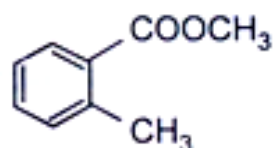


How mass spectral fragmentations confirm this ? 8



- (ii) Describe the various fragmentation modes of a compound whose mass spectrum exhibits peaks at  $m/e$  152 ( $M^+$ ), 121, 120, 92, 65 and 64. Give the structure of the compound. 8

OR

- (b) (i) What is the principle involved in mass spectrometry ? Write an account on general rules governing fragmentation of molecules in mass spectrometry. 8
- (ii) An organic compound forms a molecular ion peak at  $m/e$  114 and other prominent peaks at  $m/e$  85, 72, 57, 41 and 29. Name the compound. 8

————— ❖ —————

2016

Time : 3 hours

Full Marks : 80

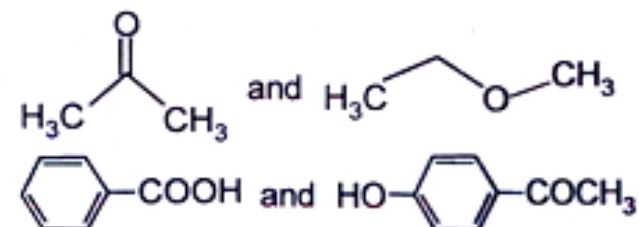
The figures in the right-hand margin indicate marks.

Answer questions from both the Sections as directed.

### (APPLICATION OF SPECTROSCOPY)

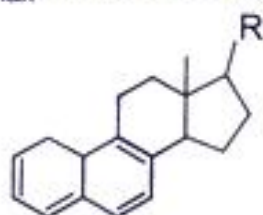
#### Section – A

1. Answer any **four** of the following : 4×4 = 16
- (a) How can you distinguish the following pair of compounds by IR spectroscopy ?



- (b) The  $^1\text{H}$  NMR spectra of DMF shows two signals at  $\delta$  2.84 and 3.0 for the methyl protons at room temperature but a single sharp signal appear at 438K. Explain.

- (c) Calculate  $\lambda_{\max}$  of the following compounds :



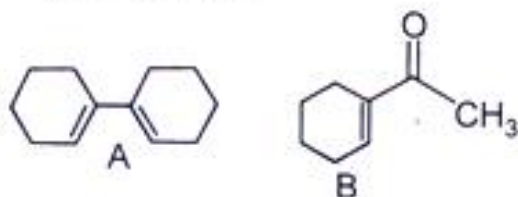
- (d) Why a polar solvent shifts the  $\pi - \pi^*$  transitions to longer wave length and  $n - \pi^*$  transition to shorter wave length ?
- (e) The position of absorption of acetone varies in different solvents : 279 nm (hexane), 272 nm (ethanol) and 264 nm (water). Explain.
- (f) Write various fragmentation mode of 1-butanol.

OR

2. Answer **all** questions from the following :

2×8 = 16

- (a) On the basis of Woodward-Fieser rules calculate absorption maximum for the following compound :



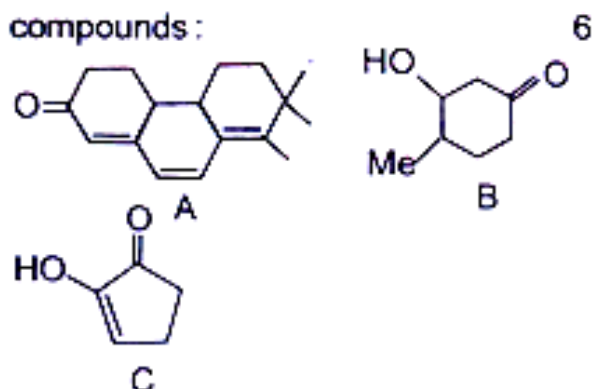
- (b) Why hydrogen bonding shifts the absorption to shorter wavelength in alcohols and amines ?
- (c) What is bathochromic shift ? Give one example of it.
- (d) Predict the number of fundamental modes of vibration of HCl.
- (e) Why water can not be used as a solvent in IR spectroscopy ?
- (f) Explain the  $^1\text{H}$  NMR splitting pattern and chemical shift values of compound 1-bromobutanoic acid.
- (g) Write down all the chemical shift values of methyl benzoate in  $^{13}\text{C}$  NMR spectroscopy.
- (h) The mass spectrum of 4-methyl-1-hexene show intense peak at  $m/z$  57 and  $m/z$  41. What fragmentation reaction account for these peaks ?

### Section – B

Answer **all** questions :

3. (a) (i) Write various transition modes in UV absorption spectroscopy. 8

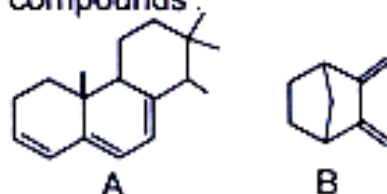
- (ii) Calculate  $\lambda_{\max}$  of the following compounds :



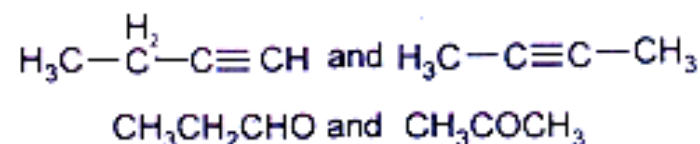
- (iii) The bands due to  $n - \pi^*$  transition in amine disappear in acid solution. Why ?

OR

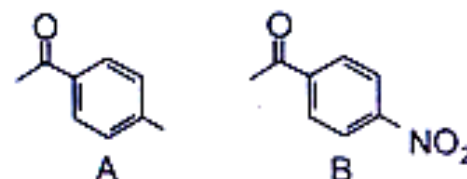
- (b) (i) What is the difference between auxochrome and chromophore ? Explain with examples.
- (ii) Write note on solvent effects on electronic transitions in UV spectroscopy.
- (iii) Calculate  $\lambda_{\max}$  of the following compounds :



4. (a) (i) How the following pairs can be distinguished by IR spectroscopy ?



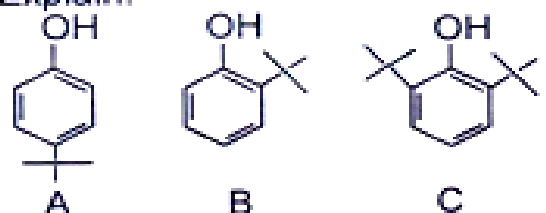
- (ii) Why the frequency of axial hydroxyl group is higher than that of equatorial in cyclohexanols ?
- (iii) From the following compounds, which one is expected to show lower  $\text{C} = \text{O}$  stretching frequency and why ?



OR

- (b) (i) Write a note on the principle of FTIR spectroscopy.
- (ii) 2-Hydroxy-3-nitroacetophenone shows two carbonyl stretching frequencies at  $1692$  and  $1658 \text{ cm}^{-1}$ . Explain.

- (iii) In the substituted phenols the O-H stretching frequency is at  $3608\text{ cm}^{-1}$  in A, at  $3605\text{ cm}^{-1}$  in B and in  $3643\text{ cm}^{-1}$  in C. Explain. 4

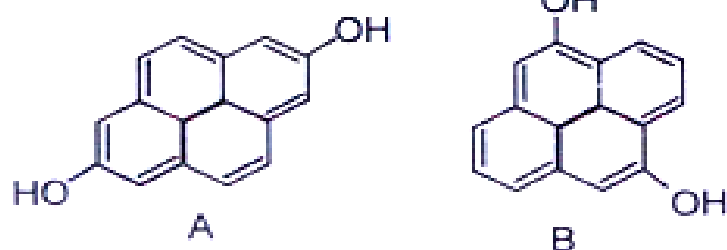


5. (a) (i) Predict the structure of an organic compound having molecular formula  $\text{C}_9\text{H}_{10}\text{O}_3$  which exhibited the following spectral data : 8

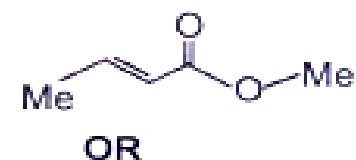
IR :  $3400, 1680\text{ cm}^{-1}$

$^1\text{H NMR}$  :  $\delta$  7.8 (1H, d,  $J = 8\text{ Hz}$ ), 7.0 (1H, d,  $J = 8\text{ Hz}$ ), 6.5 (1H, s), 5.8 (1H, s,  $\text{D}_2\text{O}$  exchangeable), 3.9 (3H, s), 2.3 (3H, s).

- (ii) In  $^{13}\text{C NMR}$  spectrum, how many signals are possible for the following compounds A and B ?  $2+2 = 4$



- (iii) Write the correct chemical shift ( $\delta$ ) values of carbon in  $^{13}\text{C NMR}$  of the following structure : 4



- (b) (i) Predict the structure of an organic compound having molecular formula  $\text{C}_{10}\text{H}_{12}\text{O}_2$  and exhibited the following  $^1\text{H NMR}$  spectral data :

$^1\text{H NMR}$  :  $\delta$  7.80 (2H, d,  $J = 8\text{ Hz}$ ), 6.80 (2H, d,  $J = 8\text{ Hz}$ ), 4.10 (2H, q,  $J = 7.2\text{ Hz}$ ), 2.4 (3H, s), 1.25 (3H, t,  $J = 7.2\text{ Hz}$ ).

- 8
- (ii) Tell precisely how you would use the  $^1\text{H NMR}$  spectra to distinguish between the following pair of compounds : 8
- (a) Propanal and Propanone
- (b) 1-butyne and 2-butyne
6. (a) (i) A compound with molecular formula  $\text{C}_9\text{H}_{10}\text{O}_2$  has the following structure.