

Total No. of Questions : 6]

SEAT No. :

**P1859**

[5323]-41

[Total No. of Pages : 7

M.Sc.

**ORGANIC CHEMISTRY**

**CH - 351 : Spectroscopic Methods in Structure Determination  
(2008 Pattern) (Semester - III)**

*Time : 3 Hours]*

*[Max. Marks : 80*

*Instructions to the candidates:*

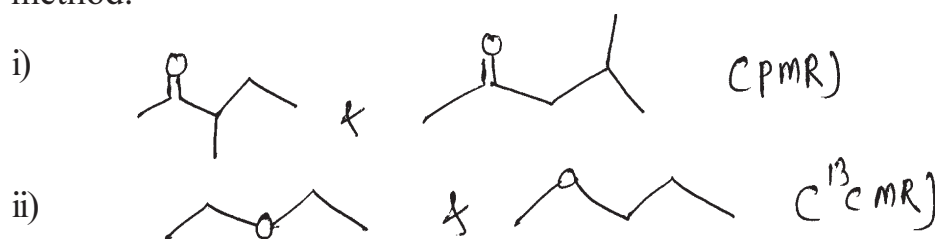
- 1) *All questions are compulsory.*
- 2) *Figures to the right indicate full marks.*
- 3) *Answers to two sections should be written in separate answer books.*
- 4) *Spectroscopic data : IR, PMR, CMR is not provided.*

**SECTION - I**

**Q1)** Explain any four of the following:

**[16]**

- a) How will you distinguish between following pairs by indicated spectral method.



- b) From the given data, deduce the structures of two isomeric Ketones.

m.f =  $C_7H_{14}O$

Compd. A

PMR = 1.2 (d) 12 mm  
2.8 (sept.) 2 mm

$^{13}CMR$  = 18 (str.), 38 (m)  
214 (w)

Compd. B

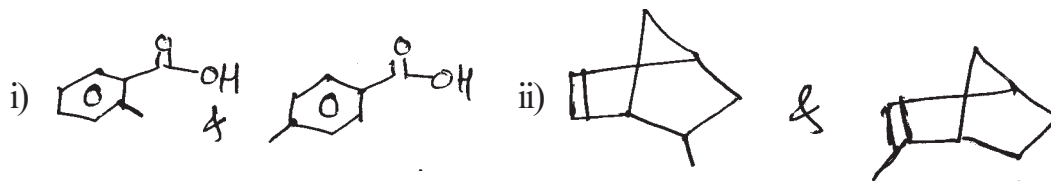
PMR = 1.0 (s) 9 mm  
2.2 (s) 3 mm  
2.31 (S) 2 mm

$^{13}CMR$  = 30 (str.), 32 (w)  
34 (w), 56 (m), 210 (w)

- c) Explain chemical ionization technique in mass spectroscopy.

**P.T.O.**

d) How will you distinguish between following pair by mass spectroscopy.

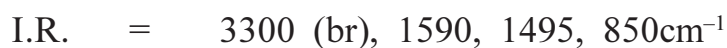
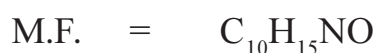


e) Explain : Protonated carbons exhibits stronger signals in  $^{13}\text{C}$ CMR. Justify with suitable example.

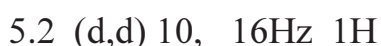
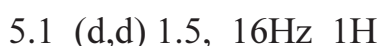
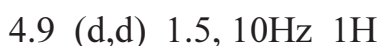
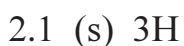
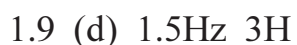
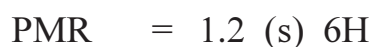
**Q2) A) Answer any three.**

**[9]**

a) Deduce the correct structure



b)  $\text{C}_{10}\text{H}_{16}\text{O}$



c)  $C_{11}H_{10}O_4$  (Compound gives + ve 2,4 DNP Test)

PMR = 3.96 (s) 12mm

6.08 (s) 8mm

6.48 (d) 8Hz 4mm

6.68 (d) 8Hz 4mm

6.70 (dd) 16, 8Hz 4mm

7.38 (d) 16 Hz 4mm

9.73 (d) 8Hz 4mm

d)  $C_{15}H_{14}O$

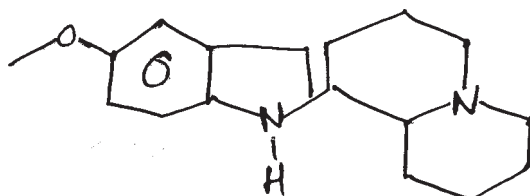
IR =  $1680\text{cm}^{-1}$

PMR = 2.4 (6H) s  $^{13}\text{CMR} = 21, 129, 133, 136, 141, 190$

7.2 (4H) d, 8Hz

7.7 (4H) d, 8Hz

B) Assign  $^{13}\text{CMR}$  signals and justify your answers with justify the assignments. [3]



$^{13}\text{CMR}$  : 22 (t), 25 (t), 26 (t), 30 (t), 54 (t), 55 (q), 56 (f), 61 (d), 106 (s), 111 (d), 117 (d), 118 (d), 121 (d), 128 (s), 136 (s), 137 (s).

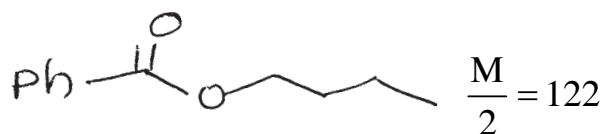
Q3) Write note on any three of the following. [12]

- Solomon's diagram in NOE.
- Factors affecting vicinal coupling.
- Cosy in spectra interpretation.
- DEPT technique.

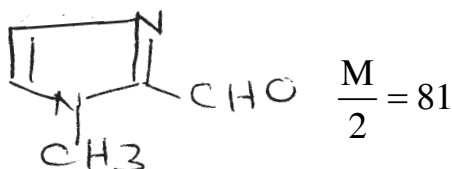
## SECTION - II

**Q4) a)** Explain the genes is of ions for any four of the following. **[8]**

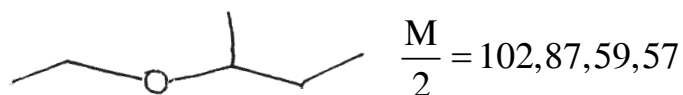
i)



ii)



iii)



iv)  $\text{HOCH}_2\text{CH}_2\text{SH}$   $\frac{M}{2} = 80, 78, 60, 48$

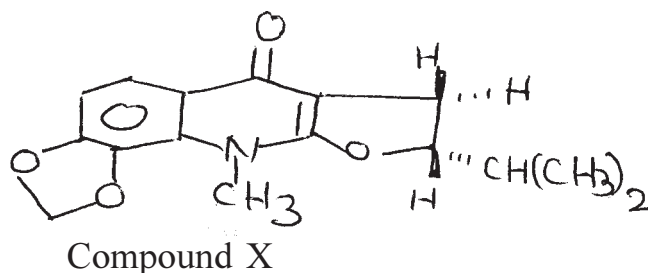
v)  $\text{H}_3\text{CCOCH}_2\text{CH}_2\text{COOH}$   $\frac{M}{2} = 116, 99, 98, 73$

b) Compound M with molecular formula  $\text{C}_6\text{H}_{12}\text{O}$  shows the following fragment ions along with the formation of metastable ions. Assign structure for M. **[4]**

$\frac{M}{2}$  : 100 (25%), 85 (5%), 57 (27%), 43 (100%), 72 (18%), 41 (27%), 29 (34%), 27 (15%).

Metastable ions : 72.25, 51.84, 25.14, 18.49.

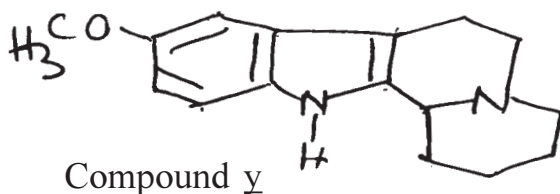
**Q5) a)** Assign the chemical shifts and comment on the observed coupling constants in compound X. **[8]**



$^1\text{H NMR}$  :  $\delta$  : 0.93 (d,  $J = 7\text{Hz}$ , 3H), 1.03 (d,  $J = 7\text{Hz}$ , 3H), 2.01 (Eight lines  $J = 7\text{Hz}$ , 1H), 2.25 (dd,  $J = 15$  &  $8\text{Hz}$ , 1H), 2.95 (dd,  $J = 15$  &  $10\text{Hz}$ , 1H), 3.80 (s, 3H), 4.76 (m, 1H), 6.02 (s, 2H), 7.03 (d,  $J = 9\text{Hz}$ , 1H), 8.07 (d,  $J = 9\text{Hz}$ , 1H)

What will be the change upon irradiation of signal at

- 2.01  $\delta$  and
  - 2.25  $\delta$  ?
- b) Assign the chemical shifts to various carbon atoms in compound y. [4]



$^{13}\text{C NMR}$  :  $\delta$  : 137 (s), 136 (s), 128 (s), 121 (d), 118 (d), 117 (d), 111 (d), 106 (s), 61 (d), 56 (t), 55 (q), 54 (t), 30 (t), 26 (t), 25 (t), 22 (t).

- c) Assign the structure to the compound using the following spectral data. [4]

Molecular formula :  $\text{C}_6 \text{H}_{11} \text{O}_2 \text{Br}$

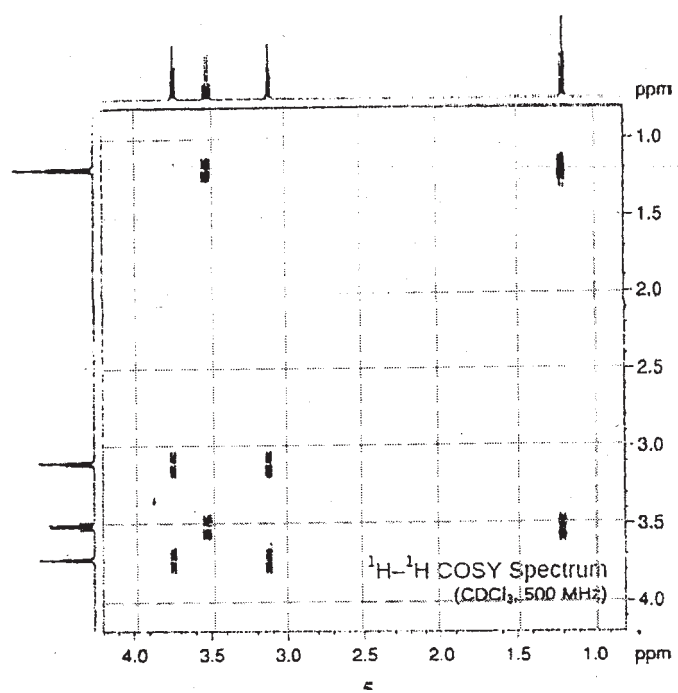
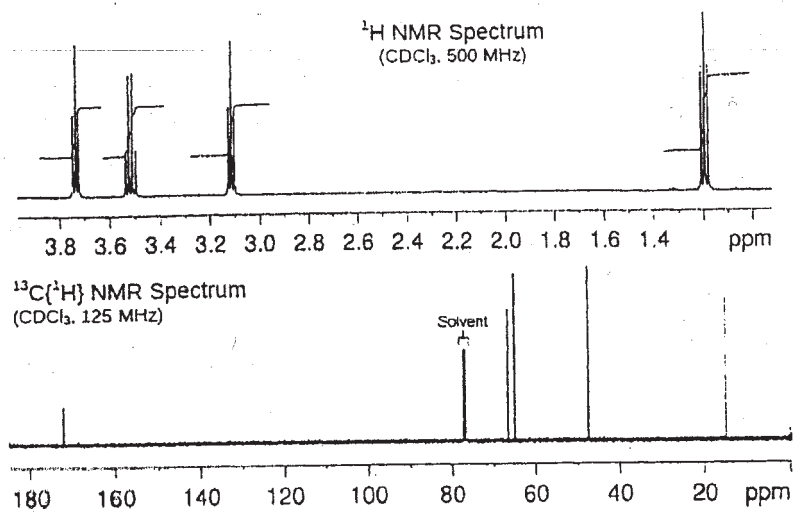
$^1\text{H NMR}$  :  $\delta$  : 1.25 (t,  $J = 6\text{Hz}$ , 3H), 2.25 (m, 2H), 2.5 (t,  $J = 6\text{Hz}$ , 2H), 3.5 (t,  $J = 6\text{Hz}$ , 2H), 4.15 (q,  $J = 6\text{Hz}$ , 2H)

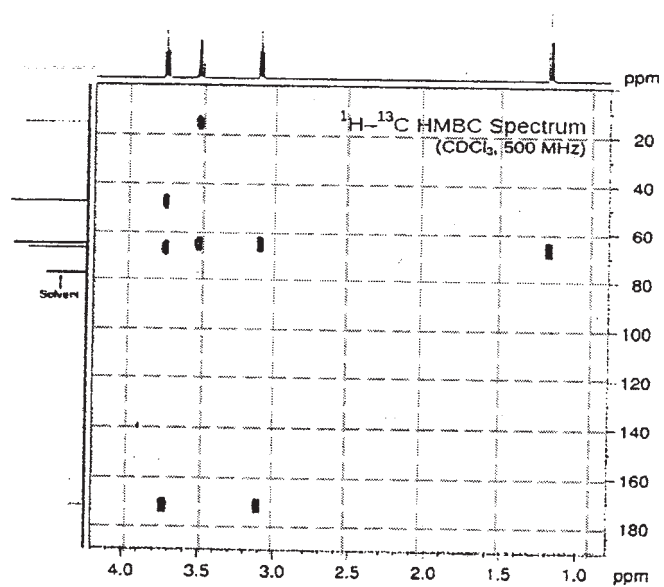
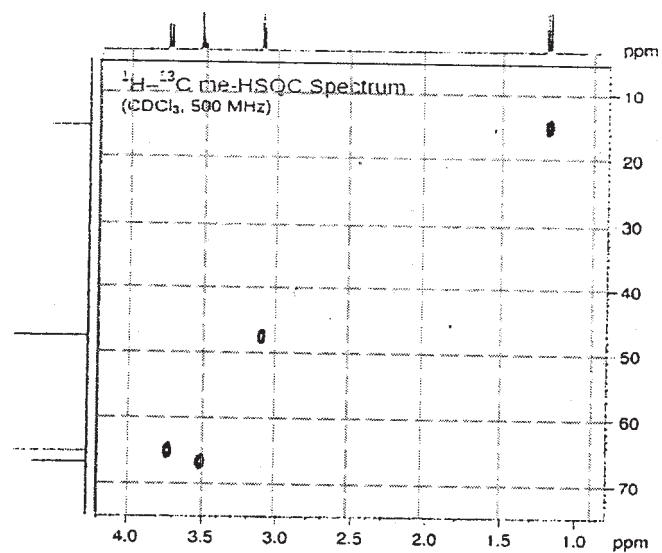
$^{13}\text{C NMR}$  :  $\delta$  : 15.0 (q), 27.0 (t), 31.2 (t), 31.5 (t), 60.0 (t), 173 (s)

**Q6)** The spectra of an unknown compound are shown on adjacent pages. [12]

Analyse the spectra and use to arrive at a correct structure of the unknown. Justify.

Molecular Formula: C<sub>5</sub>H<sub>9</sub>ClO<sub>2</sub>





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