Total No. of Questions : 6]

SEAT No. : ____

P1392

[Total No. of Pages : 5

[5123]-311
M.Sc. - II
ORGANIC CHEMISTRY
CHO - 351 : Spectroscopic Methods in Structure Determinations.
(2014 Pattern) (Semester - III) (4 - Credits)

Time : 3 Hours] ***[Max. Marks : 50***

Instructions to the candidates:

1) ***All questions are compulsory.***
2) ***Answer to the two sections to be written on two separate answer books.***
3) ***Figures to the right indicate full marks.***

SECTION - I

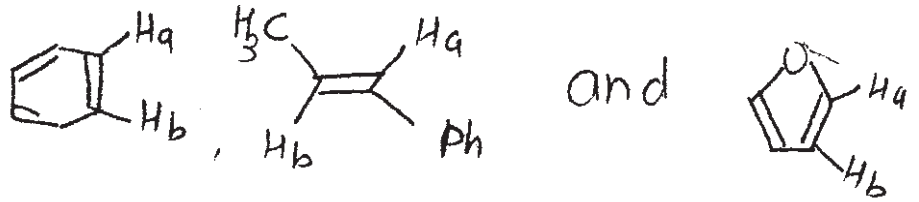
Q1) Answer any four of the following: **[8]**

a) $C_3H_6O_2$ shows two singlets of same intensities in its NMR at 2.3 & 4.0δ ppm. What is its probable structure.

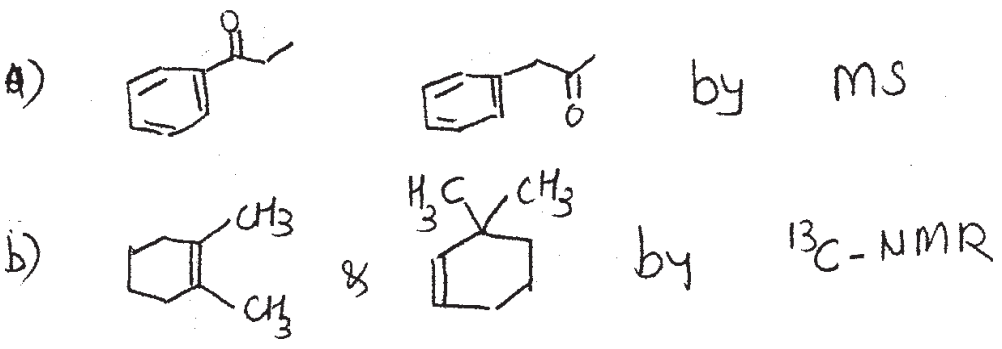
b) A compound shows Mt at 84 and base peak at 56 its PMR shows single peak at 1.4δ ppm. Assign the correct structure.

c) A compound with a molecular formula C_6H_8 shows only two signals inits ^{13}C-NMR. DEPT shows presence of CH & CH_2 assign probable structure.

d) Arrange the following compounds in decreasing order of Jvicinal. Justify your order.



e) Distinguish the following Pairs by indicated spectroscopic methods.



P.T.O.

Q2) Answer any three of the following: **[12]**

a) $C_7H_{14}O$ has two isomeric ketones whose PMR and CMR Signals are shorceu below assign the structures to each of the ketones from data provided.

i) PMR : 1.2 d (12 mm), 28(septet, 2mm

CMR : 18 (str), 38(m), 214(w)

ii) PMR : 1.0 s(9mm) 2.2 s(3mm) 2.31 (2mm)

CMR : 30(str), 32(w), 34(w), 56(m) 210(w).

b) A compound $C_6H_{10}O_2$ exhibits the following spectral data. Analyse the signals and arrive at a consistant structure. Justify your assignment.

CMR : 12(q); 13(q); 22(t); 127(s); 147(d) 174(s)

PMR : 1.17 t 7.5Hz 3H; 1.85d, 1.5Hz 3H; 2.2(dq. 7.5 & 6.3Hz 2H; 6.9, tq 1.5 & 6.3Hz 1H; 12.7 bs 1H

c) A compound with M+ 100 shows the following spectral data. Analyse the data systematicallyant arrive at a structure based on your analysis.

MS(M/z) : 100, 85, 71, 56, 44

CMR : 13(q); 20(t); 32(t); 68(t); 86(t); 152(d)

PMR : 1.0 t 7 Hz gmm; 14 m 6mm;

1.6 m 5.8 mm; 3.7 t 7Hz 6 mm

4.0 dd 9 & 2Hz 3 mm;

4.1 dd 13 & 2Hz 3 mm

6.5 dd 13 & 9 Hz 3 mm

Cosy : 6.5 $\leftrightarrow$ 4.0, 4.1

1.0 1.4

1.4 1.0, 1.6

1.6 1.4, 3.7

4.0 6.5

4.1 4.0

d) A compound with MF $C_{10}H_{12}O_2$ shows the following spectral data analyse data and arrive at a structure consistant with the data

CMR : 146; 144; 137, 132; 121. 2; 115.5; 114; 111; 56; 40

PMR : 3.3 bd 7Hz 2H; 3.87 S 3H; 4.52 bd 1H exchangeable; 5.03 ddt 17.2 & 1.2 Hz 1H; 5.15 ddt 9.7,2 & 1.2 Hz 1H; 5.95 ddt 17, 9.7 & 6.8 Hz 6.61 dd 8& 2 Hz 1H; 6.68 d 2Hz 1H; 6.85 d 8Hz 1H.

NOE : Irradiate at 6.68 $\rightarrow$ 3.32 & 3.87 line intensities increase.

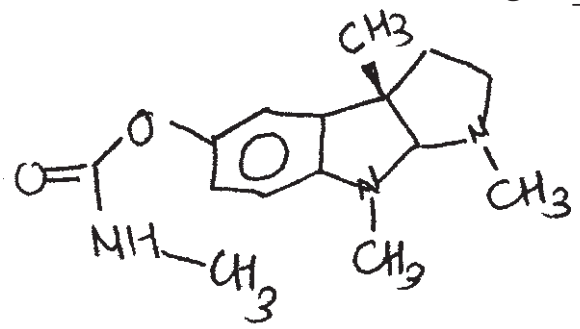
e) Assign the structure to the compound with MF $C_9H_{16}O_2$

IR : 1740 cm^{-1}

PMR : 0.9 (t, 7.6 Hz 3H); 1.3 (M, 4H); 1.65 (m.2H); 2.32(t 6.7 Hz 2H); 4.58 (d,7.8Hz, 2H); 5.21(d, 10.4Hz 1H); 5.32(d,15.9Hz 1H); 5.92 (ddt 7.8, 10.4 & 15.9 Hz 1H).

CMR : 13.9(q); 22.3(t); 24.7(t) 31.3(t); 34.2(t); 64.9(t); 118(t); 132(d) and 174(s)

Q3) Assign the signals to various protons in compound . Use decoupling data for the confirmations of the assignments justify your assignments. **[5]**



A

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1.4 2 S, 3H; 1.95 t 6Hz 2H; 2.55 s 3H; 2.7 t 6 Hz 2H; 2.82 d 6Hz 3H; 2.92 s 1H; 4.12 s 1H; 5.33q 6Hz 1H; 6.37d, 8Hz, 1H; 6.78 dd, 2Hz 1H; 6.87 dd, 8 & 2Hz 1H.

Irradiation Experiments:

a) Irradiation at 2.97 changes 2.70(t) to singlet

b) Irradiation at 2.82 changes 5.33(q) to singlet

c) Irradiation at 6.87 changes 6.37(d) & 6.78 (d) to singlet.

SECTION - II

Q4) Write the short notes on <u>any three.</u> **[9]**

a) Use of lanthanide shift reagents.

b) Spin decoupling techniques.

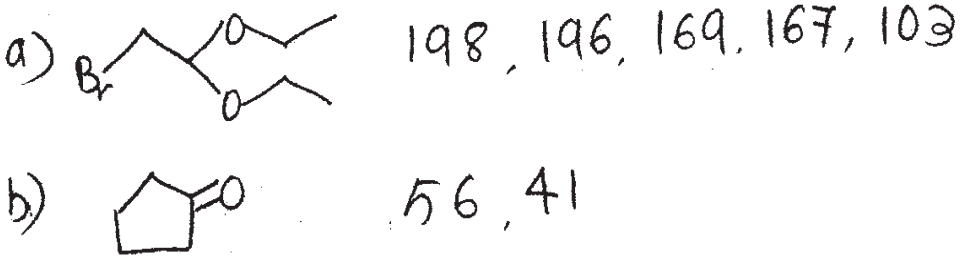
c) Factors affecting germinal coupling.

d) Double focusing technique in MS.

e) Use of DEPT & Off. resonance decoupling techniques in CMR.

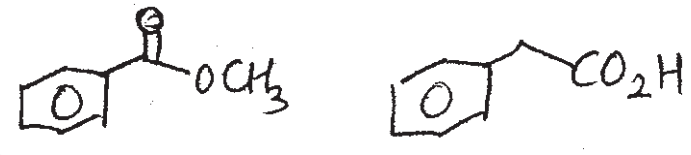
Q5) Answer any four of the following. **[8]**

a) Explain the genesis of ions in the following compounds



b) Explain in brief a working of electron impact mass spectrometry.

c) Differentiate the following compounds by MS

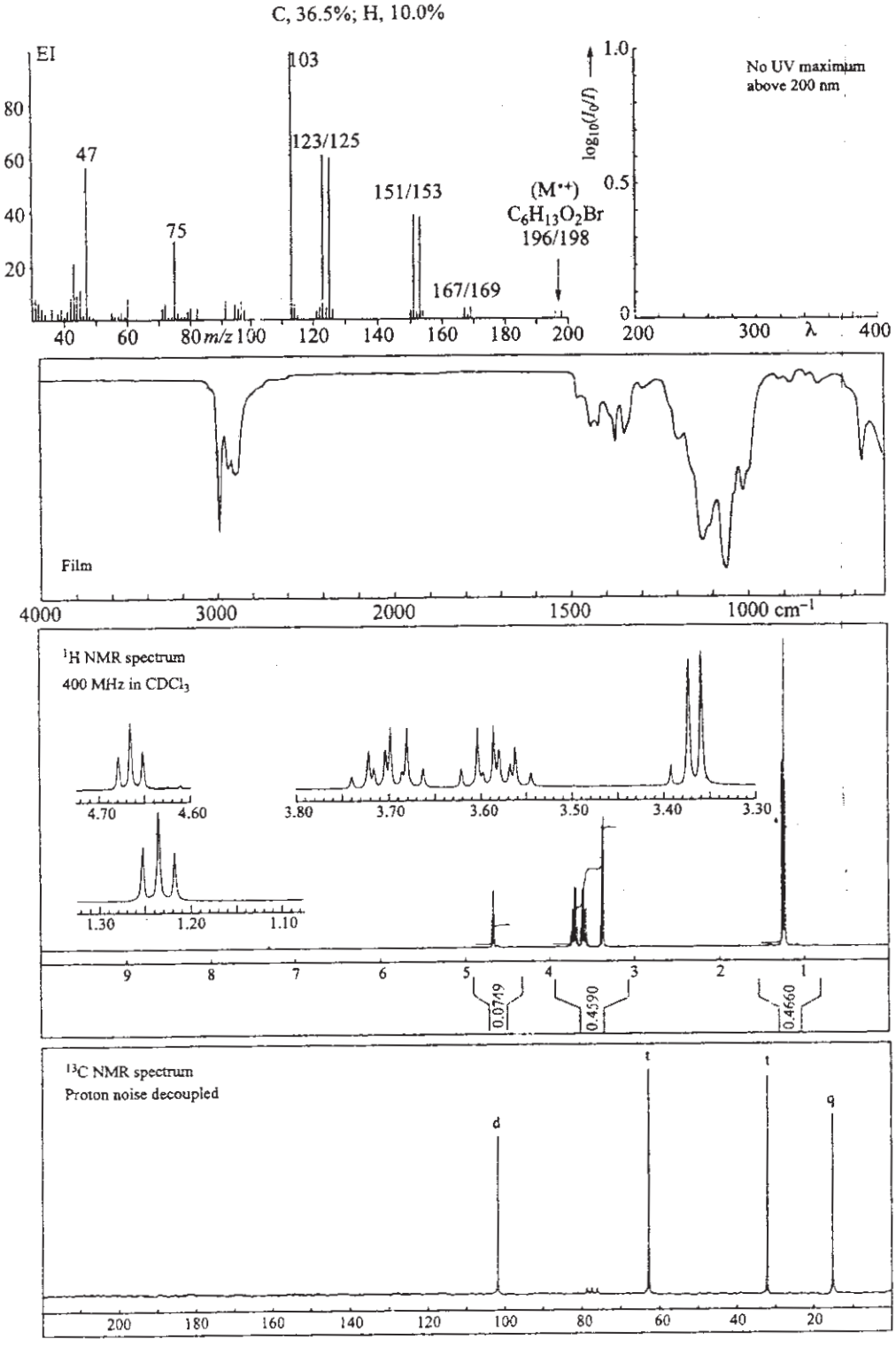


d) An amine $C_7H_{15}N$ shows the following ions in MS. Deduce probable structure

M/e:84(100%); 70, 56, 113, 98, 85

e) Explain the techniques used to arrive at the molecular formula in MS.

Q6) The spectra of all unknown compound are shown on the adjacent page Analyse the spectra and use to arrive at a correct structure of the unknown. Justify your assingnment. **[8]**


C, 36.5%; H, 10.0%
EI
103
123/125
47
75
151/153
167/169
(M•+)
C6H13O2Br
196/198
No UV maximum
above 200 nm
log10(I0/I)
m/z
λ
Film
1000 cm-1
1H NMR spectrum
400 MHz in CDCl3
13C NMR spectrum
Proton noise decoupled

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