

Reg. No

Name

18P3645

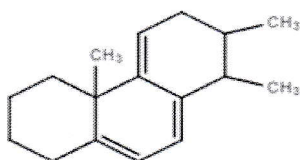
MSc DEGREE END SEMESTER EXAMINATION - OCTOBER 2018
SEMESTER 3 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY
COURSE : 16P3CHET12 / 16P3CPHT12 : SPECTROSCOPIC METHODS IN CHEMISTRY
(For Regular - 2017 Admission & Supplementary - 2016 Admission)

Time : Three Hours

Max. Marks: 75

Section A**Answer any 10 (2 marks each)**

- Acetone shows absorption maximum at 264 nm in water while at 270 nm in methanol. Explain.
- Use the Woodward rule to calculate λ_{\max} for the compound

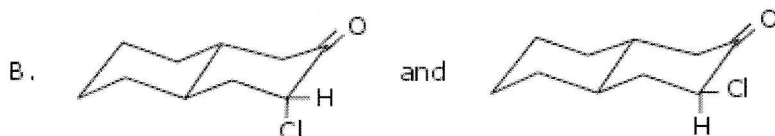


- How can you differentiate between methine and methylene groups using IR spectroscopy?
- Predict any two characteristic bands in the IR spectrum of formamide.
- How can you differentiate between *p*-nitroacetophenone and acetophenone using IR spectroscopy?
- Predict the chemical shift positions and multiplicity of the protons in 4-hydroxytoluene in proton NMR spectrum
- The ortho protons of methyl phenyl ether exhibits a chemical shift value δ 6.8. Justify the low chemical shift value.
- What is DEPT?
- Deduce the structure of the amine with molar mass 101 whose ^1H NMR taken in CDCl_3 showed two peaks – δ 1.03 (t), δ 2.53 (q).
- An unknown hydrocarbon has a molecular ion peak at $m/z = 84$, with a relative intensity of 31.3. The $M + 1$ peak has a relative intensity of 2.06. What is the molecular formula for this substance?
- Phenol shows CO loss on EI analysis. Show the mode of fragmentation.
- An organic compound ($\text{C}_4\text{H}_9\text{Br}$) shows only one signal in proton NMR spectrum. The base peak in the EI mass spectrum is an ion of m/z 57. What is the structure of the compound.
- The proton NMR spectrum of a compound ($\text{C}_4\text{H}_7\text{N}$) shows signals at δ 1.1 (d) and 2.9 (m), and IR spectrum showed a strong band at 2250 cm^{-1} . Identify the structure. **(2 x 10 = 20)**

Section B**Answer any 5 (5 marks each)**

- Discuss the effect of substituents on the λ_{\max} of benzene and its derivatives taking any three examples

15. On the basis of IR spectral data how can you differentiate between primary, secondary and tertiary amides?
16. Compare the C = O stretching frequencies in the following pairs and explain.



17. Predict the chemical shift values of the protons in vinyl acetate. Predict the splitting pattern and coupling constant of the olefinic protons. What is the notation for the coupling system of the olefinic protons?
18. An organic compound, molecular formula C_4H_8O , showed the following NMR data: Proton NMR δ 1.1 (t), 3.6(q), 3.82(dd, $J=10, J=3$), 4.02 (dd, $J=16, J=3$), 6.32(dd, $J=10, J=16$). Carbon-13-NMR δ 14(q), 63(t), 85(t), 152(d). Identify the structure and assign the data.
19. What is COSY? Explain 1H-1H COSY taking isopentyl acetate as an example.
20. What are the peaks in their mass spectra used to distinguish between 4-methyl-2-pentanone and 2-methyl-3-pentanone?
21. Propose a suitable structure of a molecule having a molecular ion peak at m/z 116 and another at 45 u. On MS/MS analysis, another peak at m/z 15 is also observed. Suggest any two prominent bands in the IR spectrum and assign them. **(5 x 5 = 25)**

Section C
Answer any 2 (15 marks each)

22. What is vicinal coupling? Discuss AX, AX₃, A₂X₂, A₂X₃ and AMX coupling systems taking one example for each.
23. Discuss in detail on Mc Lafferty Rearrangements citing at least five different systems.
24. A organic compound, molecular formula $C_6H_8Cl_2O_2$, showed the following spectra data: IR spectrum displays a strong band 1739 cm^{-1} . Proton NMR: δ 1.4, 1.6, 2.3, 3.8. Carbon-13 NMR: 18, 31, 35, 53, 63, 170. DEPT-135 showed two positive signals and one negative signal. DEPT-90 showed no signals. The H-H cosy spectrum shows only one correlation (1.4-2.3) and The HETCOR spectrum showed the following correlations (1.4 -31), (2.3 - 31), (1.6-19), (3.8-53). The EI mass spectrum showed ions of m/z 183, 147, 124. Both chlorine atoms are attached to the same carbon. Identify the molecule.
25. An organic compound having molecular formula $C_{11}H_{14}O_2$, showed the following spectral data: Proton NMR: δ 7.3, 5.1, 2.4, 1.1. Carbon NMR: δ 18, 34, 66, 135, 127, 128, 129, 178. DEPT-135 spectrum shows 5 positive signals and one negative signal. EI mass spectrum showed ions of m/z 178, 91, 71. IR 3060, 2940, 1730, 1200, identify the structure and explain the data. Sketch the predicted hetero cosy spectrum. **(15 x 2 = 30)**