

**N26-103**

**December-2014**

**M.Sc., Sem.-I**

**402 : Chemistry**

**Paper – II**

**(Organic Chemistry)**

**Time : 3 Hours]**

**[Max. Marks : 70**

- Instructions :** (1) All questions are compulsory.  
(2) Figures to right indicate full marks.

1. Answer the following :

- (A) (i) Compare,  $E_1$ ,  $E_2$  and  $E_1$  CB pathways. (12) 4  
(ii) Compare Chugaev and Cope reactions with suitable examples. (6) 3

**OR**

- (i) Explain Saytzeff's rule with two supporting evidences.  
(ii) Discuss  $E_1$  CB reaction with supporting evidence.

- (B) (i) Discuss the stereochemistry of the products obtained by the reaction of 2-bromo propionate ion separated with (i) Dilute alkali solution (ii) Strong alkali solution. (4) 4

- (ii) 2-methyl-3-butenol-2 under the influence of dilute aq. acid forms 3-methyl-2-butenol-1 as the major product. Give the mechanism of the reaction and explain why 3-methyl-2-butenol-1 is the major product. (2) 3

**OR**

- (i) Acetolysis of erythro 3-phenyl-2-tosyl butane gives erythro-3-phenyl-2-acetyl butane with retention of configuration whereas its threo isomer gives racemic mixture.

- (ii) Discuss mixed  $SN^1$  and  $SN^2$  mechanism with suitable examples.

2. Answer the following :

- (A) (i) What is azulene ? How can NMR spectra and bond length criteria be used to check aromaticity ? (2) 4  
(ii) State the Huckel's rule of aromaticity and define aromaticity, non aromaticity and antiaromaticity with one example each. (3) 3

**OR**

- (i) What is diatropic current ? Discuss its role in determining aromaticity. (6) 4  
(ii) Prepare HOMO diagram for benzene and cyclobutadiene using Frost Circle method. Discuss their aromatic character. (6) 4

(B) (i) Prove that amide ion is better base for ionizing acetylene as compared to hydroxide ion. Given  $P_{ka}$  for  $NH_3$ ,  $CH \equiv CH$  and  $H_2O$  is 35, 25 and 16 respectively.

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(ii) Discuss the application and limitation of Hammett equation.

3

OR

(i) Explain with suitable examples the effect of hybridization and field effect on the strength of acid.

(ii) Give Hammett equation. Explain all the terms involved in it and show that the Hammett equation is a linear free energy relationship.

3. Answer the following :

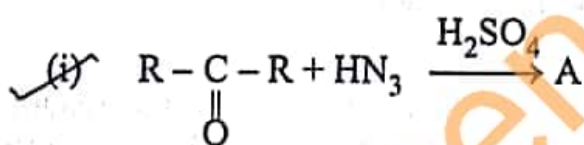
(A) (i) Discuss the mechanism for transformation of six membered cyclic ketone to seven membered lactone in presence of per acid.

4

(ii) Give introduction, mechanism and two applications for rearrangement of hydroperoxide.

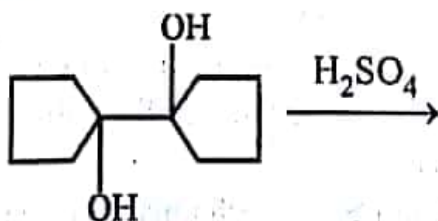
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OR



Identify product A. Name the rearrangement and offer suitable mechanism for this conversion.

(ii) Complete the following reaction and give mechanism.



(B) (i) What are nitrenes? Give two methods for generation of nitrenes? Explain Hoffman rearrangement.

(ii) Discuss three different reactions in which carbanion are a reactive intermediate.

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OR

(i) Discuss the structure and stability of Carbocation.

(ii) Discuss the structure of Carbenes.



4. Answer the following :

(A) (i) Discuss the stereochemistry of sulphoxides. 4

(ii) Discuss the stereochemistry of spirans. 3

OR

Discuss the stereochemistry of Quarternary ammonium salts. 7

(B) Explain stereoselective and stereospecific reactions. Describe any three methods for resolution of racemates. 7

OR

Discuss the stereochemistry of biphenyl compounds.

5. Answer the following :

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(i) Write conversion of tetramethelene chlorohydrine to tetra hydrofuran.

(ii)  $\beta, \beta'$  - dichlorodiethyl sulphide is hydrolysed much more readily than corresponding oxygen analogue. Give reason.

(iii) What is allylic rearrangement?

(iv) Explain Homoaromatic system.

(v) Protonation of Pyrrole is occurring on carbon and not on nitrogen. Explain.

(vi) Why compared to [14] annulene, [18] annulene is stable?

(vii) Why chloroform is more acidic than fluoroform?

(viii) Give correct order for the stability of free radicals.

(ix) Write principle of Favorskii rearrangement.

(x) What is non-classical carbonium ion?

(xi) Give example of quasi-Favorskii rearrangement.

(xii) Explain diastereotopic atoms.

(xiii) Explain helicity.

(xiv) Giving example discuss prochirality.