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Reg. No. : ....

Code No. : 5418   Sub. Code : ZCHM 31

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

Third Semester

Chemistry – Core

ORGANIC SPECTROSCOPY AND REARRANGEMENTS

(For those who joined in July 2021 onwards)

Time : Three hours   Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. A carbonyl group will cause a sharp dip at about _____ cm^{-1}.

    (a) 1700   (b) 2800

    (c) 3400   (d) 1200

2. The finger print region in IR spectroscopy is _____

    (a) 4000 to 1000 cm^{-1} (b) 1500 to 400 cm^{-1}

    (c) 200 to 1400 cm^{-1} (d) 2999 to 1200 cm^{-1}

3. A proton Hb is coupled to four equivalent protons Ha. The multiplicity and the relative intensity of lines in the signal Hb is?

    (a) Doublet, 1 : 4

    (b) Triplet, 1 : 4 : 6

    (c) Quintet, 1 : 4 : 6 : 4 : 1

    (d) Quartet, 1 : 4 : 6 : 4

4. H_2, CH_4, C_2H_6 and C_2H_4 exhibit which PMR spectra?

    (a) Singlet   (b) Doublet

    (c) Triplet   (d) Quintet

5. Which species of the following is used to bombard the sample in mass spectroscopy?

    (a) Alpha particles

    (b) Neutrons

    (c) Electrons

    (d) Protons

6. Separation of ions in mass spectrometer take place on the basis of which of the following?

    (a) Mass   (b) Charge

    (c) Molecular weight   (d) Mass to charge ratio

7. INADEQUATE is a method often used to find _____ couplings between adjacent atoms.

    (a) ^{13}C (b) ^{12}C

    (c) ^9F (d) ^{14}N

8. The first two-dimensional experiment, COSY was proposed by _____

    (a) Jean Jeener

    (b) Madam Curie

    (c) Newton

    (d) Christy Catherene Mary

9. The benzilic acid rearrangement reaction of a cyclic diketone leads to _____

    (a) Ring expansion

    (b) Ring contraction

    (c) Ring fusion

    (d) Isomers

10. Carbon to oxygen migration is seen in _____ rearrangement

    (a) Curtius   (b) Dakin

    (c) Pinacol   (d) Arndt–Eistert

PART B — (5 × 5 = 25 marks)

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

11. (a) State and explain Beer-Lambert's law.

    Or

    (b) Explain axial haloketone rule and how it is used determination of conformation.

12. (a) Compare CW and FT NMR spectra.

    Or

    (b) Explain vander Waals deshielding in NMR spectroscopy.

13. (a) (i) Explain Base peak in mass spectrometry.

        (ii) State and explain nitrogen rule in mass spectrometry.

    Or

    (b) Write a short note on Chemical ionisation technique in mass spectroscopy.

14. (a) Explain 1H-1H COSY with one example.

    Or

    (b) What is inadequate spectrum? Explain.

15. (a) Explain Migratory aptitude in molecular rearrangements.

Or

(b) What is Benzil-Benzilic acid rearrangement? Explain its mechanism.

PART C — (5 × 8 = 40 marks)

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

16. (a) Explain how maximum absorption values are affected in uv-visible absorption spectroscopy with special reference to solvent effect and hydrogen bonding.

Or

(b) State and explain how Woodward-Fieser Rules are used to calculate maximum absorption values of conjugated dienes in uv-visible absorption spectroscopy.

17. (a) Explain spin-spin coupling in NMR spectroscopy.

Or

(b) Explain chemical exchange in NMR spectroscopy.

18. (a) State Mc Lafferty rearrangement. Explain the mechanism of this rearrangement in
    (i) Pentanal
    (ii) Pentan-2-One
    (iii) Ethylacitate

Or

(b) Outline Fragmentation pattern of alcohols, aldehydes, ketones and ethics in MS

19. (a) A compound molecular mass 164 absorbs at 220 nm ε_{max} 1880. In infra red spectrum, absorption bands are formed at 3077 cm^{-1}(w), 1745 cm^{-1} (s) 1608 cm^{-1}(m), 1497 cm^{-1} (m) and 1456 cm^{-1} (m).

In NMR, the signals formed are (i) 2.7r singlet (16.5 squares), (ii) 5.70t triplet (J = 7.3 cps, 6.2 squares), (iii) 7.07 triplet (J = 7.3 cps, 6.7 squares) and (iv) 7.98r singlet (10.2 squares). Determine the structure of the compound.

Or

(b) An organic compound with molecular formula $C_7H_{12}O_4$ molecular mass 160 absorbs at 212 nm ε_{max} 60 in the ultraviolet spectrum.

(i) In infra-red, the bands are formed at (1) 2941–2857 (m), (2) 1742 (s), (3) 1460 (m), (4) 1056 (s) and (5) 1260 cm^{-1} (s). In the NMR spectrum, three signals are observed.

(ii) (1) Singlet 7.5 r (5.3 squares), (2) triplet 8.71 r (16.5 squares, J = 7.2 cps) and (3) quartet 5.84 r (10.8 squares, J = 7.2 cps). Determine the structure of the compound.

20. (a) What is Brook rearrangement? Explain mechanism and imigratory aptitude

Or

(b) Explain memory effect in molecular rearrangement with one example.

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