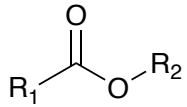
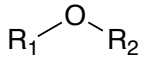
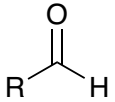
Chem 12

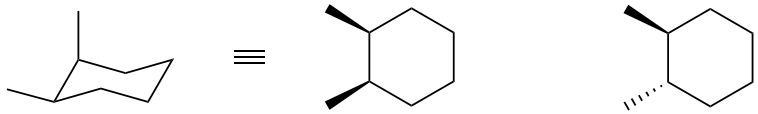
Final Exam (2021 Fall)

Grading Scheme

General Grading Principles

- All participants receive equal treatment.
- Grading schemes are used positively. Participants will be rewarded if they have given the relevant work rather than penalized for omissions.
- All the points on the grading scheme are designed to be awarded. Participants will always receive full points if deserved, i.e. if the answer matches the grading scheme. Participants may receive zero points if their response is not worthy of credit according to the grading scheme.
- Where some judgment is required, grading schemes will provide the principles by which points will be awarded and exemplification may be limited.
- Answers outside the specified answering places will not be graded.
- Low writing quality such as unclear texts and structural formulas will not be graded (or penalized for some points).
- Spelling mistakes will not be penalized **EXCEPT** in fill-in-blank questions (one point for each).
- Answers written in Chinese will be graded.

Question Number	Grading Detail	Point Awarded
1	**A is the correct answer** B is incorrect because the parent has seven carbons C is incorrect because bridgehead carbons should not be counted as ring carbons D is incorrect because the parent has seven carbons and bridgehead carbons should not be counted as ring carbons	(1)
2	**C is the correct answer** A is incorrect because an ester should have a structure of  B is incorrect because an ether should have a structure of  D is incorrect because an aldehyde should have a structure of 	(1)
3	**D is the correct answer** A is incorrect because a single bond cannot be broken when drawing resonance structures B is incorrect because the octet rule cannot be exceeded for period 2 elements only C is incorrect because the tail of a curly arrow should be placed on electrons (e.g. double bonds, lone pairs)	(1)

Question Number	Grading Detail	Point Awarded
4	**C is the correct answer** A is incorrect because BINAP is an example of atropoisomers B is incorrect because trisubstituted phosphine (with three different substituents) is chiral (*the energy barrier of flipping for the lone pair is too high*) D is incorrect because tetrasubstituted ammonium (with four different substituents) is chiral	(1)
5	**D is the correct answer**  A is incorrect because they have stereoisomerism B is incorrect because they do not have differences in bond connectivity C is incorrect because one of the chiral centers has the same configuration for both of these compounds	(1)
6	**C is the correct answer** A is incorrect because ions are not required for a free-radical rection B is incorrect because single-barbed (fishhook) arrows are used in the free-radical reaction D is incorrect because nucleophiles are not required for a free-radical rection	(1)

Question Number	Grading Detail	Point Awarded
7	**B is the correct answer** A is incorrect because an electrophile should not have a negative charge C is incorrect because an electrophile should not have a negative charge D is incorrect because an electrophile must contain something (partial) positive	**(1)**
8	**A is the correct answer** B is incorrect because primary carbocations are least stable C is incorrect because secondary carbocations are not as stable as benzyl carbocations D is incorrect because tertiary carbocations are not as stable as benzyl carbocations	**(1)**
9	**B is the correct answer** A is incorrect because C–F bond is very strong, thus C is incorrect because RO^- is not as stable as TsO^- D is incorrect because NH_2^- is not as stable as TsO^-	**(1)**
10	**C is the correct answer** A is incorrect because “double” and “electrophilic” should not be used B is incorrect because “di” should not be used D is incorrect because “two” should not be used	**(1)**

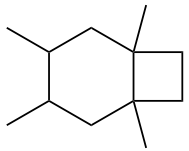
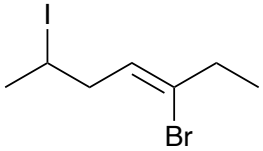
Question Number	Grading Detail	Point Awarded
11	**B is the correct answer** A is incorrect because there is not an inversion of configuration C is incorrect because Na^+ cannot function as a nucleophile D is incorrect because Na^+ cannot function as a nucleophile	(1)
12	**D is the correct answer** A is incorrect because DBN is a base rather than a nucleophile B is incorrect because the reactant has only four carbons C is incorrect because the reactant has only four carbons	(1)
13	**A is the correct answer** B is incorrect because *t*–BuOK is a large base, so a Hoffman product is produced C is incorrect because E2 is dominant for a tertiary substrate and strong base D is incorrect because E2 is dominant for a tertiary substrate and strong base	(1)
14	**D is the correct answer** A is incorrect because hydrogen should not be substituted for methyl group B is incorrect because carbocation rearrangement will occur for using H_3O^+ only C is incorrect because using H_3O^+ only is a Markovnikov's addition	(1)

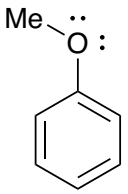
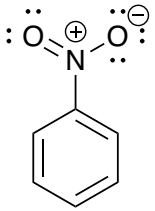
Question Number	Grading Detail	Point Awarded
15	**A is the correct answer** B is incorrect because OsO_4 dihydroxylation is a *syn* addition C is incorrect because a reductant (Na_2SO_3) is used, so a diol will be produced rather than an osmate ester D is incorrect because a reductant (Na_2SO_3) is used, so a diol will be produced rather than an osmate ester	**(1)**
16	**C is the correct answer** A is incorrect because NaOH is a small base, so a Zaitsev product is produced B is incorrect because NaOMe is a small base, so a Zaitsev product is produced D is incorrect because Cl^- is a weak base	**(1)**
17	**D is the correct answer** A is incorrect because H_2O cannot be used alone as a reagent for hydration B is incorrect because using H_3O^+ only is a Markovnikov's addition C is incorrect because oxymercuration-demercuration is a Markovnikov's addition	**(1)**
18	**C is the correct answer** A is incorrect because using Br_2 only is a halogenation rather than a halohydrin formation B is incorrect because HBr and H_2O_2 should not be used for halohydrin formation D is incorrect because BrO_3^- should not be used for halohydrin formation	**(1)**

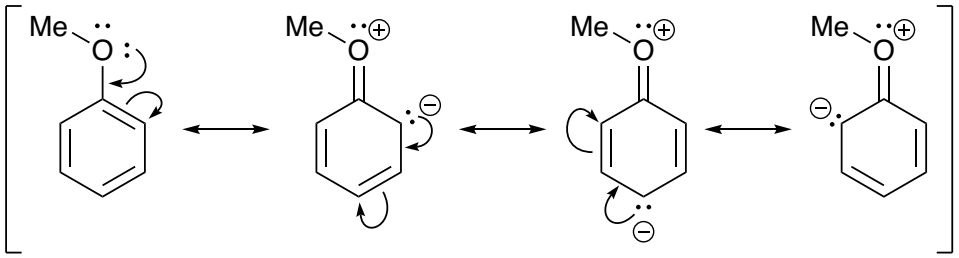
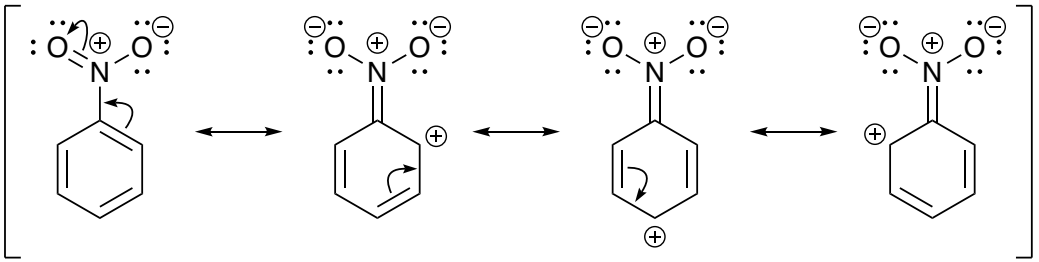
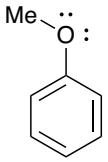
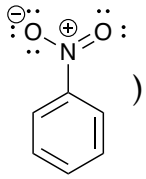
Question Number	Grading Detail	Point Awarded
19	**D is the correct answer** A is incorrect because O_2 and light are not the reactant and the condition for ozonolysis B is incorrect because a reductant should be used after the ozonide formed C is incorrect because a reductant should not be used with O_3 simultaneously	**(1)**
20	**D is the correct answer** A is incorrect because EtI should be used after the alkyne is deprotonated (by $NaNH_2$) B is incorrect because CHI_3 should not be used for ethylation C is incorrect because there is no alkyl halide present	**(1)**

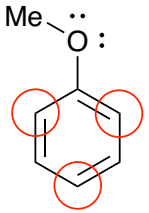
Question Number	Grading Detail	Point Awarded
21	• inversion	(2)
22	• stereospecificity	(2)
23	• negative (2) • negative (2) *low* is NOT ACCEPTED	4
24	• less *fewer* is ACCETPED	(2)
25	• When a {small(er) base / small(er) steric base / base with low(er) steric hindrance} is used, a Zaitsev product is produced (1) • When a {large(r) base / large(r) steric base / base with high(er) steric hindrance } is used, a Hoffman product is produced (1) • Producing Hoffman product is a kinetic control (1)	3

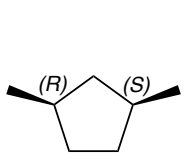
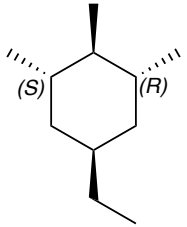
Question Number	Grading Detail	Point Awarded
26	• Stereoselectivity is to produce a pair of stereoisomers {with unequal amount / with slight difference / slight preference (to produce one in higher amount)} **(1)** • Stereospecificity {is to produce only one stereoisomer / the (stereo)configurations of product are depend on the (stereo)configurations of reactants} **(1)** • Stereospecificity is {included in stereoselectivity / a kind of stereoselectivity / the extreme condition of stereoselectivity} **(1)** isomer / configurational isomer / *Z/E* isomer / *R/S* isomer for the substitution of stereoisomer are NOT ACCEPTED	**3**
27	• Transition state is the relatively maximum on the energy curve **(1)** • …thus it {cannot exist for a long time / can only exist for a moment / can only exist for a short period / can only exist for an instant} **(1)** • Intermediate is the relatively minimum on the energy curve **(1)** • …thus it {can be stabilized / can exist for relatively long(er) time (than transition state) / can exist for a while} **(1)**	**4**

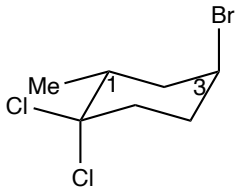
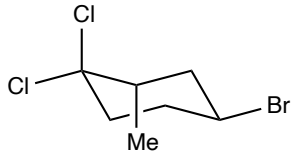
Question Number	Grading Detail	Point Awarded
28	• 1,2-diethyl-6-isopropyl-4,8-dipropylspiro[2.5]octane (2) • 4-(*tert*-butyl)*-9-chloro-3-ethyl-7-fluorodec-1-ene (2) Only the answers that fully match can get full marks; otherwise, one point will be penalized *Parentheses are not required	4
29	•  (2) 1,3,4,6-tetramethylbicyclo[4.2.0]octane •  (2) (*Z*)-3-bromo-6-iodohept-3-ene Only the answers that fully match can get full marks; otherwise, one point will be penalized Name under the structure is not required	4

Question Number	Grading Detail	Point Awarded
30(a)	•  (2) **A** •  (2) **B** Two points for lone pairs in each structure Two points for charges in each structure	4

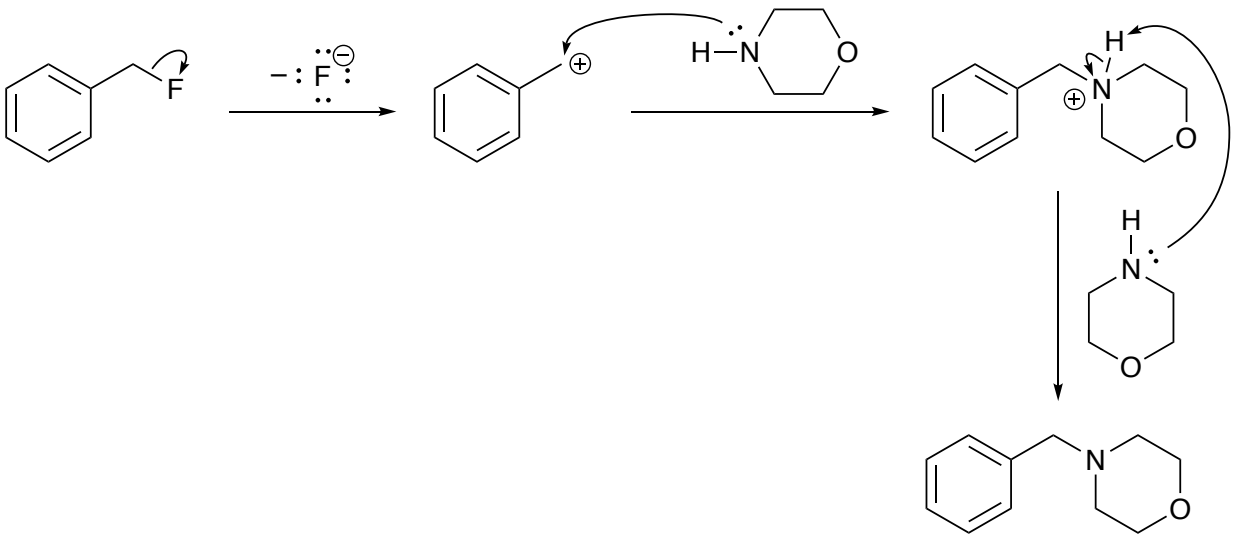
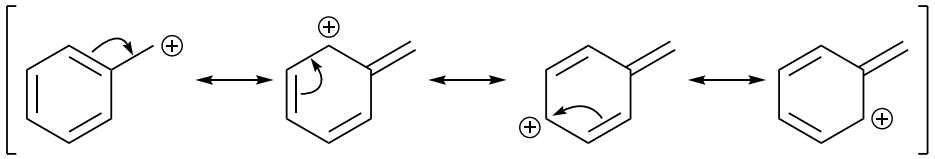
Question Number	Grading Detail	Point Awarded
30(b)	•  (3) •  (3) One point is penalized if there is a missing structure / a wrong arrow or charge or lone pair for each resonance structure If a single arrow (⟶) is used, one point is penalized (only once for the whole question) The last resonance structure (not indicated above, such as  or ) is not required; it may receive one point under certain conditions Missing brackets will not be penalized	6

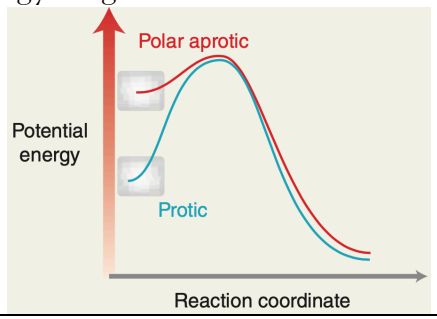
Question Number	Grading Detail	Point Awarded
30(c)	• Molecule A should be circled	(1)
30(d)	 • Circle on *para*-position **(1)** • Circles on *ortho*-positions **(1)** To receive the point for *ortho*-positions, two circles must be drawn If meta-position(s) is(are) circled with correct circles on *para-* and *ortho*-positions, one point will be penalized	2
	Total for question 30	13

Question Number	Grading Detail	Point Awarded
31(a)	  • Correct labeled chiral centers (do not need to indicate configurations) **(2)** • Correct configurations for the left compound **(2)** • Correct configurations for the right compound **(2)**	**6**
31(b)	For the left compound: • {Achiral / not chiral / does not have chirality} **(1)** • Because it has a {reflectional symmetry / mirror plane} **(1)** For the right compound: • {Achiral / not chiral / does not have chirality} **(1)** • Because it has a {reflectional symmetry / mirror plane} **(1)**	**4**

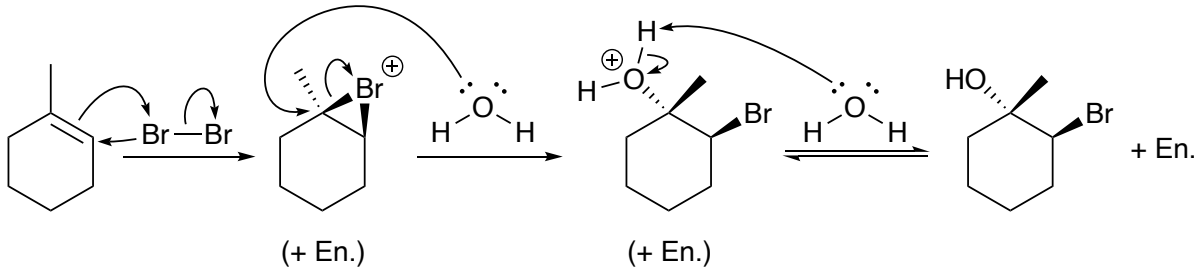
Question Number	Grading Detail	Point Awarded
31(c)	•  One point for each substituent with correct position and orientation	(4)
31(d)	•  One point for each substituent with correct position and orientation If the chair conformation is not flipped, no points can be awarded	(4)
31(e)	• {⇌ / any indication that the left conformation is preferred}	(1)
	Total for question 31	**19**

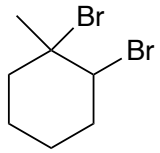
Question Number	Grading Detail	Point Awarded
32(a)	Ranking: • $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$ **(4)** Any two in the wrong order will be penalized for one point Reason: • The {atomic / ionic} radius increases from $F^{\ominus}$ to $I^{\ominus}$ **(1)** • Which means the bond are likely to be broken (for later halogens than former halogens) **(1)** Alternative explanations like conjugate acid-base strength / orbital overlap are ACCEPTED	**6**

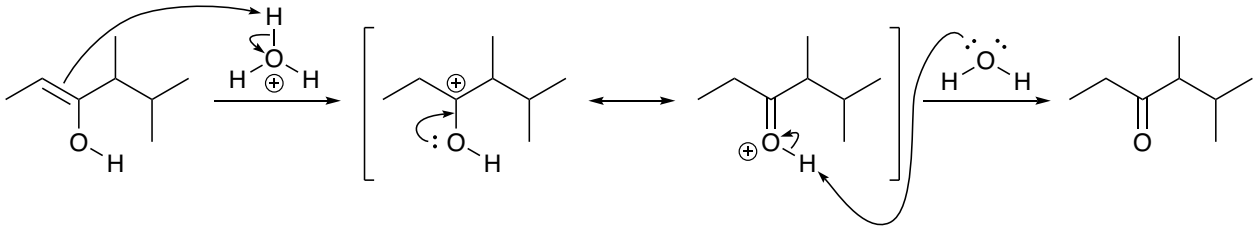
Question Number	Grading Detail	Point Awarded
32(b)	•  (3) •  (3) Any correct structure for the mechanism receives one point, up to three points Any correct structure for the resonance stabilization receives one point, up to three points **(continues)**	6

Question Number	Grading Detail	Point Awarded
32(b) **continued**	Alternative explanations of the formation of 1° carbocation are ACCEPTED, but a sufficient, clearly structured response is expected Incorrect use of arrows (e.g. using single arrows in resonance structures) will be penalized for one point (only once for the whole question) Missing brackets will not be penalized	
32(c)	• Polar aprotic solvent can stabilize cations **(1)** • But cannot stabilized the {anion / nucleophile} **(1)** • The {anion / nucleophile} is in high energy **(1)** • So {it likes to react with the substrate / this high energy provides for crossing the energy barrier} **(1)** Clearly labeled energy diagrams can also receive full points Example diagram: 	**4**

Question Number	Grading Detail	Point Awarded
32(d)	• Water can form hydrogen bond with {fluorine / fluoride} (because of the high electronegativity of fluorine) **(1)** • Which can {stabilize the fluoride ion / move the equilibrium to produce more fluorides / force the reaction to produce more fluorides} **(1)** Solvation effect / stabilized in the solution for the substitution of hydrogen bond are NOT ACCEPTED	**2**
	Total for question 32	**18**

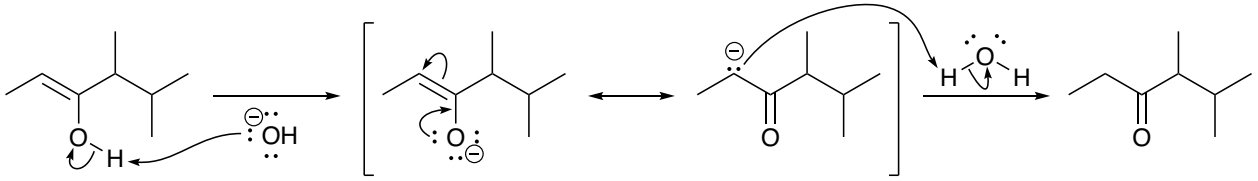
Question Number	Grading Detail	Point Awarded
33(a)	 • Correct first step with reagent and arrows **(1)** • Correct second structure and second step with reagent and arrows **(1)** • Correct third structure and third step with reagent and arrows **(1)** • Correct final structure with En. (Enantiomer) **(1)** Using (racemic) instead of En. is ACCEPTED Missing En. for intermediates will not be penalized Using the single arrow to substitute the equilibrium arrow will not be penalized	**4**

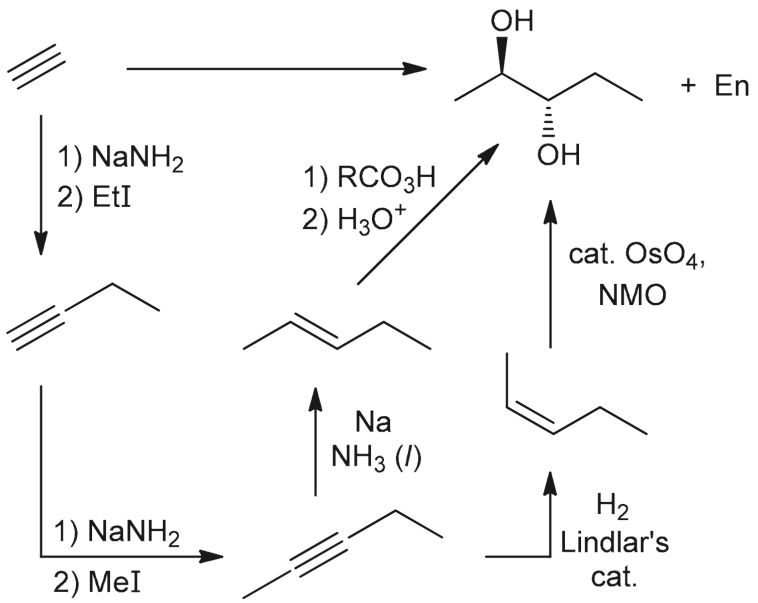
Question Number	Grading Detail	Point Awarded
33(b)	 1,2-dibromo-1-methylcyclohexane • There is no hydrogen on 1' position **(1)** • The product (a "cyclohexyne") has an extremely high ring strain / only the ring that contains more than nine carbons can hold a triple bond in it **(1)**	2

Question Number	Grading Detail	Point Awarded
33(c)		4

- Correct first step with reagent and arrows **(1)**
- Correct first resonance structure with arrow **(1)**
- Correct second resonance structure with arrow and the final step with reagent and arrows **(1)**
- Resonance arrow is used correctly **(1)**

Missing brackets will not be penalized

Question Number	Grading Detail	Point Awarded
33(d)	 • Correct first step with reagent and arrows **(1)** • Correct first resonance structure with arrow **(1)** • Correct second resonance structure with arrow and the final step with reagent and arrows **(1)** • Resonance arrow is used correctly **(1)** Missing brackets will not be penalized	**4**

Question Number	Grading Detail	Point Awarded
33(e)	 • First step with $NaNH_2$ followed by EtI **(1)** • Second step with $NaNH_2$ followed by MeI **(1)** • Third step with {Na, NH_3(l) [*anti* reduction]/ H_2, Lindlar's cat. or Ni_2B [*syn* reduction]} **(1)** **(continues)**	6

Question Number	Grading Detail	Point Awarded
33(e) **continued**	• Fourth step with {RCO_3H followed by H_3O^+ [for third step choosing *anti* reduction] / OsO_4 (catalytic) [for third step choosing *syn* reduction]} **(1)** • Any two of the intermediates with correct structures **(2)** Clear retrosynthetic analysis can earn up to two points Missing reagents / missing adding orders / wrong adding orders will be penalized for one point **each time**	
	Total for question 33	**20**