Organic Chemistry CH 352-01 (Wilson)

Exam #3

April 18, 2000

Question 1 _______ (12)
Question 2 _______ (12)
Question 3 _______ (8)
Question 4 _______ (20)
Question 5 _______ (20)
Question 6 _______ (20)
Question 7 _______ (8)
BONUS _______ (5)

TOTAL _______ (100)
“Clothes make the man. Naked people have little or no influence in society.”  -Mark Twain

(12) 1. Identify each of the following compounds as aromatic, anti-aromatic, or non-aromatic. (3 pts each)

   a.  
   b.  
   c.  
   d.  

(12) 2. Assistant Beaker has synthesized a compound which is one of the following: o-nitro styrene; m-nitro styrene; or p-nitro styrene. Use this information to answer the questions below.

   a. The aromatic region of the $^1$H NMR shows that each proton has its own signal and displays the following coupling patterns. What has Beaker made? Give reason(s)/drawing(s) to support your answer. Aromatic region coupling: d, dd, dd, d. (4 pts)
b. How has Beaker made this compound starting using some or all of the reagents below? [Hint: order may be important here.] Use the reverse of this page if needed. (8 pts)

\[
\text{Br} \quad \text{HNO}_3 \quad \text{FeBr}_3 \quad \text{Br}_2
\]

(8) 3. Rank the following from the strongest (1) to weakest (3) acid (4 pts). Give resonance forms of the conjugate base of the strongest acid which might explain why it is, indeed, the strongest acid (4 pts).

\[
\text{C}_6\text{H}_5\text{CO} \quad \text{C}_6\text{H}_5\text{OH} \quad \text{C}_6\text{H}_5\text{CHOH}
\]
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. ![Compounds A and PhCOCl, AlCl₃](attachment:Compounds.png)  
   1) PhCOCl, AlCl₃  
   2) H₂NNH₂, KOH  
   3) H₂SO₄ (add it once)

b. ![Compounds B](attachment:Compounds.png)  
   **aniline**  
   2 equivalents of **butyl chloride**  
   (AlCl₃ could be added, but is not really needed)

c. ![Compounds C](attachment:Compounds.png)  
   ![Compounds C](attachment:Compounds.png)  
   1) KOEt, HOEt  
   2) H₃O⁺  
   [Hint: Dieckmann]

d. ![Compounds D](attachment:Compounds.png)  
   3-methoxy acetophenone  
   Cl₂, AlCl₃
e. 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), MVK, benzene, bases for elimination and/or deprotonation, Lewis acids, 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 complete arrow pushing mechanisms for one out of each of the following two pairs. Be sure to include all relevant resonance structures and account for at least one product. You may use the back of this page if you wish. (10 pts each)

a. The first step (#1 over the arrow) of #4 a, c, or e.

b. Either reaction below (note I have given you the product that I want).

   i. \[
   \text{reaction with HNO}_3\rightarrow \text{product with NO}_2
   \]

   ii. \[
   \text{reaction with H}_2\text{SO}_4\rightarrow \text{product with SO}_3\text{H}
   \]
7. Assistant Beaker is working busily away in the laboratory on his unknown. He has found that it is soluble in strongly basic water (KOH), but not weakly basic water (NaHCO₃). This means that his unknown could contain a certain aromatic functional group we discussed recently in class. He has a negative nitrogen test and a positive halogen test. His IR only has interesting peaks at 3300, 1605, and 1490 cm⁻¹. Propose two possible structures for Beaker (4 pts each). There are many possibilities here – don't limit yourself!
(5) BONUS: Name one verifiable fact (name of presenter, name of moderator, approximate title of talk, etc.) from the Undergraduate Research Conference.