F 4681 (Pages : 4) Reg. No.....

Name.....

M.Sc. DEGREE (C.S.S.) EXAMINATION, JANUARY 2017

Third Semester

Faculty of Science

AN3C12/AP3C12/CH3C12/PH3C12/PO3C12—SPECTROSCOPIC METHODS IN CHEMISTRY

(Common to all Branches of Chemistry)

[2012 Admission onwards]

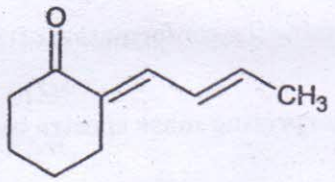
Time : Three Hours Maximum Weight : 30

Section A

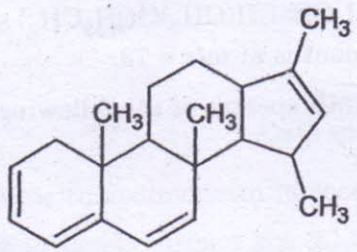
Answer **ten** *questions.*
Each question carries a weight of 1.

1. Sketch the H^1NMR spectrum of the following molecules :—
   (a) $CH_3CH_2CH_2COOH$. (2) $CH_2FCH_2CH_2CHO$.
2. Explain the UV spectra parameters λ_{max} and ε_{max}.
3. Using Woodward Fieser rules calculate the λ_{max} values for the following molecules :—

(a)



(b)



4. State and explain the 'Axial Halo' ketone rule.
5. Explain the terms Bathochromic shift and Hypsochromic shift with suitable examples.
6. When a UV light is passed through the given solution, the radiant power is reduced to 50 %. Calculate the absorbance.

Turn over

7. Explain Aniline absorbs at 280 nm (ε_{max} = 8600) but in acidic solution, the main absorption band is seen at 203 nm. (ε_{max} = 7500) which is comparable to benzene.

8. Determine the structure of the compound. Molecular formula C_3H_6O, UV–λ_{max} = 292 nm and ε_{max} = 21 ; IR (1) 2720 cm^{-1} (w) (2) 1738 cm^{-1}.

9. Arrange the following groups in order of increasing stretching frequencies. C = C ; C = O, C = N, C = S.

10. Predict the structural formula for the compounds with the following molecular formulae showing only one PMR signal. C_8H_{18} ; C_2H_6O ; C_5H_{12}.

11. What are Shift reagents ? What are their uses ? Explain with examples.

12. What are the main fragments obtained in the mass spectrum of Ethyl bromide.

13. What is a metastable peak which is seen in mass spectra ? What is its importance ? Why they appear as broad peak ?

(10 × 1 = 10)

Section B

Answer any **five** *questions.*
Each question carries a weight of 2.

14. Explain Nitrogen rule. Explain how it is useful in determining the molecular formula.

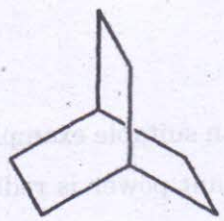
15. Explain the Octant rule. Apply this rule to 9-methyl decalone.

16. State Karplus equation. Explain how it can be used to determine the conformation of conformational isomers ?

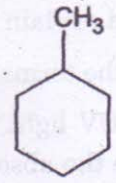
17. What is McLafferty rearrangement ? Explain its use in interpreting mass spectra using a suitable example.

18. Account for the following :— (a) The mass spectrum of 1-hexanol gives a base peak at m/z = 56. (b) The mass spectrum of ethyl Sec. butyl ether ($CH_3CH_2CH_2CH(CH_3)OCH_2CH_3$) shows a base peak at m/z = 45 and among other peaks the most prominent is at m/z = 73.

19. How many peaks are expected in the proton decoupled CMR spectra of the following :—

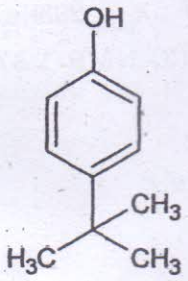
(a) 

(b) 

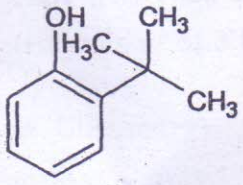
(c) 

20. In the following substituted phenols the O-H stretching frequencies are at 3608 cm^{-1} in (a) at 3605 and 3643 cm^{-1} in (b) and at 3643 cm^{-1} in (c) Explain.

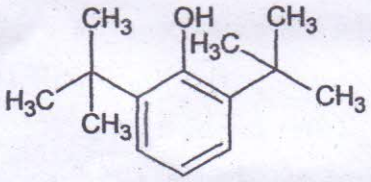
(a)



(b)



(c)



21. Explain the following soft ionization methods :—

(a) SIMS. (b) MALDI.

(c) FAB.

Compare the advantages and disadvantages of each method.

(5 × 2 = 10)

Section C

Answer any **two** *questions.*
Each question carries a weight of 5.

22. An organic compound with molecular mass 88 absorbs at 206 nm ε_{max} 50. In infra-red medium absorption bands formed are (a) 3049-2924 and (b) 1445 cm^{-1}. Also strong absorption band is formed at 1736 cm^{-1}. The following signals are formed in its NMR spectrum (a) 1.93 τ-singlet (5.9 squares), (b) 5.88 τ triplet (j = 7.0 cps, 12.2 squares), (c) 8.33 τ sextet (j = 7.0 cps, 11.6 squares) and 9.05 τ triplet (j = 7.0 cps, 18.6 squares). Arrive at the molecular formula and structure.

23. Give the important methods available in the determination of molecular formula in mass spectrometry.

24. What is optical rotatory dispersion (ORD) ? Explain the use of plane curves and Cotton curves.

25. Arrive at the structure. (1) Molecular formula – C_3H_7NO. (2) UV : λ_{max} 238nm and ε_{max}10500 (3) IR 3428 (m), 2941-2857 (w), 1681 (s), and 1452 cm^{-1} (w) (3) NMR 1.87τ singlet (1H), 7.30τ singlet (3H), and 8.1τ singlet (3H).

$(2 \times 5 = 10)$