

**M.Sc. DEGREE (C.S.S.) EXAMINATION, JANUARY 2016****Third Semester**

Faculty of Science

Branch III : Chemistry

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

(Common to all Branches of Chemistry)

[2012 Admission onwards]

Time : Three Hours

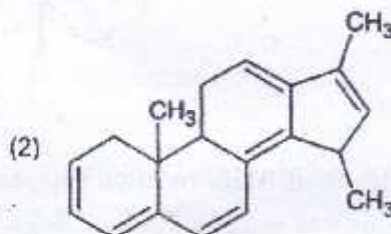
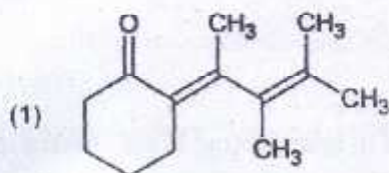
Maximum Weight : 30

**Section A**

Answer ten questions.

Each question carries a weight 1.

- Sketch the  $^1\text{H}$ NMR spectrum of the following molecules.
  - $\text{CF}_3\text{CH}_2\text{CH}_2\text{CHO}$ .
  - $\text{CH}_2\text{FCHFCH}_2\text{COOH}$ .
- Explain the effect of solvent polarity on K band and R band in UV spectra
- Using Woodward Fieser rules calculate the  $\lambda_{\text{max}}$  values for the following molecules :—



- State and explain the 'Axial Halo ketone rule.
- What structural features may produce Bathochromic shift and Hypsochromic shift ?
- $2.5 \times 10^{-4}$  M solution of a substance in a 1 cm cell at  $\lambda_{\text{max}}$  245 nm has an absorbance 1.17. Calculate the  $\epsilon_{\text{max}}$ .
- 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.
- Determine the structure of the compound. Molecular formula  $\text{C}_9\text{H}_8\text{O}$ , UV- $\lambda_{\text{max}} = 292$  nm and  $\epsilon_{\text{max}} = 21$ ; IR (1)  $2720 \text{ cm}^{-1}$  (w) (2)  $1738 \text{ cm}^{-1}$  (s).

Turn over

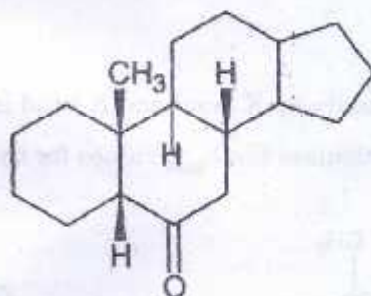
9. Arrange the following compounds in the order of increasing stretching frequencies of the carbonyl group.  $\beta$ -lactam ;  $\gamma$ -Lactam and  $\delta$ -lactam. Give the rationale behind this order.
10. Predict the structural formula for the compounds with the following molecular formulae showing only one PMR signal.  $C_8H_{16}$  ;  $C_2H_6O$  ;  $C_5H_{12}$ .
11. What are Shift reagents ? What are their uses ? Explain with examples.
12. What are the main fragments obtained in the mass spectrum of n-propyl chloride ?
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)

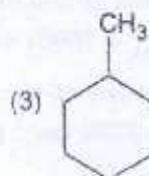
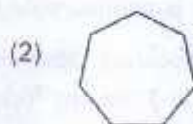
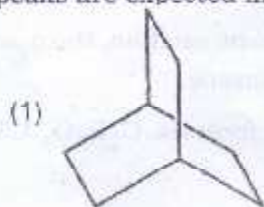
## Section B

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

14. Explain Nitrogen rule. Explain how it is useful in determining the molecular formula ?
15. State Karplus equation. Explain how it can be used to determine the conformation of conformational isomers ?
16. Explain the octant rule. Apply this rule to :

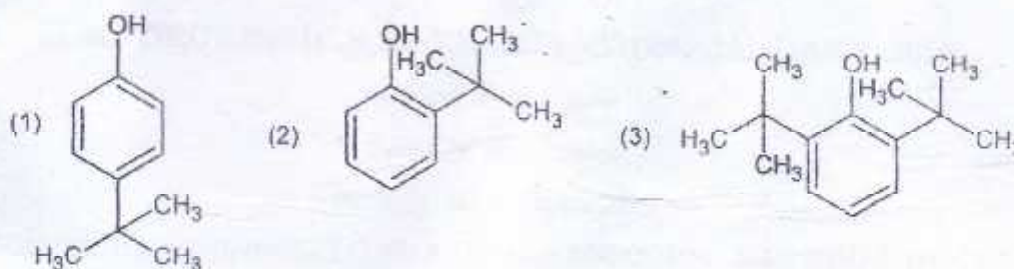


17. What is Retro Diels Alder reaction ? Explain its use in interpreting Mass spectra using a suitable example.
18. Write down the fragmentation patterns for the following class of compounds :
  - (a) Aliphatic ketones.
  - (b) Aromatic carboxylic acids.
19. How many peaks are expected in the proton decoupled CMR spectra of the following :—





20. In the following substituted phenols the O-H stretching frequencies are at  $3608\text{ cm}^{-1}$  in (1) at  $3605$  and  $3643\text{ cm}^{-1}$  (2) and at  $3643\text{ cm}^{-1}$  in (3) Explain.



21. Explain the following :—

- (a) NOE.
- (b) MALDI.
- (c) MRI.

(5 × 2 = 10)

### Section C

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

22. An organic compound with molecular mass 60 absorbs at  $222\text{ nm}$   $\epsilon_{\text{max}} = 62$ . In infra-red medium absorption bands formed are (1)  $3490$  and (2)  $3385\text{ cm}^{-1}$ . Also strong absorption band is formed at  $1675\text{ cm}^{-1}$ . It shows a broad band at  $2.5\tau$  in its NMR spectrum. 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- $\text{C}_7\text{H}_8\text{Br}$ ; (2) UV:  $\gamma_{\text{max}} = 282\text{ nm}$  and  $\epsilon_{\text{max}} = 450$  (3) IR  $3033$  (m),  $1646$  (m),  $1602$  (m),  $1582$  (v),  $820$  (s) and  $710\text{ cm}^{-1}$  (3) NMR  $2.62$ - $2.74\tau$  (Asymmetrical pattern 18.9 squares),  $4.30\tau$  doublet of doublet (4, 7 squares),  $3.30\tau$  doublet of doublet (4.9 squares) and  $4.86\tau$  doublet of doublet (5.0 squares).

(2 × 5 = 10)