

NQ-127
December-2015
M.Sc., Sem.-I
402 : Chemistry
(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) Explain how meso (erythro) 1,2-dibromo 1,2-diphenyl ethane yields cis product while its dl (threo) form gives trans product through E2 reaction. 4
- (ii) Discuss E1CB reaction with supporting evidences. 3

OR

- (i) Explain Hofmann's and Saytzeff's rule of elimination with suitable illustrations.
- (ii) Compare Chugaev and Cope reaction with suitable examples.
- (b) (i) Base catalysed hydrolysis of β -dichloro diethyl sulphide in dioxane proceeds thousand times faster as compound to β -chloro diethyl ether. Explain. 4
- (ii) Conversion of trans 5-methyl-2-cyclohexenol to trans 3-chloro-5-methyl cyclohexene with retention of configuration. Name the reaction and explain giving mechanism. 3

OR

- (i) Ethanolsis of conjugate base of 2-(p-hydroxy phenyl) ethyl bromide occurs much faster than 2-(p-methoxy phenyl) ethyl bromide. Explain giving suitable mechanism.
- (ii) Discuss mixed SN1 and SN2 mechanism with suitable examples.

2. Answer the following :

- (a) (i) What is diatropic current ? Discuss its role in determining aromaticity. 4
(ii) Prepare HMO diagram for cyclopropenyl anion and cycloheptatrienyl cation using frost circle method. Discuss their aromatic character. 3

OR

- (i) State the Huckel's rule of aromaticity and explain the terms antiaromaticity and non-aromaticity.
(ii) Discuss the aromaticity in different annulenes.
- (b) (i) Explain with suitable example hybridisation and field effect on the strength of acid. 4
(ii) Give Hammett equation. Explain the terms involved in it. 3

OR

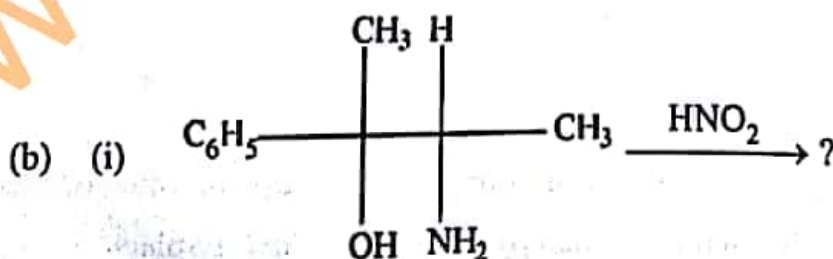
- (i) Guanidine is stronger base than amine. Explain.
(ii) Discuss the application and limitations of Hammett equation.

3. Answer the following :

- (a) (i) What are free radicals ? How they are generated ? Discuss their stability. 4
(ii) Discuss the structure of and stability of carbocation. 3

OR

- (i) What are carbenes ? Discuss the stereo selectivity of singlet and triplet carbenes with suitable examples.
(ii) Discuss any three reactions in which carbanion is a reactive intermediate.



Identify the rearrangement and offer suitable mechanism for this conversion.

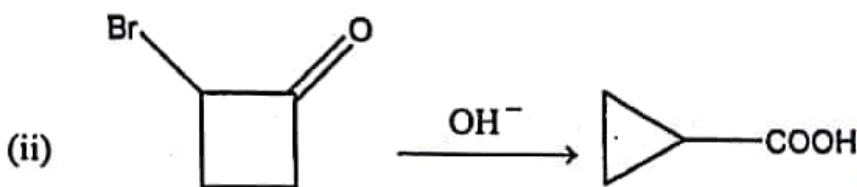
4

- (ii) Discuss the mechanism and application of Baeyer-Villiger rearrangement. 3

OR

- (i) Ethyl aceto acetate + $\text{HN}_3 \xrightarrow{\text{H}_2\text{SO}_4} ?$

Complete the reaction, identify the rearrangement and give its mechanism.



Identify the rearrangement and give its mechanism.

4. Answer the following :

- (a) Discuss the stereoselective and stereospecific reactions. Describe any three methods of resolution of racemates. 7

OR

Discuss the stereochemistry of quaternary ammonium salts.

- (b) Discuss the stereochemistry of spiranes and sulphoxides. 7

OR

Discuss the stereochemistry of allenes.

5. Answer the following :

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- (i) Write conversion of tetramethylene chlorohydrine to tetrahydrofuran.
(ii) Explain anchimeric assistance.
(iii) Write mono hydrolysis product of mustard gas.
(iv) Give example of Single Electron Transfer (SET) reaction.
(v) What is homoaromatic system ?
(vi) Why compared to [14] annulene, [18] annulene is stable ?

- (vii) Explain the effect of hydrogen bonding in determining the strength of acid.
 - (viii) What are bridged carbocations ?
 - (ix) Write principle of Favorsky rearrangement.
 - (x) What are nitrenes ?
 - (xi) Define homotopic and enantiotropic atom.
 - (xii) Mention various types of configurational isomers.
 - (xiii) Explain helicity.
 - (xiv) How acid azides are converted to corresponding urethanes ?
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