Exam. Code : 210401
Subject Code : 4821

M.Sc. Chemistry 1st Semester

SPECTROSCOPY A : TECHNIQUES FOR STRUCTURE ELUCIDATION OF ORGANIC COMPOUNDS

Course—IV

Time Allowed—Three Hours] [Maximum Marks—75

Note :— Candidates are to attempt **FIVE** questions, **ONE** from each Section. **Fifth** question may be attempted from any Section. All questions carry equal marks.

SECTION—A

1. (a) Explain, why NMR spectrum of benzene is obtained at a lower field whereas that of acetylene at higher field strength ?

   (b) How many different type of protons are in allyl bromide ? Explain.

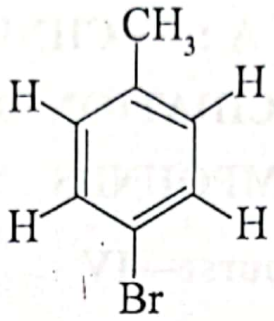
   (c) Discuss the significance of following :

   (i) Nuclear magnetic double resonance

   (ii) Karplus relationship. 6+3+6

2. (a) What are chemical shifts reagents ? Discuss their importance.

(b) Discuss the following compounds in terms of spin system :

(i) 

(ii) CH_3CH_2Br ;

(iii) $H_2C = C(F)(F)$

(c) Out of given formulae identify the structural formulae for the compound that show only one signal in NMR spectra :

C_5H_{12}, C_2H_6O, C_3H_6O, $C_2H_4Br_2$

(d) List the differentiating features in the ^{1}HNMR of phenylacetate and methylbenzoate. 4+6+2+3

SECTION—B

3. (a) Explain the following with example :

(i) Nitrogen rule

(ii) Chemical ionization technique.

(b) Comment upon salient features of the mass spectra of compound containing one chlorine and two bromine atoms.

(c) How will you account for the appearance of prominent peaks at m/z 31, 42 and 70 in the mass spectrum of n-pentanol ?

(d) Explain, how 3-Methylcyclohexene and 4-Methyl-cyclohexene can be distinguished with the help of mass spectrometry ? 6+3+2+4

4. (a) Distinguish the following isomeric pair on the basis of mass spectrometry :

(i) 2-Pentanone and 3-Pentanone

(ii) 1-Butanol, 2-Butanol and 2-Methyl-2-Propanol.

(b) Predict the fragmentation pattern of following compounds :

(i) Cyclohexanone

(ii) Nitrobenzene.

(c) Discuss giving one example Retro-diels alder reactions and its mass spectrum. 6+6+3

SECTION—C

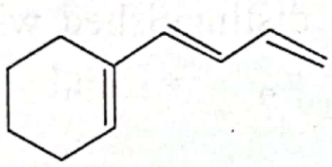
5. (a) Define and explain the following terms :

(i) Molar extinction coefficient

(ii) Absorbance

(iii) Transmittance.

(b) Giving justification, arrange the following compounds in increasing order of λ_{max} :



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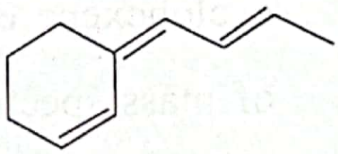
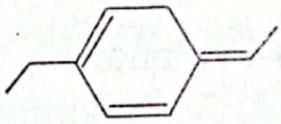


II



III

(c) Explain, why the bands obtained in ultra-violet spectra are broad as compared to infra-red spectra ?

(d) Taking the example of acetylacetone, discuss the characteristic peaks and various stretching and bending vibrations encountered in β-diketones.

3+6+2+4

6. (a) How will you distinguish the following pairs of compounds with the help of IR spectrum ?

(i) CH_3CH_2OH and $CH_3–O–CH_3$

(ii) CH_3CH_2CHO and $CH_3–CO–CH_3$

(b) Giving suitable examples explain the effect of hydrogen bonding on wavelength of absorption in IR.

(c) Arrange the following non conjugated carbonyl compounds in order of increasing carbonyl stretching frequency, explain giving reasons : aldehydes, esters, amides, acyclic ketones, acid fluorides and acid chlorides. 6+3+6

SECTION—D

7. (a) A cyclic ketone **A** on reaction with $NaOCH_3$ gives a product **B**. The spectral data of these compounds are given below :

Compound A; IR (cm^{-1}) : 1720; ^{1}H-NMR ($CDCl_3$) : δ 2.02 (4H, m), 2.60 (4H, m); ^{13}C-NMR : 219.8, 39.2, 23.1; EI-MS : 84 (M^+), 55.

Compound B; IR (cm^{-1}) : 1740; ^{1}H-NMR ($CDCl_3$) : δ 0.92-1.22 (7H, m), 2.20 (2H, t, J = 5.8), 3.60 (3H, s); ^{13}C-NMR : 175.2, 51.9, 33.2, 27.1, 22.1, 13.7. EI-MS : 116 (M^+), 85, 74, 59, 57, 29.

Deduce the structure of compounds **A** and **B**.

(b) An organic compound with molecular formula $C_7H_{10}O_3N_2$ gave the following spectral data :

UV, λ_{max}	:	216 nm (ε 80)
IR (ν cm^{-1})	:	3534 (m), 2941-2857 (m), 2247 (m), 1745 (s), 1681 (s), 1634 (s) and 1460 (m)
^{1}HNMR (δ)	:	6.77 (1H, bs), 5.53 (1H, d, J = 6.7 Hz), 4.39 (2H, q, J = 7.2), 2.34 (3H, s), 1.38 (3H, t, J = 7.2)

Explaining all the spectral data, deduce the structure of the organic compound. 8+7

8. (a) When compound **A** is treated with a halogen containing compound **B** under basic conditions (ethanolic sodium hydroxide) forms yellow colored compound **C**. Compounds **A**, **B** and **C** gives the following spectral data :

Compound A : IR : 1720 cm^{-1}, ^{1}H-NMR : δ 2.14 (singlet), EI-MS : m/z 58 ($M^{+\cdot}$), 43 (base peak), 15.

Compound B : IR : 3024, 2852, 2751, 1705, 1601, 1444 cm^{-1}, ^{1}H-NMR : δ 9.82 (singlet, 1 H), 7.83 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H), m/z : 140.00 (100.0%), 141.01 (7.7%), 142.00 (32.0%), EI-MS : m/z 142, 140, 139, 111.

Compound C : IR : 3076, 3033, 1676, 1610, 1599, 1422 cm^{-1}, ^{1}H-NMR : δ 7.82 (d, J = 17.2 Hz, 2H), 7.68 (d, J = 7.7 Hz, 4H), 7.42 (d, J = 7.7 Hz, 4H), 7.02 (d, J = 17.2 Hz, 2H), m/z : 302 (100.0%), 304 (63.9%), 306 (10.2%).

Explain all the spectral data and deduce the structure of these compounds.

(b) A compound $C_6H_{10}O_2$ shows a significant IR band at 1770 cm^{-1}, and three ^{1}HNMR signals at δ 4.2, 2.5 and 1.0 with relative intensity 1 : 1 : 3 respectively. Deduce the structure of the compound.

10+5