Massachusetts Institute of Technology

Organic Chemistry 5.13

September 10, 2003
Prof. Timothy F. Jamison

Problem Set #1

Organic Structure Determination

DUE DATE: Thursday, September 18, 2003 at 12 noon

NOTE: If mass spectrometry (MS) data are provided, the highest molecular ion given corresponds to the molecular ion (M^+), unless otherwise noted.

1. In class we derived a formula for calculating the "index of hydrogen deficiency," which is equal to the sum of the number of rings and π-bonds in an organic molecule. We showed that number of atoms of each element is multiplied by a factor (hereafter called "deficiency factor") in this equation (C: 1, H: –1/2, O: 0, etc.).

a. Derive the deficiency factor for phosphorus (P), using triphenylphosphine $(C_6H_5)_3P$, a common laboratory reagent (e.g. Wittig reactions), as the basis for your calculations.

b. Derive the deficiency factor for phosphorus (P), using triphenylphosphine oxide $(C_6H_5)_3P{=}O$ (a byproduct in the Wittig reaction), as the basis for your calculations.

c. Why are the two factors derived different? In other words, what do you need to know about each element in a particular organic molecule? Based on these considerations, write a general mathematical expression for the deficiency factor for any element.

2. a. Draw the structures of the 4 compounds that satisfy the following experimental data:

EA (found): C, 60.96; H, 15.35; N, 23.70

MS: 59

b. There is a broad signal at 2970 cm^{-1} in the IR spectrum of this unknown compound. Which of the structure(s) that you drew for your answer to 2a can you eliminate from consideration based on this information? Explain.

3. a. Draw the structures of the 6 molecules that satisfy all of the following experimental data, including enantiomers, diastereomers, alkene isomers:

EA (found): C, 66.63; H, 11.18

MS: 72

IR: 3435 (broad), 1645 (weak)

b. When this unknown compound is treated with pyridinium chlorochromate, the signal at 3435 cm^{-1} disappears from the IR spectrum, and a strong, sharp signal at 1685 cm^{-1} appears. Which of the structures(s) that you drew for your answer in 3a can you eliminate from consideration based on this information?

c. How would you distinguish between the 2 remaining structures?

4. In the following problems, determine the structure of each unknown:

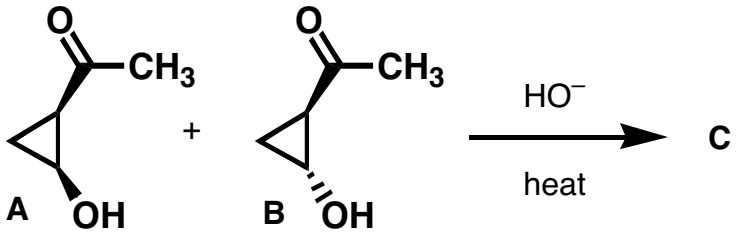
a. EA (found): C: 73.43; H, 10.27
MS: 98
^{13}C NMR: 208.2, 43.0, 32.0, 25.8.

b. EA (found): C, 93.06; H, 6.94
MS: 116, 77
IR: 2075 (weak)
^{13}C NMR: 132.1, 128.2, 128.1, 122.3, 86.8, 81.0, 1.1.

c. EA (found): C, 66.63; H, 11.18
MS: 72
^{13}C NMR: 203.7, 45.8, 14.5.

5. When treated with lithium aluminum hydride in tetrahydrofuran, two isomeric compounds **1** (IR: 1735 cm^{-1}) and **2** (IR: 1705 cm^{-1}) (both $C_8H_8O_2$) each gave two different products (i.e. all 4 products (total) in the 2 reactions are different from one another). Deduce the structures of **1** and **2**.

6. Compounds **A** and **B** were both treated with NaOH, producing a single compound, **C**.

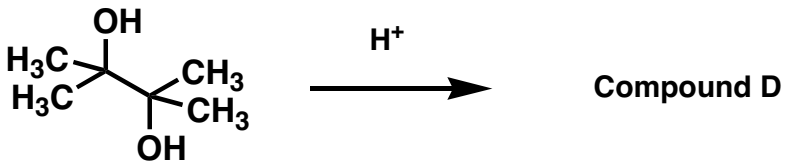


Data for **C**:

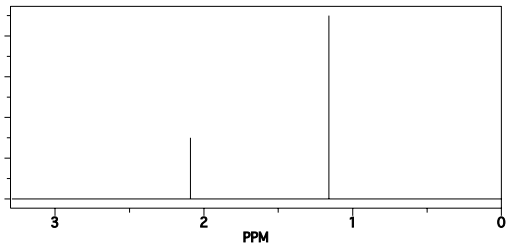
EA (found): C: 68.18%; H: 8.82%
^{13}C NMR: 210.1, 164.6, 134.5, 34.0, 29.0.

a. What is the relationship of **A** and **B**?
b. Using the data provided above and the spectra provided below, deduce the structure of **C**.
c. Write out a stepwise mechanism that accounts for the formation of **C**.

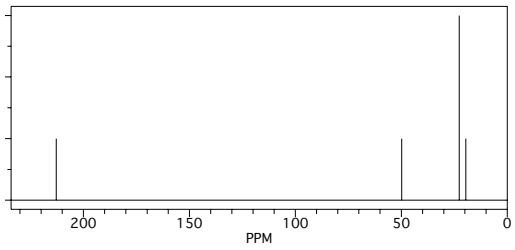
7. Compound D, the product of the reaction below, was characterized by ^{1}H NMR and ^{13}C NMR (spectra below). Draw the structure of the product and a stepwise mechanism for its formation in this reaction.



^{1}H NMR of compound D (truncated, nothing downfield of 3 ppm):



^{13}C NMR of compound D:



8. a. Propose two possible structures for Compound **E** using the information provided below.

EA (found): C: 75.01%; H: 6.59%

MS: 176, 161

^{13}C NMR: 166.9, 144.5, 134.4, 130.1, 128.8, 128.0, 118.2, 60.4, 14.3.

b. The coupling constant between the signals at 6.4 ppm and 7.8 ppm in the ^{1}H NMR spectrum is 15 Hz. Based on this information, which of the two structures that you proposed in part (a) is more likely to be the structure of **E**? Explain.

9. Sometimes it is possible to determine the structure of an organic molecule even with what appears to be an incomplete set of information. Using the data below, propose a structure for compound **F**.

EA (found): C: 75.99%, H: 9.02%

MS: 93, 92. (The molecular ion was not observed.)

^{1}H NMR: sharp singlet (1 H) at 2.50 ppm, broad singlet (1 H) at 2.38 ppm, all other signals between 1.5 and 2.0 ppm.

^{13}C NMR: 5 signals, all between 0.0 and 90.0 ppm.

IR: very broad, very strong signal centered at 3400 cm^{-1}, weak signal at 2110 cm^{-1}.

10. Propose a structure for compound **G** using the information provided below:

MS: 100, 85

^{13}C NMR: 215.2, and 4 other signals, all between 0.0 and 45.0 ppm (5 signals total).