

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

Faculty of Science

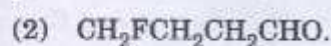
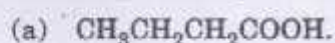
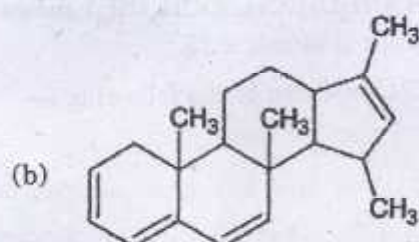
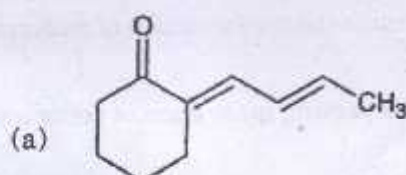
**AN3C12/AP3C12/CH3C12/PH3C12/PO3C12—SPECTROSCOPIC METHODS
IN CHEMISTRY**

(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 :—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 :—

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

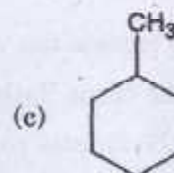
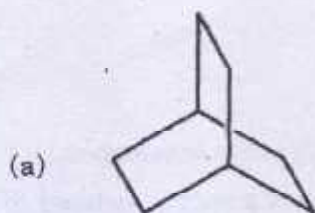
7. Explain Aniline absorbs at 280 nm ($\epsilon_{\text{max}} = 8600$) but in acidic solution, the main absorption band is seen at 203 nm. ($\epsilon_{\text{max}} = 7500$) which is comparable to benzene.
8. Determine the structure of the compound. Molecular formula $\text{C}_3\text{H}_6\text{O}$, $\text{UV-}\lambda_{\text{max}} = 292 \text{ nm}$ and $\epsilon_{\text{max}} = 21$; IR (1) 2720 cm^{-1} (w) (2) 1738 cm^{-1} .
9. Arrange the following groups in order of increasing stretching frequencies. $\text{C} = \text{C}$; $\text{C} = \text{O}$, $\text{C} = \text{N}$, $\text{C} = \text{S}$.
10. Predict the structural formula for the compounds with the following molecular formulae showing only one PMR signal. C_8H_{18} ; $\text{C}_2\text{H}_6\text{O}$; 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 \times 1 = 10)

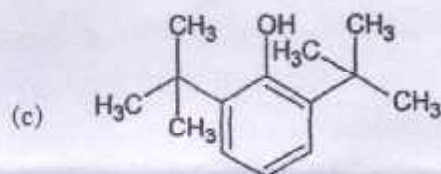
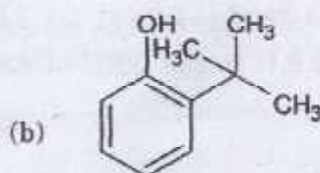
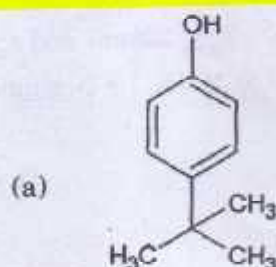
Section B

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 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}_3$) 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 :—



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



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) $3049\text{--}2924$ 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) $1.93\text{ }\tau$ -singlet (5.9 squares), (b) $5.88\text{ }\tau$ triplet ($j = 7.0\text{ cps}$, 12.2 squares), (c) $8.33\text{ }\tau$ sextet ($j = 7.0\text{ cps}$, 11.6 squares) and $9.05\text{ }\tau$ triplet ($j = 7.0\text{ cps}$, 18.6 squares). Arrive at the molecular formula and structure.

Turn over

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 1.87 τ singlet (1H), 7.30 τ singlet (3H), and 8.1 τ singlet (3H).

(2 \times 5 = 10)