Seat No. : 237

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.

(ii) Compare E_1, E_2 and E_1 CB Pathways.

OR

(i) Explain Zaitsev's rule and Hoffmann's rule of elimination reaction. Explain E_1 and E_2 eliminations in "Me_2 CH CH MeS$^+$ 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.

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

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.

(ii) Write a note on azulenes.

OR

(i) Discuss : Aromaticity and ring current.

(ii) Prepare HMO diagram for benzene and cyclobutadiene using Frost circle method. Discuss their aromatic character.

(b) (i) Guanidine is a strong base. Explain. 7

(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. 7

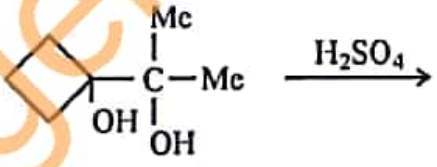
(ii) Discuss the stability of carbocations.

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. 7



(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.

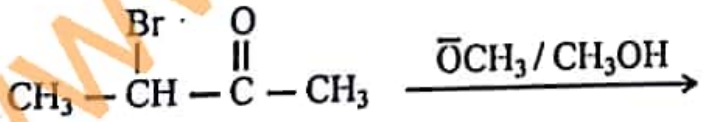
(7) Which acid is the strongest acid of the following acids ? Due to which effect ?

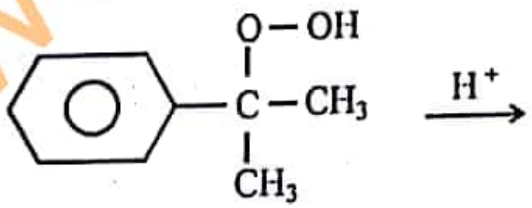
HCOOH, $Cl\,CH_2COOH$, CH_3COOH, FCH_2COOH

(8) Explain non-classical carbocations.

(9) Give one method to generate carbenes.

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



(11) 

(12) Explain diastereotopic atoms.

(13) Explain Helicity.

(14) What is atropisomerism ?