

Seat No. : _____

MR-129
December-2016
M.Sc., Sem.-I
402 : Chemistry
(Organic Chemistry)

Time : 3 Hours]

[Max. Marks : 70

- Instructions :** (1) All questions are compulsory.
(2) Figures to the right indicate full marks of that question.

1. (a) Answer the following : 7
- (1) Explain why meso-2,3-dibromobutane in presence of iodide ion undergoes elimination to give trans-2-butene, while that of d/l isomer gives cis-2-butene. Justify.
- (2) Discuss orientation in elimination reaction giving suitable example.

OR

- (a) Answer the following :
- (1) Discuss pyrolysis of esters with mechanism.
- (2) Explain why erythro-1,2-dibromo-1,2-diphenylethane gives cis product while that of threo isomer yields trans product in E2 reaction.

- (b) Answer the following : 7
- (1) Ethanolysis of β -(para-hydroxyphenyl) ethyl bromide is much faster than its β -(para-methoxyphenyl) ethyl bromide – Justify with mechanism.
- (2) Reaction of 2-methyl-3-buten-1-ol in presence of dilute aq. acid gives 3-methyl-2-buten-1-ol as the major product – Justify giving its mechanism.

OR

- (b) Answer the following :
- (1) Discuss why (S)-bromopropionic acid when reacts with Conc. KOH gives (R)-lactic acid, while the same reaction in presence of dilute aq. KOH and Ag_2O gives (S)-lactic acid.
- (2) Discuss NGP in base catalysed hydrolysis of mustard gas.

2. (a) Answer the following :

7

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

OR

(a) Answer the following :

- (1) What is azulene ? How can NMR spectra and bond length criteria are useful to determine aromaticity ?
- (2) Cyclopropenyl cation is aromatic, while cyclopropenyl anion is antiaromatic – Justify.

(b) Answer the following :

7

- (1) Write Hammett equation, explain each term and show that Hammett equation is a linear free energy relationship.
- (2) Discuss effect of H-bonding and solvation effect on the strength of acid.

OR

(b) Answer the following :

- (1) Discuss the applications and limitations of Hammett equation.
- (2) Discuss the effect of hybridization and field effect affecting the acidity giving suitable example.

3. (a) Answer the following :

7

- (1) What are nitrenes ? Give two methods for the generation of nitrenes.
- (2) Discuss methods to distinguish singlet and triplet carbenes.

OR

(a) Answer the following :

- (1) Discuss three different reactions in which carbocation is a reactive species.
- (2) What are free radicals ? How they are generated ? Discuss their stability.

(b) Answer the following :

7

- (1) Discuss reaction mechanism and application of Pinacol-pinacolone rearrangement.
- (2) Name the rearrangement used for the conversion of ethyl phenyl acetate to benzyl amine. Give its mechanism.

OR

(b) Answer the following :

- (1) Discuss reaction mechanism and applications of Favorskii rearrangement.
- (2) Which rearrangement is used in the conversion of $\text{RCOOH} \rightarrow \text{RCOOR}$? Discuss with mechanism.

4. (a) Answer the following :

7

- (1) Discuss required conditions for biphenyls to be optically active.
- (2) Discuss stereochemistry of quaternary ammonium salts.

OR

(a) Answer the following :

- (1) Discuss stereochemistry of oxyphosphines.
- (2) Write a note on asymmetric synthesis.

(b) Answer the following :

7

- (1) Discuss chemical and biochemical techniques for resolution.
- (2) Discuss stereoselectivity and stereospecificity with suitable example.

OR

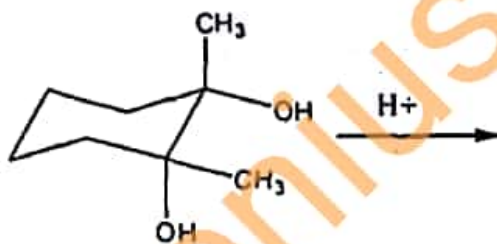
(b) Answer the following :

- (1) Discuss prochirality giving suitable example.
- (2) Discuss stereochemistry in allenes.

5. Short questions :

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- (1) Arrange the ascending order of nucleophilicity for Se, O and S.
- (2) Define Eclipsing effect in E^2 .
- (3) Why NGP assisted SN_2 reaction gives product with retention of configuration ?
- (4) Give only the reaction equation for xanthate undergoing pyrolysis.
- (5) What is allylic rearrangement ?
- (6) State Huckel Rule of aromaticity.
- (7) Define helicity giving one example.
- (8) Define antiaromaticity.
- (9) Cyclobutatrienyl anion is aromatic or non-aromatic ?
- (10) Complete the reaction and name the rearrangement :
 $RCOOH + N_3H / H_2SO_4 \rightarrow ?$
- (11) Complete the reaction and name the rearrangement :



- (12) What is Criegee intermediate ?
 - (13) Define Atropes.
 - (14) Draw a structure of spiro [4, 3] octane.
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