

**L-7/2050**

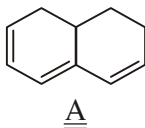
APPLICATIONS OF ORGANIC MOLECULAR  
SPECTROSCOPY-421  
(Semester-IV)

Time : Two Hours]

[Maximum Marks : 55

**Note** : Attempt any *four* questions. All questions carry equal marks.

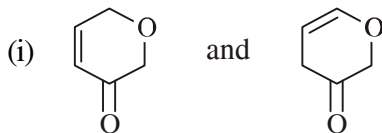
- I. (a) Discuss briefly the effect of polarity of solvent on  $\underline{n} - \underline{\pi}^*$  and  $\underline{\pi} - \underline{\pi}^*$  absorption bands in  $\alpha$ ,  $\beta$ -unsaturated ketones.
- (b) Catalytic hydrogenation of triene A with one equivalent of hydrogen could give three isomers with molecular formula,



$C_{10}H_{14}$ . Write their structures. Explain how the  $\lambda_{\max}$  values could distinguish these isomers ?

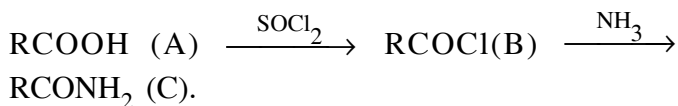
- II. (a) How does IR spectroscopy help us in distinguishing between inter and intra-molecular hydrogen bonding ?

- (b) Distinguish between the following pairs of compounds on the basis of IR data :



- III. (a) What is the significance of metastable peaks in the mass spectrometry ? Explain with two examples.  
(b) Outline the mass spectrum fragmentation of anisole.

- IV. (a) Consider the following sequence of reactions :



How can IR spectroscopy be used to distinguish between the products (A), (B) and (C) ? Give proper reasoning for your answer.

- (b) Distinguish 2-methylbutanal and 3-methylbutanal by mass spectrometry.  
(c) Compare the acid character of (i) phenol and (ii) benzoic acid in the ground and the excited states ?
- V. (a) Explain shielding and deshielding of protons in NMR spectroscopy. Explain why methyl protons in acetonitrile are more shielded than those of methyl chloride ?

- (b) Write all the isomers of 1,2-dimethyl cyclopropane. Which of these will show four different types of hydrogens in its  $^1\text{H-NMR}$  spectrum ? Give reason for your answer.
- (c)  $(\text{CH}_3)_2\text{N-CHO}$  shows two signals at 82.70 and 2.84 in the  $^1\text{H NMR}$  spectrum. Explain why ?
- VI. (a) What do you mean by coupling constant ? On what factors does it depend ? How can coupling constants be used to determine the structure and stereochemistry of organic compounds ?
- (b) What are enantiotropic and diastereotropic protons ? Explain why the former have the same but the latter have different chemical shifts ?
- VII. (a) Comment upon the advantages of  $^{13}\text{C-NMR}$  over  $^1\text{H-NMR}$ .
- (b) With one example in each case explain the difference between proton coupled (off-resonance decoupling) and proton coupled  $^{13}\text{C-NMR}$  spectra.
- (c) The peak sizes and integrals in proton decoupled  $^{13}\text{C-NMR}$  spectra are usually not reliable. Explain.
- (d)  $\text{CDCl}_3$  in  $^{13}\text{C-NMR}$  shows a triplet at  $\delta 76, 77, 78$ . Why ?

- VIII. (a) Highlight the utility of APT and DEPT technique as used in  $^{13}\text{C}$ -NMR spectroscopy. Discuss briefly the DEPT-45, DEPT-90 and DEPT-135 spectra of menthol.
- (b) Give one example of nuclear overhauser effect in the study of molecular geometry.
- IX. (a) List all the possible electronic transitions in vinyl chloride,  $\text{H}_2\text{C}=\text{CHCl}$  and arrange them in order of increasing energy difference ( $\Delta E$ ).
- (b) UV absorption spectra generally consist of bands while IR spectra consist of peaks. Explain why ?
- (c) How will you distinguish  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$  and  $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$  by IR spectroscopy ?
- (d) What is nitrogen rule ? Explain its use in structure determination.
- (e) Write the geometrical isomers of  $\text{C}_2\text{H}_2\text{BrCl}$  and identify them on the basis of values.
- (f) How many methyl signals would you expect in the proton decoupled  $^{13}\text{C}$ -NMR spectrum of cis-1,2-dimethylcyclohexane ?
- (g) Write the fragmentation ions corresponding to  $m/z$  57, 59 and 88 in the mass spectrum of methyl propanoate.
- (h) Write the structure of a compound,  $\text{C}_5\text{H}_8$  which shows a singlet in its  $^1\text{H}$ -NMR spectrum.

- (i) With suitable examples explain how can UV spectroscopy be used to distinguish between conjugated and cross-conjugated diamond ?
  - (j) What are symmetric and asymmetric stretching vibrations ? Discuss briefly the use of these vibrations in the identification of certain functional groups.
  - (k) What is the difference between FT and CW NMR and comment upon the advantages of the former ?
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