



III Semester M.Sc. Examination, January 2018
(CBCS)
CHEMISTRY
C – 303 – IC/PC/AC : Spectroscopy – II
(Common to Analytical Inorganic and Physical Chemistry)

Time : 3 Hours

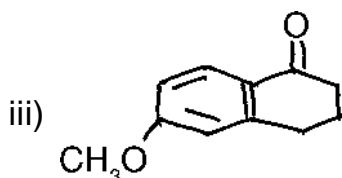
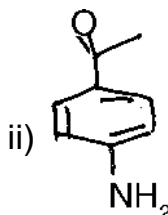
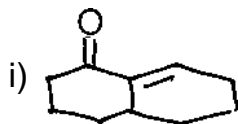
Max. Marks : 70

Instruction: Answer question number 1 and **any five** of the remaining.

1. Answer **any ten** of the following : **(10×2=20)**
- a) Distinguish chromophores and auxochromes with suitable examples.
 - b) Discuss the effect of increasing conjugation on λ_{\max} of polyenes.
 - c) How do you distinguish between the C = O group of a ketone, carboxylic acid and amide by their IR spectra ?
 - d) Name the most commonly used internal reference in proton NMR spectroscopy. Why it is preferred ?
 - e) How are (E) and (Z) – 2 – butene's differentiated by proton NMR ?
 - f) What is Nuclear overhauser effect ?
 - g) Sketch the broad band and off resonance ^{13}C NMR peaks of methyl and methylene groups.
 - h) How 1, 3, 5-trinitrobenzene and 1, 2, 3-trinitro benzene are differentiated by ^{13}C NMR spectroscopy ?
 - i) What are metastable ions ? How are they recognized in a mass spectrum ?
 - j) Explain the reason for the existence of M and M + 2 peaks for molecules containing bromine substituent.
 - k) Predict the mass spectral fragmentation pattern for 2-heptanone.
 - l) Define Nitrogen rule and explain taking suitable examples.
2. a) Describe the effect of intramolecular and intermolecular hydrogen bonding on the position of absorption frequency of a compound with suitable example.
- b) Distinguish between the following pairs of compounds using infrared technique.
- i) Ethanol and diethyl ether
 - ii) Propanal and propanone. **(5+5)**



3. a) Outline the Woodward-Fieser rules for conjugated dienes.
 b) Calculate the λ_{max} for the following compounds : Woodward Fieser rules.

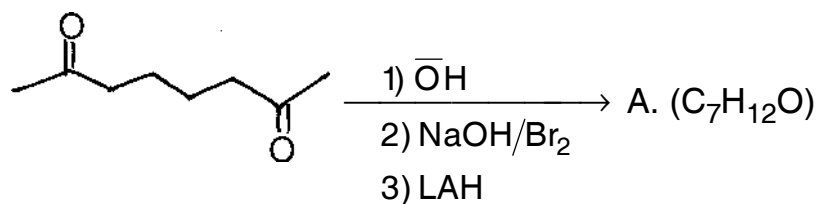


(5+5)

4. a) What are Lanthanide shift reagents ? How are they useful in ^1H NMR spectroscopy ?
 b) Explain the mechanism of spin-spin splitting and the rules for first order splitting in ^1H NMR. (5+5)
5. a) Describe anisotropic effects prevalent in aromatic hydrocarbons.
 b) Beckmann rearrangement of a bromoacetophenone oxime ($\text{C}_8\text{H}_8\text{BrNO}$) gives a major product having the following :
 ^1H NMR (δ , ppm) : 9.89 (s, 1H), 7.88 (s, 1 H), 7.45 (d, 1H, $J = 7.2$ Hz), 7.17 (m, 1H), 7.12 (d, 1H, $J = 7.0$ Hz), 2.06 (s, 3 H). Give the structure of the compound. (5+5)
6. a) Explain McLafferty rearrangement taking suitable example.
 b) Write a note on chemical exchange phenomenon in NMR spectroscopy. (5+5)
7. a) Write a note on fast atom bombardment and laser desorption ionisation.
 b) Two isomeric methyl esters with molecular formula $\text{C}_5\text{H}_{12}\text{O}$ have the following mass spectra :
 X : 88, 56, 45 (100), 41, 29, 27
 Y : 73, 59 (100), 45, 41, 29.
 Identify X and Y. Give justification to your answer. (5+5)



8. a) How is High Resolution Mass Spectrometry (HRMS) useful to determine the exact molecular formula of an organic compound ?
- b) A diketone undergoes following reaction giving a cyclic compound A, which shows following spectral data. Find the structure of the compound A and assign the values.



UV : 210 nm IR : 3400 cm⁻¹.

¹H NMR : δ 1.63 (s, 3H), 1.7 – 1.8 (m, 2H), 2.0 (bs exchangeable), 2.33 – 2.44 (m, 4H) 4.11 (s, 2H).

¹³C NMR : 13.7 (Q), 21.6 (t), 34.2 (t), 89.1 (t), 134.3 (s), 135.7 (s).

(5+5)

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