**PARUL UNIVERSITY**
**PARUL INSTITUTE OF APPLIED SCIENCES**
**MID SEMESTER INTERNAL EXAMINATION, SEPTEMBER-2019**
**M.Sc. Chemistry Semester III**

**Paper Name:** Pericyclic Reactions, Photochemistry and Free Radicals **Date: 03/09/2019**
**Paper Code:** 11205201 **Time: 1.5 hrs.**
**Max. Marks:** 40

**Instructions:**
1. All questions are compulsory and options are in first and second question only.
2. Numbers to the right of question indicate the marks of respective question.
3. Give your answers with appropriate **EXAMPLES** where it is necessary.

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**Q. 1** Attempt any one question of the following. **(08)**

I. Discuss in detail the Molecular Orbitals (MOs) of allyl system.

II. Explain Claisen rearrangement of allyl vinyl ether. Explain the solvent effect on this reaction. Why this reaction is irreversible?

**Q. 2** Attempt any three questions of the following. **(12)**

I. Draw and explain the molecular orbitals of 1,3,5-hexatriene.

II. Explain Woodward–Hoffman sigmatropic shift nomenclature with example.

III. With suitable diagram explain why 1,3-dipolar cycloaddition is thermally allowed but photochemically forbidden?

IV. Why thermal [2+2] cycloaddition of ethylene is forbidden whereas photo-chemically allowed?

V. Discuss the mechanism of Sommelet- Hauser rearrangement.

**Q. 3** Do as directed. Attempt all five questions. **(05)**

I. Draw and explain the dis- and con-rotatory motion of orbitals?

II. What is HOMO and LUMO?

III. What is meant by bonding and antibonding Molecular orbitals?

IV. What are fluxional molecules?

V. Why NMR spectra of bullvalene give a sharp singlet in spite of having single and double bonded carbons?

**Q. 4** Write correct option in your answer sheet for following 15 multiple choice questions. **(15)**

MCQ 1 Which one is a dipolarophile

(A) Ethene (B) Propene
(C) 1-butene (D) All of these

MCQ 2 A substituent moves from one part of a π-bonded system to another part in an intramolecular reaction with simultaneous rearrangement of π system in

(A) Sigmatropic rearrangement (B) Cycloaddition reaction
(C) Electrocyclic reaction (D) All of these

MCQ 3 Examples of sigmatropic rearrangements

(A) Cope rearrangement (B) Claisen rearrangement
(C) Carroll rearrangement (D) All of these

MCQ 4 The molecular rearrangements in which the main product is indistinguishable from the main reactant is called

(A) Degenerate rearrangement (B) Degeneracy
(C) Degeneration (D) All of these

MCQ 5 Which one is true?

(A) Claisen rearrangement is irreversible (B) Cope rearrangement is reversible
(C) Both A and B (D) None of these

MCQ 6 Bullvalene formula is

(A) $C_5H_{10}$ (B) $C_{10}H_{10}$
(C) $C_5H_{20}$ (D) $C_{10}H_{20}$

MCQ 7 In sigmatropic rearrangements, number of pi-bonds

(A) Increases (B) Decreases
(C) Remains constant (D) Can increase or decrease

MCQ 8 Number of nodes present in LUMO of 1,3-butadiene

(A) 0 (B) 1
(C) 2 (D) 3

MCQ 9 The HOMO-LUMO energy gap in 1,3-butadiene is

(A) Lower in energy than ethene (B) Greater in energy than hexatriene
(C) Greater in energy than ethene (D) Both A and B

MCQ 10 An example of concerted reaction

(A) $S_N2$ reaction (B) Claisen rearrangement
(C) Both of these (D) None of these

MCQ 11 Two new sigma bonds and one pi bond are formed at the same time as three pi bonds are lost in

(A) Cycloaddition reaction (B) Electrocyclic reaction
(C) Group transfer (D) Sigmatropic rearrangement

MCQ 12 As per MO theory, number of pi electrons in a simplest allyl free radical is

(A) 1 (B) 2
(C) 3 (D) 4

MCQ 13 For Lowest energy MO which is/are correct

(A) It has zero nodes (B) All p orbitals in same phase
(C) Both A and B (D) None of these

MCQ 14 For highest energy MO which is/are correct

(A) It has zero nodes (B) All p orbitals in same phase
(C) Both A and B (D) None of these

MCQ 15 As per MO theory, which is/are correct

(A) N atomic orbitals combine to form N molecular orbitals (B) LUMO is the highest energy MO
(C) HOMO is the lowest energy MO (D) All of these

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