 2365–2367.
2. Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. I* **1991,** 223–228.
3. Jiménez, M. C.; Miranda, M. A.; Tormos, R. *Chem. Commun*. **2000,** 2341–2342.
4. Ünaldi, N. S.; Balci, M. *Tetrahedron Lett*. **2001,** *42*, 8365–8367.
5. Altundas, R.; Dastan, A.; Ünaldi, N. S.; Güven, K.; Uzun, O.; Balci, M. *Eur. J. Org. Chem*. **2002,** 526–533.
6. Zimmerman, H. E.; Chen, W. *Org. Lett*. **2002,** *4*, 1155–1158.
7. Tanifuji, N.; Huang, H.; Shinagawa, Y.; Kobayashi, K. *Tetrahedron Lett*. **2003,** *44*, 751–754.
8. Dura, R. D.; Paquette, L. A. *J. Org. Chem.* **2006,** *71*, 2456–2459.
9. Singh, V.; Chandra, G.; Mobin, S. M. *Synlett* **2008,** 2267–2270.
10. Cox, J. R.; Simpson, J. H.; Swager, T. M. *J. Am. Chem. Soc*. **2013,** *135*, 640–643.

Zincke reaction

The Zincke reaction is an overall amine exchange process that converts *N*-(2,4-dinitrophenyl)pyridinium salts, known as Zincke salts, to *N*-aryl or *N*-alkyl pyridiniums upon treatment with the appropriate aniline or alkyl amine.





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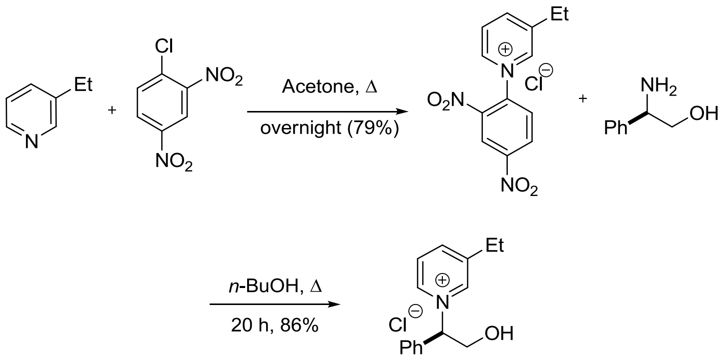
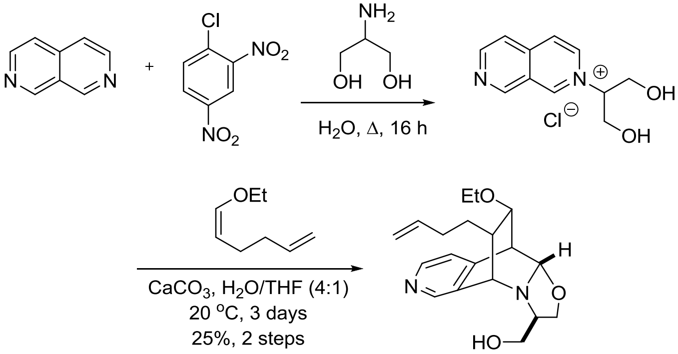
DOI 10.1007/978-3-319-03979-4_299,

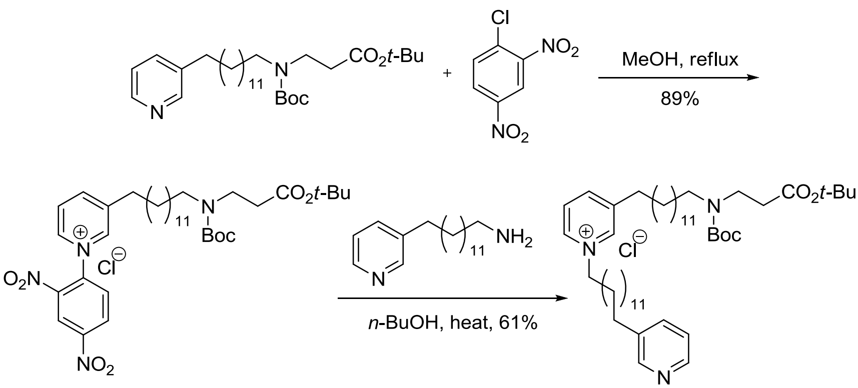
Example 1[5]



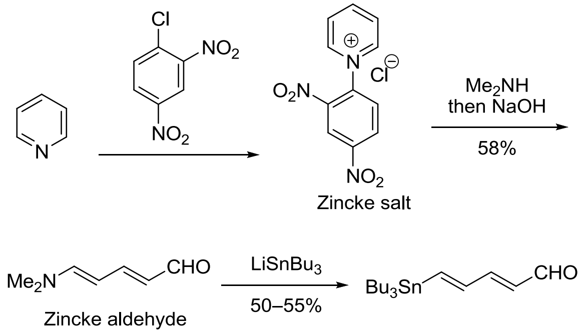
Example 2[6]



Example 3[9]



Example 4[10]

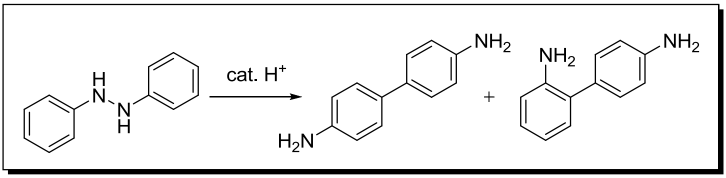


References

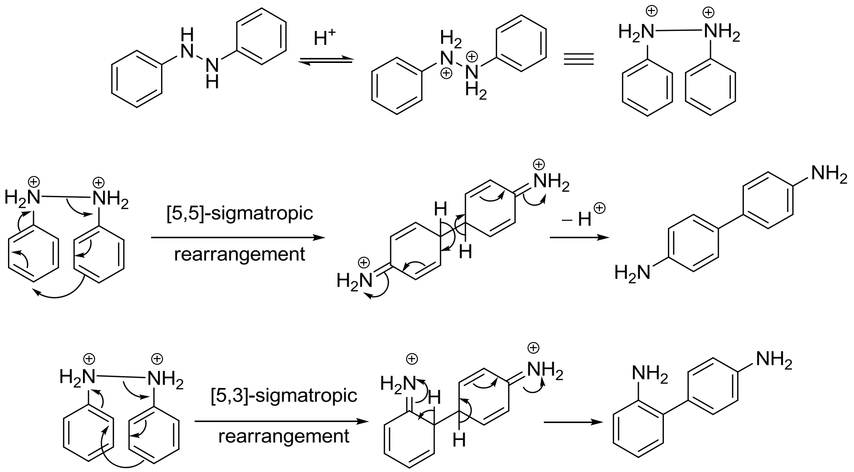
1. (a) Zincke, Th. *Ann.* **1903,** *330*, 361–374. (b) Zincke, Th.; Heuser, G.; Möller, W. *Ann.* **1904,** *333*, 296–345. (c) Zincke, Th.; Würker, W. *Ann.* **1905,** *338*, 107–141. (d) Zincke, Th.; Würker, W. *Ann.* **1905,** *341*, 365–379. (e) Zincke, Th.; Weisspfenning, G. *Ann.* **1913,** *396*, 103–131.
2. Epszju, J.; Lunt, E.; Katritzky, A. R. *Tetrahedron* **1970,** *26*, 1665–1673. (Review).
3. Becher, J. *Synthesis* **1980,** 589–612. (Review).
4. Kost, A. N.; Gromov, S. P.; Sagitullin, R. S. *Tetrahedron* **1981,** *37*, 3423–3454. (Review).
5. Wong, Y.-S.; Marazano, C.; Gnecco, D.; Génisson, Y.; Chiaroni, A.; Das, B. C. *J. Org. Chem.* **1997,** *62*, 729–735.
6. Urban, D.; Duval, E.; Langlois, Y. *Tetrahedron Lett.* **2000,** *41*, 9251–9256.
7. Cheng, W.-C.; Kurth, M. J. *Org. Prep. Proced. Int.* **2002,** *34*, 585–588. (Review).
8. Rojas, C. M. *Zincke Reaction*. In *Name Reactions in Heterocyclic Chemistry*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2005,** pp 355–375. (Review).
9. Shorey, B. J.; Lee, V.; Baldwin, J. E. *Tetrahedron* **2007,** *63*, 5587–5592.
10. Michels, T. D.; Rhee, J. U.; Vanderwal, C. D. *Org. Lett.* **2008,** *10*, 4787–4790.
11. Vanderwal, C. D. *J. Org. Chem.* **2011,** *76*, 9555–9567. (Review).

Zinin benzidine (semidne) rearrangement

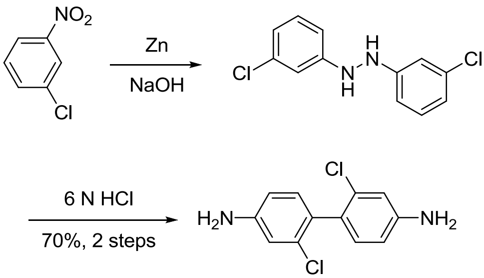
Also known as benzidine rearrangement or semidine rearrangement. Acid-promoted rearrangement of hydrazobenzene to 4,4-diaminobiphenyl (benzidine) and 2,4-diaminobiphenyl.



Hydrazobenzene 70% (benzidine) 30% (semidine)



Example 1[9,10]



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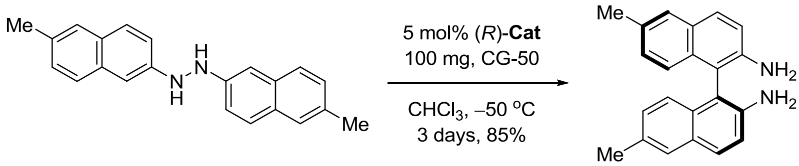
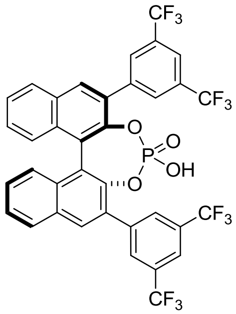
DOI 10.1007/978-3-319-03979-4_300,

Example 2, Catalytic Asymmetric Benzidine Rearrangement[9]



(*R*)-**Cat** =



CG-50, an acidic resin.

References

1. Zinin, N. *J. Prakt. Chem.* **1845,** *36*, 93–107.
2. Shine, H. J.; Baldwin, C. M.; Harris, J. H. *Tetrahedron Lett.* **1968,** *9,* 977–980.
3. Shine, H. J.; Zmuda, H.; Kwart, H.; Horgan, A. G.; Brechbiel, M. *J. Am. Chem. Soc.* **1982,** *104,* 5181–5184.
4. Rhee, E. S.; Shine, H. J. *J. Am. Chem. Soc.* **1986,** *108,* 1000–1006.
5. Shine, H. J. *J. Chem. Educ.* **1989,** *66*, 793–794.
6. Davies, C. J.; Heaton, B. T.; Jacob, C. *J. Chem. Soc., Chem. Commun.* **1995,** 1177–1178.
7. Park, K. H.; Kang, J. S. *J. Org. Chem.* **1997,** *62,* 3794–3795.
8. Benniston, A. C.; Clegg, W.; Harriman, A.; Harrington, R. W.; Li, P.; Sams, C. *Tetrahedron Lett.* **2003,** *44*, 2665–2667.
9. Hong, W.-X.; Chen, L.-J.; Zhong, C.-L.; Yao, Z.-J. *Org. Lett.* **2006,** *8*, 4919–4922.
10. Kim, H.-Y.; Lee, W.-J.; Kang, H.-M.; Cho, C.-G. *Org. Lett.* **2007,** *9*, 3185–3186.
11. De, C. K.; Pesciaioli, F.; List, B. *Angew. Chem. Int. Ed.* **2013,** *52*, 9293–9295.

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J.J. Li, *Name Reactions: A Collection of Detailed Mechanisms and Synthetic Applications*,
DOI 10.1007/978-3-319-03979-4,

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