Chemistry 3B, Midterm 2

Wednesday, November 13, 2002

Student name:

Student signature:

Write TA’s name or Lecture Only: chung Qian

1. Please make sure that the exam has 9 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed (No Calculators).

GOOD LUCK!

1. 30 points  
2. 60 points  
3. 20 points  
4. 20 points  
5. 20 points  
6. 20 points  
7. 10 points  
Total 180 points

MINI-PERIODIC TABLE

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1. Answer the following questions. Every wrong answer cancels a correct answer (30 points).

(a). Circle the carboxylic acid derivatives that upon heating with methoxide in methanol provide the methyl ester (6 points).

(b). Circle the compounds that would react with LiAlH₄ to give an alcohol after work-up (6 points).

(c). Circle the compounds that are converted into a new compound upon treatment with aqueous sodium hydroxide and heat (6 points).

(d). Rank the following carbonyl compounds from most electrophilic to least electrophilic [1 = most electrophilic, 5 = least electrophilic] (6 points).

(e). Each of these enantiomerically pure compounds is heated with H₂O, H⁺ for an extended period of time. Circle the compound(s) that become racemic (6 points).
2. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (60 points total).

(a) 
\[
\text{C} = \text{CH} \\
1. \text{H}_2\text{O}, \text{H}^+, \text{Hg}^{2+} \\
2. \text{LDA} \\
3. \text{MeI}
\]

(b) 
\[
\text{OH} \\
1. \text{MnO}_2 \\
2. \text{EtMgBr} \\
3. \text{aqueous workup}
\]

(c) 
\[
\text{Cl} \\
1. \text{LiHAI[OC(CH}_3}_2)_3 \\
2. \text{HO}^-, \Delta 
\]

(d) 
\[
\text{OH} \\
1. \text{SOCl}_2 \\
2. \text{Et}_2\text{CuLi} \\
3. \text{MeOH, H}^+
\]

(e) 
\[
1. \text{(CH}_3\text{CH}_2)_2\text{CuLi} \\
2. \text{H}_2\text{O}
\]

(f) 
\[
\text{OH} \\
1. \text{LiAI[OC(CH}_3}_3)_2\text{H} \\
2. 2 \text{CH}_3\text{CH}_2\text{MgBr} \\
3. \text{H}^+\text{/H}_2\text{O}
\]
(g) PhCHO

1. HCN
2. H⁺/H₂O / Δ

(h) Cyclohexene

1. O₃
2. Zn, AcOH
3. CF₃CO₂H

(i) Cyclohexylamine

1. Cl₂, NaOH, H₂O
2. H⁺, sieves

(j) 3-Amino-1-cyclohexene

1. CH₂N₂
2. LiAlH₄
3. aqueous work-up

(k) 3,5-Dihydroxy-6-methyl-2-cyclohexene-1-carboxylic acid

1. MeOH
2. SOCl₂

(l) PhBr

1. NaCN
2. HAI(CH₂CH(CH₃)₂)₂
3. The following reaction is extensively used in the synthesis of the important class of ionophore antibiotics. Provide a mechanism (20 points).
4. Draw the product of the below transformation and show the mechanism for its formation. Make sure to provide a mechanism for all sites of deuterium incorporation (20 points).
5. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).

\[
\begin{align*}
2 \text{OME} & \xrightarrow{\text{LiAlH}_4} 2 \text{H} \xrightarrow{\text{NaOH, H}_2\text{O}} \text{H}_2 \text{O} \\
\text{OME} & \xrightarrow{\text{LiAlH}_4} \text{H}_2 \xrightarrow{\text{H}_2\text{NET}H^+} \text{NET}_3^+ \\
\text{CH}_2 & \xrightarrow{\text{N=PPh}_3} \text{N=PPh}_3 \\
\text{OH} & \xrightarrow{} 
\end{align*}
\]
6. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).
(a) The molecules drawn below are key building blocks in the synthesis of many psychoactive drugs. Circle the compound that would have the largest $K_{eq}$ for hydrate formation. **Provide a brief explanation for your answer.** (5 points).

(b) Circle compound below that would have the largest $K_{eq}$ for hydrate formation. **Provide a brief explanation for your answer.** (5 points).

- NO$_2$ is a deactivating group