

Name _____

Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #2 - March 12, 2001

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.

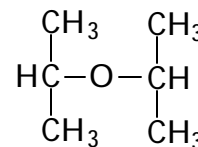
You may use a set of molecular models but no other aids during the exam.

Answer all questions. The questions on Part I are worth 2.67 points each.

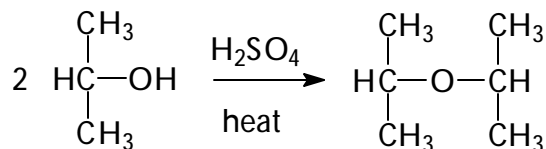
You have 90 minutes. Good luck!

1. Select the best name for the compound to the right.

- (a) diethyl ether, (b) diisopropyl ether, (c) dipropyl ether,
(d) dipropyl ketone, (e) disec-propyl ether

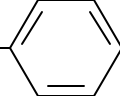
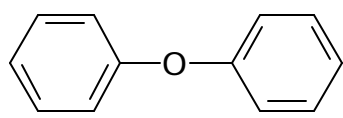


2. The ether shown in question #1 can be synthesized by bimolecular dehydration as shown to the right. Which of the following compounds is most likely to be a significant byproduct in such a synthesis?



- (a) $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{HC}-\text{O}-\text{O}-\text{CH} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ (b) $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ (c) $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{HC}-\text{O}-\text{C}-\text{OH} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ (d) $\text{H}_2\text{C}=\overset{\text{CH}}{\text{C}}-\text{CH}_3$

3. Which of the following ethers could not be synthesized by a Williamson synthesis?

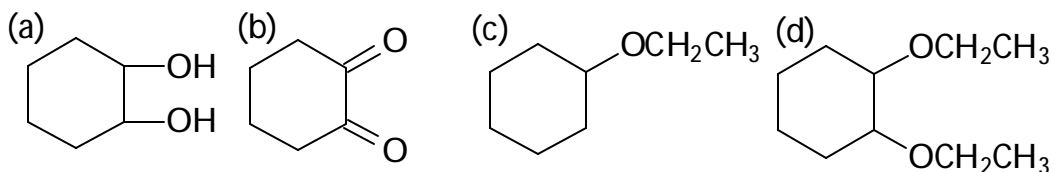
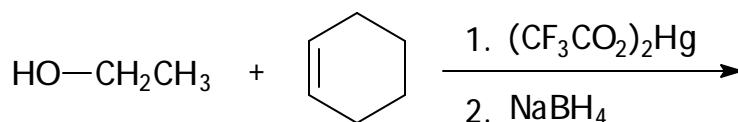
- (a) $\text{H}_3\text{C}-\text{O}-\text{CH}_2\text{CH}_3$ (b) $\text{CH}_3\text{CH}_2-\text{O}-$ 
- (c)  (d) $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{HC}-\text{O}-\text{CH} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

4. Rank the following compounds in order of decreasing reactivity in a Williamson synthesis (most reactive first).

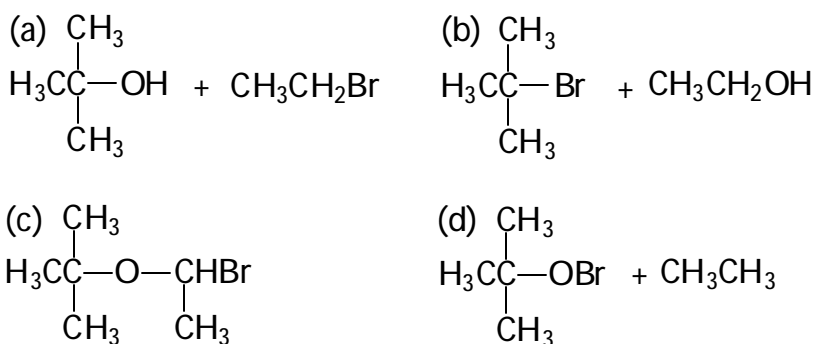
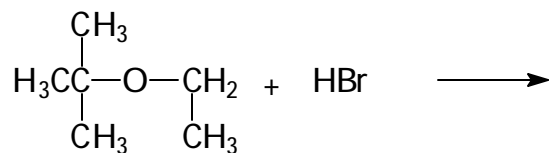
- (I) bromomethane, (II) 1-bromopropane, (III) 2-bromopropane,
(IV) 2-bromo-2-methylpropane

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

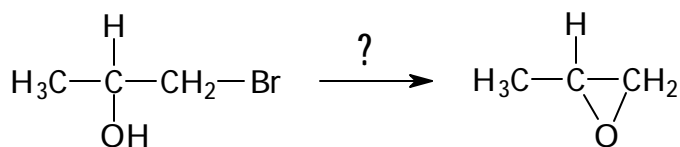
5. Select the major product of the following reaction.



6. Predict the major products of the following reaction.

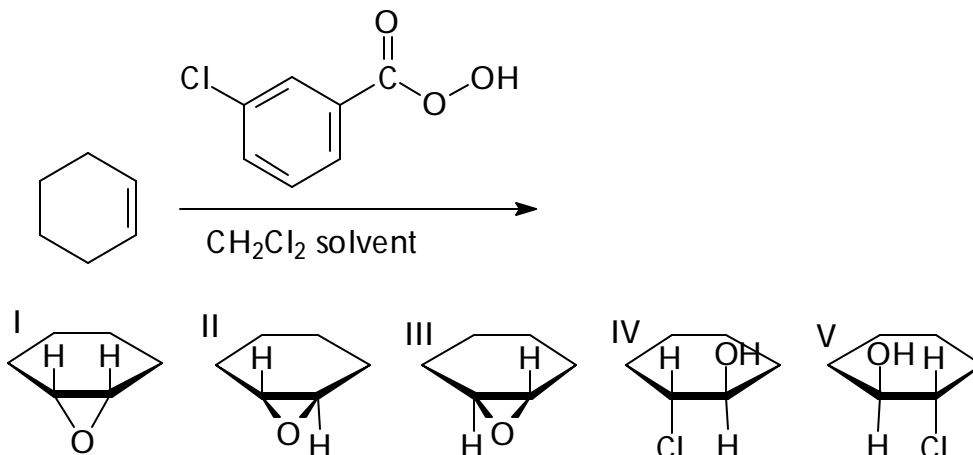


7. What reagent would you use to effect the transformation shown to the right?



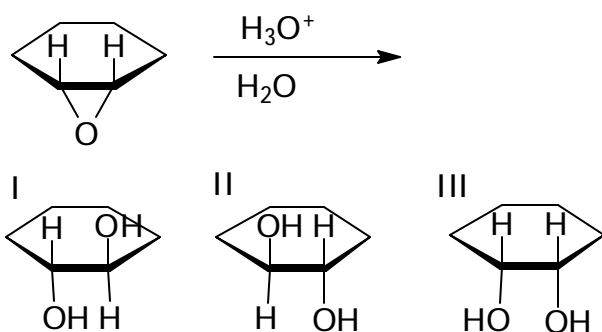
- (a) H_2SO_4 , (b) NaBH_4 , (c) KOH ,
(d) Na_2CrO_4

8. Predict the major organic product(s) in the following reaction.



(a) I, (b) II&III in equal amount, (c) II&III in unequal amount, (d) IV&V in equal amount, (e) IV&V in unequal amount, (f) I-III, with II&III in equal amount, (g) I-III, with II&III in unequal amount

9. Predict the major organic product(s) in the following reaction.

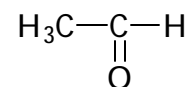


(a) I, (b) II, (c) I&II in equal amount, (d) I&II in unequal amount, (e) III, (f) I&II in equal amount, and III, (g) I&II in unequal amount, and III

10. A common reaction type for both aldehydes and ketones is

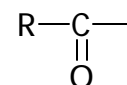
(a) electrophilic substitution, (b) nucleophilic substitution, (c) nucleophilic addition, (d) oxidation, (e) None of the previous answers is correct.

11. The compound to the right is known as



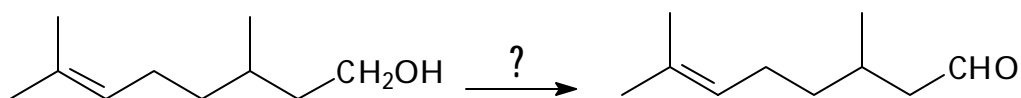
(a) acetaldehyde, (b) acetic acid, (c) acetic anhydride, (d) acetal

12. The group shown to the right is known as



(a) acetyl, (b) formyl, (c) carboxy, (d) acyl

13. Which reagent would you use to convert citronellol to citronellal, the chief constituent of citronella oil?



(a) KOH,
(b) KMnO_4 , (c) PCC / CH_2Cl_2 , (d) LiAlH_4

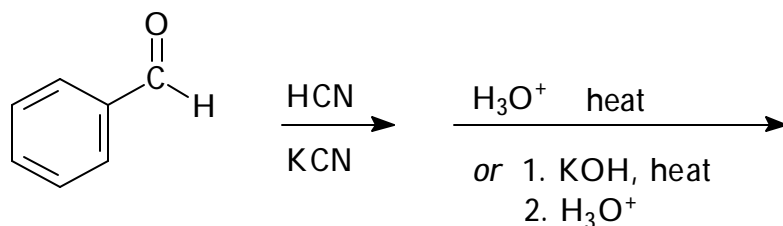
14. Which of the following methods could not be used to make a methyl ketone (a ketone in which one of the alkyl groups is methyl)?

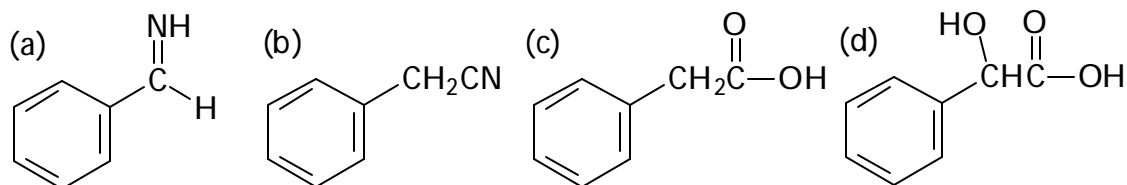
(a) oxidation of an alcohol, (b) ozonolysis of an alkene, (c) Friedel-Crafts acylation,
(d) reaction of a terminal alkyne with water in the presence of H_2SO_4 and HgSO_4 ,
(e) reaction of a carboxylic acid chloride with a diorganocopper (Gilman) reagent,
(f) Bogus premise; all of the above methods could be used.

15. In the Tollens test for aldehydes, which employs Ag_2O , ammonia, and water,

(a) Ag^{+1} is reduced to Ag^0 and the aldehyde is oxidized to the salt of a carboxylic acid.
(b) Ag^{+1} is oxidized to Ag^0 and the aldehyde is reduced to the salt of a carboxylic acid.
(c) Ag^0 is reduced to Ag^{+1} and the aldehyde is oxidized to the salt of a carboxylic acid.
(d) Ag^0 is oxidized to Ag^{+1} and the aldehyde is reduced to the salt of a carboxylic acid.

16. Select the principal product of the following synthesis



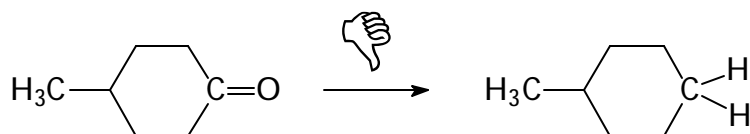


17. The oxygen in a ketone is usually ___ hybridized.

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

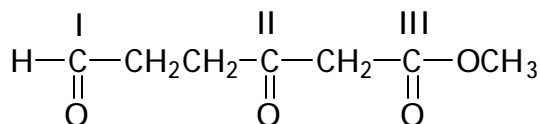
18. Which of the following sets of reagents and conditions could not accomplish the transformation shown below.

- (I) H_2N-NH_2 , KOH, diethylene glycol solvent, heat, (II) 1. $NaBH_4$, 2. H_3O^+
 (III) $HOCH_2CH_2OH$, H_3O^+ , (IV) 1. $LiAlH_4$, 2. H_2O



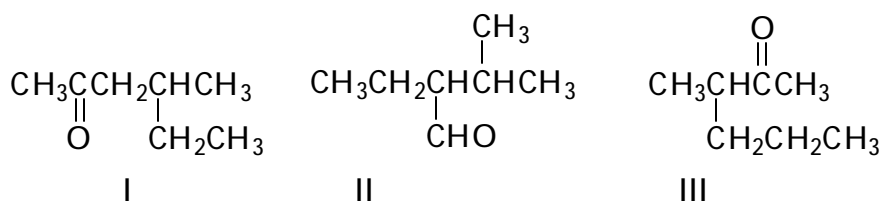
- (a) I, II, (b) I-III, (c) I, IV, (d) II, III, (e) II-IV, (f) III, IV

19. Acetals are sometimes formed from aldehydes and ketones to function as "protecting groups." If one mole of 1,2-ethanediol (ethylene glycol) were to react with the compound to the right, which of the carbonyl groups would be protected?



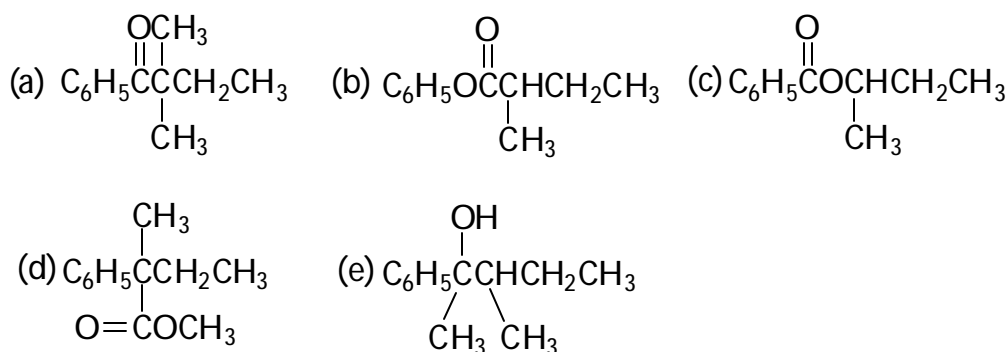
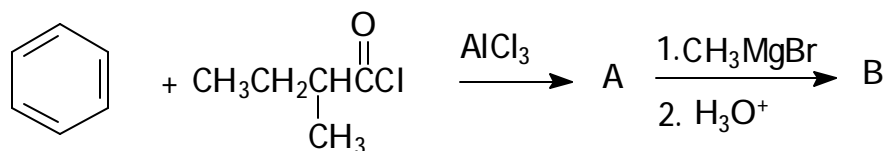
- (a) I, (b) II, (c) III, (d) I&II are about equally reactive, so in some molecules both would be protected, in some molecules one or the other would be protected and in some molecules neither would be protected, (e) I&III are about equally reactive, so in some molecules both would be protected, in some molecules one or the other would be protected and in some molecules neither would be protected.

20. Which compounds shown below are correctly named in the IUPAC system as pentane based, either as pentanals or pentanones?

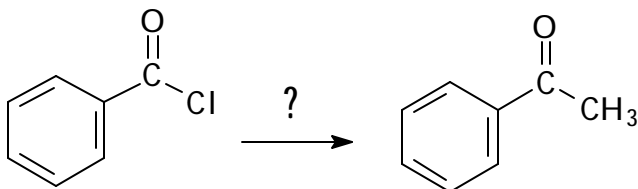


- (a) I, (b) II, (c) III, (d) I&III, (e) None of them.

21. Product B of the following sequence of reactions would be:



22. Which reagents would effect the conversion shown?



- (a) CH_3MgBr /ether, then H_3O^+ , (b) CH_3Li /ether, then H_3O^+
 (c) $\text{CH}_3\text{Br}/\text{AlCl}_3$, (d) $(\text{CH}_3)_2\text{CuLi}$ /ether, (e) $\text{CH}_3\text{OH}/\text{H}_3\text{O}^+$

23. 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 reactive than ketones toward nucleophilic substitution reactions.
- (IV) are more reactive than ketones toward nucleophilic substitution reactions.
- (V) are less easily oxidized than ketones.
- (VI) are more easily oxidized than ketones.

- (a) I&III, (b) I,III&V, (c) II&IV, (d) II, IV, &VI, (e) I&V, (f) II&VI,
- (g) None of the previous answers is correct.

24. Typical reactions of aldehydes and ketones involve attack of a(n) A reagent at the B atom of the carbonyl group.

	A	B
(a)	nucleophilic	oxygen
(b)	nucleophilic	carbon
(c)	electrophilic	carbon
(d)	radical	oxygen

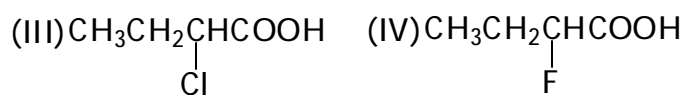
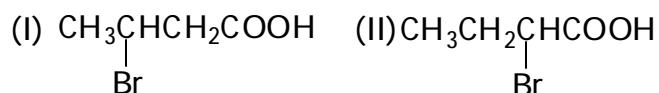
25. Carboxylic acids are stronger acids than alcohols because

- (a) the carboxylate anion is stabilized by resonance to a greater extent than the carboxyl group and neither the alcohol nor its alkoxide anion is stabilized by resonance.
- (b) the carboxylate anion is destabilized by resonance to a greater extent than the carboxyl group and neither the alcohol nor its alkoxide anion is destabilized by resonance.
- (c) the carboxyl group is very unstable because of a high energy C-O bond and it therefore ionizes readily.
- (d) the carboxyl group is stabilized by resonance to a greater extent than the carboxylate anion and neither the alcohol nor its alkoxide anion is stabilized by resonance.
- (e) Way bogus, dude! Alcohols are like way more acidic than carboxylic acids.

26. A solution of 1-decanol and butanoic acid in ether is shaken with excess aqueous sodium bicarbonate solution in a separatory funnel. Which answer below correctly describes the major organic contents of each of the two resulting solutions?

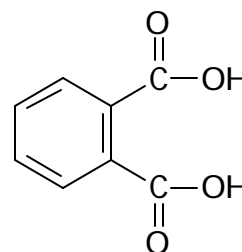
	<u>Ether Solution</u>	<u>Aqueous Sodium Bicarbonate Solution</u>
(a)	decanol	butanoic acid
(b)	decanol	sodium butanoate
(c)	butanoic acid	decanol
(d)	sodium butanoate	decanol

27. The correct order of acidity of the acids shown below (most acidic first) is

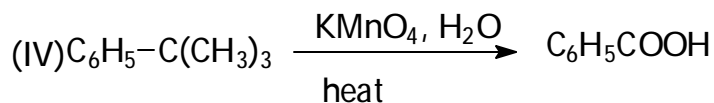
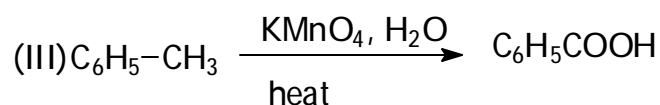
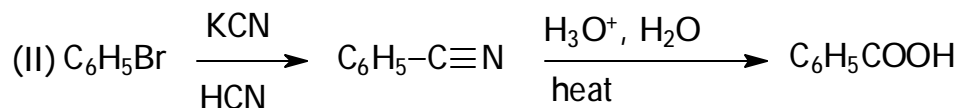
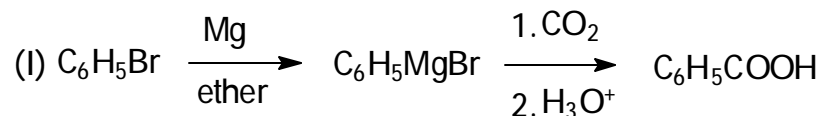


- (a) I>II>III>IV, (b) II>IV>I>III, (c) IV>II>I>III, (d) IV>III>II>I, (e) I>II>IV>III
28. The common name for the acid shown to the right is

- (a) succinic acid, (b) valeric acid, (c) maleic acid,
(d) toluic acid, (e) phthalic acid

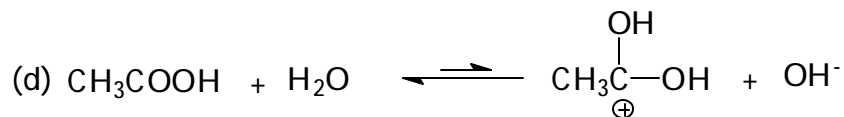
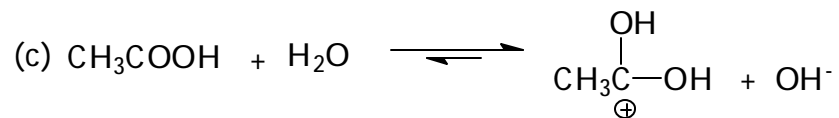
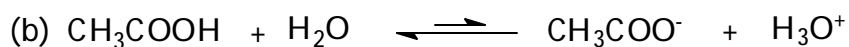
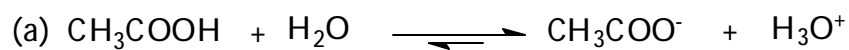


29. Which of the following syntheses would not give an acceptable yield of the indicated carboxylic acid?



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

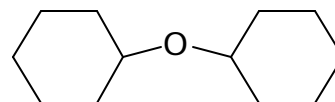
30. Which of the following is correct in both terms of products formed and the equilibrium constant implied by the arrows?



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.

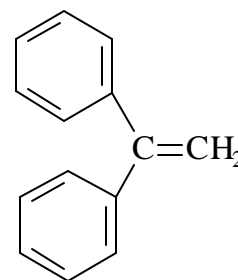
1. Synthesis. Draw an outline for each of the following syntheses. Show all materials and any special conditions employed as you write the reactions which constitute your outline. Do not balance equations or show mechanisms.

- (a) Prepare dicyclohexyl ether using a Williamson synthesis. Available starting materials are alcohols up to 6 carbons and any needed inorganic materials.

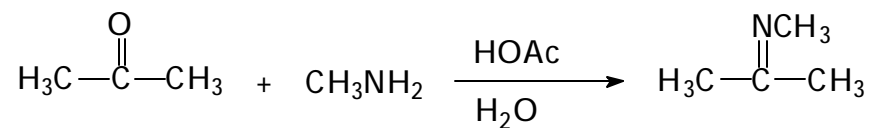


- (b) The Williamson synthesis is not ideal for making the above compound. Write down the reaction that will lead to a significant amount of byproduct in this synthesis.

- (c) Prepare 1,1-diphenylethene from benzophenone, Ph-CO-Ph, and bromomethane, CH₃Br, using any other materials you need.



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



Part I (80) _____

Part II

1. (15) _____

2. (5) _____

Total (100) _____