PG – 649

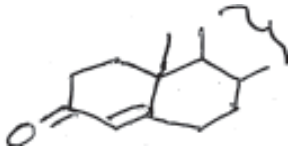
**III Semester M.Sc. Degree Examination, December 2016**
**(2010-11 Scheme) (NS) (Repeaters)**
**CHEMISTRY**
**C-304 : Spectroscopy – II**
**(Common to AC/IC/OC/PC)**

Time : 3 Hours Max. Marks : 80

***Instruction :*** *Answer question No.* ***1*** *and* ***any five*** *of the remaining.*

1. Answer **any ten** of the following : **(10×2=20)**

a) Cholest – 4 – en – 3 – one gives an enol acetate which has $\lambda_{max}$ at 238 nm. Suggest the structure for the enol.



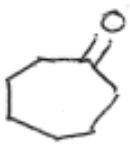
$\xrightarrow{Ac_2O}$ Enol acetate

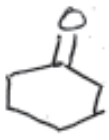
Cholest – 4 – en –
– 3 – one

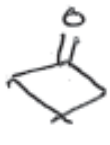
b) Aniline absorbs at 230 nm ($\in$ 8600) however, in acid solution the main absorption band is seen at 203 nm ($\in$ 7500) and is comparable with benzene. Why ?

c) A compound with molecular formula $C_4 H_9 Br$ gives the following signals in its $^1$H NMR spectrum. $\delta$ : 3.33 (d, 2H), 1.95 (m, 1H) and 1.04 (d, 6H). Assign its structure.

d) Account for the observed frequencies in the IR spectra of the following compounds :







$\nu_C = 0$ 1702 cm$^{-1}$ 1715 cm$^{-1}$ 1745 cm$^{-1}$ 1780 cm$^{-1}$.

e) How you will distinguish the following compounds using IR spectroscopy ?

$CH_3COCH_2COCH_2CH_3$ and $CH_3COCH_2CH_2CO\,CH_3$

f) N,N-Dimethylamine shows two signals for methyl groups in its $^1H$ NMR spectrum. Why ?

g) An organic compound with a molecular formula $C_6H_{10}O$ shows the following spectral data :

UV : $\lambda_{max}$ : 238 nm ($\in$ 11700)

IR ($cm^{-1}$) : 1695 and 1620

$^1H$ NMR ($\delta$) : 1.95 (s, 3H), 2.1 (s, 6H) and 6.15 (s, 1H)

Deduce its structure.

h) What do you mean by chemical and magnetic equivalence of protons ? Give an example.

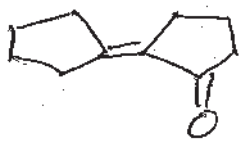
i) How will you distinguish between 3-methyl and 4-methyl-cyclohexene with the help of mass spectrometry ?

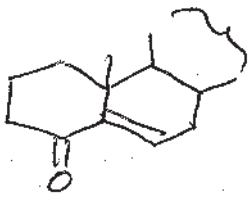
j) Predict the masses of the ions produced in the mass spectrum of 2-heptanone by the McLafferty rearrangement. Are these radical cations ?

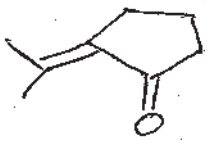
k) Ethyl benzoate in its mass spectrum show ions at M/Z = 88 and 60 and an abundant ion at M/Z = 71. Assign the structures for these fragments.

l) State nitrogen rule and mention its applications in mass spectrometry.

2. a) The following $\alpha,\beta$-unsaturated ketones have $\lambda_{max}$ at 241nm ($\in$ 4700), 254 nm ($\in$ 9550) and 259 nm ($\in$ 10790) in ethanol. Assign the values.

i) 

ii) 

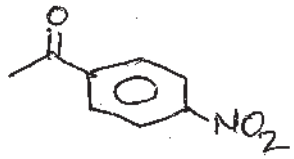
iii) 

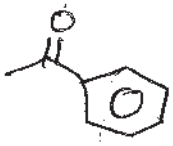
b) Discuss the theory and different types of electronic transitions in UV-Vis spectroscopy.

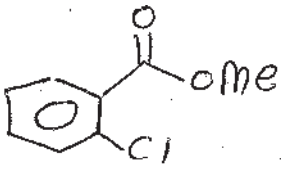
c) Explain the phenomenon of red shift and blue shift with appropriate examples. **(6+3+3=12)**

3. a) How will you distinguish the ortho- and para-aminophenols using IR spectroscopy ?

b) Explain the applications of IR spectroscopy in identification of the following compounds :

i) 


ii) 

iii) 


c) Discuss the complimentarity of IR and Raman spectroscopy with the help of suitable examples. **(3+6+3=12)**

4. a) Sketch the $^{1}H$ NMR spectra of pure and with acidic impurity of ethanol. Comment on their nature.

b) Explain why aromatic protons appear at higher $\delta$-value than the acetylene protons.

c) What are chemical shift reagents ? Discuss their applications with suitable example in $^{1}H$ NMR spectroscopy.

d) Write a note on nuclear overhauser effect. **(3+3+3+3=12)**

5. a) How will you distinguish n-butano, sec-butanol, tert-butanol and iso-butanol using $^{13}C$ NMR spectroscopy.

b) A neutral compound of molecular formula $C_{10}H_{12}O$ gave the following $^{13}C$ NMR signals,

$\delta$ : 22 (q), 68(d), 128 (d), 129 (d), 131(s),132 (d) and 166(s) with approximate observed relative intensities of 8 : 3 : 6 : 8 :1 : 3 :1. Deduce its structure. **(6+6=12)**

6. a) Describe the MALDI method of ionisation in mass spectrometry.

   b) Deduce the structure of an organic molecule having molecular formula $C_9H_8N_2O_2$ with the help of following spectral data :

   IR ($cm^{-1}$) : 3654, 2202 and 1683

   $^1H$ NMR ($\delta$) : 4-5 (s, 2H), 60(bs, 2H) and 7.1 – 8.1 (m, 4H)

   Mass (M/Z) : 176 ($M^+$), 118, 102, 77

   c) In the mass spectrum of acetophenone, predict a very stable fragment ion containing the aromatic ring and state how this will, in turn fragment.

**(4+4+4=12)**

7. a) Write briefly on off-resonance decoupled $^{13}C$-NMR spectrum.

   b) What is correlation spectroscopy (COSY) ? Sketch the COSY spectrum of m-dinitro-benzene and interprete the signals observed.

   c) Describe DEPT. Discuss its applications. **(4+4+4=12)**