61923

Reg. No. | | | | | | | | |

III Semester M.Sc. Degree Examination, March/April - 2025

CHEMISTRY

Organic Spectroscopy - II

(CBCS Scheme 2019-20 Onwards)

Paper : ch 303-IC/PC/OC

Time : 3 Hours **Maximum Marks : 70**

Instructions to Candidates:

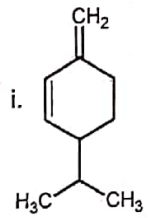
Answer question No. 1 and any five of the remaining questions.

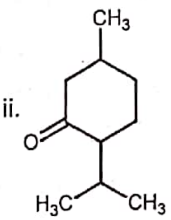
Answer any Ten of the following: **(10×2=20)**

1. a) How do you differentiate between an intramolecular and intermolecular hydrogen bonding using IR spectroscopy?

b) Define the terms chromophore and auxochromes. Give one example of each.

c) Using Woodward-Fieser rules predict the λmax for the following:

i. 

ii. 

d) Reason out why strong bands in IR spectroscopy correspond to weak bands in Raman spectroscopy?

e) In the ^{1}H NMR spectrum of cyclohexane two signals are observed at low temperature. Why?

f) A sweet smelling liquid with molecular formula $C_4H_8O_2$ gave the following ^{1}H NMR data: δ:3.67 (s, 3H), 2.32 (q, 2H) and 1.14 (t, 3H). Arrive at a structure of the compound.

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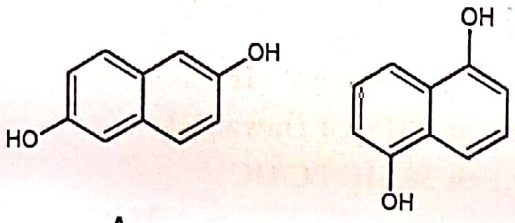
g) Indicate the number of signal and their approximate chemical shifts appearing in the broad-band decoupled 13_C-NMR spectra of A and B



A B

h) What are the cross-peaks in ^1H-^1H COSY spectra? Give their significance.

i) The mass spectrum of 1-hexanol gives a base peak at m/z 56. Account for its formation

j) The EI-MS of chlorobenzene gives a base peak at m/z 77, whereas benzyl chloride gives at m/z 91. why?

k) Illustrate the usefulness of CIDNP to detect free radical reactive intermediates.

l) Draw a diagram to illustrate the anisotropic effect in ethylene while recording ^1H NMR spectrum.

2. a) Why the band position of both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of an α,β-unsaturated carbonyl compound are shifted when the solvent is changed from hexane to ethanol? Explain with appropriate MO diagram.

b) Answer the followings:

i) Why acetone benzal (Ph-CH=CH-$COCH_3$) shows two absorption peaks in its IR spectrum due to carbonyl function?

ii) How are the isomers: 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde differentiated by IR spectroscopy? **(5+5=10)**

3. a) Write the Karplus equation and sketch the Karplus curve. Discuss the usefulness of the curve.

b) What is deuterium exchange technique? Discuss its applications in ^1H NMR spectroscopy using appropriate example.

c) Deduce the structure of an organic compound with the help of following data:

Mol.formula : $C_{10}H_{14}$

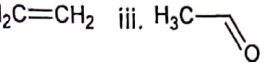
^1H NMR : δ: 7.01(S, 1H) and 2.20 (S, 6H)

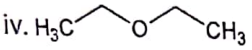
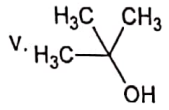
13_CNMR : δ: 133.0, 130.2 and 19.2

(4+3+3=10)

4. a) Explain the Nuclear Overhauser Effect (NOE) with example. Mention its application in NMR spectroscopy.

b) How do you identify the following compounds by 13_C NMR spectroscopy

i. $H_3C—CH_3$ ii. $H_2C=CH_2$ iii. 

iv.  v. 

(5+5=10)

5. a) Explain the differences observed in the EI and ESI Mass spectra of n - butylpropanoate.

b) Ethyl butanoate in its mass spectrum show two characteristic peaks due to odd-electron ions at m/z 88 and 60 and an abundant ion at m/z 71. Explain the fragmentation.

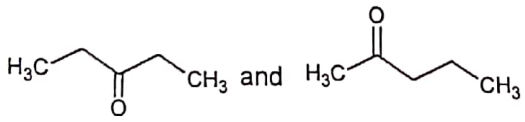
c) Deduce the structure of an organic compound with the help of following data and assign the values:

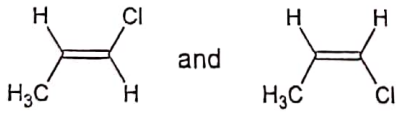
Molecular formula : $C_6H_{10}O_4$;

UV (λmax): 267 nm;

^{1}H NMR (δ, ppm): 2.11 (s, 6H), and 2.60(s, 4H). (3+3+4=10)

6. a) How will you differenttate the following pairs using ^{1}H NMR spectroscopy?

i. 

ii. 

b) Write a note on :

i) McLafferty rearrangement

ii) EI and CI methods of ionization in MS (5+5=10)

7. a) Write an account of the Woodward-Fieser rules to empirically calculate the λ_{max} of α,β-unsaturated carbonyl compounds.

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b) Deduce the structure of an organic compound with the help of following data:

Molecular formula : C_7H_7BrO
UV (λ_{max}): 261 nm;
IR (cm^{-1}) :1684, 1587, 1395, 1264, 1078 and 1010;
^1H NMR (δ, ppm): 7.82 (d, 2H, J=7.5Hz), 7.60(d, 2H, J=7.5Hz) and 2.60 (s, 3H);
^{13}C NMR (δ, ppm): 197, 136, 130, 128 and 26;
MS(m/z): 200, 198, 185, 183 (base peak), 157, 155, 77, 75 and 43 **(5+5+=10)**

8. a) Discuss the various factors influencing the chemical shifts in ^1H NMR spectroscopy

b) Describe the use of DEPT technique in ^{13}C NMR studies. **(5+5+=10)**