

Chemistry 210
“Organic Chemistry I”
Winter Semester 2003
Dr. Rainer Glaser

Quiz #3
“ ^1H - and ^{13}C -NMR-Spectroscopy”

Posted: Monday, May 3, 2004.

Collection: Wednesday, May 5, 2004, after lecture.

Name:

Answer Key

Question 1. NMR Basics	16	
Question 2. ^1H -NMR Spectrum Interpretation	12	
Question 3. ^1H -NMR Spectrum Prediction	12	
Question 4. ^{13}C -NMR Spectroscopy	10	
Total	50	

Question 1. NMR Basics. (16 points)

- (a) What does “NMR” stand for? nuclear magnetic resonance. (1 p.)
- (b) What does “MRI” stand for? magnetic resonance imaging. (1 p.)
- (c) What nucleus is being looked at in MRI? (1) **H-nucleus**. (2) C-nucleus. (1 p.)
- (d) What does “ppm” stand for? parts per million. (1 p.)
- (e) Give the approximate natural abundance of ^{13}C ? (1) 0% (2) 0.1% (3) **1%** (4) 10% (1 p.)
- (f) How large is the nuclear spin I of a ^{12}C -atom? (1) **0** (2) 0.5 (3) 1.0 (4) 1.5 (1 p.)
- (g) Once a nucleus with a magnetic moment is in a magnetic field, the nucleus’ energy depends on whether its magnetic moment is “parallel” or “antiparallel” with regard to the external field. The effect is called the Zeeman effect after its discoverer. (1 p.)
- (h) The magnetic moment of an H-nucleus aligns either “parallel” or “antiparallel” with an external magnetic field. Which orientation is energetically better? (1) **parallel** (2) antiparallel (1 p.)
- (i) NMR uses radio waves to flip nuclear spins. What is the frequency range of radio waves. (1 p.)
(1) MicroHertz (2) MilliHertz (3) **MegaHertz** (4) McHertz
- (j) An H-atom is said to be “shielded” when it is _____ (positively, **negatively**) charged and such “shielded” H-atoms show _____ (**low**, high) chemical shifts. (1 p.)
- (k) The ring current effect in benzene is due to the _____ (sigma, **pi**) electrons. It causes the effective field outside of the ring to be _____ (smaller, **larger**) than the external magnetic field. This ring current effect is a so-called non-local effect. (2 p.)

(l) Chemical shifts are relative values that are independent of the magnetic field strength of the NMR spectrometer. The chemical shift values are given relative to “TMS”. Draw the structure of TMS, provide the full name of TMS, and specify the exact chemical shift of TMS. (2 p.)

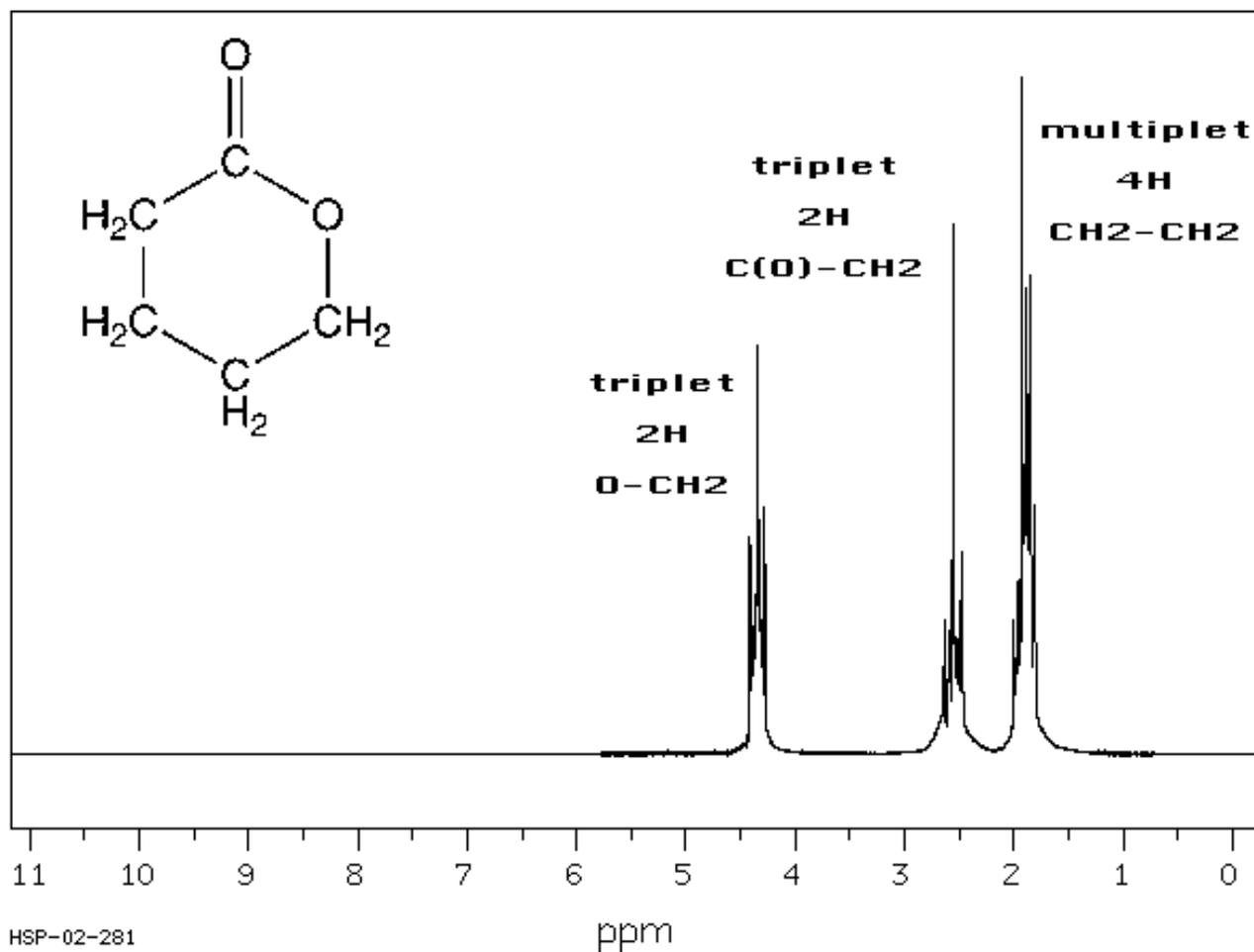
Draw $\text{Si}(\text{CH}_3)_4$
Tetramethylsilane
 $\delta = 0$ ppm

(m) Suppose that ν_S is the resonance frequency which flips the spin of a nucleus in a sample and that ν_R is the resonance frequency that flips the spin of the nucleus in the reference compound. Write down the equation for the computation of the chemical shift δ . (2 points)

$$\delta = 1,000,000 (\nu_S - \nu_R) / \nu_R \text{ ppm}$$

Question 2. $^1\text{H-NMR}$ Spectrum Interpretation. (12 points)

The H-NMR Spectrum of delta-Valerolactone.



Assign the H-NMR Spectrum of delta-valerolactone.

For each peak, write next to the peak what kind of splitting pattern the peaks shows (singlet etc.).

For each peak, write next to the peak how many H-atoms cause the peak (1H, 2H, etc.).

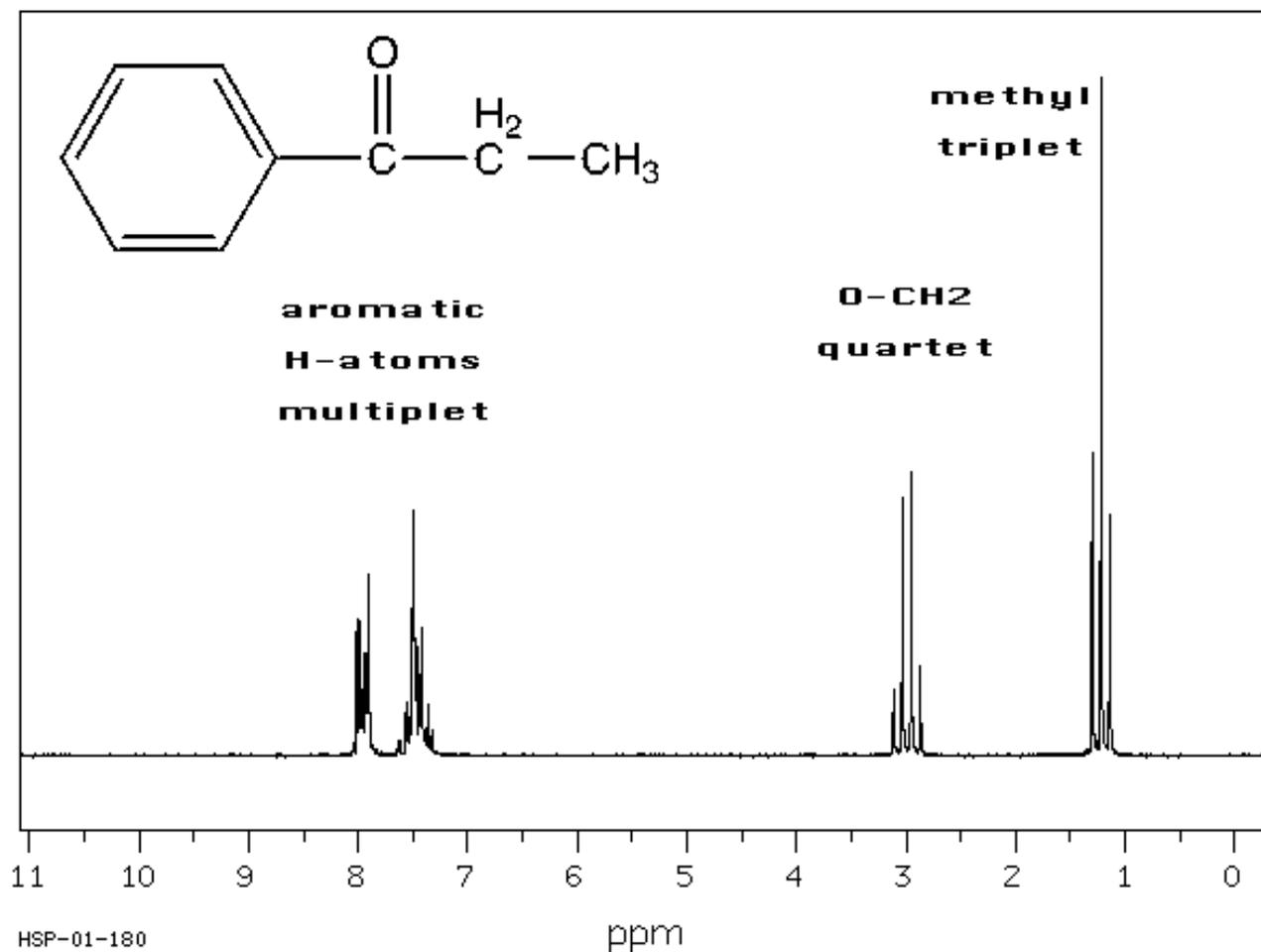
For each peak, write next to the peak which (group of) H-atom(s) causes the peak.

For the signal around 2.5 ppm, what line intensities would you expect in the ideal case (use Pascal triangle)? **An ideal triplet: 1:2:1.**

Predict the number of peaks in the C-NMR Spectrum of delta-valerolactone: 5

Question 3. $^1\text{H-NMR}$ Spectrum Prediction. (12 points)

The $^1\text{H-NMR}$ Spectrum of Propiophenone.



Predict the $^1\text{H-NMR}$ Spectrum of propiophenone.

Predict the number of peaks: 3

Predict the approximate chemical shifts of all peaks using chemical shift tables.

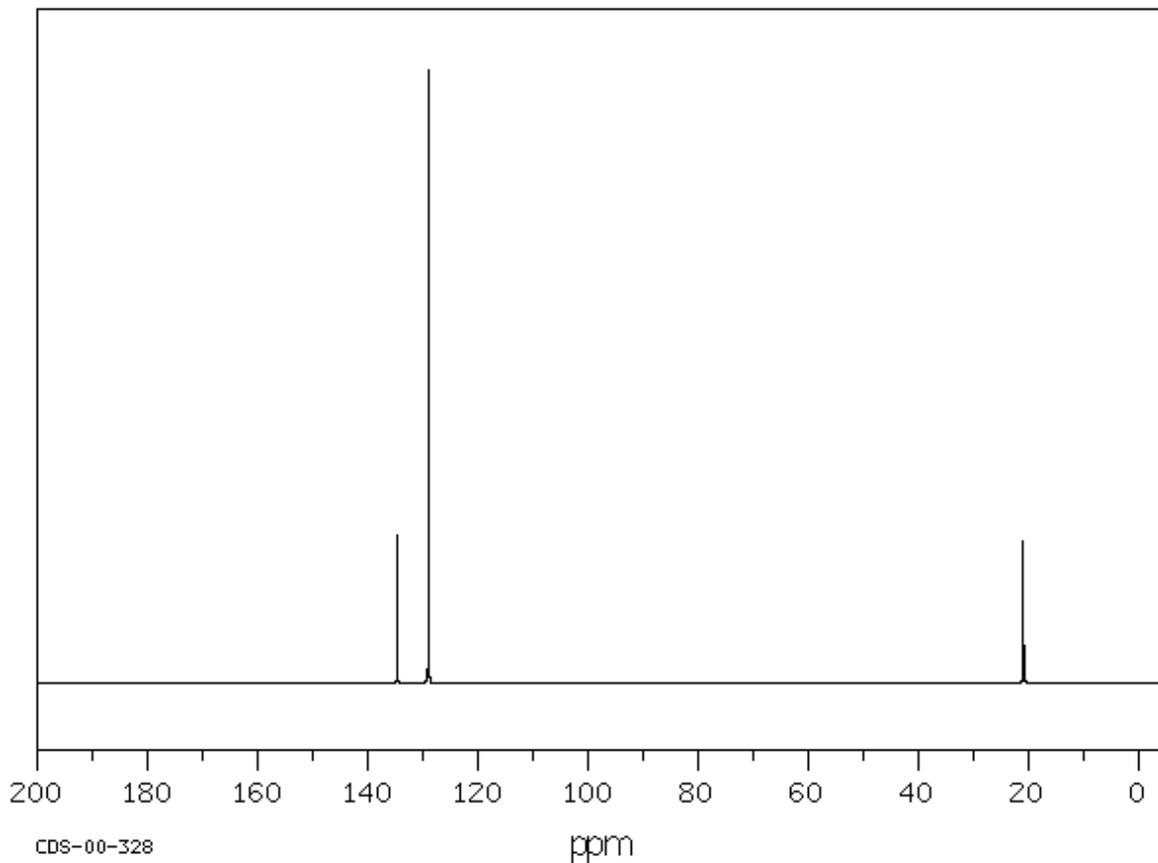
Predict the splitting patterns of all peaks. Call them singlet, triplet, quartet and so on as appropriate. If a signal is split in a more complicated way, then just call it “multiplet” and leave it at that!

Draw an approximate spectrum in the above template. The spectrum should reflect chemical shifts, signal intensities and splitting due to spin-spin coupling.

Predict the number of peaks in the $^{13}\text{C-NMR}$ Spectrum of propiophenone: 7

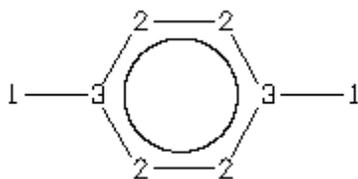
Question 4. ^{13}C -NMR Spectroscopy. (10 points)

^{13}C -NMR spectrum of (a) *ortho*-xylene, (b) *meta*-xylene or (c) *para*-xylene: (c).



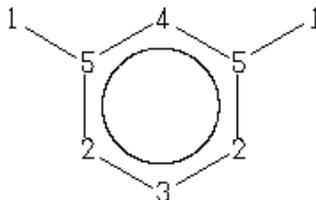
Explain your assignment:

3 signals



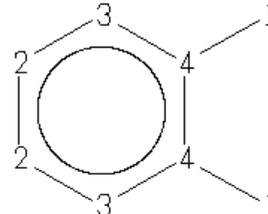
ppm	Int.	Assign.
134.66	239	3
128.97	1000	2
0.90	229	1

5 signals



ppm	Int.	Assign.
137.74	547	5
129.96	423	4
128.21	473	3
126.13	1000	2
21.31	403	1

4 signals



ppm	Int.	Assign.
136.42	383	4
129.63	960	3
125.85	1000	2
19.66	587	1