Name ____________________________
Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #2 - March 10, 1997

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 4 points each.

You have 90 minutes. Good luck!
1. Select a correct name for CH$_3$-O-CH(Ch)$_2$.

(a) sec-butyl methyl ether, (b) isobutyl methyl ether, (c) isopropyl methyl ether, (d) isopropyl methyl ketone, (e) None of the previous answers is correct.

2. Ethers are most commonly used in the laboratory as

(a) reactants, (b) solvents, (c) drying agents, (d) fuel, (e) beverages

3. Which of the following compounds would you employ in a Williamson synthesis to make the ether shown to the right?

I: CH$_3$CH$_2$OH, II: CH$_3$CH$_2$Br, III: (CH$_3$)$_3$CCH$_2$OH, IV: (CH$_3$)$_2$CCH$_2$Br

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

4. Which synthetic procedure would be best for making the ether shown to the right?

CH$_3$CH$_2$CHOC(CH$_3$)$_3$

(a) Cannizzaro reaction. (b) Diels-Alder reaction.
(c) Williamson synthesis.
(d) alkoxymercuration-demercuration reaction. (e) Pomeranz-Fritsch reaction.

5. Select the two major organic products that form when one mole of HI reacts with one mole of cyclohexyl ethyl ether.

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O—CH$_2$CH$_3$ + HI

(a) iodoethane & cyclohexanol, (b) iodocyclohexane & ethanol,
(c) 1-iodohexane & ethanol, (d) iodoethane & 1-hexanol
```
6. Select the major organic product in the following reaction.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} = \text{C} \quad \text{CH}_3 + \text{Cl} & \quad \text{C} = \text{O} \quad \text{C} = \text{O} \quad \text{OH} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{Cl} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

- (a) \(\text{H}_3\text{C} = \text{C} \text{OCH}_3\)
- (b) \(\text{H}_3\text{C} = \text{C} \text{CH}_3\)
- (c) \(\text{H}_3\text{C} \text{OCH}_3\)
- (d) \(\text{H}_3\text{C} \text{CCH}_3\)
- (e) \(\text{H}_3\text{C} \text{CCH}_3\)

7. Select the principal organic products formed when \textit{cis}-5,6-epoxydecane undergoes acid catalyzed hydrolysis.

\[
\begin{align*}
\text{H}_9\text{C}_4 & \quad \text{C} = \text{C} \quad \text{C}_4\text{H}_9 \\
\text{H} & \quad \text{O} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{H}_9\text{C}_4 & \quad \text{C} = \text{C} \quad \text{C}_4\text{H}_9 & \quad \text{H}_2\text{O} & \quad \text{H}_3\text{O}^+ \\
\text{HO} & \quad \text{C} = \text{C} \quad \text{OH} & \quad \text{H}_9\text{C}_4 & \quad \text{C} = \text{C} \quad \text{C}_4\text{H}_9 & \quad \text{H}_9\text{C}_4 & \quad \text{C} = \text{C} \quad \text{C}_4\text{H}_9 \\
\text{I} & \quad \text{H} & \quad \text{H} & \quad \text{II} & \quad \text{H} & \quad \text{H} & \quad \text{III} & \quad \text{H} & \quad \text{C}_4\text{H}_9
\end{align*}
\]

(a) I, (b) II, (c) III, (d) I&II in equal amounts, (e) I&II in unequal amounts,
(f) I-III with I&II in equal amounts, (g) I-III with I&II in unequal 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. Select all of the following compounds that are correctly named in the IUPAC system as pentane derivatives, either as pentanals or pentanones?

\[
\begin{align*}
\text{I} & \quad \text{CH}_3\text{CCH}_2\text{CHCH}_3 \\
\text{II} & \quad \text{CH}_3\text{CH}_2\text{CHCH}_3\text{CH}_2\text{CHO} \\
\text{III} & \quad \text{CH}_3\text{CHCCH}_3 \\
\end{align*}
\]

(a) I, (b) II, (c) III, (d) I&III, (e) Bogus question, dude! None of these compounds is named as a pentanal or pentanone.

10. Select the set of reagents that would carry out the following conversion in one or two steps.

\[
\text{CH}_3\text{CH}_2\text{C}═\text{CH} \quad \longrightarrow \quad \text{CH}_3\text{CH}_2\text{CCH}_3
\]

(a) H_2SO_4, HgSO_4, H_2O,
(b) 1. BH_3 2. H_2O_2, KOH, H_2O,
(c) 1. H_2/Lindlar Catalyst 2. H_2SO_4, H_2O,
(d) O_3
(e) 1. CrO_3, H_2SO_4 2. H_2/Lindlar catalyst

11. Select the set of reagents that would carry out the following conversion in one or two steps.

\[
\text{C─Cl} \quad \longrightarrow \quad \text{C─CH}_3
\]

(a) 1. CH_3MgBr/ether 2. dilute HCl
(b) 1. CH_3Li/ether 2. dilute HCl
(c) CH_3Br, anhydrous AlCl_3
(d) (CH_3)_2CuLi/ether
(e) CH_3OH, H_3O^+

12. 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) Yo, dude; another bogus question. No generalization of this type can be made.

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

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) nucleophilic</td>
<td>oxygen</td>
</tr>
<tr>
<td>(b) nucleophilic</td>
<td>carbon</td>
</tr>
<tr>
<td>(c) electrophilic</td>
<td>carbon</td>
</tr>
<tr>
<td>(d) radical</td>
<td>oxygen</td>
</tr>
</tbody>
</table>

14. To effect the conversion of acetone containing O-16 to acetone containing O-18, which reagents would you use?

(a) oxygen-18 and a nickel catalyst,
(b) Cr\(^{18}\)O\(_3\),
(c) H\(_2\)\(^{18}\)O\(_2\), NaOH,
(d) H\(_2\)\(^{18}\)O, dilute HCl,
(e) \(^{18}\)O\(_3\), then Zn and acetic acid

15. Which of the following reactions involves nucleophilic addition to a carbonyl carbon as a key step in its mechanism?

(I) \[
\begin{align*}
\text{H} & \\
\text{C}_6\text{H}_5\text{C}=\text{O} + 2 \text{CH}_3\text{OH} & \xrightarrow{\text{H}^+} \text{C}_6\text{H}_5\text{CH(OCH}_3)_2
\end{align*}
\]

(II) \[
\begin{align*}
\text{CH}_3\text{CCH}_2\text{CH}_3 & \xrightarrow{1) \text{LiAlH}_4} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\
& \xrightarrow{2) \text{H}_3\text{O}^+} \text{CH}_3\text{CHCH}_2\text{CH}_3\text{OH}
\end{align*}
\]

(a) I, (b) II, (c) I&II, (d) Neither I nor II.
16. Which of the reactions in question #15 involves activation of the carbonyl group by initial protonation of its oxygen?

(a) I, (b) II, (c) I&II, (d) Neither I nor II.

17. Cyclic acetals of the sort shown here 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) LiAlH₄, (b) CrO₃, (c) CH₃MgBr, (d) alkoxide anions, (e) dilute H₂SO₄

18. Which reagent below will not react with benzaldehyde to form an imine?

(a) C₆H₄NH₂, (b) (CH₃)₂CHNH₂, (c) (CH₃)₂NH, (d) (CH₃)₂CNH₂, (e) Sham query, dude! All of these amines will react with essence of maraschino cherry to give an imine.

19. Which compounds from the list below would you select as starting materials to prepare 2,4-dimethyl-3-hexene by the Wittig method?

(I) CH₃CHCH₂Br    (II) CH₃CHBr    
    CH₃

(III) CH₃CCH₃    (IV) CH₃CHCHO    (V) CH₃CCH₂CH₃

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

20. Which of the following is the weakest acid?

(a) ClCH₂CH₂COOH, (b) FCH₂CH₂COOH, (c) ClCH₂COOH, (d) FCH₂COOH

21. A carboxylic acid having 8 carbon atoms is likely to be soluble in _____, but not in _____.

(a) dilute acid, dilute base, (b) water, dilute base, (c) dilute base, water, (d) water, dilute acid.
22. What is (are) the product(s) of the following reaction?

\[
\text{CH}_3\text{COH} + \text{CH}_3\text{MgBr} \rightarrow \text{OMgBr}
\]

(a) \((\text{CH}_3)_2\text{COH}\)  (b) \(	ext{CH}_3\text{C(CH}_3)_2\)

(c) \(	ext{CH}_3\text{C}_2\text{H}_3 + \text{HOMgBr}\)  (d) \(	ext{CH}_3\text{COMgBr} + \text{CH}_4\)

23. Which of the following sequences does not yield a carboxylic acid?

(a) \(	ext{CH}_3\text{CH}_2\text{MgBr} \xrightarrow{\text{CO}_2} \text{HCl}/\text{H}_2\text{O}\)

(b) \(	ext{CH}_3\text{CHCH}_3 \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} \)

(c) \(	ext{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{KCN}} \text{H}_2\text{SO}_4\text{ heat}\)

(d) \(	ext{CH}_3\text{CH}_2\text{C}=\text{O} \xrightarrow{\text{Ag(NH}_3)_2\text{NO}_3} \text{HCl}/\text{H}_2\text{O}\)

24. Which of the following sequences yields benzoic acid?

(I) \[
\text{MgBr} \xrightarrow{\text{HCO}_2\text{H}} \text{HCl}/\text{H}_2\text{O}
\]

(II) \[
\text{CH}_3 \xrightarrow{\text{KMnO}_4\text{ heat}} \text{HCl}/\text{H}_2\text{O}
\]

(III) \[
\text{Br} \xrightarrow{\text{KCN}} \text{H}_2\text{SO}_4\text{ heat}
\]

(IV) \[
\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} 
\]

(a) I,  (b) II,  (c) III,  (d) IV,  (e) I&II,  (f) III&IV,  (g) I&IV,  (h) II&III
25. Select the major organic product of the following reaction sequence.

\[
\text{[Diagram of reaction sequence with options (a) to (d)]}
\]

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

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\[\text{C} = \text{O} \quad \text{CH}_3\]
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(c) Prepare the aldehyde shown below, starting with bromobenzene. You may use any other materials you need.

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\[\text{H} \quad \text{C} = \text{O}\]
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2. Show the mechanism for the reaction below. Show all intermediates, drawing all important resonance structures. Do not show transition states.

$$2 \text{ benzaldehyde} \xrightarrow{\text{concentrated aqueous KOH}} \text{ benzoate potassium} + \text{ benzyl alcohol}$$