CHEM 2311
E5 practice-ii (answers provided)

COPIES OF TABLES 2.7, 9.1, and 9.2 are attached
You may use a calculator on this exam

Atomic Masses: H, 1.008; C, 12.01; N, 14.007; O, 15.999

1. (32 points) Circle the letter *on the right* which corresponds to the answer to each question. There is only one correct answer for each question.

(i) What type of electromagnetic radiation is absorbed during the NMR experiment? **A B C D**

A. X-ray **B.** microwave **C.** ultraviolet **D.** radio frequency

(ii) In the **^{1}H** NMR spectrum of ethanol, the protons of the methyl group appears at δ = 1.2 ppm as a triplet. What principle allows you to predict that it would be a triplet? **E F G H**

E. integration **F.** chemical shift **G.** N + 1 rule **H.** shielding

(iii) Predict the splitting pattern you would observe for the proton at C3 of 2,3-dimethyl-2-phenylbutane.? **I J K L**

I. singlet **J.** sextet **K.** quartet **L.** septet

(iv) How many **^{13}C** signals would 1,3-dichlorobenzene give? **M N O P**

M. 3 **N.** 4 **O.** 5 **P.** 6

(v) The protons of the methyl groups of tetramethylsilane (TMS) are highly shielded and appear at δ = 0.00 ppm. In the corresponding carbon compound, 2,2-dimethylpropane, the methyl groups appear at δ = 1.00 ppm. How can this difference be explained? **Q R S T**

Q. carbon is more electropositive than silicon **R.** silicon is larger than carbon
S. silicon is more electropositive than carbon **T.** there is no coupling of H to Si

(vi) A C_7 compound which gives 3 signals in the **^{13}C** NMR spectrum could be: **U V W X**

U. 2-Methylhexane **V.** 3,3-Dimethylpentane
W. 2,4-Dimethylpentane **X.** 2,2,3-Trimethylbutane

(vii) A compound, $C_5H_{11}Cl$, which exhibits only two singlets in the **^{1}H NMR** spectrum must be: **Y Z AA BB**

Y. 1-Chloro-3-methylbutane **Z.** 3-Chloropentane
AA. 1-Chloro-2,2-dimethylpropane **BB.** 1-Chloro-2-methylbutane

(viii) In **^{13}C** NMR spectroscopy, the signal due to which type of carbon occurs furthest downfield. **CC DD EE FF**

CC. C-O **DD.** C-F **EE.** C=C **FF.** C=O

2. (24 points)

(a) Provide a single structure consistent with the following data (there is a single correct answer for each part).

(i) Compound **A**: C_3H_6O which boils at 78 °C (the highest boiling C_3H_6O compound)

(ii) Compound **B**: C_3H_7Br
^{1}H NMR: a septet (1H) downfield from a doublet (6H)

(iii) Compound **C**: $C_5H_{12}O$
^{1}H NMR: two singlets

(iv) Compound **D**: $C_8H_8Cl_2$
^{1}H NMR: two singlets

(b) Compound **E**, which contains only C, H, and O gives a combustion analysis of C55.82%; H 6.94%

(i) What is the *empirical formula* of **E**? _____

(ii) What is the *smallest possible molecular formula* for **E**? _____

3. (19 points) Refer to the data provided on the next page. *NOTE: Parts (a)-(i) are worth TWO POINTS each, (j) is worth ONE POINT. Each part is graded independently, without reference to other answers*

Analysis of Combustion Analysis/Mass Spectrum/Empirical Formula

(a) What is the *molecular formula*? _____

(b) What is the value of SODAR? _____

Analysis of the ^{13}C NMR spectrum:

(c) How many types of carbon are there in the molecule: _____

(d) Is a carbonyl present? (circle one) Yes No

(e) How many types of aromatic carbons are there?_____

Analysis of IR spectrum (in conjunction with formula and ^{13}C NMR)

(f) Which of the following are present? (circle all that are present)

O-H C-O C=O

Analysis of ^{1}H NMR spectrum

(g) How many types of proton are there in the molecule?_____

(h) What is the ratio of the number of each type of proton? (*i.e.*, 6:3:2:1)_____

(i) How many aromatic hydrogens are there?_____

Putting it all together

(j) Suggest a single structure for the molecule.

INFRARED ABSORPTION VALUES

Group	*Frequency Range (cm^{-1})*	*Intensity*
A. Alkyl		
C-H (stretching)	2583-2962	(m-s)
Isopropyl, $-CH(CH_3)_2$	1380-1385	(s)
	and 1365-1370	(s)
tert-butyl, $-C(CH_3)_3$	1385-1395	(m)
	and ~1365	(s)
B. Alkenyl		
C-H (stretching)	3010-3095	(m)
C=C (stretching	1620-1680	(v)
R-CH=CH_2	985-1000	(s)
	and 905-920	(s)
$R_2C=CH_2$	880-900	(s)
cis-RCH=CHR	675-730	(s)
trans-RCH=CHR	960-975	(s)
C. Alkynyl		
≡C-H (stretching)	~3300	(s)
C≡C (stretching)	2100-2260	(v)
D. Aromatic		
Ar-H (stretching)	~3030	(v)
Aromatic substitution type (C-H out-of-plane bendings)		
Monosubstituted	690-710	(very s)
	and 730-770	(very s)
o-Disubstituted	735-770	(s)
m-disubstituted	680-725	(s)
	and 750-810	(strong s)
p-disubstituted	800-860	(strong s)
E. Alcohols, Phenols, and Carboxylic Acids		
O-H (stretching)		
Alcohols, phenols (dilute solution)	3590-3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)	3200-3550	(broad, v)
Carboxylic acids (hydrogen bonded)	2500-3000	(broad, v)
F. Aldehydes, Ketones, Esters and Carboxylic Acids		
C=O (stretching)	1630-1780	(s)
Aldehydes	1690-1740	(s)
Ketones	1680-1750	(s)
Esters	1735-1750	(s)
Carboxylic Acids	1710-1780	(s)
Amides	1630-1690	(s)
G. Amines		
N-H	2200-2500	(m)
H. Nitriles		
C≡N	2220-2260	(m)

s = strong; m = medium, w = weak, v = variable

APPROXIMATE PROTON CHEMICAL SHIFTS

Type of Proton	*Chemical Shift (δ, ppm)*
1° Alkyl, RCH_3	0.8-1.0
2° Alkyl, RCH_2R	1.2-1.4
3° Alkyl, R_3CH	1.4-1.7
Allyllic, $R_2C=C-CH_3$ (R on C)	1.6-1.9
Ketone, $RCCH_3$ (O on C)	2.1-2.6
Benzylic, $ArCH_3$	2.2-2.5
Acetylenic, RC≡CH	2.5-3.1
Alkyl iodide, RCH_2I	3.1-3.3
Ether, $ROCH_2R$	3.3-3.9
Alcohol, $HOCH_2R$	3.3-4.0
Alkyl bromide, RCH_2Br	3.4-3.6
Alkyl chloride, RCH_2Cl	3.6-3.8
Ainylic, $R_2C=CH_2$	4.6-5.0
Vinylic, $R_2C=CH$ (R on C)	5.2-5.7
Aromatic, Ar-H	6.0-9.5
Aldehyde, RCH (O on C)	9.5-10.5
Alcohol hydroxyl, ROH	0.5-6.0
Amino, RNH_2	1.0-5.0
Phenolic, ArOH	4.5-7.7
Carboxylic, RCOH (O on C)	10-13

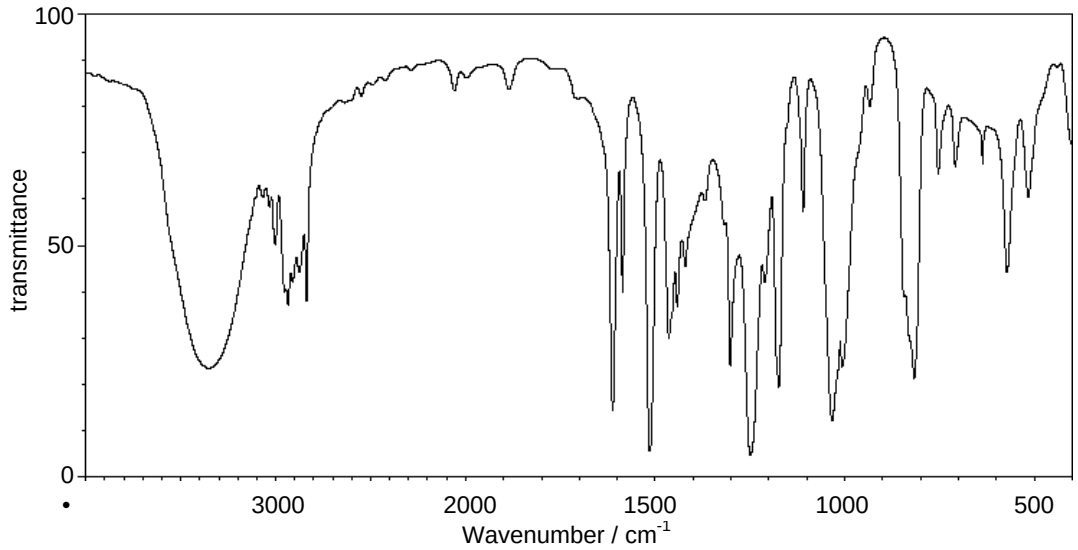
APPROXIMATE CARBON-13 CHEMICAL SHIFTS

Type of Carbon	*Chemical Shift (δ, ppm)*
1° Alkyl, RCH_3	0-40
2° Alkyl, RCH_2R	10-50
3° Alkyl, R_3CH	15-50
Alkyl halide or amine, C-X	10-65
Alcohol or ether, -C-O	50-90
Alkyne, , -C≡	60-90
Alkene, -C=	100-170
Aryl,	100-170
Nitriles, -C≡N	120-130
Amides, -C(=O)-N-	150-180
Carboxylic acids , esters, -C(=O)-O-	160-185
Aldehydes, ketones, -C(=O)-	182-215

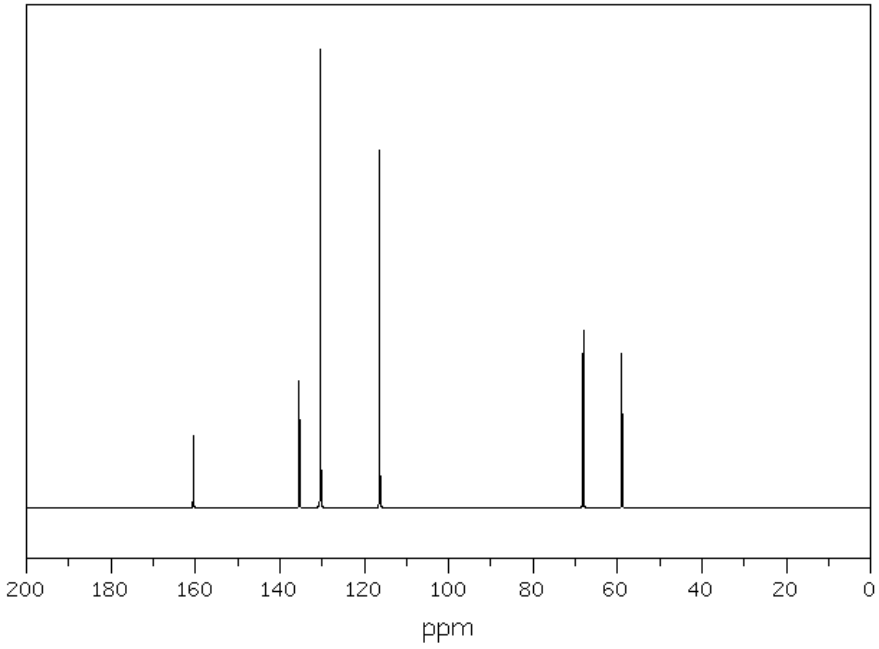
E1 Practice-i, q3

Empirical Formula: C_4H_5O
Mass Spec: M^+ *m/e*= 138

IR



^{13}C NMR



^{1}H NMR