PG – 562

III Semester M.Sc. Examination, December 2016
(CBCS)
CHEMISTRY
303 : Spectroscopy – II
(Common to AC/IC/PC)

Time : 3 Hours Max. Marks : 70

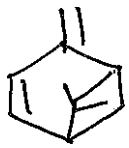
Instruction *: Answer Question No.* ***1*** *and* ***any five*** *of the remaining questions.*

1. Answer **any ten** of the following :

a) Predict the λ_{max} .

i)

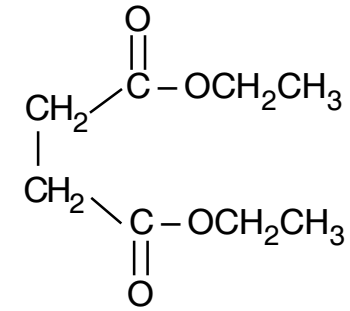
ii)



b) What is Pascal's triangle ? Explain with an example.

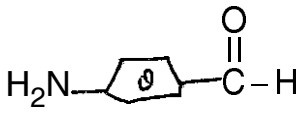
c) How many peaks are observed in the PMR spectrum of the following compounds ?

i)



ii) $HO - CH_2 - CH_2 - OH$

d) Give the important IR bands for the given compound.



e) Which is fingerprint region in IR spectroscopy ? Give its significance.

f) Illustrate using a diagram, how AX and AB ^{1}H-NMR spectra are distinguished ?

g) Illustrate nitrogen rule.

h) What is a mass spectrum ? Explain with an example.

i) Draw the components of a mass spectrometer.

j) Give the names of any two ionizing reagents used in CI-MS. Explain their role.

k) Give the possible fragmentation pathways for n-hexane.

l) How are benzamide and benzonitrile distinguished using IR spectroscopy ?

2. Write a note on the following :

a) Chemical shift reagents.

b) Nuclear Overhauser Effect (NOE). **(5+5=10)**

3. a) Each of the following compounds are characterised by ^{1}H-NMR spectrum consists of only one peak. Propose the structures and give the chemical shift values in δ scale.

i) C_4H_6

ii) C_3H_4

iii) C_4H_8.

b) Account for the peaks observed in the mass spectrum of the following compounds :

i) $CH_3 - (CH_2)_4 - CH_2Br$ – m/z = 135, 137, 85

ii) $(CH_3)_2 - CH - O - (CH_2)_4 - CH_3$ – m/z = 115, 71. **(6+4=10)**

4. Write a note on the following :

a) McLaffertry rearrangement.

b) Utility of IR spectroscopy in determination of hydrogen bonds. **(5+5)**

5. a) Summarize the Woodward rules for predicting λ_{max} for α, β-unsaturated aldehydes and ketones. Illustrate the use of these rules with two examples.

b) Use of HRMS to determine exact molecular weight of organic compounds. **(5+5)**

6. a) Deduce the structure of a compound with molecular formula C_3H_4O with the following data :

   IR : 2200, 3300, 3600 cm^{-1}

   ^{1}H-NMR : 2.5 (t, 1H)

   2.82 (br, s, 1H, D_2O exchangable)

   4.28 (d, 2H)

   ^{13}C-NMR : 67, 80, 62.

   b) Discuss the influence of ring size on carbonyl IR absorption in cyclic ketones.

   c) Write a note on molecular ion peak and base peak. **(3+3+4=10)**

7. a) Deduce the structure of the following compound from the given data and assign the values :

   Molecular formula : C_7H_9NO

   UV λ_{max} : 292 nm

   IR : 3457, 3370, 2905, 1617, 1411, 1076 cm^{-1}

   ^{1}H-NMR : δ = 7 – 0 – 6.89 (br, m), 3.97 (br, 2H) and 3.79 (s, 3H)

   ^{13}C-NMR : δ = 147, 136, 121, 118, 115, 110 and 55.

   MS (m/z crelabundance) : 123 (6%), 122 (2%), 94 (63%), 65 (100%), 28 (19%), 27 (22%).

   b) Explain the retro-Diels-Alder fragmentation in the mass spectrum. **(6+4)**

8. Write a note on the following :

   a) Chemical shift

   b) Tetramethyl Silane (TMS)

   c) Coupling constant. **(3+3+4=10)**