CHEM 2311
E6 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) Which of the following is a valid molecular formula?

**A.** $C_8H_9$ **B.** $C_6H_{13}BrN$ **C.** $C_7H_{11}N_3$ **D.** $C_9H_{24}$ **A B C D**

(ii) In *IR* spectroscopy which of the following bonds stretches (vibrates) at the lowest *frequency*?

**E.** $sp^2$ C-H **F.** C-O **G.** C=O **H.** C=C **E F G H**

(iii) What is the principle that allows us to use *mass spectrometry* to determine the molecular weight of a compound?

**I.** higher molecular weight compounds are less volatile
**J.** higher molecular weight compounds are more dense
**K.** a beam of higher molecular weight cations is deflected less by a magnetic field
**L.** ions with higher molecular weight absorb higher frequencies of light **I J K L**

(iv) Which of the following features accounts for the *downfield shift* of the protons of benzene in the $^1H$ *NMR* spectrum?

**M.** The presence of electronegative elements **N.** The N+1 rule
**O.** Ring currents that reinforce the applied field **P.** The presence of six identical protons **M N O P**

(v) What is the splitting pattern in an $^1H$ *NMR* spectrum for the signal arising from the protons on C2 of 1,4-dichlorobutane?

**Q.** singlet **R.** doublet **S.** triplet **T.** triplet of triplets **Q R S T**

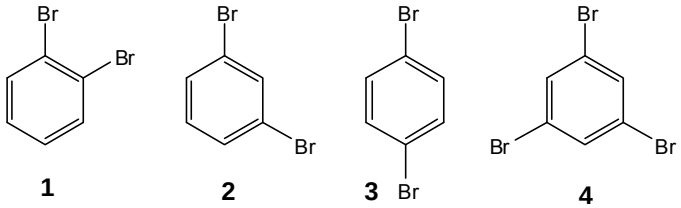
(vi) What is the relative area of the seven peaks in a septet in an $^1H$ *NMR* spectrum?

**U.** 1:2:3:3:2:1 **V.** 1:3:6:12:6:3:1 **W.** 1:3:5:6:5:3:1 **X.** 1:6:15:20:15:6:1 **U V W X**

(vii) How many signals appear in the $^{13}C$ *NMR* spectrum of 2,3-dimethylhexane?

**Y.** 5 **Z.** 6 **AA.** 7 **BB.** 8 **Y Z AA BB**

(viii) Which of the following compounds would give a $^1$H NMR spectrum consisting of two doublets and a $^{13}$C NMR consisting of consisting of three signals?




**1** **2** **3** **4**

**CC.** only **1** **DD.** only **2**
**EE.** only **1** and **3** **FF.** **1**, **2**, **3** and **4** **CC DD EE FF**

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**: $C_8H_9$
$^1$H NMR: $\delta$ 1.2 (doublet, 1H)
$\delta$ 2.9 (septet, 6H)
$\delta$ 7.0-7.2 (broad singlet, 5H)

Compound **B**: $C_4H_8Cl_2$
$^1$H NMR: $\delta$ 1.9 (triplet, 4H)
$\delta$ 3.6 (triplet, 4H)

Compound **C**: $C_6H_{12}Cl_2$
$^1$H NMR: $\delta$ 0.9 (singlet)
$^{13}$C NMR: two peaks

Compound **D**: $C_5H_{12}O$
$^1$H NMR: $\delta$ 0.9 (singlet, 9H)
$\delta$ 3.4 (singlet, 2H)
$\delta$ 3.5 (singlet, 1H)
$^{13}$C NMR: $\delta$ 80, $\delta$ 37, $\delta$ 21 ppm
IR: peak at 3500-3000 $cm^{-1}$ (and others)

(ii) (8 points) Compound **E** gives a combustion analysis of C 41.42%; H 6.95%, N 24.14%.

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

(b) What is the smallest possible molecular formula of **E**?

(c) What is the value of **SODAR** for the *smallest possible molecular formula* of **E**?

3. (19 points) Refer to the data provided on the following page. *Each part is graded independently 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 bonds are present? (circle all that are present) O-H C-O C=O

Based on this analysis, what type of functional group(s) is/are 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)_____.

Describe the multiplets (*i.e.*, s, d, t, q) at: $\delta$ 7.2 ppm _____, and $\delta$ 1.3 ppm _____.

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?_____.

*Putting it all together*

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

*Note that this structure is only worth 1 point, most of the credit for this problem comes from answering the questions above in the spaces provided.*

## 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

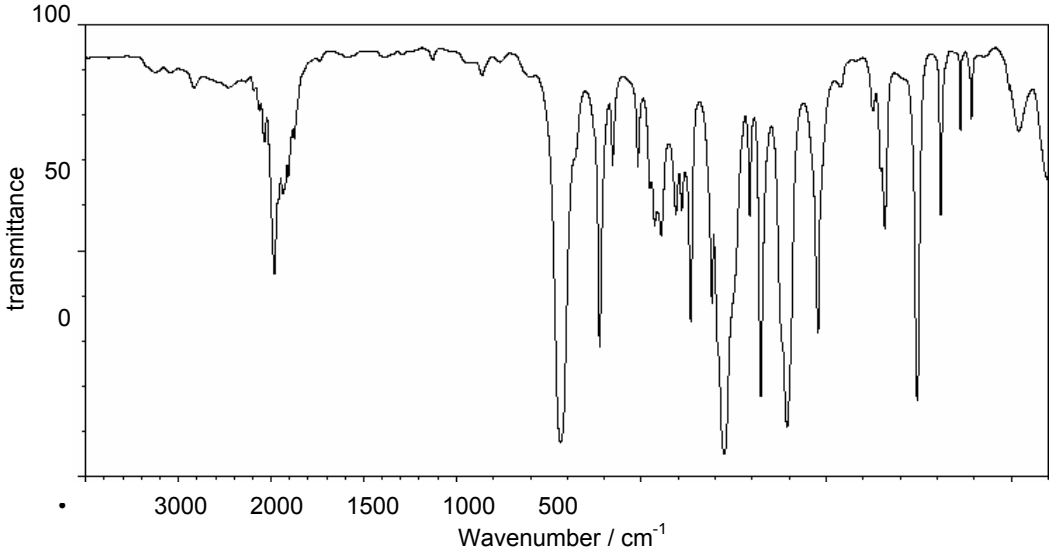
| *Type of Proton* | *Chemical Shift (δ, ppm)* |
|---|---|
| 1° Alkyl, $RCH_3$ | 0.8-1.0 |
| 2° Alkyl, $RCH_2R$ | 1.2-1.4 |
| 3° Alkyl, $R_3CH$ | 1.4-1.7 |
| Allyllic, $R_2C=C-CH_3$ (R on C) | 1.6-1.9 |
| Ketone, $RCCH_3$ (O on C) | 2.1-2.6 |
| Benzylic, $ArCH_3$ | 2.2-2.5 |
| Acetylenic, RC≡CH | 2.5-3.1 |
| 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

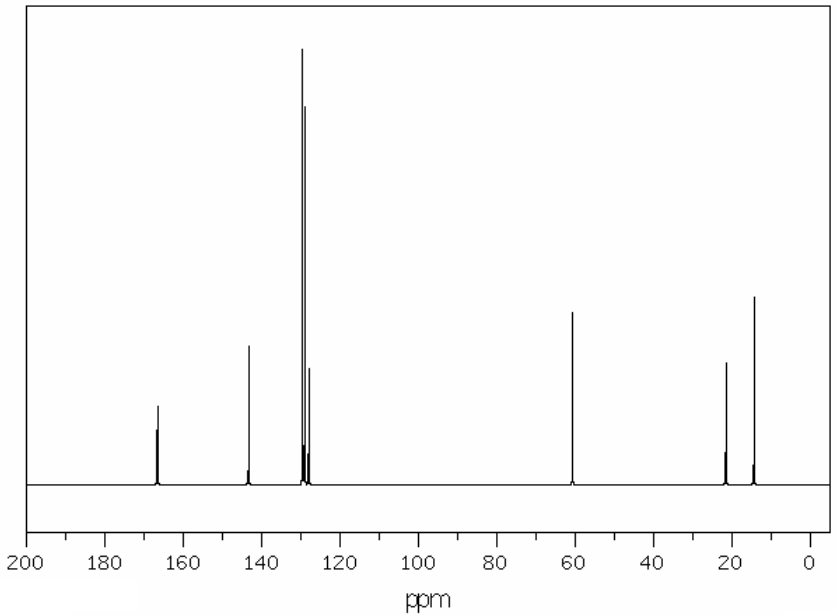
| *Type of Carbon* | *Chemical Shift (δ, ppm)* |
|---|---|
| 1° Alkyl, $RCH_3$ | 0-40 |
| 2° Alkyl, $RCH_2R$ | 10-50 |
| 3° Alkyl, $R_3CH$ | 15-50 |
| Alkyl halide or amine, C-X | 10-65 |
| Alcohol or ether, -C-O | 50-90 |
| Alkyne, , -C≡ | 60-90 |
| Alkene, -C= | 100-170 |
| Aryl, | 100-170 |
| Nitriles,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

**Empirical Formula: $C_5H_6O$**
**Mass Spec: $M^+$ *m/e*= 164**

**IR**




**$^{13}$C NMR**




**$^{1}$H NMR**