CHE 297 Organic Workshop
Problem Set 6B
February 26, 2007

1. (20 pts.) Draw the major product of each of the following reactions. Do not draw mechanisms! Assume aqueous workup in all cases (that is, draw neutral products).

(a)  

(b)  

(c)  

(d)  

2. (20 pts.) Design a synthesis of the ketones below. All of the C atoms in the product must be derived from one or both of the two starting materials shown, but you may use any other reagents to accomplish the necessary transformations. Your synthesis will require more than two steps. Show each intermediate compound and all reagents you will need for each step. (Don’t panic if you can’t remember the reagents for a particular step; partial credit will be given.) Do not show mechanisms.

3. (20 pts.) The following reaction is a model for the hydrolysis of sucrose to fructose and glucose. Draw a reasonable mechanism for it.

4. (5 pts. each, 20 pts. total.) Your summer job is to clean up an organic chemistry laboratory after a flood has partially destroyed the labels on many of the bottles. In each problem below, choose a method for distinguishing the two possibilities by MS, IR, 1H NMR, 13C NMR, or optical activity, and precisely describe the differences that you can expect to see in the spectra of the two compounds that will allow you to identify the sample unambiguously. You may use each method no more than twice in this problem!

(a) Bottle 1 contains one of the following:

(b) Bottle 2 contains one of the following:

(c) Bottle 3 contains one of the following:

(d) Bottle 4 contains one of the following:

5. (20 pts. total) Draw in all of the H atoms in the following compound.

6. (5 pts) Label equivalent H's with the same letter and inequivalent H's with different letters, as we did in class.

(b) (15 pts.) Predict the 1H NMR spectrum of the compound, indicating the approximate chemical shift, integration, and multiplicity for each resonance that you expect to see. You can find a table of 1H NMR chemical shifts at the front of this exam.

2. (20 pts. total) Draw in all of the H atoms in the following compound.

(a) (5 pts.) Label equivalent H atoms with the same letter and inequivalent H atoms with different letters, as we did in class.

(b) (15 pts.) Predict the 1H NMR spectrum of the compound, indicating the approximate chemical shift, integration, and multiplicity for each resonance that you expect to see. You can find a table of 1H NMR chemical shifts at the front of this exam.

3. (30 pts. total) The last three pages of this exam show the MS, IR, and 1H NMR spectra of an organic compound. Answer the following questions using these spectra.

(a) (3 pts.) How many N, Cl, and Br atoms are present in this compound?

N:

Cl:

Br:

(b) (8 pts.) Based on the MS spectrum, propose three reasonable formulae for this compound, and indicate the number of degrees of unsaturation for each.

Formula 1:

Degrees of unsaturation:

Formula 2:

Degrees of unsaturation:

Formula 3:

Degrees of unsaturation:

(c) (4 pts.) Name two absorbances in the IR spectrum and the functional groups whose presence they indicate.

(d) (3 pts.) What functional group do the two doublets at 6.8 and 7.4 ppm in the 1H NMR spectrum indicate?

(e) (6 pts.) Given your answers to (b-d), propose a formula for this compound. The formula may be the same as or different from one of the formulae in your answer to (b).

(f) (4 pts.) Draw any structure consistent with your answers to (e-o). The structure need not be fully consistent with the 1H NMR spectrum, but it should have the formula you gave in (e) and the functional groups you gave in (c) and (d).

(g) (4 pts.) Draw a structure consistent with all three spectra. It may be the same as or different from your answer to (f).
4. (5 pts. each, 30 pts. total) Explain each of the following observations in one or two coherent, grammatically correct English sentences free of misspellings. Feel free to draw pictures to illustrate your explanations.

(a) One doublet is observed in the 1H-decoupled 13C NMR spectrum of CF3C6H4.

(b) In the 1H NMR spectrum of 4-methyphenol, the H atom ortho to the OH group resonates much farther upfield than the H atoms ortho to the Me group.

(c) A C=O stretch is not observed in the IR spectrum of 4-octene.

(d) Bromobenzene weighs 157.0 g/mol, but its MS spectrum shows a molecular ion at 156 amu, not at 157 amu.

(e) Knoevenagel's reaction (condensation followed by separation of isomeric aldol products) was used at the turn of the last century to distinguish α-, β-, and γ-dihaloanisoles, but now we can just use a 1H NMR spectrum to distinguish them.

(f) The 1H NMR spectrum of 2-isododecane shows five (not four) resonances.
2. (30 points) Predict the product of the following reactions. If you believe that no reaction will occur, write "no reaction." DO ANY 4 OF THE 12 GIVEN.

a) 
\[ \text{Catalytic TsOH} \]

b) 
1. LiAlH₄ \\
2. H₂O, HCl

c) 
\[ PBr₃ \]

d) 
1. HNO₃ \\
2. \[ \text{Br}^- \]

e) 
\[ \text{K₂Cr₂O₇} \]

2. \[ H₂SO₄ \]

f) 
1. \[ \text{Gibbs-Hyde-MgBr} \]

2. \[ H₂O, HCl \]

g) 
1. LDA \\
2. \[ \text{Br}^- \]

h) 
1. Ph₃P \\
2. BuLi \\
3. \[ O \]

i) 
1. LiAlH₄ \\
2. \[ H₂O, HCl \]

Note: a) D is deuterium; b) show the resulting stereochemistry

j) 
\[ \text{Catalytic TsOH} \]

k) 
1. C₂H₅Li \\
2. \[ H₂O, HCl \]

l) 
1. LDA \\
2. \[ \text{HCl, H₂O} \]

3. (10 points) Show how 1-pentanol can be converted to the various products shown. More than one step may be required. If so, indicate 1) reagent 1; 2) reagent 2, etc. DO ANY TWO OF THE FOUR.

a) 
\[ \text{OH} \]

b) 
\[ \text{OH} \]

c) 
\[ \text{CH₃} \]

d) 
\[ \text{CH₃} \]

4. (10 points) Show how n-hexane can be prepared from tails of 3 carbons or less.

5. (10 points) Provide a viable mechanism for the following reaction. Pay attention to the use of mechanism arrows, and watch every proton transfer step! NOTE: DO NOT ADD ANY ADDITIONAL REAGENTS!

6. (20 points) Provide viable syntheses for the compounds below, using only benzene, inorganic reagents, triethylphosphine, LDA, and organic reagents of 3 carbons or less. DO ANY 2 OF THE 4 BELOW.

a) 
\[ \text{OH} \]

b) 
\[ \text{OH} \]

c) 
\[ \text{OH} \]

d) 
\[ \text{OH} \]

1. (20 points) The following MS and IR are to be used to solve this problem. Values in parentheses are the relative intensities. 4 pts for each answer.

\[ \text{MS} \]

171 (100), 173 (90)

3191

2470

3364

3191

1616

172 (68), 174 (62)

1. (a) What is the molecular mass of this compound (the molecular ion)?

1. (b) What heteroatoms are present and state how you know this from the MS?

1. (c) How many carbons are present? Show calculation. You shouldn't need a calculator for this one.

1. (d) Now you should be able to propose a molecular formula. What is it?

1. (e) Draw a structure which is consistent with all the above. Isomers are possible. Don't worry about that.
2. (10 points) Please provide a mechanism for the following conversion (retro to acetal).

3. (10 points) Draw in all the protons in the following compound. Label with small letters all of the different types of protons. Next to each different type of proton, write the multiplicity you would expect in a $^1$H NMR spectrum.

4. (20 points) Match each of the following compounds with the appropriate $^1$H NMR spectrum. Write the letter of each compound in the lower left corner of the correct spectrum. One compound will be omitted. Recall that you cannot treat the intensities of peaks in $^1$H NMR spectra as all or some equal.

5. (20 points) Match each of the following compounds with the appropriate $^1$H NMR spectrum. Write the letter of each compound in the lower left corner of the correct spectrum. One compound will be omitted. You will need to label all different protons within each compound and predict multiplicity.

6. (20 points) Match each of the following compounds with the appropriate $^1$H NMR spectrum. Write the letter of each compound in the lower left corner of the correct spectrum. Two compounds will be omitted. It will help if you first label all different protons within each compound and predict multiplicity.