

(7 pages)

Reg. No. :

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Sub. Code : ZCHM 31

M.Sc. (CBCS) DEGREE EXAMINATION,
NOVEMBER 2023

Third Semester

Chemistry – Core

ORGANIC SPECTROSCOPY AND
REARRANGEMENT

(For those who joined in July 2021–2022 onwards)

Time : Three hours

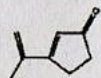
Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. λ_{\max} for the following compound is



- (a) 262nm (b) 298nm
(c) 245nm (d) 255nm

2. Solution of Iodine in benzene shows an intense band around 300nm due to ———.

- (a) $\pi - \pi^*$ transition
(b) $n - \pi^*$ transition
(c) charge transfer complex
(d) extensive conjugation

3. The separation between the centers of the peaks of a doublet (in Hz) is called as ———.

- (a) spin constant
(b) coupling constant
(c) spin-spin coupling
(d) chemical shift

4. The $^1\text{H-NMR}$ spectrum of $\text{CH}_3\text{OCHClCH}_2\text{Cl}$ will exhibit

- (a) 3 proton doublet, 1 proton singlet and 2 proton doublet
(b) 3 proton singlet, 1 proton singlet and 2 proton doublet
(c) 3 proton singlet, 1 proton triplet and 2 proton doublet
(d) 3 proton triplet, 1 proton triplet and 2 proton triplet

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5. Which of the following compounds undergoes McLafferty rearrangement?

- (a) acetone (b) butanone
(c) pentan-3-one (d) pentan-2-one

6. The mass of metastable ion produced when a fragment of m/z 77 decomposes by loss of acetylene to a fragment of m/z 51 is _____.

- (a) 116.25 (b) 0.66
(c) 33.7 (d) 26

7. Signals are not visible for _____ in HETCOR.

- (a) methyl carbon
(b) methylene carbon
(c) quaternary carbon
(d) all the above

8. Which of the following carbons produces a negative peak in DEPT-135 spectrum?

- (a) CH (b) CH₂
(c) CH₃ (d) R₄C

9. Reagent used in Dakin rearrangement is _____.

- (a) H₂O₂/NaOH (b) CF₃CO₃H
(c) SeO₂ (d) HIO₄

10. Oxidation of acetophenone using perbenzoic acid gives

- (a) acetone
(b) phenyl acetate
(c) benzaldehyde
(d) methylbenzoate

PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 250 words.

11. (a) State Axial haloketone rule. Discuss two applications of the rule.

Or

(b) What are the factors that affect IR absorption frequency of Carbonyl compounds?

12. (a) How is NOE useful in stereochemical analysis?

Or

(b) Briefly explain chemical exchange.



13. (a) Write a short note on McLafferty rearrangement.

Or

- (b) With examples explain the fragmentation pattern in alcohols and acids.
14. (a) Explain ^1H - ^{13}C COSY spectrum with an example.

Or

- (b) Write a short note on DEPT.
15. (a) Discuss the mechanism and migratory aptitude of groups in dienone-phenol rearrangement.

Or

- (b) Describe the steps involved in Von-Richter rearrangement.

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 600 words.

16. (a) Discuss the effect of solvents and hydrogen bonding on λ_{max} values.

Or

- (b) State octant rule. Explain how it is used to determine stereochemistry of steroids.

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17. (a) Explain the factors influencing chemical shift of protons.

Or

- (b) Write short notes on non-first order spin-spin splitting.

18. (a) Explain the following techniques

(i) FAB

(ii) CI

Or

- (b) How is MALDI-MS and TOF techniques useful in ionization?

19. (a) Propose a structure for a compound of molecular formula $\text{C}_9\text{H}_8\text{O}$, whose mass spectrum shows molecular ion peak at m/z 132, base peak at m/z 131 and a significant peak at m/z 103. Its IR spectrum has a strong absorption at 1690cm^{-1} . The UV spectrum has an intense band at 284nm and weak band at 308nm. The compound shows following ^1H NMR absorptions: δ 6.7(1H dd, $J = 16\text{Hz}$ $J = 8\text{Hz}$), 7.4 (5H m), 7.45 (1H d, $J = 16\text{Hz}$), 9.75 (1H d, $J = 8\text{Hz}$).

Or

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- (b) A compound with molecular formula $C_8H_8O_2$ shows bands at 3200cm^{-1} and 1700cm^{-1} in its IR spectrum. The ^1H NMR spectrum shows peaks at $\delta = 10.9\text{ppm}$ (1H s), 7.2ppm (5H s) and 3.6ppm (2H s). The ^{13}C NMR has four peaks at $\delta = 130\text{ppm}$, one peak at $\delta = 178.3\text{ppm}$ and another peak at $\delta = 41\text{ppm}$. Its mass spectrum shows a strong molecular ion peak at m/z 136 and base peak at m/z 91. Suggest a structure for the compound.

20. (a) (i) Explain the term memory effect.
(ii) Show Ring contraction or enlargement in rearrangement with Demjanov reaction as example.

Or

- (b) Discuss the mechanism and migratory aptitude of groups in
(i) Dakin rearrangement
(ii) Benzilic acid rearrangement

