Organic Chemistry CH 352-02 (Wilson)

Exam #3

April 14, 1998

Question 1 _______ (20)
Question 2 _______ (15)
Question 3 _______ (20)
Question 4 _______ (20)
Question 5 _______ (11)
Question 6 _______ (6)
Question 7 _______ (8)
BONUS _______ (5)

TOTAL _______ (100)

“Never think that you’ve seen the last of anything...” -Eudora Welty
1. Supply the missing products for five out of the following six equations. Indicate only five for grading. If none are indicated, the first five will be graded. Be mindful of details!

a. \[
\begin{align*}
&\text{H} \\
&\text{O} \\
&\text{LiCu(n-Bu)}_2 \\
&\text{THF} \\
\end{align*}
\]

(HINT: Michael)

b. \[
\begin{align*}
&\text{O} \\
&\text{1) aniline, TsOH} \\
&\text{2) LAH, EtOH} \\
\end{align*}
\]

c. \[
\begin{align*}
&\text{CO}_2\text{H} \\
&\text{1) SOCl}_2 \\
&\text{2) NH}_3 \\
&\text{3) LAH, EtOH} \\
\end{align*}
\]

d. \[
\begin{align*}
&\text{NO}_2 \\
&\text{Bu} \\
&\text{H}_2, \text{Pt} \\
\end{align*}
\]

e. \[
\begin{align*}
&\text{Br} \\
&\text{1) NH}_3 (10 \text{ eq.}) \\
&\text{2) MeI (xs)} \\
&\text{3) Ag}_2\text{O} \\
&\text{4) heat} \\
\end{align*}
\]

f. \[
\begin{align*}
&\text{O} \\
&\text{O} \\
&\text{KOH} \\
\end{align*}
\]
2. Give reagents or starting materials for five out of the following six reactions. Give answers for only five. If none are indicated, the first five answers will be graded. Be mindful of details such as solvent, temperature, and stereochemistry.

a. \[ \text{CO}_2\text{H} \rightarrow \text{CO}_2\text{H} \]

b. \[ \text{CN} \text{Et} \]

1) NaNO\(_2\), HCl, cool, dil.
2) CuCN

\[ \text{CN} \text{Et} \]

c. \[ \text{BuNH}_2 \rightarrow \text{H} \text{N} \text{Bu} \]

d. \[ \text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{CO}_2\text{H} \]

1) ClCCl
2) methyl amine
3) LAH, EtOH

\[ \text{CH}_2\text{Br} \text{CO}_2\text{H} \]

e. \[ \text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{CO}_2\text{H} \]

1) MeOC\(\Theta\)CO\(_2\)Me
2) H\(_3\)O\(^+\), heat

\[ \text{CH}_2\text{CO}_2\text{H} \]
3. Propose synthesis routes for **two out of the following three compounds**. Legal starting materials include **monofunctional** organic compounds of **four carbons** or less, benzene, and any inorganic reagent or solvent required to carry out the transformation. Keep in mind there are many correct synthesis routes for each compound.

Any nitrogen containing compound should derive the nitrogen from an inorganic source (i.e.: NH₃, NaCN, NaN₃, HNO₃, etc.)

![Chemical structures](image-url)
4. Write out the mechanism for **two** out of the following **three** transformations. Be sure to include all intermediates, resonance structures where applicable, and arrow pushing to show the flow of electrons. Use back of this page or previous page if needed.

**A.**
\[
\left(\begin{array}{c}
\text{O} \\
\text{O} \\
\text{Hg}^2+ \\
\text{Br}_2
\end{array}\right) \xrightarrow{\text{Br}_2} \text{HgBr}_2 \xrightarrow{\Delta} \text{Br}^- + \text{CO}_2 + \text{HgBr}_2
\]

**B.**
\[
\text{N}_2\text{Cl}^+ + \text{PhOPh} \rightarrow \text{PhN=NNPh} + \text{HCl}
\]

**C.**
\[
\text{CH}_3\text{COOH} + \text{HOEt} \xrightarrow{\text{TsOH}} \text{CH}_3\text{COEt} + \text{H}_2\text{O}
\]
5. An oxidation product of a particular aldehyde was treated with base, washed with diethyl ether, then treated with acid. This “clean” product gave the IR and NMR spectra shown below. Use these spectra to answer the following questions.

a. Explain the relevant peak(s) in the IR spectrum. (4 pts)

b. Explain the relevant peak(s) in the $^1$H NMR spectrum. (4 pts)

c. What is the structure of this compound? (2 pts)

d. What is the structure of the starting aldehyde? (1 pts)
6. You have not seen this problem in class! Given the following amino acid (phenylalanine), the pKₐ of the acid portion is 5 and the pKₐ of the base portion is 4. What is the first thing that happens when this amino acid is placed in water? (2 pts) If this is now heated, a dimerization takes place between two amino acids, what new bond is formed? [Draw a picture of what you think this new product might look like] (4 pts)

7. Assistant Beaker has been cleaning out the stockroom, and he found a bottle of an organic compound whose label has long since discolored and fallen off. While wearing gloves, Beaker took a small amount of the unknown and found that it is soluble in water and the pH of the aqueous solution is neutral indicating that it could be a monofunctional alcohol, aldehyde, ketone, ester, nitrile, or amide of five carbons or fewer. The unknown also has a positive nitrogen test and negative halogen test after sodium fusion. The only peak of interest in the IR is a moderate stretch at 2234 cm⁻¹. What have all these tests told Beaker (analyze all the data given!)? To what general class of compound could the unknown belong? Suggest a possible structure for the unknown.
(5) Bonus: (O’Reilly is grading this one!) An example of a polyamide would be what? (2 pts) Name the chemical company which first marketed this polyamide (3 pts).