

D-504

December-2011

Sem - I

Time : 3 Hours]

| Max. Marks : 70

- Instructions : (1) Figure to the right indicates full marks.
 (2) All questions are compulsory.

1. Answer the following :

- (a) (i) 2 - Methyl cyclohexanol undergoes dehydration to yield a mixture of 1 - methyl cyclohexene and 3 - methyl cyclohexene. Formulate and explain giving suitable reason. 7
 (ii) Compare E_1 , E_2 and E_1 CB Pathways. 3

OR

- ✓ (i) Explain Zaitsev's rule and Hoffmann's rule of elimination reaction. Explain E_1 and E_2 eliminations in " $\text{Me}_2\text{CH}-\overset{+}{\text{C}}\text{H}-\text{Me}_2$ ".

- ✓ (ii) What are xanthate esters? Discuss their preparation and pyrolysis.

- (b) (i) β , β' - dichloro diethyl sulphide is hydrolysed much more readily than corresponding oxygen analogue. Explain. 7

- (ii) What is allylic rearrangement? Explain allylic rearrangement giving suitable example. 6

OR

- ✓ (i) β - (p - Hydroxy Phenyl) ethyl bromide undergoes ethanolysis more than 100 times faster than β - (p - methoxy phenyl) ethyl bromide. Explain giving mechanism.

- ✓ (ii) Explain Single Electron Transfer (SET) mechanism by giving suitable example.

2. (a) (i) Prepare HMO diagram for cycloheptatrienyl ions using Frost circle method. Discuss their aromatic character. 7

- (ii) Write a note on azulenes. 6

OR

- ✓ (i) Discuss : Aromaticity and ring current.

- ✓ (f) Prepare HMO diagram for benzene and cyclobutadiene using Frost circle method. Discuss their aromatic character.
- (b) (i) Guanidine is a strong base. Explain.
- ✓ (ii) Discuss the applications & limitations of Hammett equation. Explain deviation from Hammett equation.

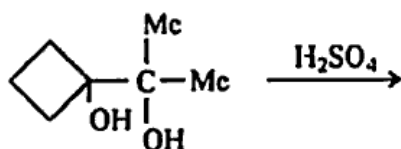
OR

- (i) Comment on the acidity of C – H bond in a Haloform.
- (ii) Give Hammett equation. Explain all the terms and show that the Hammett equation is a linear free energy relationship.

3. (a) (i) Compare the reactions of carbenes with that of nitrene.
- ✓ (ii) Discuss the stability of carbocations.

OR

- (i) Discuss methods of generating free radicals and also discuss their stability.
- (ii) Discuss three different reactions in which carbanion is a reactive intermediate.
- (b) (i) Predict the product for the following reaction and explain its formation.



- (ii) Give the conversion of Ethyl Phenyl Acetate to Benzyl Amine. Give the mechanism of the reaction.

OR

- (i) Discuss migratory aptitudes of different aryl groups in Baeyer Villiger rearrangement.
- (ii) Discuss the mechanism & applications of Schmidt rearrangement.
4. (a) (i) Discuss dynamic resolution.
- (ii) Discuss the stereochemistry of Sulphonium salts.

OR

- ✓ (i) Explain : Stereoselective and Stereospecific reactions.

- ✓ (ii) What are spirans ? Discuss their stereochemistry.
 (b) Discuss the stereochemistry of nitrogen compounds.

7

OR

✓ Discuss the stereochemistry of Allenes.

5. Answer the following questions in brief :

14

- (1) Give one example of nucleophilic substitution reaction involving mixed SN^1 and SN^2 mechanism.

✓ (2) Give one example of anchimeric assistance.

✓ (3) What is COPE reaction ?

✓ (4) Explain Homoaromaticity.

✓ (5) Give limitations of Huckel's rule.

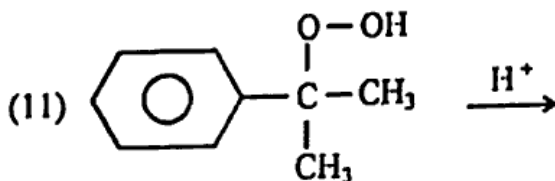
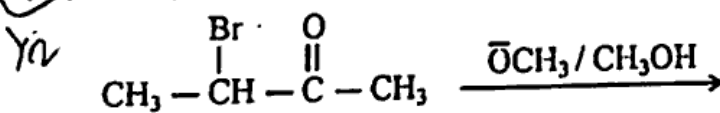
- (6) $\sigma_{p(NO_2)} = + 0.78$ and ρ value of benzoic acid ionization is 1.0. From these values how will you predict that p - nitrobenzoic acid is nearly six times stronger acid than benzoic acid.

✓ (7) Which acid is the strongest acid of the following acids ? Due to which effect ?
 $HCOOH$, $ClCH_2COOH$, CH_3COOH , FCH_2COOH

(8) Explain non-classical carbocations.

✓ (9) Give one method to generate carbenes.

✓ (10) Complete the following reaction & identify the rearrangement :



(12) Explain diastereotopic atoms.

(13) Explain Helicity.

(14) What is atropisomerism ?