Organic Chemistry CH 352-01 (Wilson)

Exam #3

April 13, 1999

Question 1 _______ (9)
Question 2 _______ (6)
Question 3 _______ (10)
Question 4 _______ (20)
Question 5 _______ (20)
Question 6 _______ (25)
Question 7 _______ (10)

BONUS _______ (5)

TOTAL _______ (100)

“Sometimes you’re the windshield, sometimes you’re the bug.” -Mark Knopfler
1. Assistant Beaker was performing an electrophilic aromatic substitution in laboratory hoping to obtain the product shown below. Beaker purified the single product and obtained the $^1$H NMR spectrum shown. Did Beaker get what he wanted (yes or no – 2 pts)? Why or why not (7 pts)? You DO NOT need spectral sheets to answer this question.
(6) 2. Rank each of the following from the strongest (1) to weakest (3) acid or base, as indicated.

a. (ACID)

b. (BASE)

(10) 3. **We have not seen this in class**, but use the following aromatic compound (adenine) to answer these questions. There are five nitrogens in this compound, three are fairly basic, and two are relatively less basic. Classify each of the nitrogens as more basic by circling them, and less basic by putting a square around them (5 pts). In the presence of a reasonable electrophile (like a resonance stabilized carbocation shown), adenine will add as shown. Explain this reactivity from the perspective of the adenine. You need not draw a complete mechanism, but resonance structures may help your explanation (5 pts).
4. Supply the missing products for **four** of the following five equations. Give answers for **only** four, and indicate which problems you would like graded.

a. 

\[
\begin{align*}
\text{PhSO}_3H & \xrightarrow{1) \text{C}_2, \text{AlCl}_3} \text{Cl}_2, \text{AlCl}_3 \\
& \xrightarrow{2) \text{H}_2, \text{Pt}} \text{H}_2, \text{Pt}
\end{align*}
\]

b. 

\[
\begin{align*}
\text{PhCCl}_2O & \xrightarrow{1) \text{PhCCl}_2, \text{AlCl}_3} \text{PhCCl}_2O \\
& \xrightarrow{2) \text{Zn(Hg)}, \text{HCl(aq}}} \text{Zn(Hg), HCl(aq)}
\end{align*}
\]

c. 

\[
\begin{align*}
aniline & \xrightarrow{1) \text{CH}_3\text{Cl}_2, \text{Cl}_2} \text{CH}_3\text{Cl}_2, \text{Cl}_2 \ (\text{NO AlCl}_3!!!) \\
& \xrightarrow{2) \text{Br}_2, \text{FeBr}_3} \text{Br}_2, \text{FeBr}_3 \\
& \xrightarrow{3) \text{H}_3\text{O}^+} \text{H}_3\text{O}^+
\end{align*}
\]

d. 

\[
\begin{align*}
p\text{-bromo phenol} & \xrightarrow{1) \text{HNO}_3, \text{H}_2\text{SO}_4} \text{p\-bromo phenol} \\
& \xrightarrow{2) \text{KOH}, \text{H}_2\text{O}} \text{KOH, H}_2\text{O} \\
& \xrightarrow{3) \text{PhCH}_2\text{Br}, \text{THF}} \text{PhCH}_2\text{Br, THF}
\end{align*}
\]

e. 

\[
\begin{align*}
\text{C}_2 & \xrightarrow{1) \text{B}_2, \text{FeB}_3} \text{B}_2, \text{FeB}_3 \\
& \xrightarrow{2) \text{Mg, Et}_2\text{O}} \text{Mg, Et}_2\text{O} \\
& \xrightarrow{3) \text{H}_3\text{O}^+} \text{H}_3\text{O}^+
\end{align*}
\]
5. Propose synthesis routes for **TWO** out of the following three compounds. Legal starting materials include **mono**-functional compounds of four carbons or less (carboxylic acid derivatives are **NOT** monofunctional), benzene, bases for elimination, and any inorganic reagent or solvent required to carry out the transformation. For any step of your synthesis, you may separate ortho from para products if you show them both! Keep in mind there are many correct synthesis routes for each compound.
6. Give the product or products for **BOTH** of the following reactions (10 pts). Choose **ONE** of the reactions and **ONE** of the products, and give a step-by-step arrow pushing mechanism to account for the formation of this product (10 pts). Be sure to include all resonance structures. Briefly (two sentences or less) state the reason(s) why you got the product you did (ortho, meta, para) (5 pts).

A. 

\[
\text{anisole} \xrightarrow{\text{CH}_3\text{Cl}} \text{AlCl}_3
\]

B. 

\[
\text{acetophenone} \xrightarrow{\text{H}_2\text{SO}_4}
\]
7. Assistant Beaker is working busily away in the laboratory on his unknown. He has found that it is insoluble in everything but sulfuric acid, indicating that it could be a ketone of more than seven carbons, an aldehyde of more than seven carbons, or an ether of more than seven carbons. He has a negative nitrogen test and a positive halogen test. His IR only has interesting peaks (the ones above 1500 cm\(^{-1}\), remember – below 1500 cm\(^{-1}\) are iffy) at 1610 and 1520 cm\(^{-1}\). Propose two possible structures for Beaker (5 pts each). There are many possibilities here – don’t limit yourself!

(5) BONUS: On April 2, we took time out from class to watch a videotape. Give the approximate storyline for one of the “short stories” we watched. Be brief!