Winter 2013
Chemistry 108B
First Midterm
February 7
version 1

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Problem 1 (36 points)

I) Consider the following compounds and the list of pK_a values shown below. Match each compound to a pK_a value from the list. Write the pK_a value in the space provided under each compound. (8 points)

\[\text{pK}_a: 7.15, 9.26, 10.3, 16.0\]

II) Consider the compounds shown below and circle the one that is more strongly activated for an electrophilic aromatic substitution and box the one that is more strongly deactivated for the same reaction. (8 points)

III) Circle the correct name for the following structure (only one): (4 points)

a) benzyl vinyl ether
b) allyl benzyl ether
c) phenyl vinyl ether
d) phenyl propyl ether
e) none of the above

IV) The reaction of the following ketone with propylmagnesium bromide (\(\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}\)) followed by acid hydrolysis gives only one of the compounds written below. Circle it. (4 points)

ketone:

a) 2-methyl-3-hexanol
b) 2-methyl-2-hexanol
c) 5-methyl-3-hexanol
d) 3-methyl-3-hexanol
e) none of the above

V) Circle the best organohalide to use in a Williamson ether synthesis (only one). (4 points)

a)

b)

c)

d)

e)
VI) The following reaction is an example of one (and only one) of the following mechanisms. Circle it. (4 points)

$$\begin{array}{c}
\text{PhCO}_2\text{CH}_3 + HI \xrightarrow{\text{heat}} \text{PhOH} + \text{CH}_3I \\
\end{array}$$

a) E2  
b) E1  
c) S_N^1  
d) S_N^2  
e) Nucleophilic addition

VII) Consider the formation of imines from aldehydes and ketones shown below. Which curve better represents the variation of the reaction rate with pH? Circle it. (4 points)

Circle one:

a)  
b)  
c)  
d)  

![Graphs](image.png)
Problem 2 (24 points; 4 points each)
The following reactions are incomplete. The starting material, the reagent, or the product is missing. The missing chemicals are indicated by "?" and the possible options for the missing chemicals are shown. In each case only one option is correct. Circle that option.

I)

\[
\text{CH}_3\text{O} + \text{HBr} \rightarrow ?
\]

Circle the correct option (only one):

a) \( \text{H}_3\text{C} \text{CH}_2 \text{Br} \text{OH} \quad \text{b)} \quad \text{CH}_3 \text{Br} \text{CH}_2 \text{OH} \quad \text{c)} \quad \text{H}_3\text{C} \text{Br} \text{OH} + \text{CH}_3 \text{Br} \text{CH}_2 \text{OH} \quad \text{d)} \quad \text{H}_3\text{C} \text{Br} \text{OH} + \text{CH}_3 \text{Br} \text{CH}_2 \text{OH}
\]

II)

\[
? \quad \text{CH}_3\text{CH}_2\text{NH}_2 \quad \text{pH 4-5} \rightarrow \quad \text{N}
\]

Circle the correct option (only one):

a) \( \text{CH}_3\text{CH}_2\text{NH}_2 \quad \text{b)} \quad \text{CH}_3\text{CH}_2\text{OH} \quad \text{c)} \quad \text{CH}_3\text{CH}_2\text{Br} \quad \text{d)} \quad \text{CH}_3\text{CH}_2\text{Br}
\]
III)

\[ \text{?} \xrightarrow{\text{HgSO}_4, \text{H}_2\text{SO}_4} \xrightarrow{\text{H}_2\text{O}} \text{only organic product} \]

Circle the correct option (only one):

a) \( \text{CH}_3\text{CH}_2\text{C}≡\text{C-CH}_3 \)

b) \( \text{CH}_3\text{CH}_2\text{CH}≡\text{CH-CH}_3 \)

c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}≡\text{CH}_2 \)

d) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{C}≡\text{CH} \)

IV)

\[ \text{Cl} \xrightarrow{\text{CH}_3\text{Cl}} \xrightarrow{\text{AlCl}_3, \text{O}^\circ} ? \]

Circle the correct option (only one):

a) \( \text{NO}_2 \)

b) \( \text{NO}_2 \)

c) \( \text{NO}_2 \)

d) \( \text{NO}_2 \) No reaction
Problem 3 (25 points; 5 points each)
In each case circle all the correct options (it could be more than one). EAS stands for Electrophilic Aromatic Substitution.

I) The cyano group (-CN) is:
   a) an electron-withdrawing group by resonance effect
   b) an electron-donating group by inductive effect
   c) a deactivator
   d) ortho-para orienting in the EAS
   e) meta orienting in the EAS

II) The amino group ( -NH₂) is:
   a) electron-donating by resonance effect
   b) electron-withdrawing by inductive effect
   c) a strong deactivator
   d) meta orienting in the EAS
   e) ortho-para orienting in the EAS
III) The methyl group is:
   a) electron-donating by inductive effect
   b) a weak deactivator
   c) a strong deactivator
   d) a weak activator
   e) ortho-para orienting in the EAS

IV) Circle all the correct statements about protecting groups:
   a) silyl ethers are used to protect the carbonyl group of aldehydes and ketones
   b) acetals are used to protect the carbonyl group of aldehydes and ketones
   c) silyl ethers are removed by hydrolysis under acidic conditions
   d) acetals are stable under basic conditions
   e) acetals are obtained by the reaction of aldehydes with chlorotrimethylsilane in the presence of an amine

V) Circle all the options that would allow you to prepare the following ether successfully:

\[
\begin{align*}
\text{a) Williamson ether synthesis using:} \\
\text{b) Williamson ether synthesis using:} \\
\text{c) Alkoxymercuration using:} \\
\text{d) Alkoxymercuration using:} \\
\text{e) Alkoxymercuration using:}
\end{align*}
\]
Problem 4 (48 points; 4 points each)
In the following transformations, the starting material, the product(s) or the reagent(s) (compounds over the arrows) is missing. Complete the reactions by writing the missing chemicals. Do not show mechanisms.

1. \( \text{CH}_2\text{OH} \xrightarrow{\text{Jones or KMnO}_4 \text{ or Na}_2\text{Cr}_2\text{O}_7 \text{ or Bleach}} \text{CO}_2\text{H} \)

2. \( \text{KMnO}_4, \text{H}_2\text{O}, \text{heat} \xrightarrow{} \text{HO}_2\text{C} = \text{O} \text{CO}_2\text{H} \)

3. \( \text{PCC, CH}_2\text{Cl}_2 \xrightarrow{\text{or DMP (Dess-Martin)}} \text{CO}_2\text{H} \)

4. \( \text{OH} \xrightarrow{\text{1) LiAlH}_4} \text{OH} \xrightarrow{\text{2) H}_3\text{O}^+ \text{(or H}_2\text{O)}} \text{OH} \)

5. \( \text{BrOH} \xrightarrow{\text{HCN, } \text{CN}} \text{HCN} \)

6. \( \text{Br} \xrightarrow{\text{1) S=O}_2\text{NH}_2} \xrightarrow{\text{2) H}_2\text{O, HO}} \text{SH} \)

(instead of Br; Cl, I could be used)
\[
\text{OCH}_3 \quad \text{HNO}_3, \text{H}_2\text{SO}_4 \quad \text{OCH}_3 \quad \text{NO}_2 \\
\text{OCH}_3 \quad \text{major} \quad \text{minor}
\]

\[
\text{HA} \quad \text{OH} \quad \text{OH} \quad \text{OH}
\]

\[
\text{DN}_6 \text{BH}_4 \quad 2) \quad \text{H}_3\text{O}^+ \quad \text{or} \quad 3) \text{LiAlH}_4 \quad 2) \quad \text{H}_3\text{O}^+
\]

\[
\text{H}_2\text{SO}_4, \text{heat} \quad \text{(major)} \quad \text{(minor)} \quad \text{two isomeric products}
\]

\[
\text{POCl}_3, \text{pyridine}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH-P(Ph)}_3 \quad \Theta \quad \Theta \quad \text{THF}
\]