III SEMESTER

OC H 511: ORGANIC REACTION MECHANISM

Course Outcome

- Students will learn about the mechanism and synthetic utility of various kinds of molecular rearrangement reactions with diverse examples.
- Students will gain knowledge on principles of photochemistry and diverse types of photochemical reactions of organic molecules with multiple examples.
- Students will learn various concepts of pericyclic reactions, diverse types of electrocyclic, cycloaddition and sigmatropic reactions with multiple examples.
- Students will learn several name reactions that involve synthesis of heterocyclic molecules with reaction mechanism and examples.

UNIT-I **[12 Hours]**

Molecular Rearrangements: General mechanistic treatment ofnucleophilic, electrophilic and free radical rearrangements. Intermolecular and Intramolecular migration, nature of migration and migratory aptitudes. Mechanism and synthetic utilities of Wagner-Meerwein, Dienone-Phenol, Pinacol-Pinacolone, Demyanov, Wolff, Favorskii, Neber, Benzidine, Lossen, Curtius, Schmidt, Stevens, Baker-Venkatraman and Amadori rearrangement.

UNIT-II Organic Photochemistry **[12 Hours]**

Bonding and antibonding orbitals, singlet and triplet states, relative energies, Jablonski diagram and quantum yield, Photodissociation, Photoreduction, Photochemical isomerisation and Photocyclisation. Norrish Type-I, Type-II reactions and Yang cyclisation. Barton reaction and Photo Fries rearrangement, Paterno-Buchi reaction, Photochemistry of alkenes, benzenes, Di-pi methane rearrangement, Photodegradation of polymers. Photocatalysis, Photooxidation and photoreduction reactions. Photochemical cells, energy conversion and storage. Photochemistry of vision.

UNIT-III **[12 Hours]**

Pericyclic Reactions: Characteristics and classifications of pericyclic reactions. Aromatic Transition States (ATS)/Perturbation Molecular Orbitals (PMO) approach for the interpretation of mechanism of pericyclic reactions. Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl systems. Woodward-Hoffmann correlation diagram and FMO approach.

Electrocyclic Reactions: Introduction, Con-rotatory and dis-rotatory Process, 4n and 4n+2 systems. Reactions of cations and anions, formation and cyclisation of dipolar molecules. **Cycloaddition reaction:** Suprafacial and Antarafacial addition, notation of cycloadditions,2+2 and 4+2 systems, 2+2 additions of ketones and chelotropic reactions. 1,3-Dipolar cycloaddition

reactions. **Sigmatropic reactions:** Suprafacial and Antarafacial shift of H, [1,3] [1,5] and [3,3]-sigmatropic shifts. Walk, Claisen, Cope, Oxy-Cope and Aza-Cope rearrangements.

UNIT-IV Name reactions in heterocyclic synthesis **[12 Hours]**

Corey-Chaykovsky reaction, Hoch-Cambell aziridine synthesis, Blum aziridine synthesis, Feist-Bénary furan synthesis, Hoffmann Loffler-Freytag reaction, Fiesselmann thiophene, Gewald aminothiophene synthesis, Fischer oxazole synthesis, Gassman indole synthesis, Larock indole synthesis, Grabe-Ullmann carbazole synthesis, Bockiheide reaction, Gabriel-Colman rearrangement, Gould-Jacobs reaction, Meth–Cohn quinoline synthesis, Combes quinoline synthesis, Pomeranz-Fritsch reaction and Bischler-Napieralski isoquinolines synthesis.

References

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