

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 E^2 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 E^2 reaction with NaOC_2H_5 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 Hammett equation, explain each term and show that Hammett 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 Hammett 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

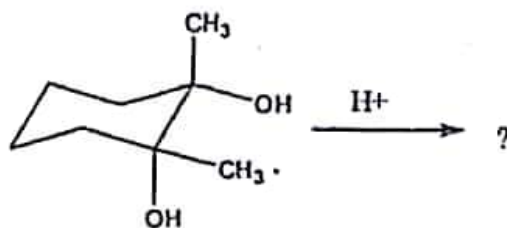
Answer the following :

- (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.

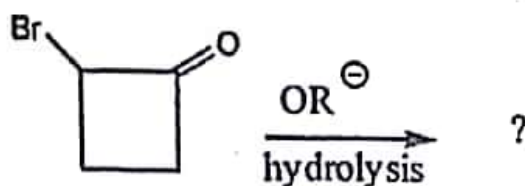


- (2) Discuss Wagner-Meerwein rearrangement with mechanism and applications.

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 :

- (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 :

Write a note on Prelog generalization.

OR

Discuss stereoselectivity and stereospecificity in addition of 2-hexene.

5. Short questions :

(1) Arrange the ascending order of nucleophilicity for F, Br, Cl and I.

(2) Define Eclipsing effect in E^2 .

(3) Give only the reaction equation for Cope reaction.

(4) Which rearrangement is used in the conversion of $\text{RCOOH} \rightarrow \text{RCOOR}$?

(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.