

Name _____

**Department of Chemistry
SUNY/Oneonta**

**Chem 322 - Organic Chemistry II
Examination #2 - March 13, 1995**

INSTRUCTIONS ---

This examination has two parts. Part I is in multiple choice format and the answers should be placed on the "Test Scoring Answer Sheet" which must be turned in and will be machine graded.

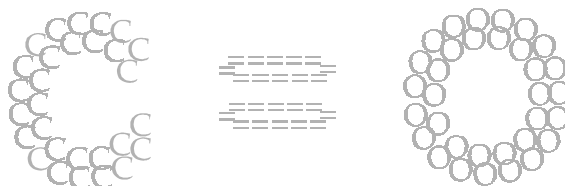
Part II requires your responding to questions by writing answers into the spaces provided in this booklet. This entire Exam Booklet must be handed in and will be returned to you with a grade. Write your name in the space above NOW.

On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places): your name, instructor's name, your student (Social Security) number, course number (30032201) and the test number (02); darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

You may use a set of molecular models but no other aids during the exam.

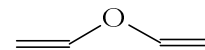
Answer all questions. The questions on Part I are worth 3 points each.

You have 90 minutes. Good luck!



1. A correct name for the compound on the right would be

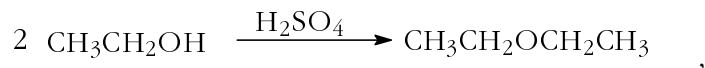
- (a) allyl vinyl ether. (b) divinyl ether. (c) diallyl ether.
(d) diethyl ether. (e) anisole.



2. The oxygen in an ether is usually ___ hybridized.

- (a) sp , (b) sp^2 , (c) sp^3 , (d) d^2sp^3 ,
(e) None of the above answers is correct.

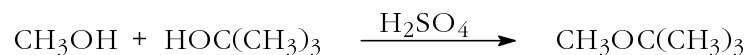
3. When diethyl ether is prepared by the bimolecular dehydration of ethanol,



the reaction takes place *via*

- (a) an S_N1 reaction of an ethyl carbocation with a molecule of ethanol.
(b) an S_N2 reaction of an ethyl carbocation with a molecule of ethanol.
(c) an S_N2 reaction of an ethoxide anion with ethanol.
(d) an S_N2 reaction of an ethoxide anion with protonated ethanol.
(e) an S_N2 reaction of an ethanol molecule with a protonated ethanol molecule.
(f) an E2 reaction between an ethoxide anion and an ethanol molecule.

4. When *t*-butyl methyl ether is prepared by the bimolecular dehydration of a mixture of *t*-butyl alcohol and methanol,



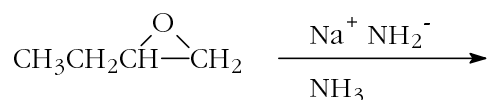
the reaction takes place *via*

- (a) an S_N1 reaction of a *t*-butyl carbocation with a molecule of methanol.
(b) an S_N1 reaction of a methyl carbocation with a molecule of *t*-butyl alcohol.
(c) an S_N2 reaction of a *t*-butoxide anion with methanol.
(d) an S_N2 reaction of a methoxide anion with *t*-butyl alcohol.
(e) an S_N2 reaction of a *t*-butoxide anion with protonated methanol.
(f) an S_N2 reaction of a methoxide anion with protonated *t*-butyl alcohol.

5. To prepare *t*-butyl ethyl ether *via* a Williamson synthesis one might (I) try to react sodium ethoxide with *t*-butyl bromide or (II) try to react sodium *t*-butoxide with ethyl bromide. Which of the following statements best describes what would actually happen in these cases.

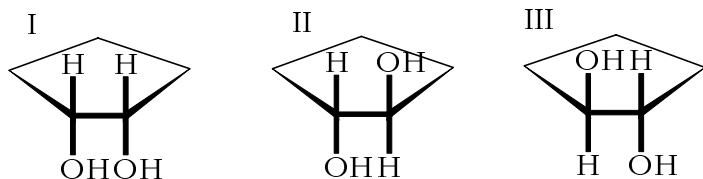
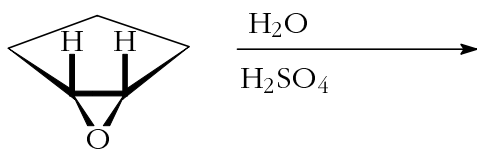
- (a) Each would give *t*-butyl ethyl ether in reasonable yield.
 (b) (I) would give *t*-butyl ethyl ether in reasonable yield, but (II) would give ethylene and *t*-butyl alcohol.
 (c) (I) would give isobutylene, $\text{CH}_2=\text{C}(\text{CH}_3)_2$, and ethanol, but (II) would give *t*-butyl ethyl ether in reasonable yield.
 (d) (I) would give isobutylene, $\text{CH}_2=\text{C}(\text{CH}_3)_2$, and ethanol, and (II) would give ethylene and *t*-butyl alcohol.

6. Predict the major product in the following reaction.



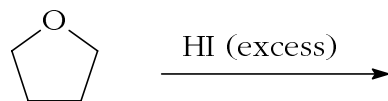
- (a) racemic $\text{CH}_3\text{CH}_2\underset{\text{NH}_2}{\text{C}}\text{HCH}_2\text{OH}$ (b) (R)- $\text{CH}_3\text{CH}_2\underset{\text{NH}_2}{\text{C}}\text{HCH}_2\text{OH}$ (c) (S)- $\text{CH}_3\text{CH}_2\underset{\text{NH}_2}{\text{C}}\text{HCH}_2\text{OH}$
 (d) racemic $\text{CH}_3\text{CH}_2\underset{\text{OH}}{\text{C}}\text{HCH}_2\text{NH}_2$ (e) (R)- $\text{CH}_3\text{CH}_2\underset{\text{OH}}{\text{C}}\text{HCH}_2\text{NH}_2$ (f) (S)- $\text{CH}_3\text{CH}_2\underset{\text{OH}}{\text{C}}\text{HCH}_2\text{NH}_2$

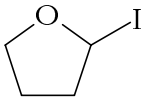
7. Predict the major product(s) in the following reaction.



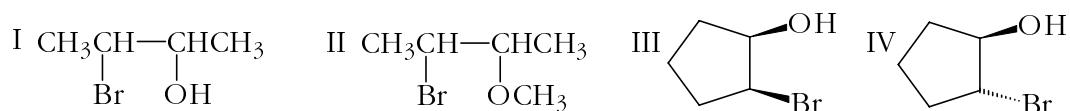
- (a) I, (b) II, (c) III,
 (d) II & III in unequal amounts,
 (e) II & III in equal amounts,
 (f) I, II and III with II & III in unequal amounts,
 (g) I, II and III with II & III in equal amounts

8. Alcohols are less volatile than ethers of the same molecular weight, but the two classes of compound have approximately the same solubility in water. This is because
- (a) only alcohols can form hydrogen bonds to water, but both compounds can form hydrogen bonds with other molecules of the same type.
 - (b) only ethers can form hydrogen bonds with water, but both compounds can form hydrogen bonds with other molecules of the same type.
 - (c) both compounds can form hydrogen bonds with water, but only ethers can form hydrogen bonds with themselves.
 - (d) both compounds can form hydrogen bonds with water, but only alcohols can form hydrogen bonds with themselves.
9. Which synthesis would you chose to make *t*-butyl isopropyl ether, $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}(\text{CH}_3)_2$, in the highest yield?
- (a) $(\text{CH}_3)_3\text{CO}^- \text{K}^+ + (\text{CH}_3)_2\text{CHBr}$
 - (b) $(\text{CH}_3)_3\text{CBr} + (\text{CH}_3)_2\text{CHO}^- \text{Na}^+$
 - (c) $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{H}_3\text{C} \end{array} + (\text{CH}_3)_2\text{CHOH} \xrightarrow[\text{NaBH}_4]{\text{Hg}(\text{OCOCF}_3)_2}$
 - (d) $(\text{CH}_3)_3\text{COH} + (\text{CH}_3)_2\text{CHOH} \xrightarrow[\text{heat}]{\text{H}_2\text{SO}_4}$
10. Only one of the following reagents will react with a simple ether (which is not an epoxide). Which is it?
- (a) hot concentrated hydrobromic acid, (b) hot concentrated sodium hydroxide,
 - (c) hot concentrated potassium permanganate, (d) lithium aluminum hydride,
 - (e) sodium metal
11. Select the product in the following reaction.



- (a) HOCH₂CH₂CH₂CH₂OH (b) HOCH₂CH₂CH₂CH₂I (c) ICH₂CH₂CH₂CH₂I
 (d) CH₃CH₂CH₂CH₂I (e) 

12. Which of the following compounds would readily form a 1,2-epoxide on treatment with base?



- (a) I&II, (b) I&III, (c) I&IV,
 (d) II&III, (e) II&IV, (f) III&IV

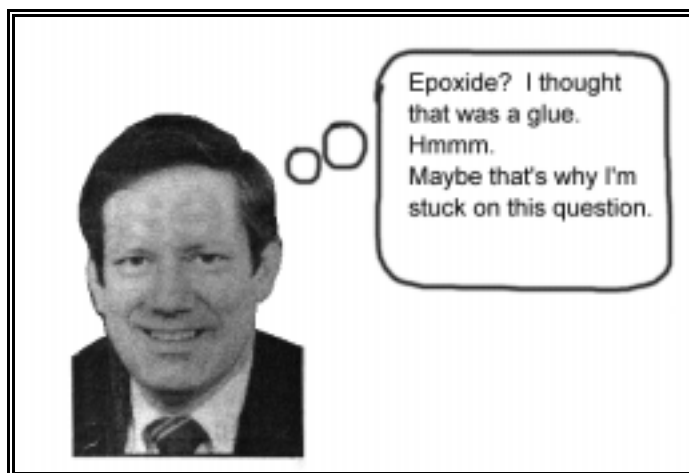
13. Which of the following sets of reagents and conditions could **not** accomplish the transformation shown below.

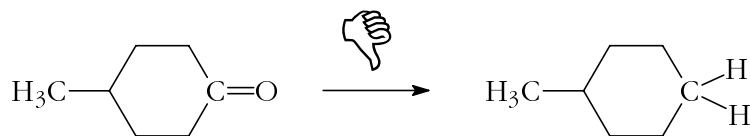
(a) H₂N-NH₂, KOH, diethylene glycol solvent, heat,

(b) Zn(Hg), HCl,

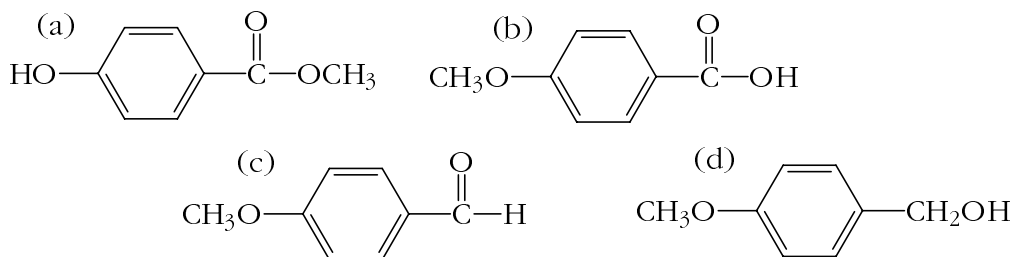
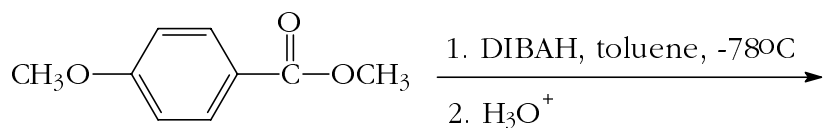
(c) 1. HSCH₂CH₂SH, HCl,
 2. Raney Ni, ethanol,

(d) 1. LiAlH₄, 2. H₂O

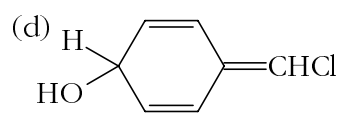
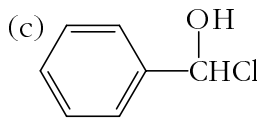
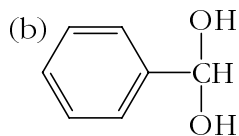
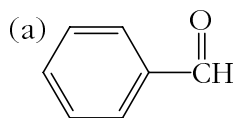
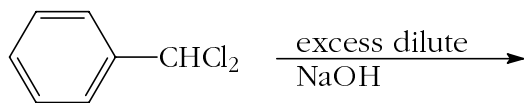




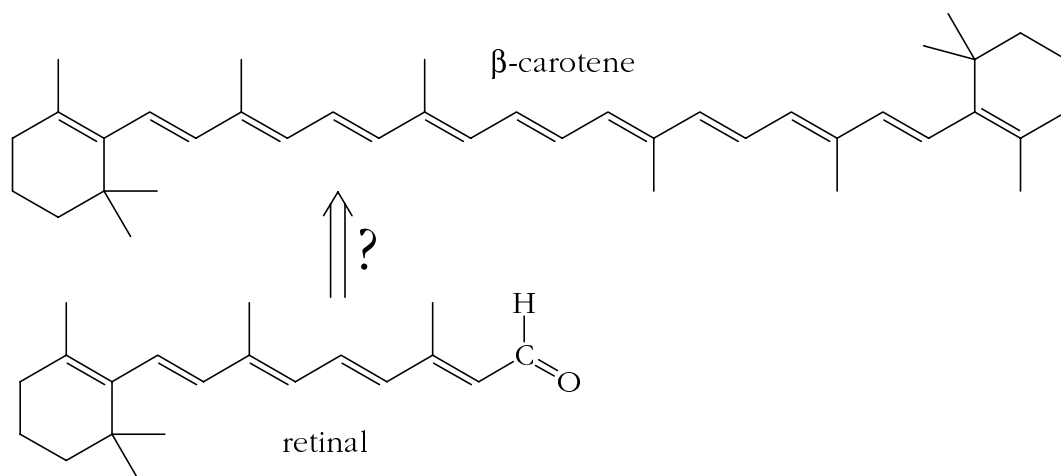
14. CH₃COOC₂H₅ is an example of a(n)
- (a) ether, (b) acid anhydride, (c) carboxylic acid, (d) ketone, (e) ester
15. The IUPAC name for CH₃-CO-CH₂CH₃ is
- (a) butanal. (b) butanone. (c) butyric acid. (d) acetyethane. (e) 1-methylacetone.
16. Which of the following classes of compound typically undergo nucleophilic addition as opposed to nucleophilic substitution?
- (I) aldehydes, (II) carboxylic acids, (III) esters, (IV) ketones
- (a) I&II, (b) II&III, (c) III&IV, (d) I&IV, (e) I&III, (f) II&IV
17. Select the principal product of the following reaction.



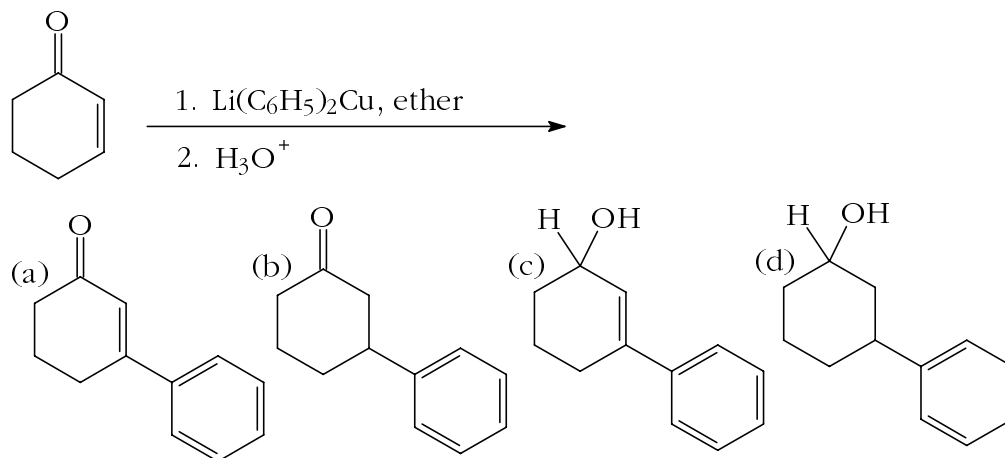
18. Select the principal product of the following reaction.



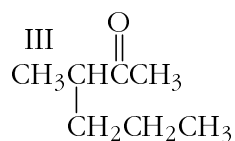
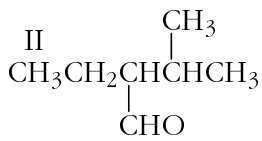
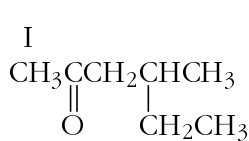
19. Which of the following reactions is a critical step in a synthetic method for converting retinal to β -carotene?



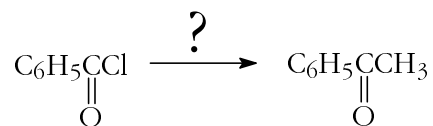
- (a) Wolff-Kishner reaction, (b) Clemmensen reduction, (c) Hunsdiecker reaction,
(d) Diels-Alder reaction, (e) Wittig reaction
20. Select the principal product of the following reaction.



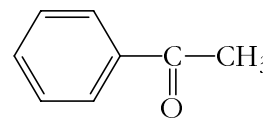
21. Which of the compounds shown below are correctly named as pentane derivatives, either as pentanals or pentanones?



- (a) I, (b) II, (c) III, (d) I&III, (e) None of them.
22. Which reagents would you use to bring about the conversion shown to the right?
- (a) CH_3MgBr , ether, -78° , then dil. HCl,
 (b) CH_3Li , ether, -78° , then dil. HCl,
 (c) CH_3Br , AlCl_3 ,
 (d) $(\text{CH}_3)_2\text{CuLi}$, ether, -78° ,
 (e) CH_3OH , H_3O^+ , catalyst

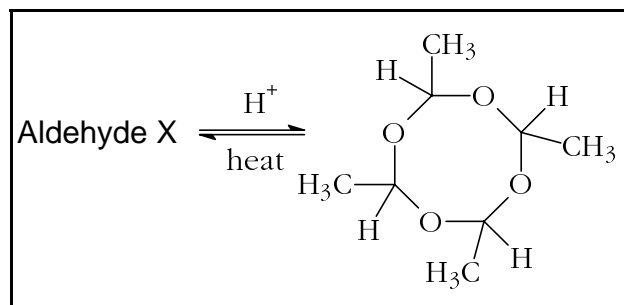


23. The compound shown to the right is used as an artificial flavor in pistacio ice cream. What is its name?



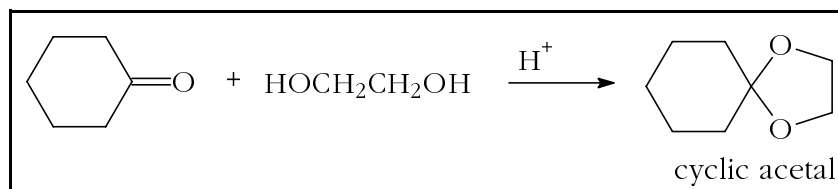
- (a) acetophenone, (b) benzophenone, (c) acetone, (d) benzoic acid, (e) methyl benzoate

24. Metaldehyde is used as a bait and poison for snails and slugs. It is a *tetramer* of a common aldehyde, "Aldehyde X", and is formed from that aldehyde under acid catalysis. Heating metaldehyde will form "Aldehyde X". What is Aldehyde X?

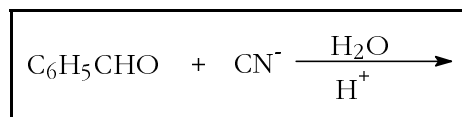


- (a) H_2CO , (b) CH_3CHO , (c) CH_3COCH_3 ,
 (d) $\text{CH}_3\text{CH}_2\text{CHO}$, (e) None of these answers is correct.
25. Aldehydes differ from ketones in that they
- (I) are less reactive than ketones toward nucleophilic addition reactions.
 (II) are more reactive than ketones toward nucleophilic addition reactions.
 (III) are less easily oxidized than ketones.
 (IV) are more easily oxidized than ketones.
- (a) I&III, (b) I&IV, (c) II&III, (d) II&IV,
 (e) None of the above answers is correct.
26. Typical reactions of aldehydes and ketones involve attack of a(n) **A** reagent at the **B** atom of the carbonyl group.
- (a) **A** = nucleophilic, **B** = oxygen, (b) **A** = nucleophilic, **B** = carbon,
 (c) **A** = electrophilic, **B** = carbon, (d) **A** = radical, **B** = oxygen,
 (e) Bogus question. Neither aldehydes nor ketones undergo any reactions.
27. Cyclic acetals of the sort shown below are frequently prepared during the course of a synthetic sequence, for the purpose of "protecting" a carbonyl group. Such an acetal is inert to each of the reagents listed below, **except**

- (a) LiAlH_4 ,
 (b) CrO_3 ,
 (c) CH_3MgBr ,
 (d) alkoxide ions,
 (e) dilute H_2SO_4

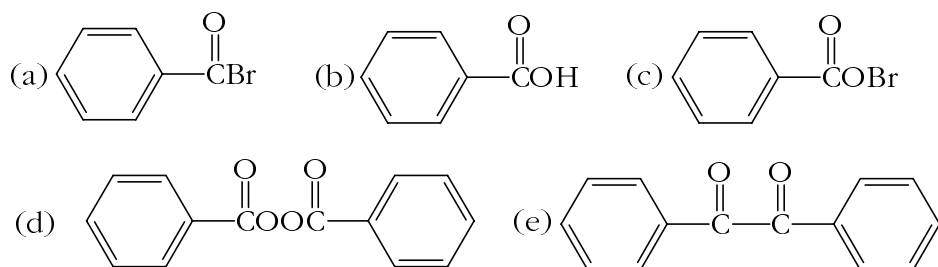
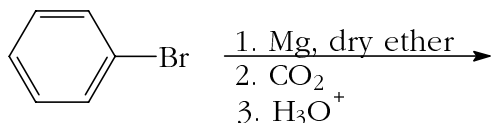


28. The product of the reaction to the right is



- (a) optically active. (b) achiral. (c) racemic.
 (d) a meso compound. (e) a pair of diastereomers.

29.



30. What is the structure of formic acid?

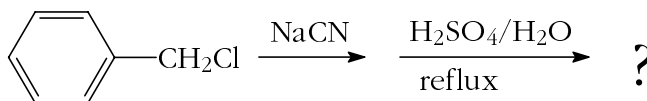
- (a) HCOOH , (b) CH_3COOH , (c) $\text{CH}_3\text{CH}_2\text{COOH}$, (d) $(\text{CH}_3)_2\text{CHCOOH}$

31. Arrange the following compounds in order of decreasing acid strength (strongest acid first).

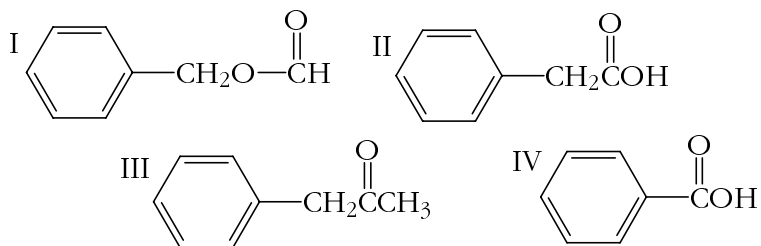
- (I) $\text{H-C}\equiv\text{C-H}$, (II) HCl , (III) HCOOH , (IV) CH_3OH

- (a) $\text{I} > \text{II} > \text{III} > \text{IV}$, (b) $\text{IV} > \text{III} > \text{II} > \text{I}$, (c) $\text{II} > \text{III} > \text{IV} > \text{I}$, (d) $\text{II} > \text{I} > \text{III} > \text{IV}$,
 (e) None of the above answers is correct.

32. What is the final product of the reaction sequence shown?



- (a) I, (b) II, (c) III, (d) IV,
(e) II&IV



33. Arrange the following compounds in decreasing order of acidity (most acidic first).

(I) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, (II) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$, (III) $\text{CH}_3\text{CHClCH}_2\text{COOH}$,
(IV) $\text{CH}_3\text{CH}_2\text{CHClCOOH}$

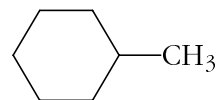
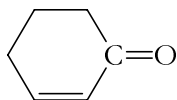
- (a) I>II>III>IV, (b) IV>III>II>I, (c) I>IV>III>II, (d) III>II>IV>I
(e) None of the above answers is correct.

L Do Not Detach These Sheets From The Rest Of The Exam!

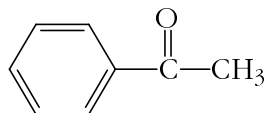
Part II. Enter your answers in the space provided. If there is inadequate room, continue on the back of the page and clearly indicate on the front of the page that you have done this. Hand in this entire exam booklet when you are finished; it will be returned to you with your grade. Make sure your name is on the front sheet.

1. Synthesis. Draw an outline for each of the following syntheses. Show all materials and any special conditions employed as you write the reactions which constitute your outline. Do not balance equations or show mechanisms.
- (a) Prepare hexyl methyl ether, $\text{CH}_3(\text{CH}_2)_5\text{-O-CH}_3$, starting with 1-hexyne. You may use any other materials you need.

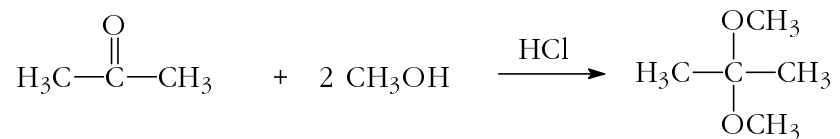
- (b) Prepare methylcyclohexane starting with 2-cyclohexenone. You may use any other materials you need.



- (c) Prepare the ketone shown below, starting with bromobenzene. You may use any other materials you need.



2. (a) Show the mechanism for the reaction below. Show all intermediates, drawing all important resonance structures. Do not show transition states.



Part I (100) _____

Part II

1. (15) _____

2. (10) _____

3. (2) _____

Total (125) _____

3. What is the snail at the bottom of page 8 doing?