CH 301
ORGANIC CHEMISTRY - FINAL EXAM
May 6, 2000

My Mom/Dad calls me ________________

DIRECTIONS: This examination is in two parts. PART I consists of fifteen multiple choice questions (each worth 4 points). Circle the correct answer. PART II (140 points) involves questions of general nature requiring write-up on your part. Be brief, clear and to the point.

READ AND UNDERSTAND EACH QUESTION CAREFULLY BEFORE ATTEMPTING TO ANSWER IT. IF YOU ARE IN DOUBT ABOUT ANY QUESTION, PLEASE CHECK WITH ME BEFORE YOU ANSWER IT.

GOOD LUCK
RELAX, STAY CALM AND DO YOUR BEST

PART I: MULTIPLE CHOICE QUESTIONS (60pts.)

I. Which of the following can't undergo nucleophilic substitution reactions under normal conditions?

CH\textsubscript{3}-CH=CH-CH\textsubscript{2}-Br

\begin{itemize}
  \item 1
  \item \[\text{\textbullet}\]
  \item 2
  \item 3
  \item 4
\end{itemize}

(A) 1   (B) 2   (C) 3   (D) 4   (E) More than one of these

II. Consider the following experimental data for the rate of the reaction given below:

\[\text{Ph}_3\text{C}-\text{Br} + \text{R}_{\text{aq}}\cdot \text{NaOH} \rightarrow \text{Ph}_3\text{C}-\text{OH} + \text{NaBr}\]

<table>
<thead>
<tr>
<th>Expt #</th>
<th>[\text{Ph}_3\text{C}-\text{Br}]</th>
<th>[\text{OH}^-]</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>0.01</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>0.01</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>0.01</td>
<td>0.02</td>
<td>1</td>
</tr>
</tbody>
</table>

What is the mechanism for the reaction?

(A) SN\textsubscript{1}   (B) SN\textsubscript{2}   (C) E\textsubscript{1}   (D) E\textsubscript{2}   (E) Both B and D
III. Which of the following best explains why SN$_2$ reactions are slower in polar solvents?
(a) The substrate is less soluble in polar solvent.
(b) The nucleophile is solvated by polar solvent.
(c) The substrate can react with polar solvent
(d) The transition state is not stabilized by polar solvent.
(e) More than one of the above.

IV. When compared to the keto form, the enol form of which of the following compounds is most stable?

\[
\begin{array}{cccc}
\text{1} & \text{2} & \text{3} & \text{4} \\
\end{array}
\]

(A) 1  (B) 2  (C) 3  (D) 4

V. Which of the following would be the best way to accomplish the following conversion?

\[
\begin{array}{c}
\text{OH} \\
\end{array} \xrightarrow{?} \text{CN}
\]

(A) $\text{H}^+, \text{H}_2\text{O}$; then HCN
(B) $\text{HO}^-$; then NaCN
(C) $\text{Br}_2/\text{H}^+$; then NaCN
(D) HBr; then NaCN
(E) HCN

VI. The tautomeric form of cyclohexanone can be best described as:
(A) Carbocation
(B) Carbanion
(C) Carbene
(D) Free Radical
(E) None of the above
VII. What would be the product of the following reaction?

\[
\text{CH}_3 - \text{CH}_2 - \text{NO}_2 + \text{C}_6\text{H}_5\text{CH} \rightarrow ?
\]

A) \( \text{C}_6\text{H}_5\text{CH} = \text{CH} \cdot \text{NO}_2 \)

B) \( \text{C}_6\text{H}_5\text{CCH}_2\text{CH}_2 - \text{NO}_2 \)

C) \( \text{C}_6\text{H}_5\text{CH} = \text{C} - \text{NO}_2 \)

D) \( \text{OH} \cdot \text{C}_6\text{H}_5\text{CHCH}_2\text{CH}_2 - \text{NO}_2 \)

E) \( \text{OH} \cdot \text{C}_6\text{H}_5\text{CCH}_2\text{CH}_2 - \text{NO}_2 \)

VIII. What would be the product, \( E \), of the following reaction sequence?

\[
\text{C}_6\text{H}_5\text{CH} + \text{KMnO}_4 + \text{H}^+ \rightarrow \text{C} \rightarrow \text{D} \rightarrow \text{E} \rightarrow \text{E}
\]

A) \( \text{C}_6\text{H}_5\text{COCH}_3 \)

B) \( \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \)

C) \( \text{p} - \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_3 \)

D) \( \text{p} - \text{CH}_3\text{C}_6\text{H}_4\text{CH}_3 \)

E) \( \text{C}_6\text{H}_5\text{-COOC}_2\text{H}_5 \)

IX. What starting compound(s) would you use in an aldol reaction to prepare

A) I

B) II

C) III

D) IV

E) V
X. What is the major product of the following reaction?

\[
\text{Ph-CH}_2\text{-Br} + \text{Ph-O Na} \xrightarrow{\text{EtOH}} ?
\]

A) \[
\text{Ph-CH}_2\text{-Ph}
\]

D) \[
\text{Ph-CH}_2\text{-OEt}
\]

B) \[
\text{Ph-O-Ph}
\]

E) \[
\text{Ph-O Na}
\]

C) \[
\text{Ph-CH}_2\text{-O-Ph}
\]

XI. Which of the following methods could be used to synthesize 4, 4-dimethyl-2-hexyne?

A) \[
\text{CH}_3 \quad \text{C}_2\text{H}_5\text{-C=C:Na}^+ + \text{CH}_3\text{-I} \xrightarrow{\text{CH}_3} \]

B) \[
\text{CH}_3\text{-C=C:Na}^+ + \text{C}_2\text{H}_5\text{-C-Br} \xrightarrow{\text{CH}_3} \]

C) \[
\text{CH}_3\text{-CH}_2\text{-CBr}_2\text{-C}_2\text{H}_5\text{ NaNH}_2 \text{ (excess)} \xrightarrow{\text{liq. NH}_3} \]

D) A and B

E) A and C

XII. Which of the following statements is true when used to compare the reaction of chlorine with isopropylbenzene, and the reaction of bromine with isopropylbenzene?

A) Bromine is the less reactive and less selective.

B) Chlorine is the less reactive and more selective.

C) Chlorine is the more reactive and more selective.

D) Bromine is the less reactive and more selective.

E) None of the above.
XIII. Which compounds could be used in a Diels-Alder synthesis of roach killer, chlordane?

A) I and II   B) I and IV   C) II and III   D) III and IV   E) None of these

XIV. Which of the following statements concerning nitriles is incorrect?

A) Nitriles can be hydrolyzed to carboxylic acids.
B) Nitriles can be formed from alkyl halides by nucleophilic substitution by with cyanide ion.
C) Nitriles can be reduced with excess lithium aluminum hydride to primary amines.
D) Nitriles react with Grignard reagents to form tertiary alcohols.
E) Nitriles can be made by the dehydration of amides.

XV. What new compound will be formed when gaseous HCl is added to a solution of Ph-C\(^\equiv\)CH\(_3\) in 1,2-ethanediol?

A) Ph-C\(^\equiv\)CH\(_2\)-OCH\(_2\)OH   B) Ph\(\begin{array}{c}
\text{HC} \\
\text{Cl}
\end{array}\)

C) Ph\(\begin{array}{c}
\text{H}_3\text{C} \\
\text{OC}_2\text{H}_5
\end{array}\)

D) Ph

E) None of the above
PART II:  WRITE-UP TYPE QUESTIONS

II. How will you chemically separate a mixture of the following substances into pure components? Describe in details with reactions involved. (12 pts.)

\[ \begin{align*}
\text{OH} & + \text{OH} & + \text{OH} \\
& & & \\
\end{align*} \]

III. Predict the major organic product(s) in each of the following reactions. Specify stereochemistry wherever applicable. Write NR for no reaction. (66 pts.)

(1) \[ \text{CN} \text{O} \text{H} + \text{H}_2\text{SO}_4 \xrightarrow{\text{cold, H}_2\text{O}} \] 
(2) \[ \text{OH} + \text{H}_2\text{SO}_4 \xrightarrow{\Delta} \] 
(3) \[ \text{NH} \text{O} \xrightarrow{\text{H}_2\text{O, } \Delta} \] 
(4) \[ \text{CH} = \text{CH} \xrightarrow{\text{CH}_2\text{N}_2, PH}_3 \] 
(5) \[ \text{C} \equiv \text{C} + \text{H}_2\text{MnO}_4 \xrightarrow{\Delta} \]
(16) \[
\text{Br} + \text{Ph}_3\text{P}, \text{then BuLi, then CO}_2\text{EtOH}
\]

(17) \[
\text{Br} + \text{CHO} + \text{NH}_2\text{Cl} + \text{NaCN} \rightarrow
\]

(18) \[
+ \text{Ac}_2\text{O} \rightarrow
\]

(19) \[
+ \text{Ac}_2\text{O} \rightarrow \text{AlCl}_3
\]

(20) \[
+ \text{pH}, \text{then } \text{H}_2\text{O}_2
\]

(21) \[
+ \text{HCl}, \text{then } \text{H}_2\text{O}_2
\]

(22) \[
+ \text{PhSO}_2\text{Cl} \rightarrow \text{NaOH}
\]

IV. In a stepwise manner, show with equations the mechanism involved in each of the following reactions: (18 pts.)

(1) \[
\text{CHO} + \text{NaOH} + \text{CO}_2 \rightarrow \text{COOH}
\]
(3) Ph-Br + Mg/Et_2O, then PhCN, then H_3O^+ \rightarrow Ph-CO-Ph

V. Starting with benzene and/or C_1-C_4 alkanols, any solvents and any inorganic reagents, write out all steps in a synthesis of each of the following. Be sure to specify the reaction condition for each step you propose. (27 pts.)

(1) Advil (Ibuprofen):
(2) Banana oil (Isoamyl acetate):

\[
\begin{align*}
&\text{CH}_3 \cdot \text{C} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_3 \\
&\text{CH}_3
\end{align*}
\]

(3) Sulfanilamide, a precursor of all sulfa drugs:

\[
\begin{align*}
&\text{NH}_2 \\
&\text{SO}_2 \cdot \text{NH}_2
\end{align*}
\]
VI  An organic compound, Δ of M.F. C_{11}H_{14}O_{3} shows a strong infrared absorption peak at 1710 cm^{-1} and gives the following NMR data:

δ 2.6 (2H, d) ; δ 3.2 (6H, s) ; δ 4.7 (1H, t) ; and δ 7.1 (5H, m)

Treatment of Δ with iodine in aqueous sodium hydroxide does not give a yellow precipitate. When Δ is treated with ammonical silver nitrate no reaction occurs. However, when Δ is first treated with dilute sulfuric acid and then with ammonical silver nitrate, a silver mirror is formed. Deduce the structure of Δ. Show your reasoning clearly and completely with all the reactions involved. Assign the spectral data to the appropriate structural feature(s) in the compound Δ. (15 pts.)

YOUR COMMENTS ARE WELCOME ....
(You win these points no matter what you write.) (Bonus 2 pts.)