CHEM 2311
E6 Practice-iii (answers *not* 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; 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 species is formed upon bombardment of a molecule with high energy electrons in a *mass spectrometer*? **A B C D**

A radical anion **B.** A radical cation **C.** A radical **D.** A carbene

(ii) What feature of a molecule effects the chemical shift (δ) of a signal in the ^{13}C *NMR* spectrum? **E F G H**

E. the number of types of carbon
F. the number of a particular type of carbon
G. the number of neighboring carbons
H. the electronic environment of the carbon

(iii) Predict the splitting pattern you would observe for the proton on C3 of 2-bromo-3-methylbutane in an ^{1}H *NMR* spectrum? **I J K L**

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

(iv) How many signals would 1,3-dimethylbenzene (*m*-xylene) give in the ^{13}C *NMR* spectrum? **M N O P**

M. 4 **N.** 5 **O.** 6 **P.** 8

(v) What is the relative area of the six peaks in a sextet in an ^{1}H *NMR* spectrum? **Q R S T**

Q. 1:2:3:3:2:1 **R.** 1:3:6:6:3:1 **S.** 1:5:10:10:5:1 **T.** 1:6:15:15:6:1

(vi) Which of the following does *not* give a ^{13}C *NMR* spectrum consisting of 2 peaks? **U V W X**

U. propane **V.** 2-methylbutane
W. 2,2-dimethylpropane **X.** 2,3-dimethylbutane

(vii) Which of the following is a valid molecular formula? **Y Z AA BB**

Y. C_8H_{22} **Z.** $C_6H_{13}Br_2FN$
AA. $C_7H_{11}N_3$ **BB.** $C_9H_{18}N$

(viii) In *IR* spectroscopy which of the following bonds stretches (vibrates) at the lowest *frequency*? **CC DD EE FF**

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

2. (24 points)

(i) (4 points each) Provide a single molecular structure consistent with the following data. The NMR data is complete. The IR spectra have a number of peaks, only the most relevant are provided.

Compound **A**: $C_5H_{10}O$
^{1}H NMR: δ 1.1 (doublet, 6H)
δ 2.1 (singlet, 3H)
δ 2.5 (septet, 1H)
IR: peak at 1720 cm^{-1} (and others)

Compound **B**: C_8H_9Br
^{1}H NMR: δ 2.0 (doublet, 3H)
δ 5.2 (quartet, 1H)
δ 7.3-7.4 (multiplet, 5H)

Compound **C**: C_6H_6ClN
^{1}H NMR: δ 3.6 (singlet, 2H)
δ 6.6 (doublet, 2H)
δ 7.1 (doublet, 2H)
IR: 3520 (broad), 3400 (broad), 3050 cm^{-1} (and others)

Compound **D**: C_5H_8O
^{13}C NMR: δ 22, 38, 220
IR: 1742 cm^{-1} (and others)

(ii) (4 points each) Compound **E** gives a combustion analysis of C 69.59%; H 7.29%

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

(b) What is the value of **SODAR** for the *smallest possible molecular formula* of **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 <u>independently</u>, without reference to other answers*

Analysis of Combustion Analysis/Mass Spectrum

What is the *molecular* formula? _____

What is the value of SODAR? _____

Analysis of IR spectrum (in conjunction with formula)

Which of the following are present? (circle all that are present) O-H C-O C=O

What type of functional group is present? _____

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

How many types of carbon are there in the molecule? ____

How many types of aromatic carbons are there in the molecule? _____

Is there a peak arising from a carbonyl in the ^{13}C NMR spectrum? (circle one) Yes No

How many types of sp^3 carbons are there?____

Analysis of ^{1}H NMR spectrum

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

What is the ratio of the number of each type of proton, proceeding from left to right across the spectrum? (*i.e.*, 6:3:2:1)_____

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

Et iPr tBu vinylic H (i.e. an alkene) aromatic H

How many aromatic hydrogens are there?____

How many substituents are there on the benzene ring?____

Describe the multiplets (*i.e.*, s, d, t, q) at: δ 1.7 ppm _____, and δ 2.9 ppm _____

Putting it all together

Suggest a single structure for the molecule which is consistent with all of the data presented.

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

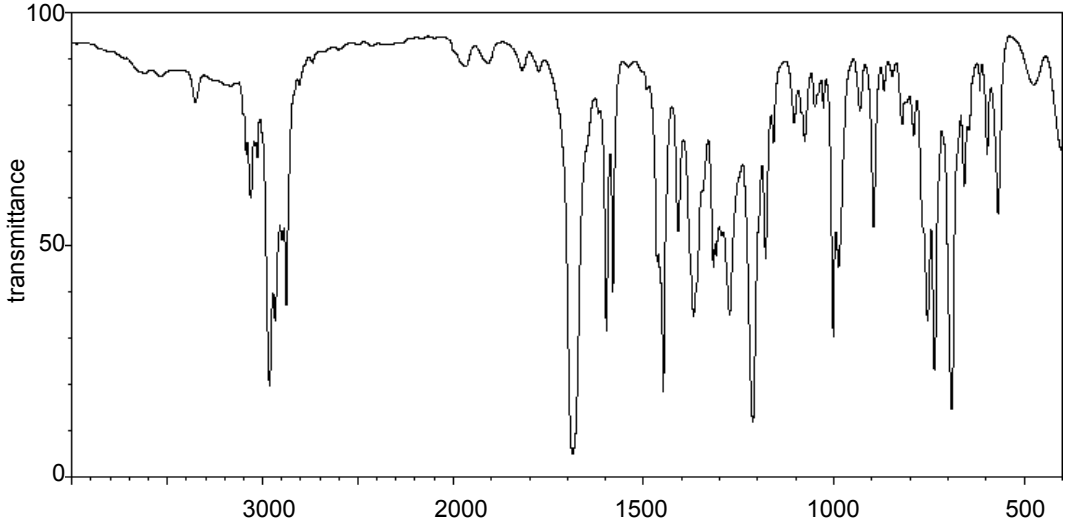
Type of Proton	*Chemical Shift (δ, ppm)*
1° Alkyl, $RC\mathbf{H}_3$	0.8-1.0
2° Alkyl, $RC\mathbf{H}_2R$	1.2-1.4
3° Alkyl, $R_3C\mathbf{H}$	1.4-1.7
Allyllic, $R_2C=C-C\mathbf{H}_3$ (R on C)	1.6-1.9
Ketone, $RCC\mathbf{H}_3$ (O on C)	2.1-2.6
Benzylic, $ArC\mathbf{H}_3$	2.2-2.5
Acetylenic, $RC{\equiv}C\mathbf{H}$	2.5-3.1
Alkyl iodide, $RC\mathbf{H}_2I$	3.1-3.3
Ether, $ROC\mathbf{H}_2R$	3.3-3.9
Alcohol, $\mathbf{H}OC\mathbf{H}_2R$	3.3-4.0
Alkyl bromide, $RC\mathbf{H}_2Br$	3.4-3.6
Alkyl chloride, $RC\mathbf{H}_2Cl$	3.6-3.8
Ainylic, $R_2C=C\mathbf{H}_2$	4.6-5.0
Vinylic, $R_2C=C\mathbf{H}$ (R on C)	5.2-5.7
Aromatic, Ar-**H**	6.0-9.5
Aldehyde, $RC\mathbf{H}$ (O on C)	9.5-10.5
Alcohol hydroxyl, $RO\mathbf{H}$	0.5-6.0
Amino, $RN\mathbf{H}_2$	1.0-5.0
Phenolic, $ArO\mathbf{H}$	4.5-7.7
Carboxylic, $RCO\mathbf{H}$ (O on C)	10-13

APPROXIMATE CARBON-13 CHEMICAL SHIFTS

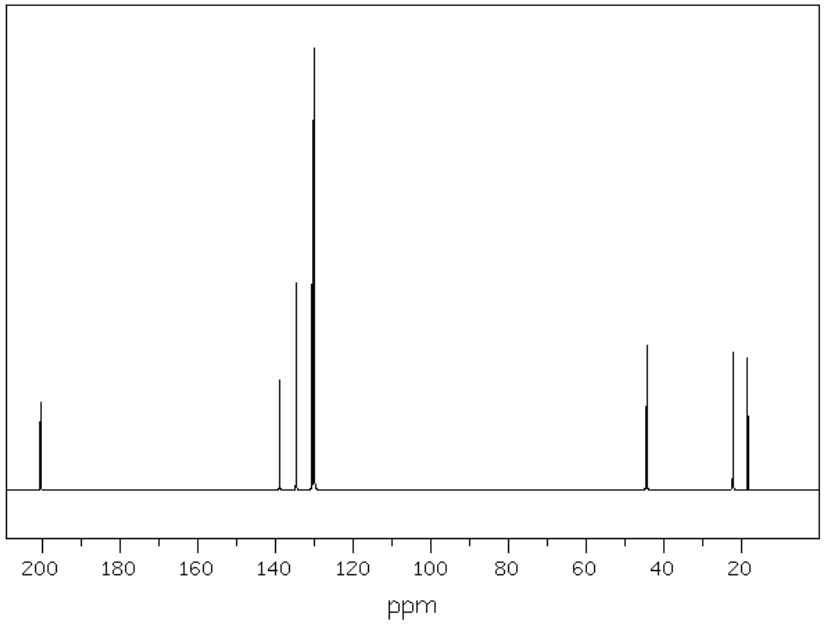
Type of Carbon	*Chemical Shift (δ, ppm)*
1° Alkyl, $R\mathbf{C}H_3$	0-40
2° Alkyl, $R\mathbf{C}H_2R$	10-50
3° Alkyl, $R_3\mathbf{C}H$	15-50
Alkyl halide or amine, **C**-X	10-65
Alcohol or ether, **-C**-O	50-90
Alkyne, , **-C**≡	60-90
Alkene, **-C**=	100-170
Aryl,	100-170
Nitriles, **-C**≡N	120-130
Amides, **-C**-N- (O on C)	150-180
Carboxylic acids , esters, **-C**-O- (O on C)	160-185
Aldehydes, ketones, **-C**- (O on C)	182-215

E5 Practice-ii, q3

Empirical Formula: $C_{10}H_{12}O$
Mass Spec: M^+ *m/e*= 148



^{13}C NMR



^{1}H NMR