Organic Chemistry CH 352-01 (Wilson)

Exam #2

March 28, 2000

Question 1 _______   (8)
Question 2 _______  (18)
Question 3 _______  (25)
Question 4 _______ (20)
Question 5 _______ (20)
Question 6 _______  (9)
BONUS _______    (5)

TOTAL     _______ (100)

“A stale mind is the devil's breadbox.” -Mary Bly, English professor, U.C. Davis
1. Assistant Beaker is performing a reduction of an ester (see reaction below). Instead of running the reaction at –78°C as he was supposed to, he let the reaction warm to room temperature. Did Beaker get the product he expected based on the $^1$H NMR spectrum? Why or why not? What product did Beaker isolate? Give support for your answer.
2. Given the following two "roadmaps," supply the structures for A, B, and C. There is only one correct answer for each compound, which will match the molecular formula given. Partial credit may be awarded for incorrect structures carried through the sequence.

(a)

\[
\text{OH} \quad 1) \text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4 \\
2) \text{mCPBA, CH}_2\text{Cl}_2
\]

A \[ \text{C}_5\text{H}_8\text{O}_2 \]

\[
1) \text{H}_3\text{O}^+ \\
2) \text{NH}_3, \text{TsOH}
\]

B \[ \text{C}_5\text{H}_{11}\text{O}_2\text{N} \]

\[
1) \text{Br}_2, \text{NaOH} \\
2) \text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4
\]

C \[ \text{C}_5\text{H}_{11}\text{O}_2\text{N} \]

A = 

B = 

C = 

(b)

\[
\text{O} \quad 1) \text{MeMgBr, Et}_2\text{O} \\
2) \text{H}_3\text{O}^+
\]

A \[ \text{C}_8\text{H}_{10}\text{O} \]

\[
1) \text{PCC, CH}_2\text{Cl}_2 \\
2) \text{LDA, THF, -78}^\circ\text{C} \\
3) \text{Br}
\]

B \[ \text{C}_{13}\text{H}_{18}\text{O}_3 \]

\[
1) \text{H}_2\text{NNH}_2, \text{TsOH} \\
2) \text{KOH, heat}
\]

C \[ \text{C}_{13}\text{H}_{18}\text{O}_2 \]

A = 

B =
3. Supply the missing products for **five** of the following six equations. Give answers for **only** five, and CLEARLY indicate which problems you would like graded.

a. 1) nBuLi, hexane
2) isopropyl bromide
3) HgCl$_2$, H$_2$O, CH$_3$CN

b. 1) pyrrolidine, TsOH
2) CH$_3$COCl
3) H$_3$O$^+$

c. 1) SOCl$_2$
2) EtOH
3) DIBAL, toluene, -78$^\circ$C

d. 1) PBr$_3$
2) NH$_3$
3) LAH, EtOH

e. 1) NaH, THF
2) acetone
3) H$_3$O$^+$
4. Propose synthesis routes for two out of the following three compounds. Legal starting materials include mono functional compounds of four carbons or less, bromobenzene, toluene, pyrrolidine and morpholine, and bases for elimination or deprotonation (like KOTBu, LDA, KH, etc.), and any inorganic reagent or solvent required to carry out the transformation. Carboxylic acid derivatives, for this exam, are not monofunctional. Keep in mind there are many correct synthesis routes for each compound.
This space left blank for your work.
5. Give the complete, arrow pushing mechanism for two of the following three transformations. Choose ONLY two. Be sure to include all resonance structures and all intermediates from starting materials to products.

A. 

\[ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3\text{CH}═\text{CH}_2 \] 

B. 

\[ \text{C}_2\text{H}_5\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{C}_2\text{H}_5\text{COOH} + \text{NH}_3 \] 

C. 

\[ \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \xrightarrow{\text{Br}_2, \text{NaOH}} \text{C}_6\text{H}_5\text{NH}_2 \]
This space left blank for your work.
6. Assistant Beaker is following a reductive amination reaction by TLC (shown below). Beaker felt the need and has run to Starbucks™ for a double latte. Professor Bunsen Honeydew walks into the laboratory and, just by looking at Beaker’s last TLC, can tell if the reductive amination is done or not. Is the reaction done? Give specific details that tell you if the reaction has gone to completion and why.

![TLC diagram with reaction, co-spot, and aldehyde labels]
(5) **BONUS:** List a reaction for which we have seen the “molecular movie” in class. Give an example of that kind of reaction (it need not be the specific substrate we saw).