

Seat No. : _____

DM-132

December-2017

M.Sc., Sem.-I

402 : 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 *erythro*-1-bromo-1, 2-diphenylpropane gives cis product while that of *threo* isomer gives trans product in E² reaction.
- (2) Discuss orientation rules in elimination reaction giving suitable example.

OR

Answer the following :

- (1) Discuss Chugaev reaction with mechanism.
- (2) Cis-tert-butylcyclohexylbromide undergoes E² reaction with NaOC₂H₅ in ethanol at 75 °C while its trans isomer does not undergo elimination at all _____. Justify giving mechanism.

(B) Answer the following : 7

- (1) In alkaline medium 2-chlorocyclohexanol forms epoxide more readily than its cis-isomer – Justify with mechanism.
- (2) Explain methanolysis of α-bromopropionate in presence of alkali giving α-methoxypropionate anion occurs with retention configuration – Justify giving mechanism.

OR

Answer the following :

- (1) Discuss reaction mechanism of alcohol undergoing S_N reaction with thionyl chloride giving alkyl halide with retention of configuration.
- (2) Discuss NGP in base catalyzed 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) What is diatropic ring current ? Discuss its role in determining aromaticity.

OR

Answer the following :

- (1) Discuss aromaticity in different annulenes.
 - (2) Cyclooctatetrene is non-aromatic while its dication is aromatic – Justify.
- (B) Answer the following : 7
- (1) Write Hemmette equation, explain each term and show that Hemmette equation is a linear free energy relationship.
 - (2) Discuss effect of H-bonding and Resonance on the strength of acid.

OR

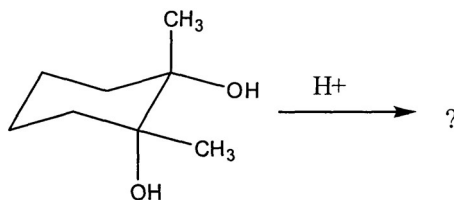
Answer the following :

- (1) Discuss the applications and limitations of Hemmette equation.
 - (2) Discuss the effect of hybridization and solvent effect on acidity giving suitable example.
3. (A) Answer the following : 7
- (1) Write a note on nitrenes.
 - (2) What are free radicals ? Give three methods for their generation. Discuss their stability.

OR

Answer the following :

- (1) Discuss three different reactions in which carbanion is a reactive species.
 - (2) Discuss methods to distinguish singlet and triplet carbenes.
- (B) Answer the following : 7
- (1) Complete the following reaction, name the rearrangement involved, also give its mechanism.

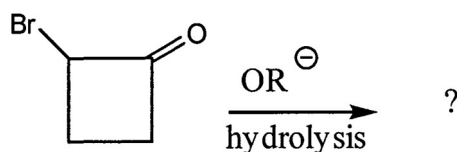


- (2) Discuss Wagner-Meerwein rearrangement with mechanism and applications.

OR

Answer the following :

- (1) Discuss Curtius rearrangement with Principle, mechanism and applications.
- (2) Complete the following reaction, name the rearrangement involved, also give its mechanism.



4. (A) Answer the following : 7

- (1) Discuss why biphenyls are optically active even in absence of chiral centre.
- (2) Discuss stereochemistry of quaternary ammonium salts.

OR

Answer the following :

- (1) Discuss stereochemistry of phosphonium compounds.
- (2) Discuss chemical and biochemical techniques for resolution.

- (B) Answer the following : 7

Write a note on Prelog generalization.

OR

Discuss stereoselectivity and stereospecificity in addition of 2-hexene.

5. Short questions : 14

- (1) Arrange the ascending order of nucleophilicity for F, Br, Cl and I.
- (2) Define Eclipsing effect in E².
- (3) Give only the reaction equation for Cope reaction.
- (4) Which rearrangement is used in the conversion of RCOOH → RCOOR ?
- (5) What is allylic rearrangement ?
- (6) How symmetry criterion is useful to determine prochirality ?
- (7) Define Helicity giving one example.
- (8) Define antiaromaticity giving one example.
- (9) Cyclobutatrienyl anion is aromatic or not. Why ?
- (10) Name the rearrangement where isocyanate is formed as an intermediate.
- (11) How many shielded protons are present in 18 annulene ?
- (12) What is yield ? Give one example.
- (13) Name the rearrangement used for the conversion O-acylated hydroxamic acid to amines.
- (14) Draw a structure of spiro [5, 3] nonane.

