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**B.M.S. COLLEGE FOR WOMEN AUTONOMOUS**
**BENGALURU-560004**
**SEMESTER END EXAMINATION-APRIL/MAY- 2023**

**M.Sc. Chemistry-III Semester**

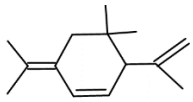
**ORGANIC SPECTROSCOPY**

**Course code: MCH303T** **QP Code: 13008**
**Time: 3 Hours** **Max marks: 70**

***Instruction: Answer Question No 1 and any Five of the remaining.***

**1.** Answer any ***TEN*** questions **(2×10=20)**

a) With the help of neat diagram indicate the allowed electronic transitions in organic molecule.
b) How do you distinguish between the C=O group of ketone, carboxylic acid and amide by their IR spectra?
c) Predict the $\lambda_{max}$ in the following:

(i).  (ii). 

d) Name the most commonly used internal reference in proton NMR spectroscopy. Why it is preferred?
e) On a 60MHz NMR a particular proton shows a separation of 150Hz. What is its chemical shift in ppm? Where it should resonance on a 300MHz instrument?
f) How are labile protons identified by dynamic $^{1}$H-NMR spectroscopy? Illustrate with an example.
g) What is broad band decoupling in $^{13}$C-NMR spectroscopy?
h) Formulate the number of $^{13}$C signals for barrelene in the coupled and decoupled CMR spectra.

**Barrellene**

i) Predict the PMR spectrum of $HPF_2$.
j) State Audier-Stevenson rule. Highlight its importance in EI-MS fragmentation.
k) Define Nitrogen rule. Give its significance in mass spectrometry.
l) What are metastable ions? How are they recognized in a mass spectrum?

**2.** a) Briefly discuss the factors which affect IR group frequencies.
b) Explain the effect of conjugation and polarity of solvents on
(i) $\pi \longrightarrow \pi^*$ transitions (ii) $n \longrightarrow \pi^*$ transitions
c)Write briefly on the complementarity of IR and Raman spectroscopy. **(3+3+4=10)**

**3.** a) Summarize the Woodward rules for predicting $\lambda_{max}$ for α,β-unsaturated aldehydes and ketones.

b) Explain the mechanism of spin-spin splitting and the rules for the first order splitting in $^1$H-NMR. **(5+5=10)**

**4.** a) Explain the terms Chemical shift and Coupling constants.

b) An organic compound has molecular formula $C_4H_{10}O$. Give the structures of possible isomeric alcohols and predict multiplicity of non-equivalent sets of protons.

c) Give an account of the principle and instrumentation of an FT-NMR instrument**.**

**(3+3+4=10)**

**5.** a) Write a note on Nuclear Overhauser effect and explain its significance.

b) Give the expansion of CIDNP. Discuss its applications.

c) Write short notes on:

i) DEPT and ii) INADEQUATE **(3+3+4=10)**

**6.** a) Propose a plausible structure for the compound using the following spectral data. Give reasons.

MF: $C_6H_{13}O_2N$

IR: 1735 $cm^{-1}$

$^1$H-NMR, δ: 1.30 (t, 3H), 2.40 (s, 6H), 3.20 (s, 2H), 4.20 (q, 2H)

b) Identify the structure of the compound from the below given data and interpret the data to the structure arrived at. Molecular formula: $C_5H_7NO_2$, $^1$H NMR ($CDCl_3$) δ: 4.3 (quartet, 2H, J = 7.5 Hz), 3.5 (singlet, 2H), 1.3 (triplet, 3H, J = 7.5 Hz); $^{13}$C NMR ($CDCl_3$)δ: 165, 115, 62, 25, 15. **(5+5=10)**

**7.** a) Describe the MALDI method of ionization in mass spectrometry.

b) Account for the peaks observed in the mass spectrum of the following compounds:

(i) $CH_3(CH_2)_4CH_2Br$: m/z=135, 137 and 85

(ii) $(CH_3)_2CH\text{-}O\text{-}(CH_2)_4CH_3$: m/z=115 and 71. **(5+5=10)**

**8.** a) What is McLafferty rearrangement? Explain its mechanism with suitable examples.

b) Deduce the structure of a compound with the following data. Explain the fragmentation pattern based on the proposed structure.

MF: $C_7H_8NBr$

IR: 3400, 3300, 3200, 2900, 1620, 1600, 1500, 1380, 880, 820 $cm^{-1}$

$^1$H NMR, δ: 7.20 (1H, d, J=9 Hz), 6.50 (1H, d, J=3.5 Hz), 6.30 (1H, dd, J=9 and 3.5 Hz), 3.50 (2H, broad s) and 2.30 (3H, s) ppm

Mass, m/z: 29(8), 39(40), 65(30), 93(20), 121(90) and 122(100) **(5+5=10)**

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