(8 pages) Reg. No. : .....

Code No. : 7418 **Sub. Code : ZCHM 31**

M.Sc. (CBCS) DEGREE EXAMINATION, NOVEMBER 2024.

Third Semester

Chemistry – Core

ORGANIC SPECTROSCOPY AND REARRANGEMENTS

(For those who joined in July 2021 and 2022 only)

Time : Three hours Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. Why is a weak band near 1750 cm^1 formed in IR spectrum of Benzoylchlorid?
   (a) Inductive effect
   (b) Fermi resonance between C = 0 band and first overtone
   (c) Conjugation effect
   (d) Hyperconjugation effect

2. What is the number of vibrational degrees of freedom in $C_6H_5CH_3$?
   (a) 39 (b) 15
   (c) 18 (d) 40

3. Coupling constant of two nuclei is defined as
   (a) Ratio of chemical shifts
   (b) Distance between splitted peaks in Hz
   (c) Difference of chemical shifts
   (d) Ratio of absorption frequencies

4. Which of the following produces magnetic anisotropy?
   (a) Aromatic ring system
   (b) Hydrogen bonding
   (c) Electronegativity
   (d) pH

5. Which of the following ionization method uses aromatic compounds and organic solvents to achieve ionization?
   (a) ESI
   (b) Chemical ionization
   (c) FAB
   (d) MALDI

6. Which of the following cannot be used as a MALDI matrix compound?

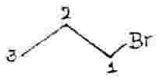
(a) α-Cyano-4-hydroxycinnamic acid

(b) Sinapinic acid

(c) 3-Hydroxypicolinic acid

(d) 2,3-Dihydroxybenzoic acid

7. The effect of electronegative atom in ^{13}C *NMR* will be more in



(a) 1 (b) 2

(c) 3 (d) All are equal

8. How many signals does the aldehyde $(CH_3)_3CCH_2CHO$ have in ^1H NMR and ^{13}C *NMR* spectra?

(a) Five ^1H signals and six ^{13}C signals

(b) Three ^1H signals and four ^{13}C signals

(c) Five ^1H signals and four ^{13}C signals

(d) Three ^1H signals and six ^{13}C signals

9. Arndt-Eistert synthesis is used to convert an acetyl chloride into

(a) A methyl ester

(b) A diazoketone

(c) A ketone $(R-CH=C=O)$

(d) A higher acid (RCH_2COOH)

10. The benzylic acid rearrangement reaction of a cyclic diketone leads to

(a) Ring expansion

(b) Ring contraction

(c) Ring fusion

(d) Isomers

PART B — $(5 \times 5 = 25$ marks)

Answer ALL questions, choosing either (a) or (b).
Each answer should not exceed 250 words.

11. (a) Write a note on effect of solvents in finding λ max.

Or

(b) What is cotton effect and Octant rule.

12. (a) Write briefly about chemical shift and any two factors affecting it.

Or

(b) Write a note on coupling constants.

13. (a) Write briefly about fragmentation pattern of amines.

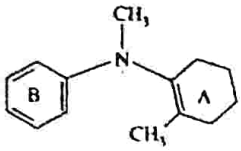
Or

(b) Write a note on Nitrogen rule and Molecular ion.

14. (a) Write briefly about DEPT technique in elucidating the structure of organic molecules.

Or

(b) How many peaks you expect in the proton decoupled ^{1}H NMR spectra of.



15. (a) Write the mechanism involved Benzil-Benzilic in acid rearrangement.

Or

(b) Write the steps involved in the mechanism of Curtius rearrangement.

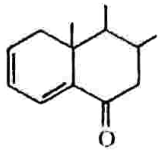
PART C — (5 × 8 = 40 marks)

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

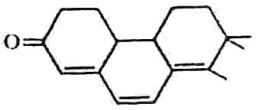
Each answer should not exceed 600 words.

16. (a) Calculate λ max for

(i)



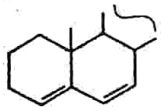
(ii)



Or

(b) Calculate the absorption maximum for the compound in ethanol.

(i)



(ii)

17. (a) Discuss the NMR spectrum of ethyl chloride, vinyl chloride.

Or

(b) Discuss the principles involved ^{13}C *NMR*.

18. (a) Discuss the principles involved in ESI-MS, FAB.

Or

(b) Discuss the principles involved in MALDI-MS, TOF.

19. (a) Molecular weight = 154
Molecular formula – $C_9H_{10}O_2$.

UV : λ max 274 $m\mu\varepsilon$ max 2050

IR : 3031(v), 2941(w), 1725 (s), 1608, 1504(w), 1060 (s) and 830 cm^{-1}(s).

NMR :

(i) Singled 7.65 τ (3H),

(ii) Singlet 6.18 τ (3H),
Unsymmetrical pattern 2.15 – 2.8 τ (4H)

Or

(b) A compound with molecular weight 116 gave the following spectral information :

(i) UV : 283 $m\mu\varepsilon$ max 22

(ii) *IR* 3000 – 2500 (b), 1715 (s), 1342 cm^{-1}(w)

(iii) *NMR* : 7.88τ Singlet (3H), 7.40 τ Triplet (2H), 7.75 τ Triplet (2H) and — 1.1 τ singlet (1 H).

Find the structural formula of the compound.

20. (a) Discuss about Lossen rearrangement and Neber rearrangement.

Or

(b) Discuss the steps in Dienone-phenol rearrangement and Von-Richter rearrangement.

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