北京师大二附中PGA高中课程班2021-2022学年度

高三年级 有机化学 第一学期期末测试题

考试时间：150分钟　试卷总分：138分

原班级：_____ 姓名：_____ 学号：_____

Attention! All writing in this box will NOT be graded!

Use this box to do any rough work.

Chem 12 (2021 Fall)

Final Exam

Time Allowed: 150 min **Total Score: 138**

Instructions

- You have 150 minutes to complete this exam. Any submission after the 150-minute mark is not accepted, so please submit your exam before this point, even if you are not done.
- This is a closed-book exam. You are not allowed to check your notes, the workbook, the previous quizzes, and any documents that may be related to today's exam. You may use molecular models, which should be provided on the exam's day. You may not use any electronic devices or collaborate or consult with any other person.
- This exam includes three parts: multiple-choice questions, fill-in-blank and short answer questions, and free-response questions. The score points allocated for each part are shown in the part directions. Use them as indicators to manage your time to answer questions.
- All pages of the exam must be turned in.
- **Be NEAT!** Non-legible structure drawings and writings will not be graded.

Good luck!!!

Personal Information

Name: _____

Class: _____

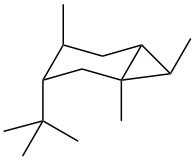
Student ID: _____

Part I Score	Part II Score	Part III Score	Total Score

Part I: Multiple-Choice Questions (29.0%)
Directions • *There are 20 questions.* • *Each question is worth 2 points.* • *There are 40 points in total.* • *Write your answer in the box below. Answers that are written before the question number/after the question will not be graded!*

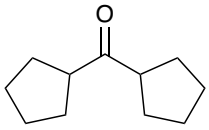
1	2	3	4	5	6	7	8	9	10
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**

1. **(2 pts)** Choose the correct name for the following cycloalkane.



A. (1*R*,3*S*,4*S*,6*R*)-3-(*tert*-butyl)-1,4,7-trimethylbicyclo[4.1.0]heptane
B. (1*R*,3*S*,4*S*,6*R*)-3-(*tert*-butyl)-1,4,7-trimethylbicyclo[4.1.0]hexane
C. (1*R*,3*S*,4*S*,6*R*)-3-(*tert*-butyl)-1,4,7-trimethylbicyclo[6.3.0]heptane
D. (1*R*,3*S*,4*S*,6*R*)-3-(*tert*-butyl)-1,4,7-trimethylbicyclo[6.3.0]hexane

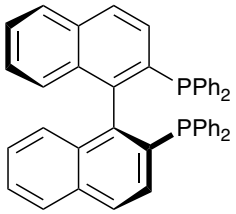
2. **(2 pts)** What is the classification of this compound?

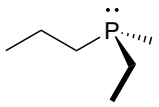


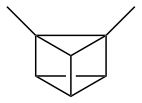
A. ester
B. ether
C. ketone
D. aldehyde

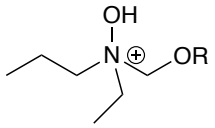
3. **(2 pts)** When drawing resonance structures:
   A. a single bond can be broken
   B. the octet rule cannot be exceeded for period 3 elements
   C. the tail of a curly arrow should be placed on a positive charge
   D. only π or p electrons can be moved (delocalized)

4. **(2 pts)** Which of the following molecule is achiral (*hint: some of the chiral centers may not be indicated by using wedges and dashes!*):

A. 

B. 

C. 

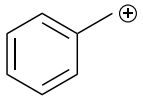
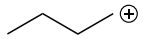
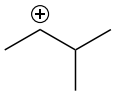
D. 

5. **(2 pts)** Determine the relationship between these two compounds:

   A. identical compound
   B. constitutional isomer
   C. enantiomer
   D. diastereomer

6. **(2 pts)** Free-radical reaction:
   A. contains positively and/or negatively charged particles in each of the steps of the reaction
   B. usually uses double-barbed arrows to represent the reaction mechanism
   C. undergoes a homolysis reaction process
   D. must have at least one nucleophile to initiate the reaction

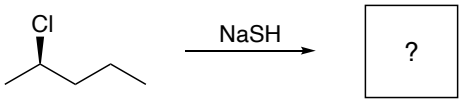
7. **(2 pts)** Which of the following species is an <u>electrophile</u>:
   A. hydride (H^-)
   B. carbocation (C^+)
   C. hydroxide (OH^-)
   D. ethanol (CH_3CH_2OH)

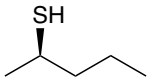
8. **(2 pts)** Which of the following carbocation is the most stable:
   A. 
   B. 
   C. 
   D. 

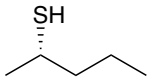
9. **(2 pts)** Which of the following species is the best leaving group:
   A. fluoride (–F)
   B. tosylate (–OTs)
   C. alkoxide (–OR)
   D. amino group ($–NH_2$)

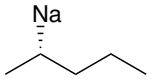
10. **(2 pts)** What is E2 stands for:
   A. double-molecular electrophilic reaction
   B. dimolecular elimination reaction
   C. bimolecular elimination reaction
   D. two-molecular electrophilic reaction

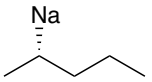
11. **(2 pts)** Identify the major product of the following reaction:



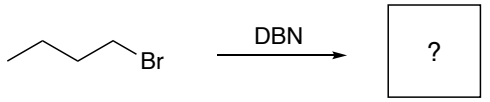
A. 

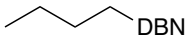
B. 

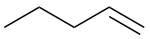
C. 

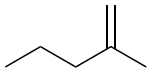
D. 

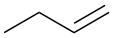
12. **(2 pts)** Identify the major product of the following reaction:



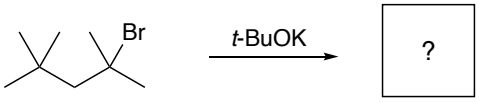
A. 

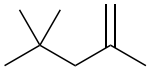
B. 

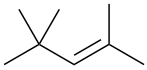
C. 

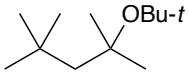
D. 

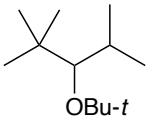
13. **(2 pts)** Identify the major product of the following reaction:



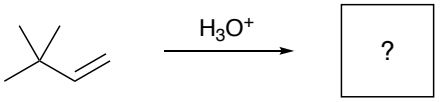
A. 

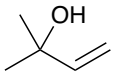
B. 

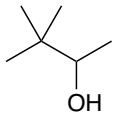
C. 

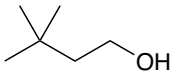
D. 

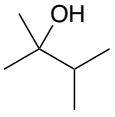
14. **(2 pts)** Identify the major product of the following reaction:



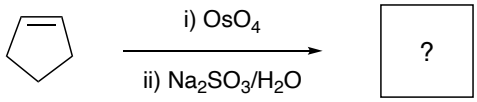
A. 

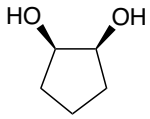
B. 

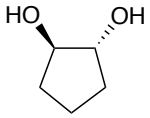
C. 

D. 

15. **(2 pts)** Identify the major product of the following reaction:



A. 

B. 

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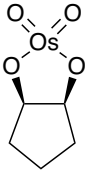
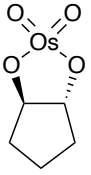
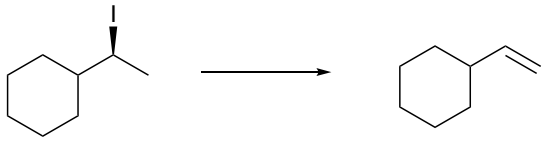
C. 

D. 

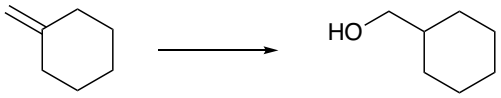
+ En.

16. **(2 pts)** Identify the reagent used for the following transformation:



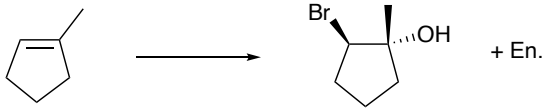
A. NaOH
B. NaOMe
C. *t*-BuOK
D. Cl^-

17. **(2 pts)** Identify the reagent(s) used for the following transformation:



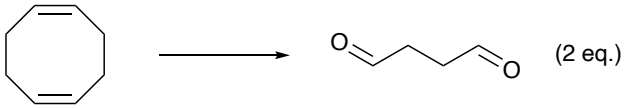
A. H_2O
B. H_3O^+
C. 1) $Hg(OAc)_2$, H_2O; 2) $NaBH_4$
D. 1) $BH_3 \cdot THF$; 2) H_2O_2, NaOH

18. **(2 pts)** Identify the reagent(s) used for the following transformation:



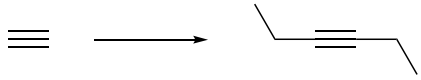
A. Br_2
B. HBr/H_2O_2
C. Br_2/H_2O
D. 1) BrO_3^-; 2) H_2O

19. **(2 pts)** Identify the reagent(s) used for the following transformation:



A. $O_2/h\nu$
B. O_3
C. O_3/DMS
D. 1) O_3; 2) DMS

20. **(2 pts)** Identify the reagent(s) used for the following transformation:



A. $NaNH_2$/EtI (2 eq.)
B. $NaNH_2/CHI_3$ (2 eq.)
C. 1) Na; 2) NH_3 (2 eq.)
D. 1) $NaNH_2$; 2) EtI (2 eq.)

Part II: Fill-in-Blank and Short Answer Questions (14.5%)
Directions • *There are 7 questions.* • *For the fill-in-blank questions, one space (the blank that needs you to fill) is worth 2 points.* • *For the short answer questions, the point worth is indicated at the beginning of each of the questions.* • *There are 20 points in total.* • *Write your answer on the line in each of the questions.*

21. **(2 pts)** To explain the slight difference between the stereochemical outcomes of the S_N1 products, Winstein proposes a theory called the *intimate ion pair mechanism*, which indicates the product that has a(n) _____ of configuration is more than the product that has a retention of configuration.

22. **(2 pts)** E2 reaction is an *anti*-coplanar elimination. This feature is called _____.

23. **(4 pts)** Because the addition reaction has a _____ value of ΔG at low temperature, and its ΔS is _____, heat should not be added for a greater yield.

24. **(2 pts)** *anti*-Markovnikov addition is to add hydrogen to the carbon which links to _____ hydrogen atoms.

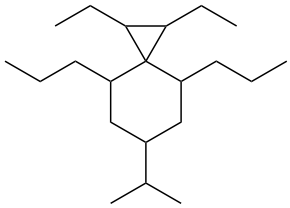
25. **(3 pts)** Describe that, in what condition, an E2 reaction will produce a Zaitsev product or a Hofmann product, and then indicate whether producing a Hofmann product is a thermodynamic control or a kinetic control.

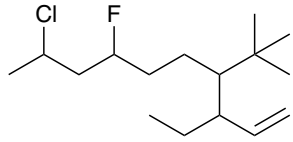
26. **(3 pts)** Explain the relationship between stereoselectivity and stereospecificity.

27. **(4 pts)** Briefly explain why, for a unimolecular reaction, a transition state cannot be separated, but an intermediate can be separated.

Part III: Free-Response Questions (56.5%)
Directions • *There are 6 questions.* • *The point worth is indicated at the beginning of each of the questions.* • *There are 78 points in total.* • *Only answers located within or very close to the answer boxes (or located at the question required places) will be graded.*

28. **(4 pts)** Name each of the following molecules.

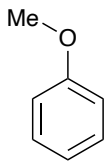




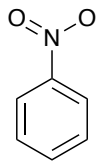
29. **(4 pts)** Draw the structure associated with each name.

1,3,4,6-tetramethylbicyclo[4.2.0]octane (Z)-3-bromo-6-iodohept-3-ene

30. **(13 pts)** While resonance is often used to compare the relative stability of two different molecules, it can be also used to compare the relative reactivity of those molecules. Consider the two molecules below:



A



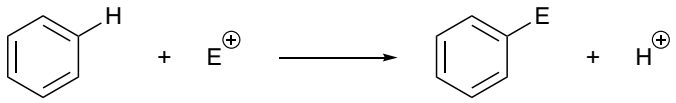
B

(a) **(4 pts)** Draw all lone pairs and identify all non-zero formal charges on each of the structures above.

(b) **(6 pts)** For each molecule, draw all resonance structures that involve the substituent and do not increase the number of formal charges on the molecule by more than 2. For example, if the original structure has one formal charge, none of your resonance structures should have more than three formal charges.

Molecule A:
Molecule B:

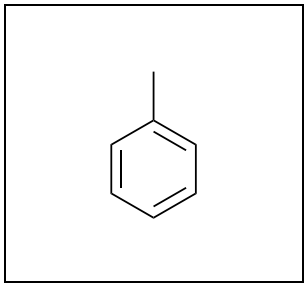
Now consider the reaction shown below:



(c) **(1 pts)** Although we have not learned this reaction before, we can predict the relative reactivity of **molecules A** and **B** by considering the resonance structures you drew in part (b). Based on these resonance structures, predict which of these two molecules will more readily react with E^+, a generic positively charged molecule.

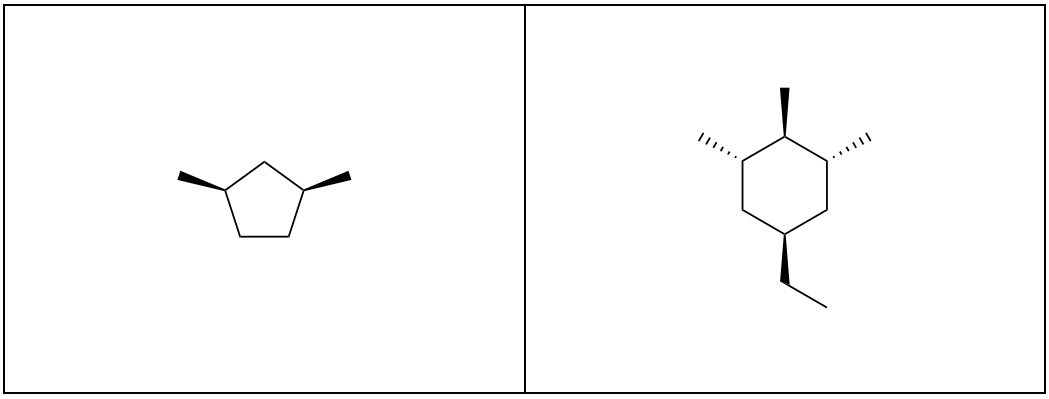
Circle your choice: **Molecule A** **Molecule B**

(d) **(2 pts)** Modify the structure in the box below so it matches the molecule you have chosen **(Molecule A** or **B)**, then **circle the positions on the ring** that are most likely to react with E^+.



31. **(19 pts)** This question is about cycloalkanes.

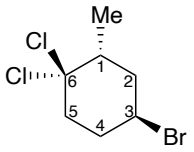
(a) **(6 pts)** Due to the rigid structure of the ring, cycloalkanes often have chiral centers. Label every chiral center of the cycloalkanes listed below, and clearly indicate the stereochemical configuration of each of the chiral centers.



(b) **(4 pts)** Are these two compounds chiral? Justify your answer by indicating the symmetry factor.

	Chirality	
	Justification	

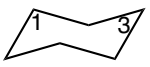
Substituted cyclohexanes are especially important in conformational analysis. For parts c to d, you may refer to the molecule below to answer the questions.



(c) **(4 pts)** Draw the substituents in the proper orientation on the chair structure provided below.

(d) **(4 pts)** Draw the chair-flipped structure in the box on the right.

(e) **(1 pts)** Given that the methyl group has a greater steric hindrance than the chlorine atom, predict the direction of this dynamic conversion of conformation by drawing an appropriate equilibrium arrow in the box below.

	equilibrium arrow	chair-flipped structure

32. **(18 pts)** It was discovered that the presence of water as a cosolvent enables the reaction of activated alkyl fluorides for bimolecular nucleophilic substitution reactions.

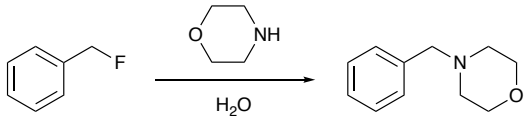
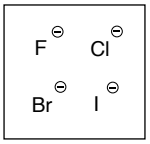


Figure 1. The reaction scheme.

(a) **(6 pts)** Rank the stability of the following leaving groups, and briefly explain the reason.



Ranking	
Reason	

(b) **(6 pts)** Once this reaction is discovered, researchers supposed that this reaction should be an S_N1 process. Propose a plausible mechanism, and explain why the hypothetical 1° carbocation intermediate can be stabilized. (*Hint: Your answer may include several resonance structures*)

(c) **(4 pts)** The experimental result and DFT (*density functional theory*) analysis concurrently show that this reaction undergoes an S_N2 process. With a mixture of protic and polar aprotic solvents, the conversion rate can be much higher than just using water (**Figure 2**). Use your knowledge, briefly explain why the addition of polar aprotic solvent can speed up this S_N2 reaction. You are free to draw any diagrams to assist your explanation.

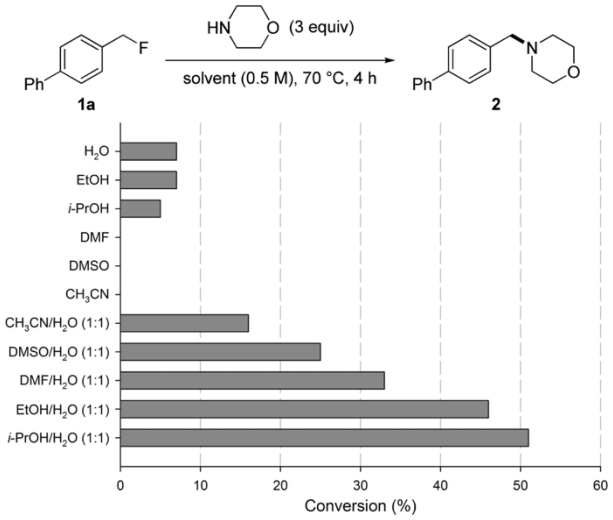


Figure 2. Evaluation of the effect of the solvent on the S_N2 reaction of benzyl fluoride **1a** with morpholine.

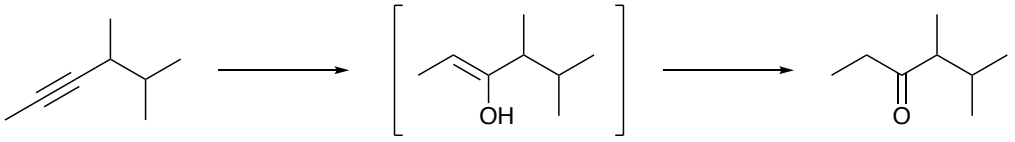
(d) **(2 pts)** Why does the presence of water can enable this transformation? Explain the reason. (*Hint: You may consider the high electronegativity of fluorine*)

33. **(20 pts)** Alkenes and alkynes are crucial raw materials in our modern chemical industry.

(a) **(4 pts)** Draw the reaction mechanism of 1-methylcyclohex-1-ene with bromine water.

(b) **(2 pts)** When using liquid bromine only, the product of part a is 1,2-dibromo-1-methylcyclohexane. Explain why an alkyne cannot be obtained by using elimination twice on this vicinal dibromocyclohexane.

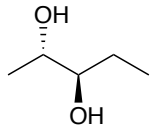
(c) **(4 pts)** When alkynes undergo hydration, a hydroxyl-containing compound (enol) cannot be isolated normally. Instead, a ketone is formed. Propose a plausible mechanism for the acid-catalyzed enol-keto tautomerization shown below. (*Only the mechanism of the <u>second step</u> is needed!*)



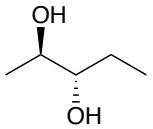
(not isolated)

(d) **(4 pts)** For the reaction shown in part c, a base (for example, NaOH) can also catalyze the tautomerization. Propose another mechanism that uses NaOH to catalyze the enol-keto conversion.

(e) **(6 pts)** Devise a synthesis route to prepare a racemic mixture of (2*R*,3*S*)- and (2*S*,3*R*)-pentane-2,3-diol. You can choose any inorganic reagents, but for organic reagents, only compounds with no more than **TWO** carbons are allowed. Retrosynthetic analysis is recommended. If your synthesis route is not correct, but you have provided a clear retrosynthetic analysis, you can still earn parts of points.



(2*S*,3*R*)-pentane-2,3-diol



(2*R*,3*S*)-pentane-2,3-diol