

Seat No. : _____

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) Ethanolysis 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

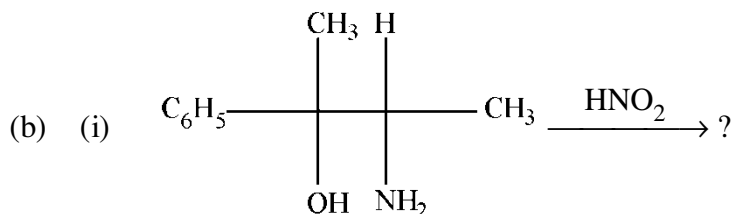
- (i) Guanidine is stronger base than amine. Explain.
(ii) Discuss the application and limitations of Hammett equation.

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.



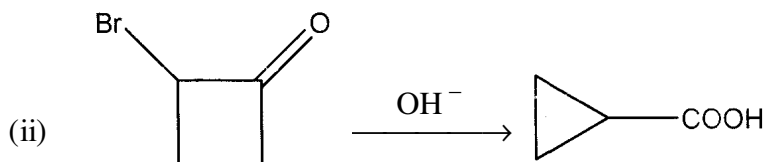
Identify the rearrangement and offer suitable mechanism for this conversion. **4**

- (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 quarternary ammonium salts.

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

OR

Discuss the stereochemistry of allenes.

5. Answer the following : 14

- (i) Write conversion of tetramethelene chlorohydrine to tetra hydrofuran.
- (ii) Explain anchimetric 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 ?
-