

Seat No. : 246

E-687

December-2010
Sem - I

Time : 3 Hours]

[Max. Marks : 70

1. (a) (i) Explain eclipsing effect in E_2 elimination with suitable examples. 7
(ii) Explain Saytzeff and Hoffmann's rule of elimination with illustrations.

OR

- (i) Compare E_1 , E_2 and $E1CB$ pathways.
(ii) Compare Chugaev and Cope reactions by citing suitable examples.
(b) (i) Discuss single electron transfer mechanism in nucleophilic substitution reactions giving proper examples. 7
(ii) Acetolysis of erythro 3-phenyl-2-tosylbutane gives erythro-3-phenyl-2-acetyl butane with retention of configuration, while its threo isomer gives racemic mixture. Explain.

OR

- (i) Discuss mixed SN_1 and SN_2 mechanism with suitable examples.
(ii) Discuss nucleophilic substitution at an allylic carbon.

2. (a) (i) Prepare HMO diagram for benzene and cyclobutadiene using frost-circle method. Discuss their aromatic character. 7
(ii) Discuss aromaticity in different annulenes.

OR

- (i) What is diatropic current ? Discuss its role in determining aromaticity.
(ii) Benzene is aromatic but its isomer fulvene is non-aromatic. Explain.
(b) (i) Give Hammett equation and explain all the terms of the equation. 7
(ii) Explain : Salicylic acid is more acidic than p-hydroxy benzoic acid.

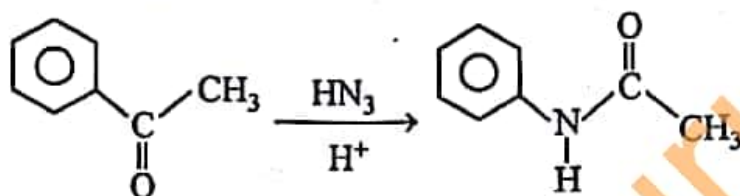
OR

- (i) Discuss the importance and limitations of Hammett equation. Explain deviation from Hammett equation.
(ii) Discuss the effect of resonance on the strength of an acid giving suitable examples.

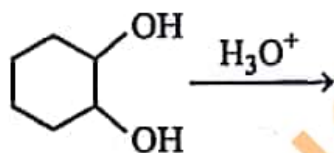
3. (a) (i) Discuss the structure of carbenes. 7
 (ii) Explain with illustrations the stability and reactivity of free radicals.

OR

- (i) What are nitrenes? Give two methods of generation of nitrenes.
 (ii) Explain the stability of aliphatic carbocations on the basis of resonance energy and electron density.
- (b) (i) Identify the rearrangement in the following transformation and give the mechanism: 7

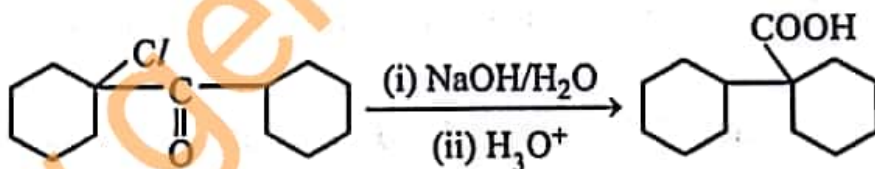


- (ii) Complete the following reaction and give its mechanism.



OR

- (i) Identify the rearrangement in the following transformation and give the mechanism



- (ii) Give introduction, mechanism and two applications of rearrangement of hydroperoxides.

4. (a) Discuss the stereochemistry of sulphoxides with suitable examples. 7

OR

Discuss the stereochemistry of allenes.

- (b) (i) Discuss dynamic resolution.
 (ii) Discuss the stereochemistry of quaternary ammonium salts. 7

OR

Discuss the stereochemistry of biphenyl derivatives.

5. Answer the following questions in brief :

14

- (1) Give one example of anchimeric assistance.
- (2) Give the factors which effect the overall reactivity of elimination reactions.
- (3) β , β' -dichloro diethyl sulphide is hydrolysed much more readily than corresponding oxygen analogue. Give reason.
- (4) Explain : Antiaromaticity.
- (5) Which is the strongest base of the following ? Why ?
Pyridine, Acetonitrile, Trimethylamine.
- (6) Define Huckel's Rule.
- (7) What is the product of the following reaction ?
$$\text{CH}_3 - \underset{\text{O}}{\parallel}{\text{C}} - \underset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3 \xrightarrow{\text{RCO}_3\text{H}} ?$$
- (8) What is a non-classical carbonium ion ?
- (9) Give the probable mechanism of carbylamine reaction.
- (10) Give the order of stability of the following carbanions.
 1° , 2° , 3° , benzyl carbanion.
- (11) What is a prochiral centre ? Give one example.
- (12) Define stereospecific and stereoselective reaction.
- (13) What are spirans ?
- (14) Explain Homoaromatic system.