F 7072

Reg. No..

Name..

M.Sc. DEGREE (CSS) EXAMINATION, JANUARY 2014

Faculty of Science

Third Semester

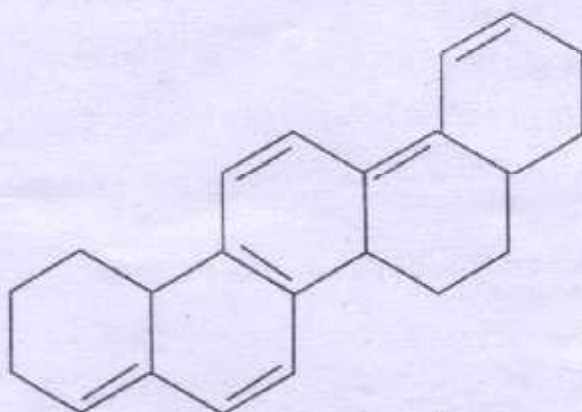AN 3C 12 / AP 3C 12 / CH 3C 12 / PH 3C 12 / PO 3C 12—SPECTROSCOPIC METHODS IN CHEMISTRY

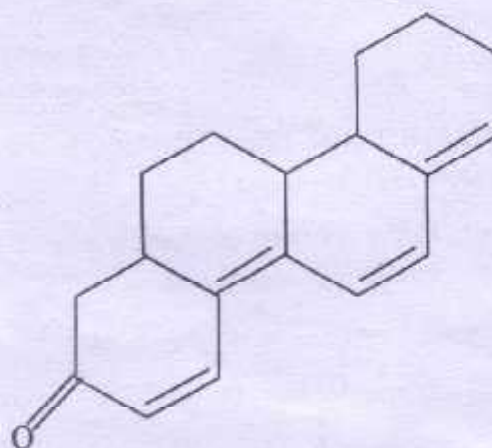(Common to all Branches of Chemistry)

Time : Three Hours

Maximum : 30 Weight

Section A

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

1. Calculate the λ_{max} for the following molecules using Woodward-Fieser Rules :

(1)   (2)

2. Explain Axial Haloketone rule using a suitable example.

3. Arrange the following in the increasing order of their carbonyl stretching frequencies Cyclohexanone, cyclopentanone, cyclopentanone, cyclo propanaone.

4. Arrange in the decreasing order of olefinic stretching frequencies of the following compounds. Cyclohexene, cyclopentene, cyclobutene, cyclopropene.

5. Write down the total number of signals obtainable in the PMR spectra of the following molecules. 2R, 3R–2, 3-Dibromopentane, Meso tartaric acid, Fumaric acid.

Turn over

6. Describe the splitting patterns in the PMR spectra of the following molecules 2 – 1, 3-Dimethylcyclopropane, 2R, 3S – 2, 3-Dibromopentane.

7. What is Selective Population Inversion (SPI) in NMR ?

8. Calculate DBE (Double bond equivalent) of the following molecules :

   (a) $C_{10}H_8O_2$.   (b) $C_{15}H_{13}Cl$.

9. What is Nitrogen Rule? What is its use in Mass spectrometry ?

10. What is MALDI? What is its use ?

11. Explain Mc-Lafferty rearrangement.

12. Using an example, explain the special advantage in HRMS.

13. Explain the use of UV spectra in distinguishing axial and equatorial conformations using a suitable example.

$$(10 \times 1 = 10)$$

Section B

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

14. What is "Cotton Effect". Explain, how it is useful in distinguishing the Enatiomeric pairs using an example ?

15. (a) In the substituted phenols given below give a suitable explanation for the difference in O-H stretching frequencies.

3608 cm⁻¹   3605 cm⁻¹ and 3643 cm⁻¹   3643 cm⁻¹
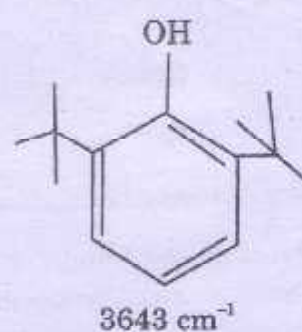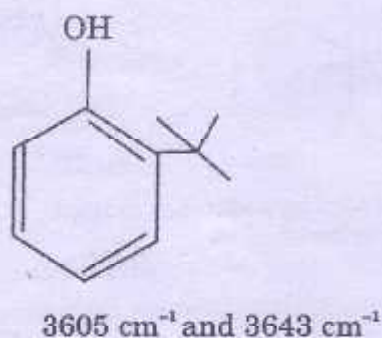
(b) The following triene on partial hydrogenation gave three products, which are separated by GLC. How UV spectroscopy is of help in identifying the products ?
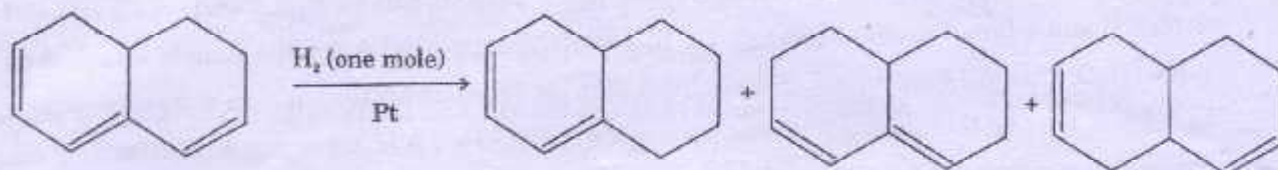
16. Sketch the ^1HNMR and $^{13}CNMR$ spectra of Hex-2-ene. Explain the spectral features.

17. What is Nuclear Overhauser Effect (NOE)? Explain its use in structural elucidations using a suitable example.

18. Explain Karplus Curve. How it is helpful in determining the conformations?

19. What are shift reagents? What is their use in NMR spectra? Name two common shift reagents used.

20. Write briefly on the theory and applications of MRI.

21. Explain the principle of 2DNMR State its advantages over normal NMR.
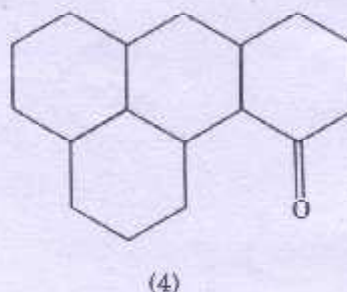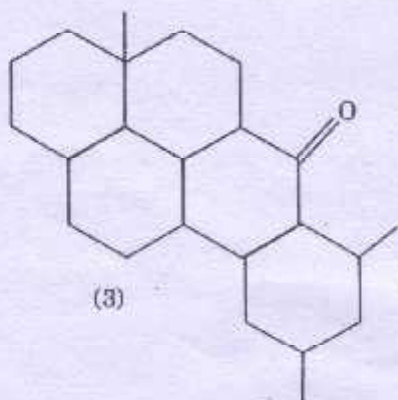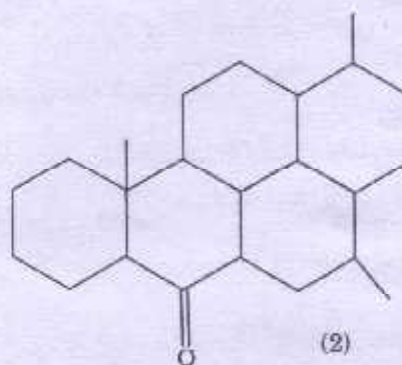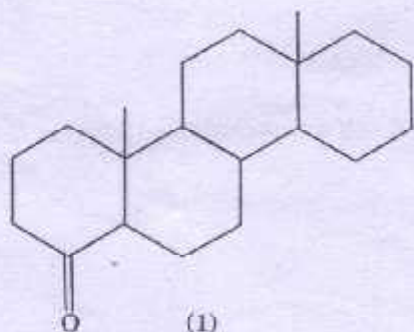
$(5 \times 2 = 10)$

Section C

Answer any two questions.

Each question carries a weight of 5.

22. (a) Write down the fragmentation pattern for the following compounds and suggest the probable mass spectra peaks :

   (i) *n*-Butyl benzene.

   (ii) 1-Hexanol.

   (b) What are Meta stable peaks? How they are identified in mass spectra. Explain the formation of a broad peak at 46.4 in the mass spectrum of Toluene.

Turn over

23. Hydrolysis of a natural product gave an aromatic compound (Molecular formula $C_9H_{10}O_4$), which is soluble in aqueous Sodium hydrogen carbonate. It had IR absorptions at 2700 (broad), 1690 and 1600 cm^{-1}. In the ^1HNMR spectrum, there were signals at $\delta_H 3.85(6H)$, 6.62(1H) and 7.15(2H) and a broad proton signal at δ_H 10.2 which disappeared when the sample was shaken with ^2H_2O. Careful inspection of the signal at $\delta_H 6.62$ showed that it was a narrow triplet (J = 1.5 H_z), while that at δ_H 7.15 was a narrow doublet (J = 1.5 H_z). Suggest a structure for the compound and account for the multiplicity of the signals.

24. The phyto toxic fungal metabolite Pyrenocine (Molecular formula-$C_{11}H_{14}O_4$) had IR absorptions at 3410, 1710 and 1640 cm^{-1} and an intense UV absorption at 284 nm. It possessed ^1HNMR signals at δ_H 1.71(3H, d, J =5.5 H_z), 2.31 (3H, S), 2.64 (1H, exchanged on shaking with D_2O), 3.86 (3H,S),5.15 (1H, d, J=7 H_z), 5.50 (1H,S) ,5.6 (1H, d, J = 15.5H_z, of q, J = 5.5 H_z) and 5.75 (1H, d, J=15.5 Hz of d, J = 7Hz). Irradiation of the signal δ_H 1.71 collapsed the multiplet at δ_H 5.60 to a doublet (J = 15.5 H_z) and irradiation of the signal at δ_H 5.15 collapsed the signal at δ_H 5.75 to a doublet (J = 15.5 H_z). The signal at δ_H 5.15 received nuclear Overhauser effect enhancements on irradiation of the signal δ_H 2.31 and 3.86, but the signal at δ_H 5.50 only received an enhancement from irradiation at δ_H 3.86. Suggest a structure for Pyrenocine.

25. State and explain "Octant Rule". Apply this rule and draw the octants for the following compounds and predict the sign of their optical activity.

(1)

(2)

(3)

(4)

(2 × 5 = 10)