Chem 51C Final Exam
197 points; 2 hours
June 10, 2013

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Academic Honesty Policy. Academic honesty is strictly enforced on quizzes, exams, and other aspects of this course. Academic dishonesty will result in a failing grade in the class and a letter in the student's file. Activities constituting academic dishonesty include:

*Cheating*
- Copying from others during an examination.
- Communicating exam answers with other students during an examination.
- Offering another person's work as one's own.
- Taking an examination for another student or having someone take an examination for oneself.
- Tampering with an examination after it has been corrected, then returning it for more credit.
- Using unauthorized materials, prepared answers, written notes, or concealed information during an examination.

*Dishonest Conduct*
- Stealing or attempting to steal an examination or answer key from the instructor.
- Allowing another student to copy off of one's own work during a test.

*Collusion*
- Any student who knowingly or intentionally helps another student perform any of the above acts is subject to discipline for academic dishonesty.

I understand and will abide by this academic honesty policy: ____________________________ (signature)

Seat: _______
1. (3 points each, 12 points)

a. Rank the following in order of increasing acidity: _____ < _____ < _____

   A. acetone
   B. diethyl malonate
   C. ethanol

b. Rank the following in order of increasing reactivity towards nucleophiles: _____ < _____ < _____

   A. benzyol chloride
   B. ethyl benzoate
   C. benzoic anhydride

c. Rank the following in order of increasing equilibrium constants: _____ < _____ < _____

   A. CH₃CHO + H₃O⁺ ⇌ CH₃CHOH⁺ + H₂O
   B. CH₃OH + H₃O⁺ ⇌ CH₃OH₂⁺ + H₂O
   C. CH₃NH₂ + H₃O⁺ ⇌ CH₃NH₃⁺ + H₂O

d. Rank the following in order of increasing basicity: _____ < _____ < _____

   A. sodium ethoxide
   B. lithium diisopropylamide
   C. n-butyl lithium

2. The enolates of thiol esters react with ketones to give β-lactones. Write a curved arrow mechanism for the following reaction. (12 points)

\[
\text{SPh} \xrightarrow{\text{LDA/THF}} \xrightarrow{\text{O}} \text{O}
\]
3. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (27 points, 3 points each)
4. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (27 points, 3 points each)
5. One overarching principle of synthetic organic chemistry is selectivity. Synthetic organic chemists often try to choose reaction conditions to give a single desired product to the exclusion of others. Reactions are chosen and developed to be selective for a particular functional group (chemoselectivity), a particular region in relation to a functional group, ring, or chain (regioselectivity), a particular diastereomer (diastereoselectivity), or one enantiomer (enantioselectivity).

Each of the following reactions lacks some type of selectivity and gives two or more products. Write the structures of the products in the boxes. (4 points each, 28 points total)

- **CH$_2$OH**
  - **NaBH$_4$**
  - **H$_2$O**

- **$\text{Ph}_3\text{P=CHCH}_3$**
  - **$\text{Ph}_3\text{P=O}$**

- **$\text{NaOMe}$**
  - **EtOH**
  - **NaCl**

- **$\text{NaOH}$**
  - **EtOH**
  - **H$_2$O**

- **$\text{LDA / THF}$**
  - **$\text{H}_3\text{O}^+$**

- **$\text{I-PrMgCl}$**
  - **$\text{H}_3\text{O}^+$**

- **$\text{NaBH}_4$**
  - **CH$_3$OH**

- **1. equiv $\text{CH}_3\text{Li}$**
  - **2. $\text{H}_2\text{O}$**

- **1. $\text{NaOH}$**
  - **EtOH**
  - **H$_2$O**

- **1. LDA / THF**
  - **2. $\text{H}_3\text{O}^+$**

- **hint: crossed aldol reaction with dehydration**

- **hint: four $\beta$-hydroxyketone stereoisomers**
6. Cocaine is an alkaloid produced by the coca tree. It used to be an ingredient in the original formula of Coca Cola, in the late 19th century, but was eventually phased out because of the addictive properties of the drug. (28 points total)

a. Cocaine is often isolated as the hydrochloride salt. Treatment with a base yields the free amine base, hence the term freebasing. Crack is a mixture cocaine hydrochloride and sodium bicarbonate (baking soda), which yields the free base upon heating. Complete the chemical equation for this reaction. (3 points)

\[
\text{Cocaine} + \text{NaHCO}_3 \rightarrow \text{Freebase} + \text{CO}_2 + \text{H}_2\text{O}
\]

b. Treatment of cocaine with lithium aluminum hydride followed by aqueous workup yield three carbon-containing products. Complete the chemical equation for this reaction. (6 points)

\[
\text{Cocaine} \xrightarrow{\text{1. LiAlH}_4} + \text{C}_3\text{H}_4 + \text{H}_2\text{O}
\]

c. Treatment with ammonia results in ammonolysis of the ester groups. Complete the chemical equation for this reaction. (6 points)

\[
\text{Cocaine} + \text{NH}_3 \rightarrow + +
\]

d. Treatment of cocaine with methyl bromide gives a salt. Complete the chemical equation for this reaction. (3 points)

\[
\text{Cocaine} \xrightarrow{\text{CH}_3\text{Br}} +
\]

e. Treatment of cocaine with sodium methoxide in methanol results in transesterification. Complete the chemical equation for this reaction. (4 points)

\[
\text{Cocaine} \xrightarrow{\text{NaOCH}_3} +
\]

f. Treatment of cocaine with methylmagnesium bromide followed by aqueous workup yield three carbon-containing products. Complete the chemical equation for this reaction. (6 points)

\[
\text{Cocaine} \xrightarrow{\text{1. CH}_3\text{MgBr}} + +
\]
7. Atropine, an alkaloid related to cocaine, is produced by the deadly nightshade plant. It dilates the pupils, increases the heart rate, and causes a variety of other physiological effects. It has been used both as a poison and a drug.

![Atropine and Cocaine Structures]

Tropinone, a chemical precursor to atropine and cocaine was synthesized by Robert Robinson in 1917 by simply mixing succinaldehyde, methylamine, and acetonedicarboxylic acid under suitable reaction conditions.

![Reaction Scheme]

The reaction may be thought of as involving two sequential reactions between iminium ions and enols (Mannich reactions) followed by two decarboxylation reactions of \( \beta \)-ketoacid groups. Write in the intermediates and mechanism in the boxes below (27 points).
8. Shown below are drawings of the eight D-aldohexoses. Under each drawing write the name of the corresponding structure. Fisher projections of the D-aldhexoses are provided for reference. (24 points)

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D-allose  D-altrose  D-glucose  D-mannose  D-gulose  D-idose  D-galactose  D-talose

Name: _______________________   Name: _______________________

Name: _______________________   Name: _______________________

Name: _______________________   Name: _______________________

9. The following questions involve the eight D-aldohexoses shown above: D-allose, D-altrose, D-glucose, D-mannose, D-gulose, D-idose, D-galactose, and D-talose, which are shown in the preceding questions. (12 points total).

a. Write the names of the two D-aldohexoses that give achiral compounds (meso compounds) upon reduction with sodium borohydride? _______________ and _______________

b. Write the names of the two D-aldohexoses that give the same optically active diacid upon oxidation with nitric acid? _______________ and _______________

c. Write the structure of the D-aldopentose formed by Wohl degradation of D-allose:

d. Subjecting this D-aldopentose (from part c, above) to Killiani-Fischer synthesis gives back D-allose and one other D-aldohexose. Write the name of that D-aldohexose: _______________

PLEASE REVIEW THE ACADEMIC HONESTY STATEMENT ON PAGE 1 AND SIGN IT IF YOU ARE ABLE