NUCLEAR MAGNETIC RESONANCE AND INTRODUCTION TO MASS SPECTROMETRY

A STUDENT SHOULD BE ABLE TO:

1. Identify and explain the processes involved in proton and carbon-13 nuclear magnetic resonance (NMR), and mass spectroscopy (MS). Important factors include:

   The relationships of energy, frequency, and wavelength in the electromagnetic spectrum. From highest to lowest energy, important types of electromagnetic radiation are: x-rays, ultraviolet, visible, infrared, microwave, radio.
   Electron impact ionization, molecular ion, mass-to-charge (m/z) ratio.
   Chemical shift, integration, shielding and deshielding of protons, signal splitting and spin-spin coupling in NMR.

2. Explain and predict experimental results in nuclear magnetic resonance spectroscopy, including:

   The number of signals a compound has in its ^{1}H-NMR or ^{13}C-NMR spectrum, which is the number of sets of equivalent protons or carbons respectively. Diastereotopic protons occur in molecules with a stereocenter.
   The relative chemical shift of given protons or carbons (from the effects of electronegativity and pi bonding).
   The splitting pattern (singlet, doublet, triplet, etc.) of a given proton NMR signal in simple systems. In these, the number of peaks equals the number of neighbors plus one; neighbors may include ^{13}C and ^{19}F, as well as protons. Note: The term multiplet often indicates that the system involved is not simple. When splitting is caused by non-equivalent protons on two adjacent carbons, the approximation of counting the total number of neighbors plus one is often effective.
   Integration ratios: The heights of the integral curves are proportional to the areas under the signals, which are in the same ratio as the number of protons causing the signal.

3. Fully analyze nuclear magnetic resonance spectra and identify unknown compounds from their NMR, MS, and/or infrared spectra. If the molecular formula is known, the index of hydrogen deficiency may be helpful--see Module 8: Alkenes: structure and properties.

4. Predict proton and C-13 spectra for a given structure. The proton spectrum should include splitting pattern, integration and chemical shift. Also calculate m/z ratio for the molecular ion in MS.

To best prepare for this module, please work Chapter 16 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 a) Which of the following types of radiation has the longest wavelength? b) Which has the highest frequency? c) Which has the lowest energy?

A. Microwaves B. Infrared C. Visible D. Radio

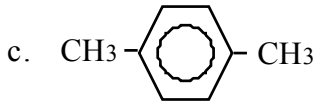
1.2 Proton and carbon magnetic resonance spectra are produced by:

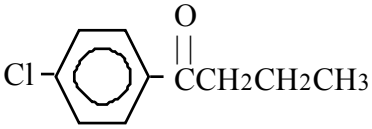
A. Carbons and protons, respectively.
B. Protons and carbons, respectively.
C. Oxygens attached to carbon.
D. Multiple bonds between carbons.

2.1 How many signals are present in the proton NMR spectra of each of the following compounds? In the ^{13}C spectra? Count similar but theoretically different benzene ring protons as different.

a. $CH_3CH(OH)CH_3$

b. $CH_3CH_2C(=O)-O-CH_2CH_3$

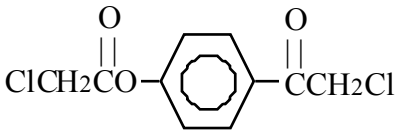
c. 

d. 

e. $CH_3CH_2CH(Br)CH_3$

f. $CH_3CH_2C(=O)-CH_3$

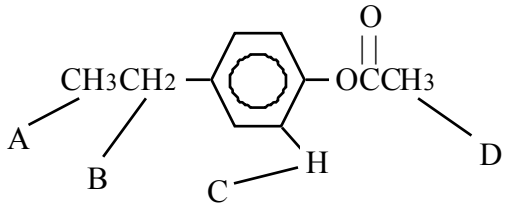
g. $CH_3OCH_2CH_2OCH_3$

h. 

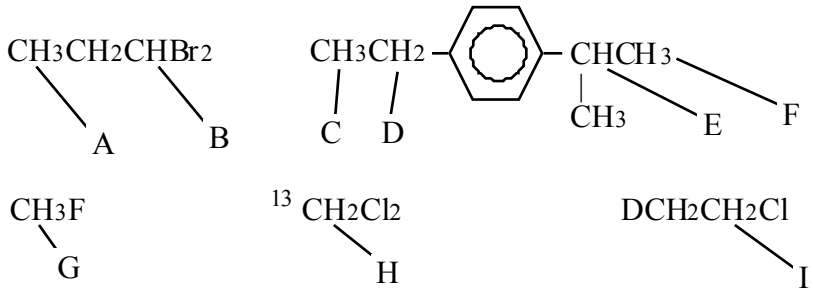
2.2 a) Which of the following compounds has the protons having the highest chemical shift (value of delta) in this set? b) Which has the lowest chemical shift?

A. $(CH_3)_2Mg$ B. $CH_3C(=O)OH$ C. $CH_3C(=O)H$ D. $(CH_3)_3N$

2.3 a) Which of the indicated proton(s) is (are) the most shielded (lowest value of delta)?
b) Which is (are) the least shielded?



2.4 What splitting pattern (singlet, doublet, triplet, quartet, quintet, etc.) is observed in the proton NMR spectrum of each of the indicated protons?



3. Identify each of the following unknowns from the given proton magnetic resonance and/or infrared spectroscopic information.

a) $C_3H_5Cl_3$
singlet, δ 2.2, 3H
singlet, δ 4.0, 2H

b) $C_5H_{10}Br_2$
doublet, δ 0.9, 6H
multiplet, δ 1.5, 1H
triplet, δ 1.85, 2H
triplet, δ 5.3, 1H

c) C_3H_8O. IR: broad peak near 3400 cm^{-1}
pmr: doublet, δ 1.2, 6H
broad singlet, δ 2.0, 1H
septet, δ 4.0, 1H

d) $C_{10}H_{12}O$. IR: peak at 1710 cm^{-1}
pmr: singlet, δ 2.1, 3H
multiplet, δ 3.0, 4H
multiplet, δ 7.1, 5H

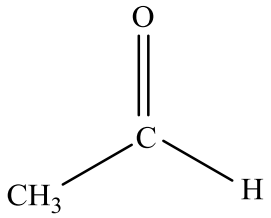
3. e) C_5H_{10}

triplet, δ 0.9, 3H
multiplet, δ 1.5, 2H
quartet, δ 2.1, 2H
multiplet, δ 4.8, 1H
multiplet, δ 5.1, 1H
multiplet, δ 5.8, 1H

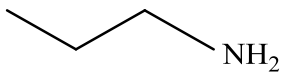
Note: The chapter on spectroscopy in your textbook contains a number of unknown identification problems that require you to propose a structure for a compound when given spectral data and the formula for that compound. Other problems give the spectrum itself (not merely spectral data). Problems 16.55-16.58, 16.62 and 16.64 are recommended.

4. Predict proton and ^{13}C NMR spectra for the following compounds. Also calculate m/z ratio for their molecular ions.

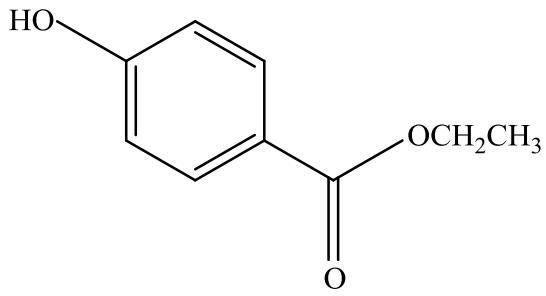
a)



b)



c)



Note: Additional problems to be considered in the textbook are 16.41 and 16.42

SOLUTIONS TO SAMPLE PROBLEMS:

1.1 a) D b) C c) D

1.2 B

2.1 Signals in the proton NMR: a) 3 b) 4 c) 2 d) 5 e) 5 f) 3 g) 2 h) 4
In the ^{13}C NMR: a) 2 b) 5 c) 3 d) 8 e) 4 f) 4 g) 2 h) 8

2.2 a) B b) A

2.3 a) A b) C

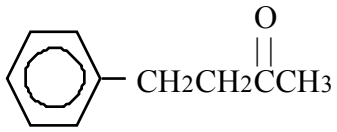
2.4

a) triplet	b) triplet	c) triplet
d) quartet	e) septet (7 peaks)	f) doublet
g) doublet	h) doublet	i) triplet

3. a) $CH_3CCl_2CH_2Cl$

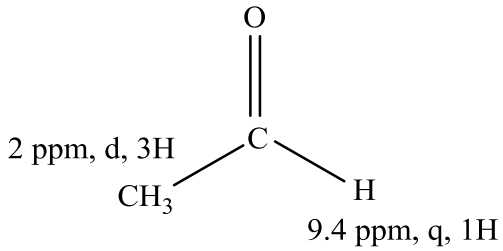
b) $(CH_3)_2CHCH_2CHBr_2$

c) $(CH_3)_2CHOH$

d) 

e) $CH_3CH_2CH_2CH{=}CH_2$

4. a) m/z 44.05

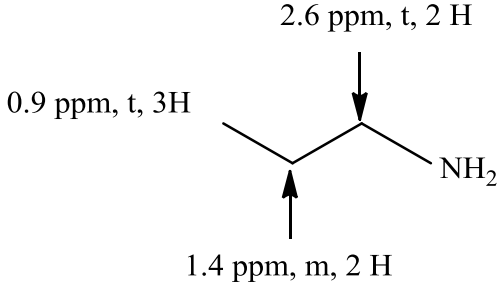


C-13:

30 ppm (CH_3)

200 ppm (C=O)

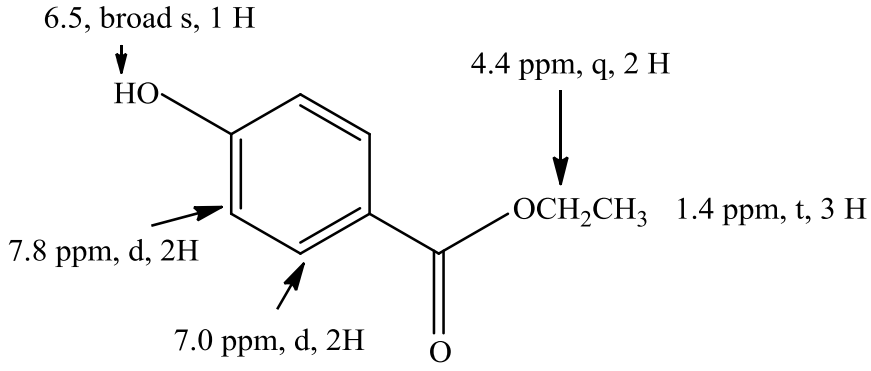
b) m/z 59.11



C-13:

15 ppm (CH_3)
25 ppm (CH_2)
45 ppm (CH_2-N)

4. c) m/z 166.18

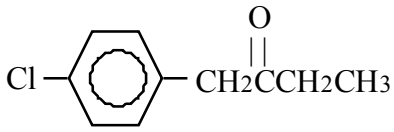


C-13:

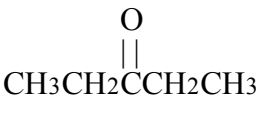
15 ppm (CH_3)
60 ppm (CH_2-O)
115 ppm (CH arom)
121 ppm (CH arom)
130 ppm (CH arom)
160 ppm (CH-O ar)
170 ppm (C=O)

Name _____ First Drill Test (Sample A)
Organic Chemistry 2220DR Answer All Questions

1. a) How many signals are present in the proton NMR spectra of each of the following compounds? Count similar but theoretically different benzene ring protons as different.
b) How many signals are present in the C-13 NMR spectrum of each?

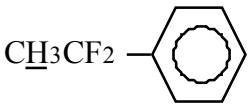


a) _____
b) _____

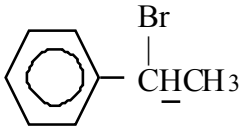


a) _____
b) _____

2. a) What splitting pattern (singlet, doublet, triplet, etc.) is observed for each of the underlined proton(s)? b) What is the m/z ratio for the molecular ion for each of the compounds? (Atomic masses: H, 1; C, 12; F, 19; Br, 80)

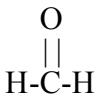


a) _____
b) _____



a) _____
b) _____

3. a) Which of the following compounds gives a signal with the highest delta value (most deshielded) in the proton NMR? b) Which gives a signal with the lowest delta value?

A. CH_3OCH_3 B.  C. $(CH_3)_4Si$ D. 

a) _____
b) _____

4. Identify each of the following unknown compounds.

a) $C_8H_{10}O$
No IR peaks near
1700 or 3400 cm^{-1}
singlet, δ2.3, 3H
singlet, δ3.8, 3H
doublet, δ6.8, 2H
doublet, δ7.1, 2H

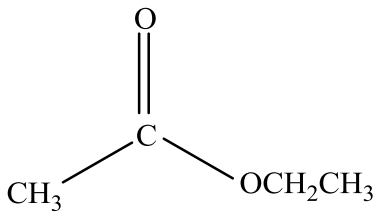
b) $C_{10}H_{14}O$
IR peak: 3400 cm^{-1}
singlet, δ1.3, 9H
singlet, δ4.9, 1H
multiplet, δ7.0, 4H

c) $C_5H_{10}O$
IR peak: 1710 cm^{-1}
doublet, δ1.1, 6H
singlet, δ2.1, 3H
septet, δ2.6, 1H

d) C_4H_7N
IR peak: 2250 cm^{-1}
triplet, δ1.07, 3H
multiplet, δ1.67, 2H
triplet, δ2.27, 2H

e) $C_3H_5ClO_2$, IR: broad peak 2500-3000 cm^{-1}, 1715 cm^{-1}.
PMR: triplet, δ2.8, 2H
triplet, δ3.8, 2H
singlet, δ11.6, 1H

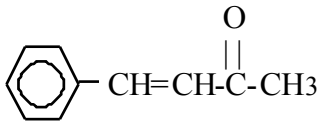
5. Predict proton and C-13 NMR spectra for the following compound. Also calculate m/z ratio for the molecular ion (radical cation). Atomic masses: H=1, C=12, O=16.



Name _____ First Drill Test (Sample B)
Organic Chemistry 2220 DR Answer All Questions

1. a) How many signals are present in the proton NMR spectra of each of the following compounds? Count similar but theoretically different benzene ring protons as different.
b) How many signals are present in the C-13 NMR spectrum of each?

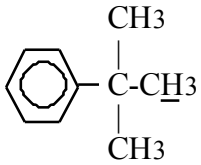
$CH_3CH_2CH_2OCH_2CH_3$ a) _____ b) _____



a) _____ b) _____

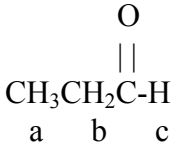
2. a) What splitting pattern (singlet, doublet, triplet, etc.) is observed for each of the underlined proton(s)? b) What is the m/z ratio for the molecular ion for each of the compounds? (Atomic masses: H, 1; C, 12; O. 16; Br, 80)

$(CH_3)_2C\underline{H}Br$ a) _____ b) _____



a) _____ b) _____

3. Which of the following indicated protons gives a signal with the highest δ value (most deshielded)? Which gives a signal with the lowest δ value? What is the m/z ratio for the molecular ion?



_____ highest δ value
_____ lowest δ value
_____ m/z ratio

4. Identify each of the following compounds from the given IR and proton NMR spectra (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

a) C_3H_7Br NMR: doublet, δ 1.7, 6H
septet (7 peaks), δ 4.3, 1H

b) C_7H_8O IR: broad peak in 3200-3550 cm^{-1} region NMR: s, δ 2.4, 1H
s, δ 4.6, 2H
m, δ 7.3, 5H

c) C_8H_9Br NMR: d, δ 2.0, 3H
q, δ 5.2, 1H
m, δ 7.4, 5H

d) $C_4H_8O_2$	IR: strong peak	NMR: d, δ 1.4, 3H
	near 1710 cm^{-1},	s, δ 2.2, 3H
	broad peak	s, δ 4.0, 1H
	near 3400 cm^{-1}	q, δ 4.3, 1H

5. Predict proton and C-13 NMR spectra for the following compound. Also calculate m/z ratio for its molecular ion (radical cation). Atomic masses: H=1, C=12, N=14, O=16.