Q.P. Code : 60777

Third Semester M.Sc. Degree Examination, January/February 2020

(CBCS Scheme)

Chemistry

Paper C 303 : OC — ORGANIC SPECTROSCOPY

Time : 3 Hours] *[Max. Marks : 70*

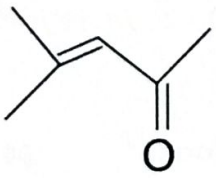
Instructions to Candidates : Answer question No. 1 and any five of the remaining.

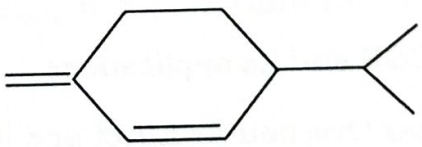
1. Answer any **TEN** of the following questions : **(10 × 2 = 20)**

(a) Explain why stretching frequency of carbon nitrogen triple bond is greater than that of single bond.

(b) Carbonyl compounds show weak bands >285 nm in their UV spectra. Account for the presence of the bands.

(c) Calculate the λmax for the followings :





(d) Mention the different types of electronic transitions in UV-Vis spectroscopy. Arrange them in the decreasing order of their energy.

(e) State the rule of multiplicity in ^{1}H NMR spectroscopy. Give an example.

(f) Name the different types of relaxation process in NMR. Which process is responsible for NMR phenomenon?

(g) Why ethylene protons are deshielded than acetylene protons?

(h) Define the terms chemical equivalence and magnetic equivalence of protons in NMR spectroscopy.

(i) What is matrix assisted laser desorption/ionization in mass spectrometry?

(j) How will you distinguish t-butyl benzene and isobutyl benzene by mass spectrometry?

(k) How will you distinguish the anthranilic acid and 4-aminobenzoic acid using IR spectrometry?

(l) How ^1H NMR spectroscopy is useful to differentiate between geometrical isomers?

2. (a) Explain why band position of both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of a compounds are shifted when solvent is changed from non-polar to polar.

(b) Discuss the factors affecting the group frequency in IR spectroscopy.

(c) Explain the applications of IR spectroscopy in the study of H-bonding. **(4 + 3 + 3 = 10)**

3. (a) Explain the first order and second order spin system with suitable examples in NMR spectroscopy.

(b) Write a note on chemical shift reagents and its applications. **(5 + 5 = 10)**

4. (a) Discuss the factors affecting the chemical shifts in ^1H NMR spectroscopy.

(b) Write briefly on :

(i) HETCOR and its applications.

(ii) Nuclear Overhauser Effect and its applications. **(4 + 3 + 3 = 10)**

5. (a) Explain MALDI and FAB methods of ionization.

(b) Write a note on McLafferty rearrangement and its applications. **(5 + 5 = 10)**

6. (a) Discuss the factors affecting the coupling constant in PMR spectroscopy.

(b) Deduce the structure of an organic compound with the help of the following data and assign the values :

Molecular formula : C_8H_8NOBr ;

UV-Vis (λ max) : 252 ; IR (cm^{-1}) : 3294, 3054, 1670, 1455, 1311 and 606 ;

^1H NMR (δ, ppm) : 10.03 (s, 1H), 7.64-7.39 (m, 4H), 2.05 (s, 3H) ;

EIMS (m/z) : 213, 211 (M^+), 173, 171, 92, 53 and 43 (base peak).

(5 + 5 = 1

7. (a) Discuss the 2-D homoannular correlation spectroscopy (COSY) with the help of suitable example.

(b) Deduce the structure of a organic compound with the help of following data and assign the values :

Molecular formula : C_8H_{14} ;

UV-Vis (λmax) : No strong band >200 nm ;

IR (cm^{-1}) : 2983, 2938, 1484 and 1338 ;

^1H NMR (δ, ppm) : 2.12 (t, 4H, J = 8Hz), 1.48 (sextet, 4H, J = 8Hz), 0.9 (t, 6H, J = 8Hz). **(5 + 5 = 10)**

8. (a) State and explain Nitrogen rule. How this rule is useful in structure elucidation of organic compounds?

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

(i) $CH_3(CH_2)_4CH_2Br$; m/z = 135, 137 and 85.

(ii) $(CH_3)_2CH-O-(CH_2)_4CH_3$; m/z = 115 and 71. **(5 + 5 = 10)**

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(CBCS Scheme)

Chemistry

Paper C 302 OC — CHEMISTRY OF NATURAL PRODUCTS

Time : 3 Hours] *[Max. Marks : 70*

Instructions to Candidates : Answer question No. 1 and any five of the remaining.

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

   (a) What is special isoprene rule? Draw the structure of limonene and mark the isoprene units.

   (b) What are terpenoids? Write the general classification of terpenoids.

   (c) Discuss the Nametkin rearrangement of camphene.

   (d) Write the synthesis of hygrine.

   (e) What is Ziesel's method? Mention its application in the alkaloid chemistry citing suitable example.

   (f) Formulate a synthesis of ephedrine.

   (g) Predict the products and name them :

   $$\text{Haemin} + \text{HI} \xrightarrow{\text{Acetic acid}} ?$$

   (h) Write the structure of purine and pyrimidine bases present in DNA.

   (i) How are hydroxyl groups of sugar in nucleic acid protected?

   (j) What are prostaglandins? Write the biological functions of prostaglandins.

   (k) What are insect pheromones? Give any two examples.

   (l) Write the structures of exo and endo-brevicomin.

2. (a) Describe the conversion of santonin into desmotroposantonin and santonic acid.

   (b) Elucidate the structure of gibberrillic acid. **(5 + 5 = 10)**

3. (a) Formulate the steps involved in the synthesis of beta-caryophyllene.

   (b) How was the structure of beta-carotene established? **(5 + 5 = 10)**