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~~ 1/2, O: 0, etc.).

+1/2 +3/2

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.

IHD = 12

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.

IHD = 13

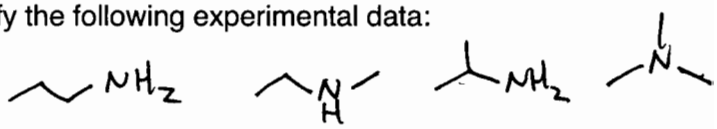
c. Why are the two factors derived different? In other words, what do you need to know about each element in a particular organic molecule? Based on these considerations, write a general mathematical expression for the deficiency factor for any element.

- OXIDATION STATE or "VALENCE"
- $X = \frac{\text{OXIDATION STATE}}{2} - 1$

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

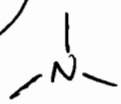
EA (found): C, 60.96; H, 15.35; N, 23.70

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.

N-H (H-BONDED)



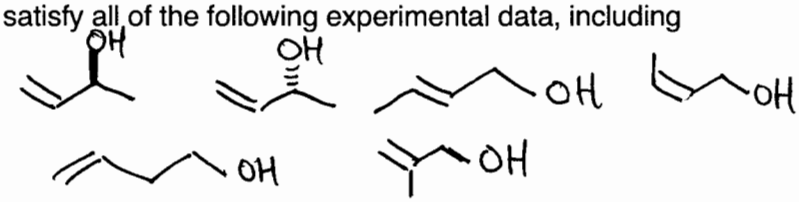
(NO N-H GROUPS)

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 OH_2 = 2

IR: 3435 (broad), 1645 (weak)

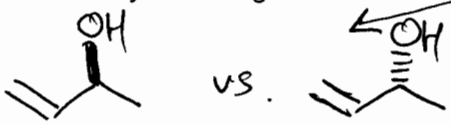


b. When this unknown compound is treated with pyridinium chlorochromate, the signal at 3435 cm^{-1} disappears from the IR spectrum, and a strong, sharp signal at 1685 cm^{-1} appears. Which of the structures(s) that you drew for your answer in 3a can you eliminate from consideration based on this information?

ALL EXCEPT 2

1715 − 30 (ketone conjugated)

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



vs.

(MANY WAYS) e.g. $[\alpha]_D$

NEED METHOD THAT DISTINGUISHES ENANTIOMERS

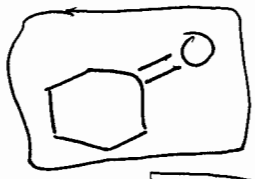
SPECIFIC ROTATION

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

a. EA (found): C: 73.43; H, 10.27 $C_6H_{10}O$ IHD = 2

MS: 98

^{13}C NMR: 208.2, 43.0, 32.0, 25.8. (probably ketone) C=O — 3 ALKYL → 2 ARE EQUIV

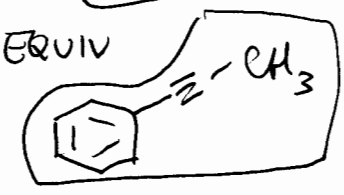


b. EA (found): C, 93.06; H, 6.94

MS: 116, 77 C_9H_8 IHD = 6

IR: 2075 (weak) C≡C — (NOT C≡C-H)

^{13}C NMR: 132.1, 128.2, 128.1, 122.3, 86.8, 81.0, 1.1. ARYL — ALKYNYL — ALKYL

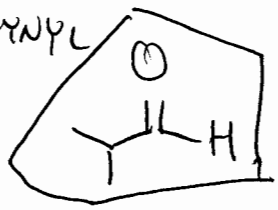


c. EA (found): C, 66.63; H, 11.18 C_4H_8O IHD = 1

MS: 72

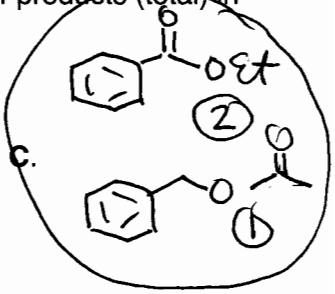
^{13}C NMR: 203.7, 45.8, 14.5. 3 DIFF ^{13}C

↑ C=O (CLOSER TO ALDEHYDE)

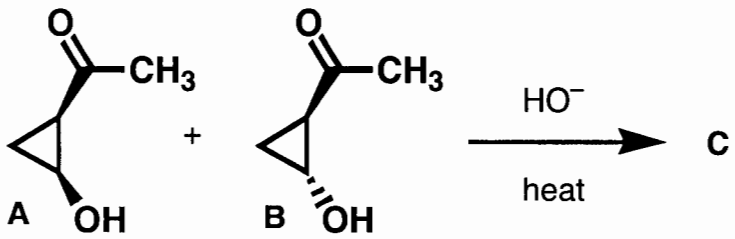


5. When treated with lithium aluminum hydride in tetrahydrofuran, two isomeric compounds **1** (IR: 1735 cm^{-1}) and **2** (IR: 1705 cm^{-1}) ~~(both $C_8H_8O_2$)~~ each gave two different products (i.e. all 4 products (total) in the 2 reactions are different from one another). Deduce the structures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

ESTER — COULD BE CONJUGATED ESTER — both $C_9H_{10}O_2$ — IHD = 5 (TRI/NK ARYL)



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



Data for **C**:

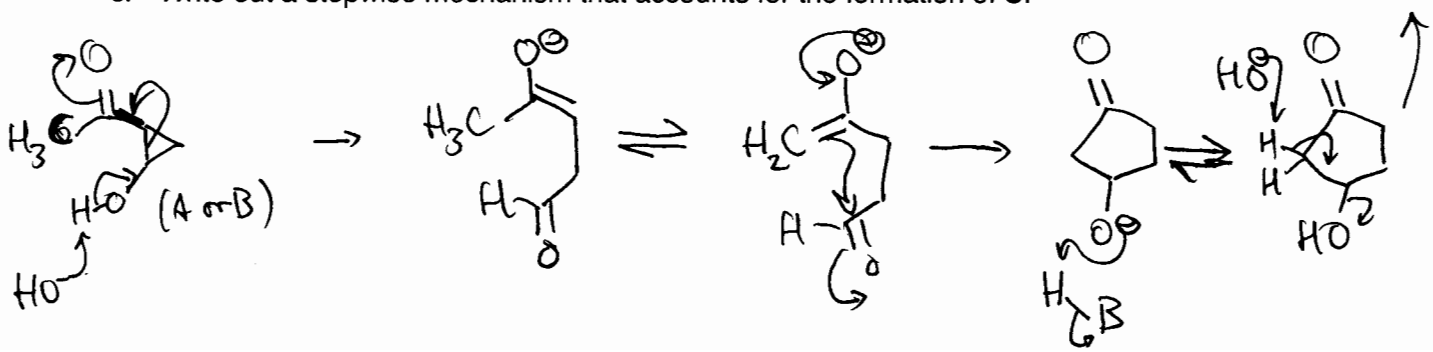
EA (found): C: 73.15%; H: 7.37%

^{13}C NMR: 210.1, 164.6, 134.5, 34.0, 29.0.

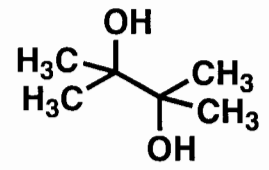
a. What is the relationship of **A** and **B**? DIASTEREOMERS

b. Using the data provided above and the spectra provided below, deduce the structure of **C**.

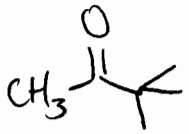
c. Write out a stepwise mechanism that accounts for the formation of **C**.



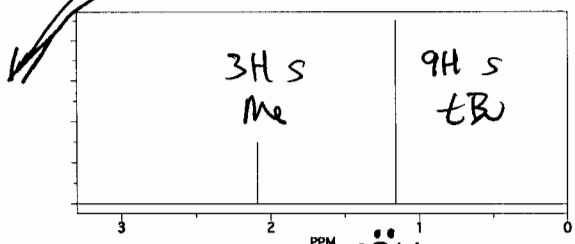
7. Compound D, the product of the reaction below, was characterized by ^{1}H NMR and ^{13}C NMR (spectra below). Draw the structure of the product and a stepwise mechanism for its formation in this reaction.



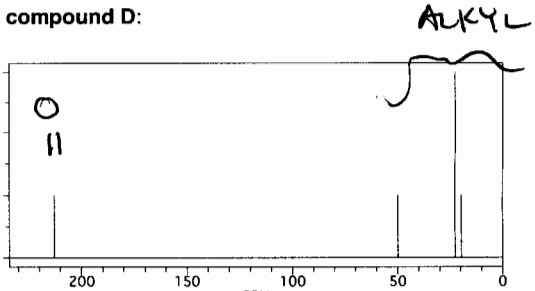
H^+ → **Compound D**

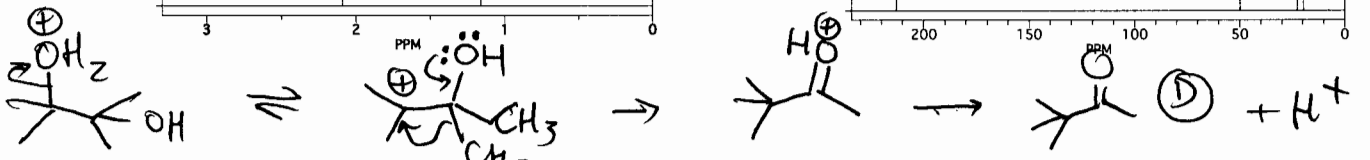


^{1}H NMR of compound D (truncated, nothing downfield of 3 ppm):



^{13}C NMR of compound D:





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

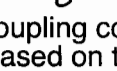
$C_{11}H_{12}O_2$

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

MS: 176, 161 ($-CH_3$)

"REAL WORLD" (i.e. ACTUAL) DATA – NOT ALWAYS EXACTLY ON EXPECTED VALUES.

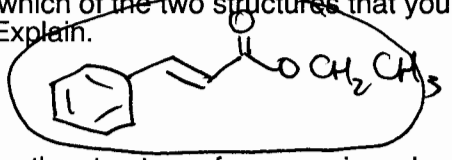
^{13}C NMR: 166.9, 144.5, 134.4, 130.1, 128.8, 128.0, 118.2, 60.4, 14.3.



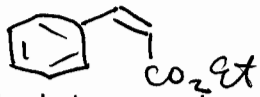
ACYL & ALKENYL — O–C — ALKYL

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.

trans →



vs.



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**.

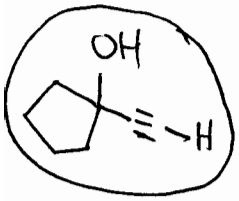
$C_7H_{10}O$

IHD = 3

← SEE NOTE FOR 8a.

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

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



OH

^{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.

C≡C–H

^{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}.

(relative to 3400 cm^{-1})

≡

ALL ALKYL (8 H)

ALL ALKYL OR ALKYNYL, 2 ARE EQUIVALENT

HO

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

MS: 100, 85 ($-CH_3$)

ALL ALKYL

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

C=O (ketone)

SO AT LEAST C_5

(SEE NEXT PAGE)

PROBLEM 10, CONTINUED

MS { MW 100
AT LEAST 1 CH_3 GROUP

^{13}C { AT LEAST 1 KETONE (NON-EQUIV)
AT LEAST 4 DIFF. ALKYL CARBONS

- $C_x H_y O_z$ $\quad x \geq 5$, $z \geq 1$

FOR $C_5H_yO_1$, $MW = 72 + y(1) = 100$

$y = 28$! (IMPOSSIBLE)

- $C_6H_yO_1$, $MW = 88 + y(1) = 100 \Rightarrow y = 12$

REASONABLE

- $C_7H_yO_1$, $MW = 100 + y(1) = 100 \Rightarrow y = 0$

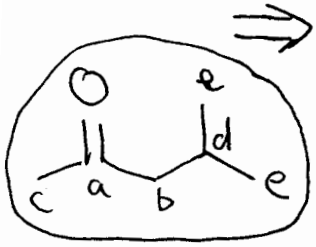
IMPOSSIBLE (HAVE CH_3 GROUP (MS))

- SO $\#C \leq 6$

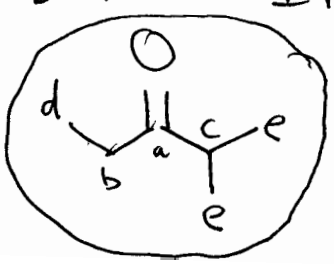
- $C_5H_yO_2$, $MW = 92 + y(8) = 100 \Rightarrow y = 8$

REASONABLE, BUT WOULD HAVE TO HAVE 2 EQUIV C=O (KETONES), LEAVING ONLY 3 ALKYL SIGNALS. $\Rightarrow$ NOT $C_5H_8O_2$

$\Rightarrow C_6H_{12}O$ $\quad IHD = 1 \rightarrow C=O$ (NO RINGS) $+ C_5H_{12}$ (ALL ALKYL, 2 MUST BE EQUIVALENT (^{13}C))



OR



ONLY STRUCTURES THAT SATISFY ALL DATA.