2024
M.Sc.
Fourth Semester
CORE – 12
CHEMISTRY
Course Code: MCHC 4.21
(Organic Chemistry - IV)

Total Mark: 70   *Pass Mark: 28*
Time: 3 hours

Answer <u>five</u> questions, taking <u>one</u> from each unit.

UNIT–I

1. (a) Calculate the vibrational absorption frequency of the carbonyl $>CO$
        group, if force constant for the double bond is $10 \times 10^5 gm/sec^2$.   5
    (b) Explain fundamentals mode of vibrations in infrared spectroscopy.   5
    (c) Explain the effect of H-bonding and solvent effect on vibrational
        frequency.   4

2. (a) Calculate the approximate frequency and wave number of C–H
        stretching vibration where $K = 5 \times 10^5$ g sec^{-2}.   6
    (b) A compound with molecular weight 108 gave the following peaks in
        its IR spectrum: 3300, 3077, 2899, 1499 and 1456 cm^{-1}. With
        alkaline potassium permanganate, it is oxidized to an acid. It gives a
        negative test with $FeCl_3$. Write the structural formula of the
        compound.   5
    (c) What is the most necessary condition for a molecule to absorb IR
        radiations?   1
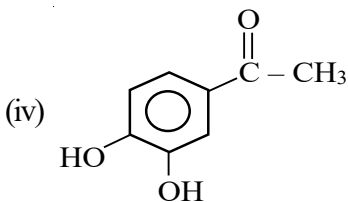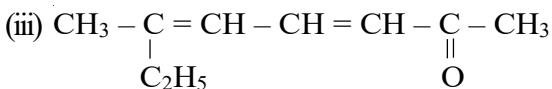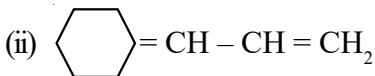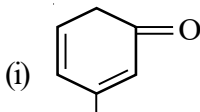   (d) Write the basic principle of molecular vibrations.   2

UNIT–II

3. (a) Explain fluorescence and phosphorescence with the help of
        Jablonski's diagram.   6

(b) Calculate the λ_{max} of the following compounds: 2×4=8

(i)

(ii)

(iii)

(iv)
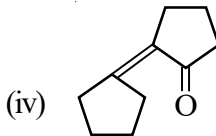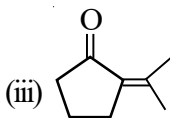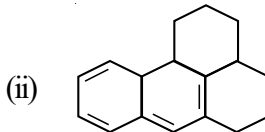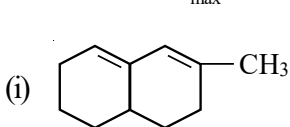
4. (a) How will you distinguish between cis and trans 1,3,5 -hexatriene by UV spectroscopy? 2

(b) There is no absorption due to $n \to \sigma^*$ transition in the spectrum of trimethyl amine in acidic solution. Explain. 2

(c) Why amines absorb at higher wavelength in UV spectrum in comparison to alcohols? 2

(d) Calculate the λ_{max} of the following compounds: 2×4=8

(i)

(ii) $\langle\ \rangle = CH - CH = CH_2$

(iii) $CH_3 - \underset{\underset{C_2H_5}{|}}{C} = CH - CH = CH - \underset{\underset{O}{\|}}{C} - CH_3$

(iv)

UNIT–III

5. (a) Write the basic principles of nuclear magnetic resonance spectroscopy. 5

(b) Write short notes on the following: 2½×2=5
   (i) Chemical shift in NMR
   (ii) Spin-spin coupling
(c) An organic compound with a molecular formula $C_6H_{12}O_2$ gave the following NMR data

   (i) Singlet, $\delta = 1.1$ (6H)   (ii) Singlet, $\delta = 2.1$ (3H)

   (iii) Singlet, $\delta = 2.6$ (2H)   (iv) Singlet, $\delta = 3.9$ (1H)

   Propose a structure consistent with the given data. Assign suitable structure to this compound with reason.   4

6. (a) An organic compound contains 66.6% carbon, 11.1 % hydrogen. In UV, it gave a characteristic band at 275 mµ ε_{max} 17. In infrared bands are formed at 2941-2857(m), 1715(s) and 1460 cm^{-1}. In NMR three signals appear at 7.52 τ quartet (2H), 7.88 τ singlet (3H), and 8.93 τ triplet (3H). Determine the structural formula of the compound.   7

(b) Predict the structure of an organic compound with molecular formula $C_9H_{14}Br$ whose pmr signals are at
   (i) Multiplate (2.25 δ) 2H   (ii) A triplet (2.75 δ) 2H
   (iii) A triplet (3.38 δ) 2H   (iv) A singlet (7.22 δ) 5H
   Assign the structure of the compound.   5

(c) Mention some important characteristics of solvent used in NMR.   2

UNIT–IV

7. (a) Write the number of signals obtained in ^{13}C NMR spectrum of 2-bromo butane.   2

(b) 3-hexanol when dehydrated forms a mixture of four unsaturated compounds.   7
   Their ^{13}C NMR spectra exhibit the following signals:
   (i) 12.30, 13.50, 23.00, 29.30, 129.70 and 130.70 δ
   (ii) 13.50, 17.20, 22.9, 35.00, 125.00 and 132.00 δ
   (iii) 14.30, 21.00 and 130.00 δ
   (iv) 14.00, 26.00 and 131.00 δ
   Analyse the data and assign the structure of four compounds.

(c) How will you distinguish among the carbonyl isomers pertaining to the molecular formula C_4H_8O on the basis of ^{13}C NMR spectroscopy? 5

8. (a) Write the application of UV, IR, NMR and mass spectroscopy for structure elucidation of organic compounds. 7

(b) A proton decoupled CMR spectrum of a compound exhibit signals at 26.3 δ, 128.2, 128.4, 137.1 and 197.6. Which of the following structures is consistent with the data? 4
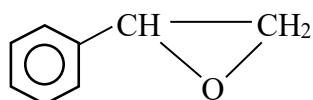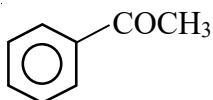
(c) Briefly explain the Fourier transform (FT) NMR. 3

UNIT–V

9. (a) Explain Mc-Lafferty rearrangement of mass spectral fragmentation and retro-Diels-Alder reaction with suitable example. 4

(b) How would you distinguish among ethylamine, diethyl amine and triethyl amine on the basis of their mass spectral studies? 5

(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. 5

10. (a) Determine the structure of the compound whose m/e values in the mass spectrum are 100, 85, 71, 57, 43 (base) and 27. 5

(b) Discuss the characteristic features of mass spectra of hydroxyl compounds. 5

(c) How would you distinguish the following on the basis of mass spectral analysis?
$CH_3 - CH = CH - CH_2 - CH_2 - CH_3$ and
$CH_2 = CH - CH_2 - CH_2 - CH_2 - CH_3$ 4