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AI—12—2017

FACULTY OF SCIENCE

M.Sc. (Second Year) (Third Semester) EXAMINATION

OCTOBER/NOVEMBER, 2017

(CBCS Pattern)

CHEMISTRY

(CH-531)

(Advanced Spectroscopic Methods)

(Friday, 10-11-2017)

Time : 2.00 p.m. to 5.00 p.m.

Time—3 Hours

Maximum Marks—75

N.B. :— (i) All questions are compulsory.

(ii) Figures to the right indicate full marks.

(iii) Multiple Choice Questions (MCQ) should be attempted only once on page number three of answer-book with complete answer.

1. Attempt any *three* of the following : 15
- (a) $h \rightarrow \sigma^*$ transition in methyl chloride is 172 mu and methyl iodide is 258 mu. Explain.
- (b) Why are water and ethanol not commonly used as solvents in IR-spectroscopy ?
- (c) Explain Hooke's law in IR.
- (d) Pentanoic acid gives m/z 60 in mass spectrum. Explain.
- (e) In PMR spectrum, aldehydic proton appears in the far region ($\delta = 9 - 10$ ppm)

P.T.O.

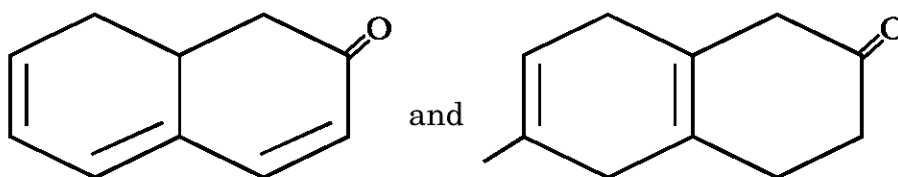
2. Attempt any *three* of the following : 15

(a) Explain the effect of the following substituents on the observable primary and secondary absorption band of benzene :

(i) —NH_2

(ii) —COOH .

(b) Using the Woodward-Fieser rules, predict λ_{max} of the following compound :



(c) What will be the force constant for the bond in CO, if fundamental vibrational frequency is $6.4296 \times 10^{13} \text{ s}^{-1}$? Given : C = 12.011, O = 15.999.

(d) Ethyl butanoate in its mass spectrum shows two characteristic peaks at m/e 88 and an abundant peak at m/e 71. Explain the fragmentation.

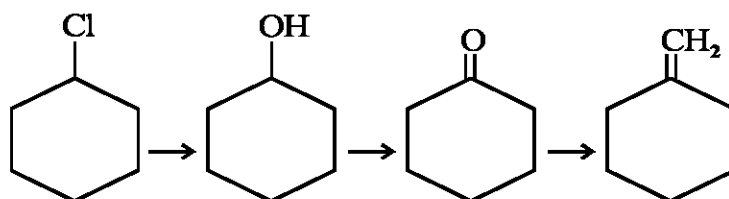
(e) Assign the structure of the compound using given PMR data :

MF : $\text{C}_8\text{H}_9\text{Br}$

$\delta_{\text{(ppm)}}$: 2.7 (2H), 3.4(2H), 7.22 (5H).

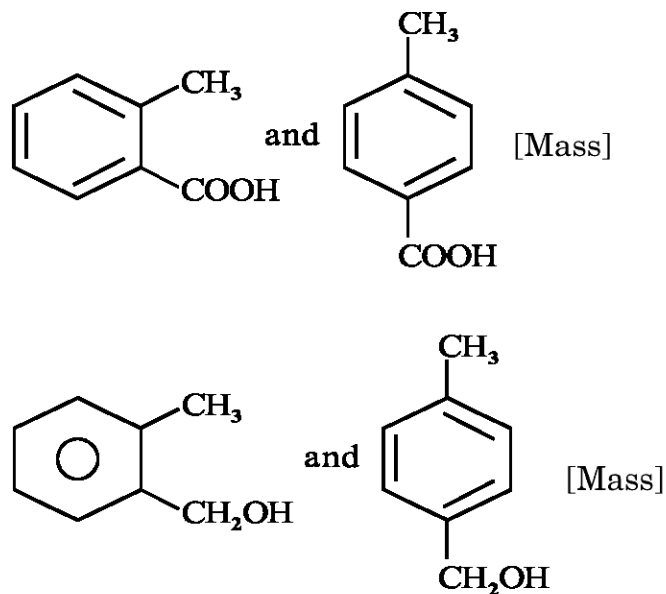
3. Solve the following :

(a) How will you follow the following sequence of reaction using IR-spectroscopy ? 7



Or

Distinguish between the following pairs by using the indicated spectral method : 7



- (b) Deduce the structure of the compound using the following spectral data : 8

MF : $C_7H_4O_4NCl$

UV : 280 nm, $\epsilon = 8000$

IR : 3300 cm^{-1} , 2700 cm^{-1} ,

1720 cm^{-1} , 1620 cm^{-1} ,

1540 cm^{-1} , 920 cm^{-1}

PMR : (δ) : 5.5 (broad singlet 7 mm)

7.9 (doublet 7 mm, $J = 7.5\text{ Hz}$)

8.4 (doublet of doublet 7 mm, $J = 7.5$ and 2.5 Hz)

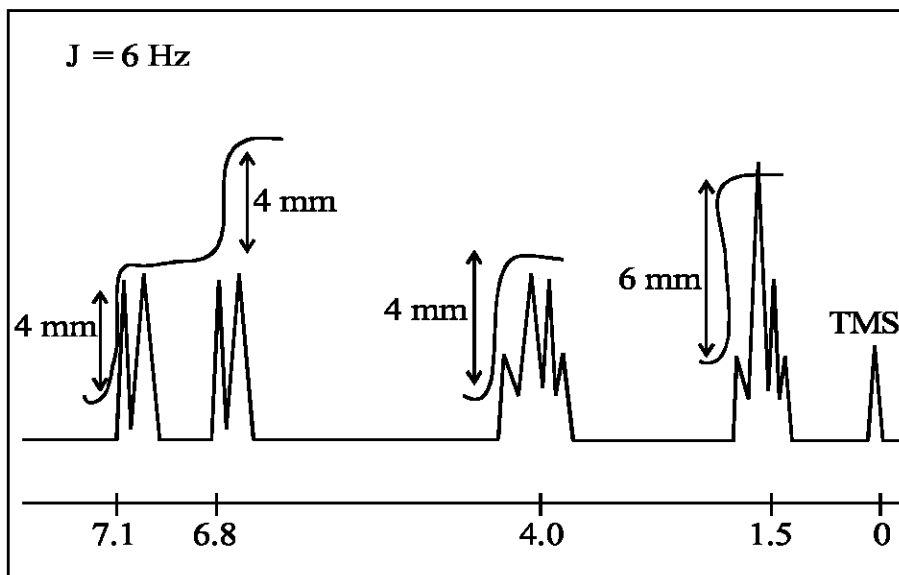
8.65 (doublet, 7 mm, $J = 2.5\text{ Hz}$)

P.T.O.

Or

A compound having molecular formula C_8H_9OBr shows the following NMR spectrum. Deduce its structure :

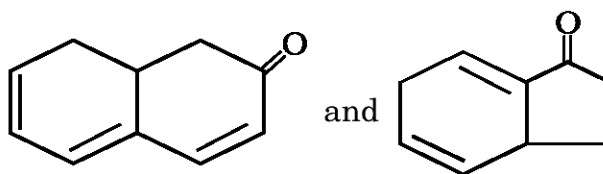
8



4. Solve the following :

(a) Distinguish between the following pairs by using the indicated spectral methods :

7

*Or*

An organic compound with molecular formula $C_{11}H_{14}O_2$ shows the following spectral data. Assign structure and justify the spectral data :

7

PMR (δ PPM) : 7.18—7.38(5 H, *m*)

5.71(2H, *q*)

4.50(2H, s)

4.06(4H, t)

2.63(1H, s)

^{13}C NMR : $\delta(\text{PPM})$: 58.5(*t*), 65(*t*)
72.5(*t*), 127.8(*d*), 127.9(*d*),
128.0(*d*), 128.5(*d*), 134.4(*d*),
137.8(*s*).

(b) Compound with MF $\text{C}_{10}\text{H}_{14}$ shows the following spectral data : 8

UV : λ_{max} 265 nm (ϵ_{max} 450)

IR : 3030, 2970, 1600, 1515, 1465 and 813 cm^{-1}

PMR : (δppm) : δ 1.2(*d*, 6H, $J = 7$ Hz)

δ 2.3(*s*, 3H)

δ 2.8(*heptet*, 1H, $J = 7\text{Hz}$)

δ 7.1(*m*, 4H).

^{13}C NMR (δppm) : 21.3(*q*), 24.2(*q*)

39(*d*), 126(*d*), 128(*d*)

139(*s*), 145(*s*).

Rationalize the spectral data and assign the structure to the compound.

Or

A compound with MF $\text{C}_6\text{H}_5\text{NO}$ displays the following spectral data : 8

UV : 265 nm

P.T.O.

IR : 2720, 1710, 1600, 1500, 850 cm^{-1}

PMR : δ 7.24(*d*, 10 mm)

8.70(*d*, 10 mm)

10.40(*s*, 5 mm).

5. (A) Select the correct answer from the following multiple choice questions and rewrite complete answer : 5

(i) The methyl proton signal in the NMR spectrum of anisole is expected around :

(*a*) 0.9 δ (b) 1.5 δ

(*c*) 2.5 δ (d) 3.9 δ

(ii) Quadruple splitting observed in IR

(*a*) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (b) $\text{Na}_2[\text{Fe}(\text{CN})_5 \cdot \text{NO}]$

(*c*) Only (*a*) (d) Both (*a*) and (*b*)

(iii) In the α -cleavage of acetone, the m/z ratio is :

(*a*) 35 (b) 43

(*c*) 45 (d) 20

(iv) In IR spectrum, due to the presence of strong hydrogen bonding, the absorption band shifts to :

(*a*) Higher wave number

(*b*) Lower wave number

(*c*) Both

(*d*) No effect

(v) Electromagnetic radiations used in ^{13}C NMR spectroscopy is :

- (a) IR (b) Microwave
(c) Radio (d) None of these

(B) Write short notes on (any *two*) : 10

- (i) MacLafferty rearrangement
(ii) Spin-spin coupling in PMR
(iii) Stretching and bending vibrations in IR-spectroscopy.