AQ – 824

First Semester M. Sc. Part–I Chemistry (CBCS) Examination

Paper – II

ORGANIC CHEMISTRY – I

P. Pages : 7

Time : Three Hours] [Max. Marks : 80

Note : All questions are compulsory and carry equal marks.

1. (a) Define the term Aromaticity. How is it related with Huckel rule ? Explain for benzenoid compounds. 6

   (b) Explain why cyclopentadiene is not aromatic while its anion is aromatic in nature ? 5

   (c) Discuss–Bonding in fullerenes. 5

OR

   (p) Comment on alternant and non–alternant hydrocarbons. 4

   (q) Which of the following species is aromatic ? Justify your answer :—

   (i) [10] Annulene (ii) [8] Annulene

   (iii) [20] Annulene 6

(r) Discuss in Brief :—

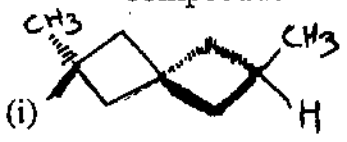
(i) Antiaromaticity

(ii) Aromatic characters of tropyllium cation. 6

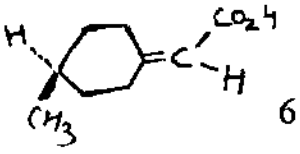
2. (a) What are diastereomers ? Bring out differences between enantiomers and diastereomers. 4

(b) What is asymmetric synthesis ? Give any two examples. 6

(c) Comment on 'optical activity' of following compounds.



(i)



(ii) 6

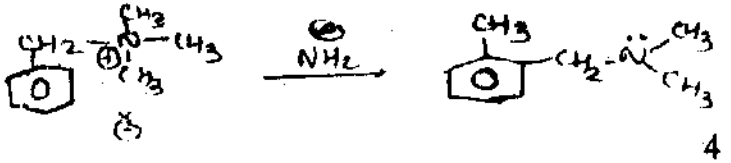
OR

(p) Write the two conformations of cis and trans isomers of 1– bromo – 4.t – butyl cyclohexane and comment on the favoured conformations in each case. 4

(q) How will you resolve racemic Lactic acid into optically active forms ? 4

(r) Comment on the chirality of unsymmetrical sulfoxides. 3

(q) Suggest the mechanism for this rearrangement.



4

(r) Discuss the Benzyne mechanism for Nucleophilic aromatic substitution. 4

(s) Comment upon cleavage of quaternary ammonium salt. 4

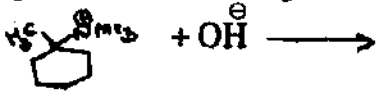
(b) Explain, how do the following factors affect the Aromatic Nucleophilic substitution.

(i) Structure of substrate.

(ii) Leaving group.

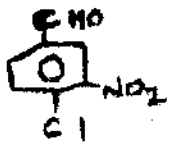
(iii) Attacking Nucleophile. 6

(c) Complete the following reactions :—

(i)  $+ \overset{\ominus}{O}H \longrightarrow$

(ii)  $\xrightarrow{CH_3I}$ $\xrightarrow{\Delta}$

(iii) $R-\underset{NO_2}{\overset{R}{C}}-\underset{NO_2}{\overset{R}{C}}-R \xrightarrow{Ca-Hg} ?$

(iv)  $+ NaOMe \xrightarrow{0^0C} ?$

4

OR

(p) State Saytzeff rule, Illustrate its mechanism by giving suitable example. 4

(s) What do you understand by symmetry elements ? Explain. 5

3. (a) Define and Illustrate the term kinetic Isotope effect. How does the knowledge of Isotope effect help is establishing the mechanism of a reaction ? Explain with suitable example. 6

(b) Comment on :—

(i) Steric effect.

(ii) Curtin–Hammet Principle. 6

(c) match the 'ϱ' (rho) value with appropriate reaction, justify your answer.

ϱ = + 2.51, ϱ = –2.69, ϱ = + 1.00, ϱ = + 0.79

(i) $ArCO_2H$ ionisation in H_2O.

(ii) $ArNH_2$ with Phcocl in C_6H_6.

(iii) $ArCO_2Et$ hydrolysis (Base) in ag etOH.

(iv) $ArCH_2$ Cl with $I^{\ominus}$ in $Me_2CO(20^0)$.

4

OR

(p) Discuss the physical significance of

(i) Reaction constant

(ii) Steric substituent parameter (Ès). 4

(q) What would be the products if the following hydrolysis were carried out in water labelled with 18_0 ? Explain.

(i) $CH_3-\overset{O}{\overset{\|}{C}}-O-C5H_{11}+H_2\overset{18}{O}\xrightarrow{\overset{\ominus}{OH}}$

(ii) $HO\,OCCH_2\,CH_2-\overset{O}{\overset{\|}{C}}-O\,C_2H_5+H_2\overset{18}{O}\xrightarrow{\overset{\oplus}{H}}$ 4

(r) Explain how T.S. resembles the reactant more than the product in exothermic reactions. 4

(s) Explain the ortho–para directing ability of (–OH) hydroxyl group in electrophilic aromatic substitution. 4

4. (a) What are carbene intermediates ? Explain the singlet and triplet structure of carbenes. 5

(b) What do you mean by ambient substrate ? With suitable example explain the regio-specificity. 5

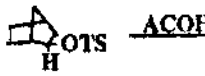
(c) Give an account of

(i) Dehydration using DCC.

(ii) Benzene intermediate. 6

OR

(p) Complete the following :—

(i)  ?

(ii) $R–Br + AgCN \longrightarrow$?

(iii) $C_2H_5-O-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{hr}$?

(iv)  $+CH_2I_2+Z_n\,(C_4)\xrightarrow{ether}$? 4

(q) What are carbanions ? Discuss the structure and stability of carbanions. 5

(r) Discuss the mechanism, stereochemistry and effect of nucleophilicity in SN^2 reaction. 5

(s) Give the structure and type of intermediate formed in the following reactions :—

(i) $CH_3CH\,(OH)\,CH_3 + H^{\oplus} \xrightarrow{\Delta} ? + H_2O.$

(ii) $CH_3\,CH_2-N=N-CH_2-H_3 \xrightarrow{\Delta} ? + N_2.$ 2

5. (a) Give an account for syn and anti elimination. 6