2022
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) Explain stretching and bending vibrations in infrared spectroscopy.   5
   (b) Calculate the vibrational absorption frequency of the carbonyl >CO group, if force constant for the double bond is 10×10^5 gm/sec^2.   5
   (c) Explain the effect of H - bonding 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}.   7
   (b) A compound with molecular weight 130 gave a negative iodoform test. In its IR spectrum the various bands are 3042, 2941, 2862, 2740, 1722, 1605, 1575 and 1462 cm^{-1}. Write the structural formula of the compound.   5
   (c) Why is methanol a good solvent for UV but not for IR determination?   2

UNIT–II

3. (a) Explain dissipation of energy with the help of Jablonski's diagram.   6
   (b) Calculate the λ_{max} of the following compounds: $3 \times 2 = 6$

   (i)

(ii)   (iii)
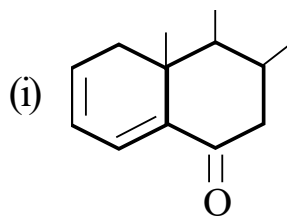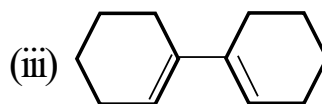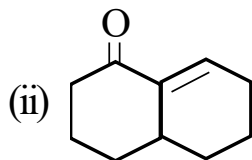
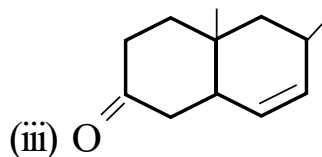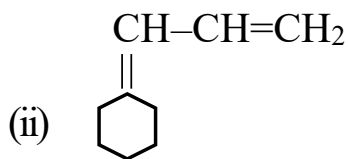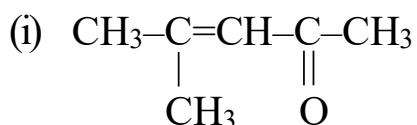(c) The wavelength of λ_{max} absorption for methyl chloride is 173 nm while for methyl iodide it is 253 nm. Explain.   2

4. (a) Explain bathochromic and hypsochromic shift.   4
   (b) Explain types of electronic transitions with suitable examples.   4
   (c) Calculate the λ_{max} of the following compounds.   2×3=6

(i) $CH_3-C=CH-C-CH_3$
              | ||
              CH_3 O

(ii)   (iii)

UNIT–III

5. (a) Write comprehensive notes on the following: 2×2=4
     (i) Chemical shift in NMR
     (ii) Spin-Spin Coupling
   (b) Describe the NMR spectrum of ethyl alcohol indicating the major set of peaks and their relative mass.   4
   (c) An organic compound with a molecular formula C_8H_9Br have the following NMR data
     (i) Triplet, $\delta = 2.79(2H)$
   (ii) Triplet, $\delta = 3.4(2H)$
     (iii) Singlet, $\delta = 7.22(5H)$
     Assign suitable structure to this compound with reason.   6

6. (a) Explain the effect of inductive effect in NMR spectrum. 2

   (b) How will you distinguish between the following pairs by NMR? Explain. 2×2=4

   (i) $ClCH_2CH_2Cl$ and CH_3CHCl_2

   (ii) CH_3COCH_3 and CH_3COOH

   (c) What do you understand by shielding and deshielding of proton in NMR? 2

   (d) An organic compound with a molecular formula $C_5H_8O_3$ gave the following NMR data 6

   (i) Singlet, $\tau = 7.88$ (3H)

   (ii) Triplet, $\tau = 7.40$ (2H)

   (iii) Triplet, $\tau = 7.75$ (2H)

   (iv) Singlet, $\tau = 1.1$ (1H)

   Assign a suitable structure to this compound with reason.

UNIT–IV

7. (a) Briefly describe C^{13} NMR spectroscopy. What are the extra advantages of it over H^1 NMR spectroscopy? 4

   (b) Let two C^{13}NMR shown below corresponds to two different constitutional isomers of C_6H_{10}. Propose a structure of each spectrum and match each carbon-carbon atom with a signal. 5×2=10

   (i) 80   40   20   0

   (ii) 100   60   40   20   0
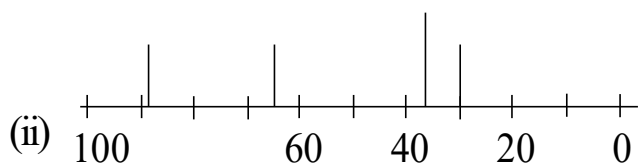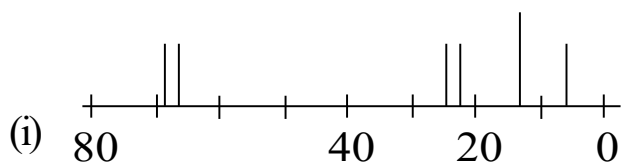
8. (a) What is the index of deficiency? Calculate the IHD of a compound with molecular formula C_8H_{10} and propose its structure. 4

(b) The C^{13} NMR spectrum has the organic compound with molecular formula $C_4H_{10}O$. It shows four signals with chemical shift 14, 23, 31, 69. Draw its possible structure and match the carbon atom with the respective chemical shift. 6


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80          40    20    0
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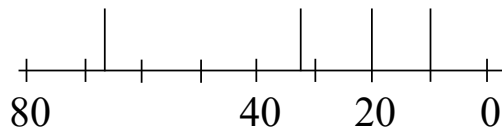
(c) Briefly explain the Fourier transform(FT) NMR. 4

UNIT–V

9. (a) Explain McLafferty rearrangement of mass spectral fragmentation. 5
   (b) Describe some important features of mass spectra of hydrocarbons. 6
   (c) Explain the appearance of strong peaks at m/e 70, 42 and 31 in the mass spectrum of n-pentanol. 3

10. (a) Discuss the characteristic features of mass spectra of hydroxyl compounds. 5
    (b) How would you distinguish between ethylamine, diethylamine and triethylamine on the basis of mass spectroscopy? 6
    (c) How would you distinguish the following on the basis of mass spectral analysis? 3
    $CH_3–CH=CH–CH_2–CH_2–CH_3$ and
    $CH_2=CH–CH_2–CH_2–CH_2–CH_3$

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