239301

December, 2019
M.Sc. Chemistry - III SEMESTER
Spectroscopy-I (CH-301A)

Time : 3 Hours]

[Max. Marks : 75

Instructions :

1. *It is compulsory to answer all the questions (1.5 marks each) of Part-A in short.*

2. *Answer any four questions from Part-B in detail.*

3. *Different sub-parts of a question are to be attempted adjacent to each other.*

PART - A

1. (a) How does the polarity of solvent affect K-band and R-band in UV-visible spectroscopy. (1.5)

   (b) Briefly explain different types of vibrational modes possible in an organic compound. (1.5)

   (c) Differentiate Fermi Resonance and overtone in IR spectroscopy. (1.5)

(d) What do you understand by chemical shift in ppm and chemical shift in Hertz? (1.5)

(e) How can we differentiate 1-Methylpentanone and cyclohexanone on the basis of IR spectroscopy? (1.5)

(f) TMS is mixed in solvents used for doing NMR spectra of compounds. Why? (1.5)

(g) Taking suitable example, define magnetic anisotropy. (1.5)

(h) What will be the effect of magnetically non-equivalent protons on ^{1}H-NMR spectra? (1.5)

(i) How the number and position of ^{13}C-NMR signals can help in identification of the following four isomeric alcohols, $C_4H_{10}O$? (1.5)
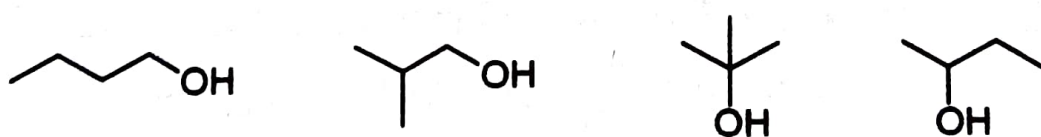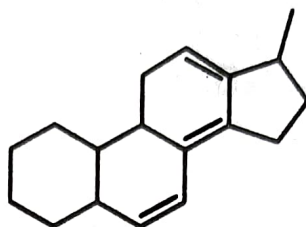

(j) What is molecular ion peak in mass spectrometery? How is it significant in structure elucidation of organic compounds? (1.5)
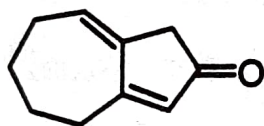
PART - B

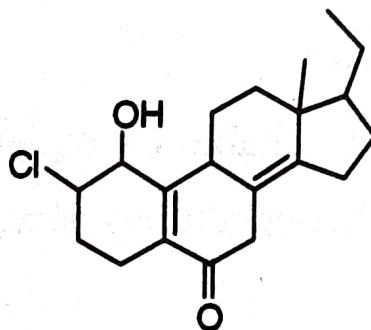2. (a) Calculate absorption maxima for the following compounds: (8)
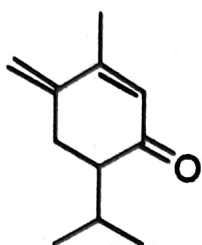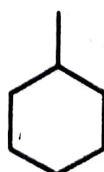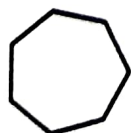

(i)

(ii)

(iii)

(iv)

(b) 3-Buten-2-one gives two peaks in its ultraviolet spectrum at 213 nm ($\varepsilon = 7100$) and 320 nm ($\varepsilon = 27$). What type of transition is possible for each absorbance? Account for the difference in molar absorptivity for the two absorptions. (4)

(c) How many peaks do you expect in proton decoupled ^{13}C-NMR spectra of the following compounds? (3)

3. **(a)** Which form of 2-bromo-4-tertiary butylcyclohexanone shows higher C=O stretching absorption in IR spectroscopy and why? (5)
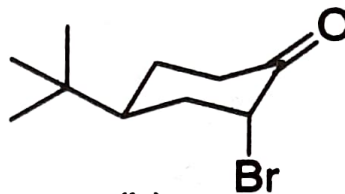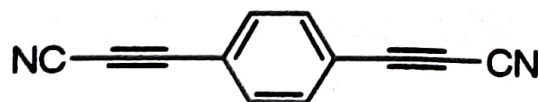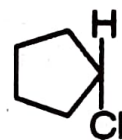

(a)   (b)

(b) How inter and intramolecular H-bonding can be distinguished by NMR studies? Explain taking suitable examples. (5)

(c) Taking suitable examples, explain virtual coupling. State the conditions necessary for virtual coupling. (5)
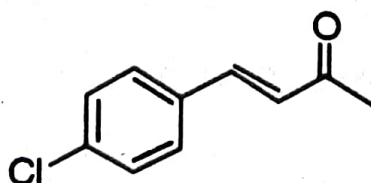
4. **(a)** Calculate the number of signals with their multiplicity in ^{1}H-NMR and proton decoupled ^{13}C-NMR spectrum of the following compounds. (6)

(i)   (ii)



(iii)

(b) What is the basic difference between 2-D NMR spectrum and a conventional NMR spectrum? List the various 2-D FT NMR techniques. (4)

(c) How will you distinguish between primary, secondary and tertiary amines on the basis of mass spectral studies? (5)

5. (a) For each of the following compounds, determine the given pair of proton as homotopic/enantiotopic/diastereotopic. (4)

(i)

(ii)
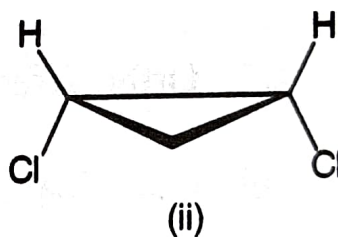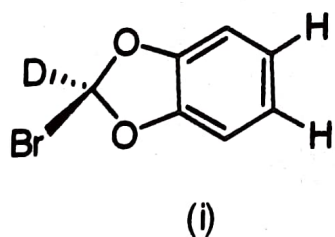
(b) Arrange the following compounds in increasing order of C=O stretching frequency. Also give suitable explaination. (5)

(i)   (ii)   (iii)
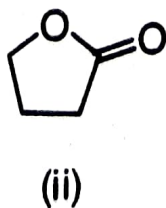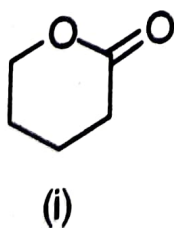
(c) How ¹H-NMR helps to know the following conversions? (6)

(i)

(ii)
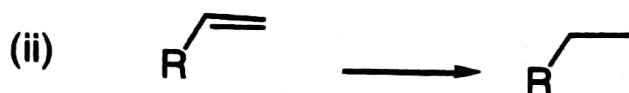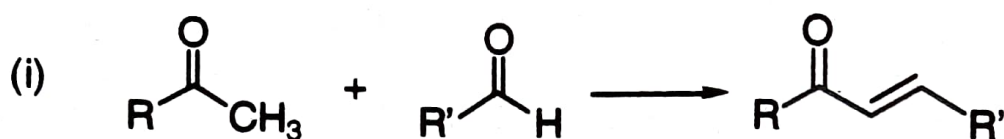
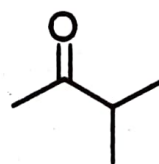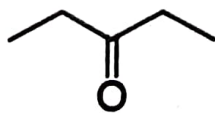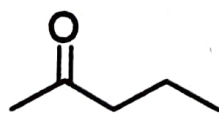6. (a) Define the following :

(i) Mclafferty Rearrangement.

(ii) Ortho effect.

(iii) Chemical shift reagents.

(iv) Long-Range coupling. (6)

(b) How mass spectrometery would help you to distinguish the following structures? (6)

(i)   (ii)   (iii)

(c) Aldehydes and ketones can easily be distinguished using IR spectral technique. Explain. (3)

7. Significant structural features of an organic compound are given below:

Molecular formula : $C_{10}H_{13}NO_2$

IR (cm^{-1}) : 3402 (s), 3318 (s), 3025 (w), 1695 (s), 1602 (s), 1580 (m)

PMR (δ, ppm) : 7.9 (2H, doublet), 6.7 (2H, doublet), 4.75 (1H, septet), 4.2 (2H, bs), 1.25 (6H, doublet)

Determine the structure of the compound and assign the data to the compound. (15)

_____