

Roll No. ....

## CHE-551

### Reaction Mechanisms, Pericyclic Reactions, Photochemistry and Stereochemistry

M. Sc. CHEMISTRY (MSCCH-12/13/16)

Second Year, Examination, 2017

**Time : 3 Hours**

**Max. Marks : 80**

**Note :** This paper is of **eighty (80)** marks containing **three (03)** Sections A, B and C. Attempt the questions contained in these Sections according to the detailed instructions given therein.

#### Section-A

##### (Long Answer Type Questions)

**Note :** Section 'A' contains four (04) long answer type questions of nineteen (19) marks each. Learners are required to answer *two* (02) questions only.

1. (a) Describe hemolytic and heterolytic fission of covalent bonds. How do these lead to the formation of carbonium ion and carbon ions ? 6  
(b) Diel's-Alder reaction is a thermally allowed process. Explain with the help of correlation diagram and FMO method. 7  
(c) Why is tertiary carbonium ion more stable than primary carbonium ion ? 6

2. (a) Explain the mechanism of Norrish type-I and Norrish type-II with suitable example. 7
- (b) Explain electrocyclic reactions with suitable examples. 6
- (c) Explain the different conformation of cyclohexane. 6
3. Explain molecular rearrangement reaction. Give their classification and explain the mechanism of pinacol-pinacolone and benzilic acid rearrangements. 19
4. Explain the following :
  - (a) Why staggered conformation of ethane is more stable than eclipsed conformation ? 5
  - (b) Mechanism of  $E_2$  and  $E_1 C_b$  reaction in detail. 7
  - (c) Jablonski diagram. 7

### Section-B

#### (Short Answer Type Questions)

**Note :** Section 'B' contains eight (08) short answer type questions of eight (08) marks each. Learners are required to answer *four* (04) questions only.

1. Give *two* methods each for the generation of the following :
  - (a) Carbocations
  - (b) Carbanions
  - (c) Free radical
  - (d) Carbenes
2. Describe the conformation of ethane in detail.
3. What is cis-trans photoisomerisation ?

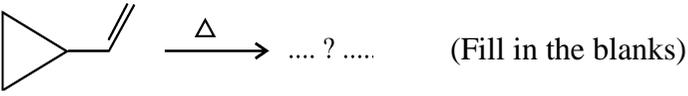
4. Explain symmetry in 2, 4-pentadienyl systems.
5. Explain the photochemistry of peroxides and diazo-compounds.
6. Explain the following :
  - (a) Backmann rearrangement
  - (b) Axial and equatorial bonds in cyclohexane
7. Explain the conformation of monosubstituted cyclohexane and disubstituted cyclohexane.
8. With the help of correlation diagram analyse the cis 3, 4-dimethyl cyclobutane  $\rightleftharpoons$  2, 4-hexadiene system, giving stereochemistry under photochemical conditions.

### Section-C

#### (Objective Type Questions)

**Note :** Section 'C' contains ten (10) objective type questions of one (01) mark each. All the questions of this Section are compulsory.

1. Reaction intermediate of  $E_1C_b$  reaction is :
  - (a) Carbocation
  - (b) Free radical
  - (c) Carbanion
  - (d) Benzyne
2. Geometry of methyl free radical is :
  - (a) Planar
  - (b) Pyramidal
  - (c) Tetrahedral
  - (d) Linear

3. Hybridization of Alkyl carbanion is :
- $sp$
  - $sp^2$
  - $sp^3$
  - $sp^2d$
4. In which of the following reaction intermediate in carbon ?
- Pinacole-Pinacolone
  - Stevens
  - Claisen
  - Wolf
5. Staggered conformation of ethane is more stable than eclipsed conformation. (True/False)
6. Tertiary carbonium ion is more stable than primary carbonium ion. (True/False)
7. The product obtained in Claisen rearrangement is ..... .
8.  (Fill in the blanks)
9. Singlet methylene is more stable than triplet methylene. (True/False)
10. The reaction intermediate formed in pinacole-pinacolone rearrangement is ..... . (Fill in the blanks)

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