

Ans

Total No. of Pages : 8

M.Sc-Chem-IIS- (409)

2017

Time : 3 hours

Full Marks : 80

The figures in the right-hand margin indicate marks.

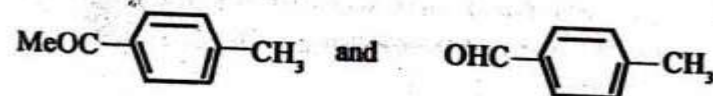
Answer from both the Section as directed.

(Application of Spectroscopy)

SECTION—A

1. Answer any *four* of the following : 4 × 4

(a) How can you distinguish the following pair of compounds by IR spectroscopy ?



(Turn Over)

(b) A compound shows ^1H NMR peak at 240 Hz downfield from TMS peak in a spectrum operating at 60 MHz. What are the values of chemical shift δ and τ in ppm relative to TMS?

(c) How would you distinguish *cis*- and *trans*-cinnamic acid by UV-visible spectroscopy?

(d) Give ^1H NMR spectra of 2-bromo-butanoic acid. Show the splitting pattern and approximate chemical shift values (δ values).

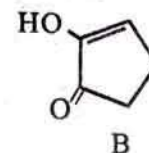
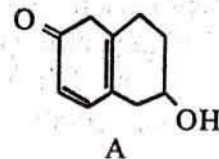
(e) Determine the structure of the compound whose peaks appear at m/e values 124, 122, 81, 79, 43 (base peak), 41, 29 and 27 in the mass spectrum.

(f) Write fragmentation ions formed in 1-Hexanol.

Or

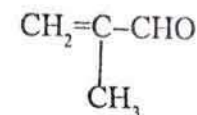
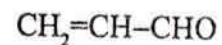
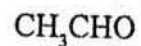
1. Answer *all* questions from the following: 2×8

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



(b) By taking examples, explain how *cis* and *trans* isomers can be distinguished by UV spectroscopy?

(c) Compare the $\text{C}=\text{O}$ stretching absorption in the following compounds. Explain it.



A (1745 cm^{-1})

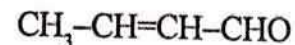
B (1723 cm^{-1})

C (1720 cm^{-1})

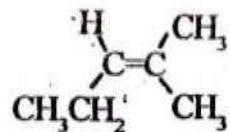
(d) Which form of 2-bromo-4-tertiary butyl cyclohexanone shows higher $\nu_{\text{C}=\text{O}}$ absorption frequencies and why?

(e) How will you verify that a particular signal arises from the proton of $-\text{OH}$, $-\text{NH}$ or $-\text{SH}$ groups?

(f) Explain the ^1H NMR splitting pattern and chemical shift values of the following compound.



- (g) How many absorption peaks will you find from the following compound in its carbon NMR spectrum?



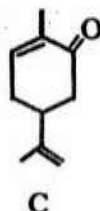
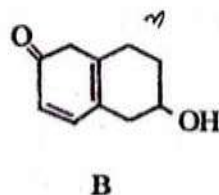
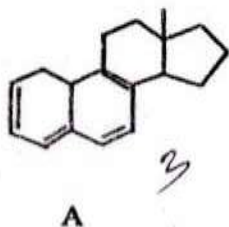
- (h) An organic compound shows peaks in the mass spectrum at m/e values 162, 134 (M^+), 120, 91 and 65. Write the structure of the compound.

SECTION-B

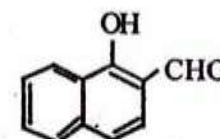
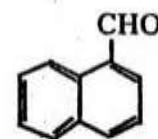
Answer *all* questions.

16 × 4

2. (a) (i) Explain in detail about the electronic excitation in UV spectroscopy. 8
- (ii) Calculate λ_{\max} of the following compounds: 6

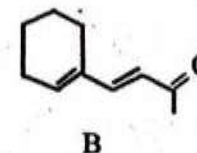
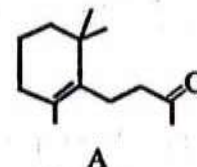


- (iii) Compare the $\nu_{C=O}$ absorption frequencies of the following compounds. 2

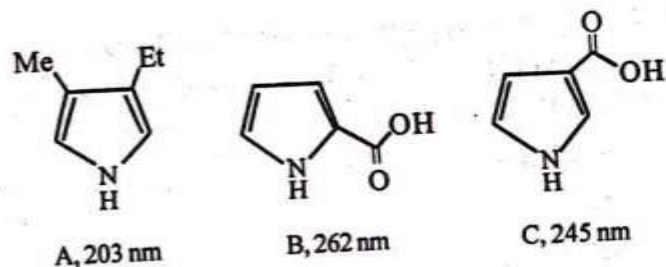


Or

- (b) (i) Write notes on UV absorption in α, β unsaturated carbonyl compounds. 8
- (ii) How the UV spectral data λ_{\max} 296 nm, ϵ_{\max} 10,700 and λ_{\max} 281 nm, ϵ_{\max} 20,800 help in deciding between structures A and B given below: 4



- (iii) The Pyrrole derivatives (A, B and C) shows the following wavelength of absorption. Explain it. 4



3. (a) (i) Describe about the instrumentation of IR spectroscopy. 8

(ii) How would you distinguish the following sets of compounds using IR spectra? 8

- (a) Cyclohexanol and cyclopentanol
- (b) Primary, Secondary and Tertiary amines
- (c) Esters and Lactones
- (d) Mono- and di-substituted benzene.

Or

(b) (i) Distinguish between maleic acid and fumaric acid using IR spectroscopy. 8

(ii) Differentiate between *o*-hydroxy benzoic acid and *m*-hydroxy benzoic acid using IR spectroscopy. 8

4. (a) (i) Determine the structure of the organic compound having molecular formula $C_9H_{12}O$ and 1H -NMR shows peak at δ ppm 7.2(s); 4.3(s); 3.2(q); 1.5(t). 8

(ii) Explain 1H -NMR spectra of furan-2-aldehyde. 8

Or

(b) (i) Write short notes on the following : 8

(a) Chemical Shift

(b) Nuclear over Hauser Effect.

(ii) The spectral features for an organic compound are given below :

Molecular formula : $C_8H_{16}O_3$, IR (cm^{-1}) : 3500-3600, 1730. 1H -NMR (δ ppm) : 4.17 (2H, q); 3.86 (1H, pentet); 2.70 (1H, t); 1.27 (3H, t); 1.17 & 1.18 (3H, s); 1.15 (1H d).

Assign the structure to the compound and explain. 8

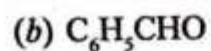
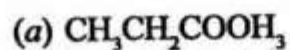
5. (a) (i) Write a note on β -cleavage in mass spectrometry. 6

(ii) Describe various fragmentation mode of 1-bromohexane. 5

(iii) Explain the mass spectrum of 1-phenyl-ethanol. 5

Or

(b) (i) Draw the fragmentation pattern in the mass spectra of the following compounds: 8



(ii) Write short notes on the following: 8

(a) Nitrogen rule,

(b) Meta stable peak.
