

CHE-551**Reaction Mechanisms, Pericyclic Reaction,
Photochemistry and Stereochemistry****M.Sc. CHEMISTRY (MSCCH-12/13/16/17)****Second Year, Examination-2019****Time: 3 Hours****Max. Marks : 80**

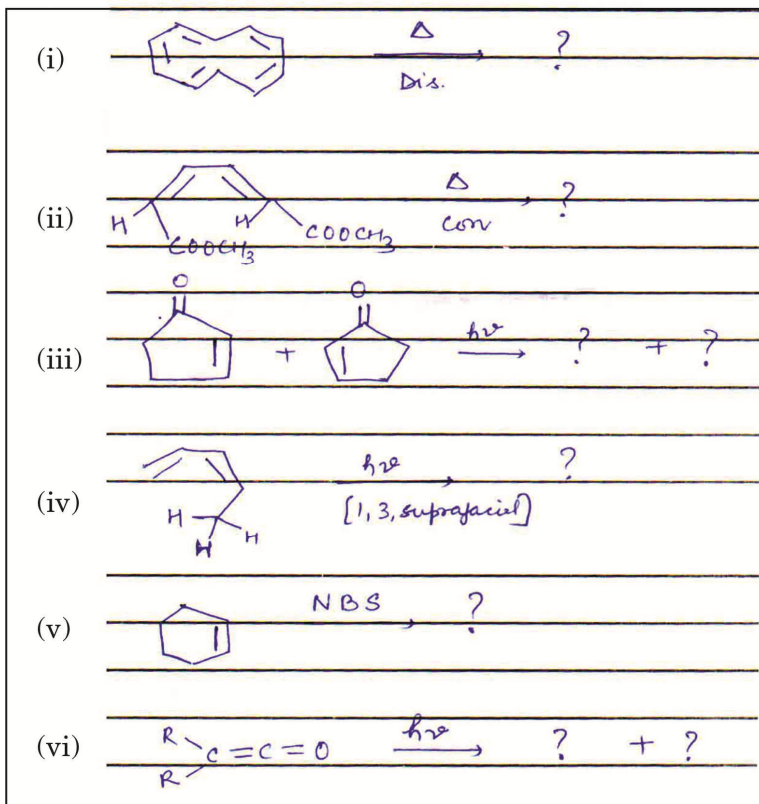
Note : This paper is of eighty (80) marks containing three (03) Sections A,B and C. Attempt the questions contained in these sections according to the detailed instructions given there in.

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.

- (a) Arrange the following consocations in increasing order of stability and discuss the stability order
Trityl cation, benzylic, allylic, tatiary, secondary.
- (b) Draw orbital symmetry correlation diagram for $\pi^4_s + \pi^2_s$ cycloaddition and show that cycloadditions symmetry allowed under thermal condition

(c) Complete the following reactions and show stereochemistry wherever possible. Image



2 . (a) Write mechanism of following reactions

- (i) Benzillic acid rearrangement
- (ii) Fries rearrangement

(b) Write notes on the followings.

- (i) 1.5 suprafacial shift of a group with retention of configuration.
- (ii) Copy rearrangement.

(c) Explain Norrish type I cleavage reactions with suitable example.

3. (a) Write explanatory notes on

(i) $\Delta i \pi$ methane rearrangement

(ii) As trans isomerization of alkenes

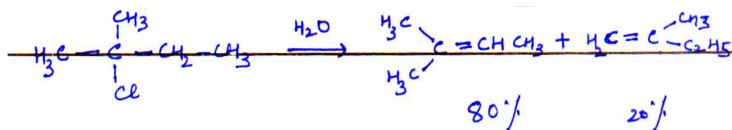
(b) Write detailed note on

(i) Hoffmann bromamide reaction

(ii) Electronic transitions.

(c) Discuss conformation of nongeminally disubstituted cyclohexanes

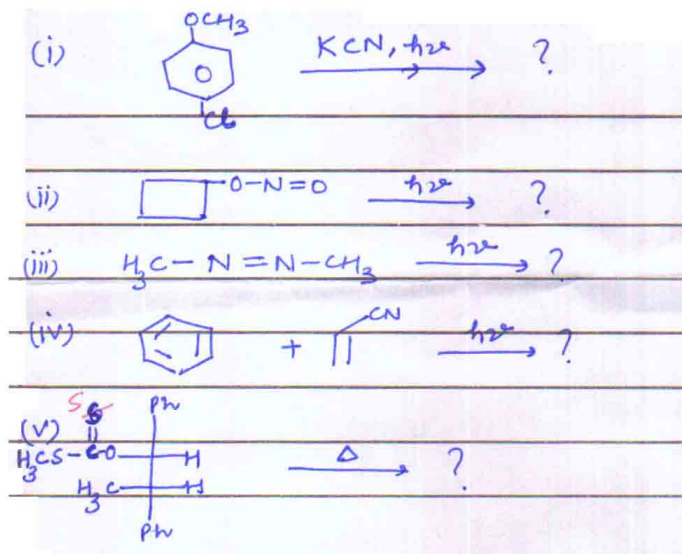
4. (a) (i) Justify the following product ratio formed



(ii) Discuss stereochemistry of E_2 reaction

(b) Write detailed note on pyrolytic reactions

(c) Complete the following reaction.



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. Discuss structure of following reaction intermediates and write one reaction involving reaction intermediate

- (a) Carbene
- (b) Aryne

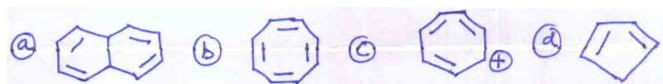
2. Write notes on conformation of
 - (a) Ethylene glycol
 - (b) Ethylene chlorohydrin
3. What do you understand by Photosensitization and triplet energy transfer.
4. Explain symmetry in π molecular orbitals of allylic system.
5. Write note on photochemical reactions of α, β unsaturated carbonyl compounds.
6. Write detailed note on photochemistry of peroxides.
7. With the help of FMO method discuss selection rules for 1,3 butadiene cyclobutene system under thermal and photo-chemical conditions
8. Explain why
 - (a) Trans 1, 4 dimethylcyclohexane is more stable than its isomer
 - (b) As 1,4 cyclohexane diol is stable in chair boat form.

Section -C

(Object Types Questions)

Note: - section 'C' contains ten (10) objective type questions of one (10) mark each. All the questions of section 'C' are compulsory.

1. Which one of the following compounds is aromatic?



2. Which of the following is nucleophile
- (a) AlCl_3 (b) BF_3
(c) SO_3 (d) H_2O
3. Which of the following molecules contain SP hybridized atom
- (a) HCOOH (b) HNO_3
(c) HNO_2 (d) HCN
4. Stability of free radicals can be explained on the basis of
- (a) Inductive effect
(b) Inductomeric effect
(c) Hyperconjugation
(d) Taictomerism

5. Which of the following cycloalkanes has the most strain energy
- (a) Cyclobutane (b) Cyclopentane
(c) Cyclohexane (d) Cycloheptane
6. Preferred conformations of 1,2 difluoroethane in liquid state is _____ conformation.
- (a) Anti (b) Gauche (c) Eclipsed
7. $\pi^4_a + \pi^2_s$ cycloaddition is symmetry allowed under photochemical condition. (True/False)
8. $n - \pi^*$ transition are low energy transitions and shows hypochromic shift in polar solvent.
(True/False)
9. P gauche conformer has dihedral angle____ and bioregional angle_____.
- (Fill in the blanks)
10. Conversion of an α diazomethyl ketone into ketene and N₂, involving an acyl carbene as intermediate, is known as.....
- (Fill in the blanks)
