

CH H 512: REAGENTS IN ORGANIC SYNTHESIS AND 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, concepts of pericyclic reactions, diverse types of electrocyclic, cycloaddition and sigmatropic reactions with multiple examples.
- Students will learn the preparation, properties, reactions and uses of organometallic reagents in organic synthesis.
- Students will know the uses of Gilman's reagent, LDA, DCC, 1,3-dithiane, TMSI, DDQ, SeO₂, Wilkinson's catalyst, PTCs, Baker's yeast, PPA, TMS-CN, Hydrosilane, chloramines-T, Woodward-Prevost hydroxylation, Zeigler-Natta catalyst, and crown ethers in organic synthesis and functional group transformation.

UNIT-I:

[12 Hours]

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

UNIT-II:

[12 Hours]

Organic Photochemistry: Bonding and antibonding orbital, Chemistry of excited states of organic molecules, Jablonski diagram and quantum yield, Photodissociation, Photoreduction, Photochemical isomerisation, Norrish Type-I and Type-II reactions, Yang cyclization, Barton reaction and Paterno-Buchi reaction, photo oxidation.

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 & dis-rotatory Process, $4n$ & $4n+2$ systems.

Cycloaddition reaction: Suprafacial and Antarafacial addition, $2+2$ and $4+2$ systems. 1,3-Dipolar cycloaddition reactions.

Sigmatropic reactions: Suprafacial and Antarafacial shift of H, $[1,3]$ & $[1,5]$ - sigmatropic shifts.

UNIT-III: Reagents in Organic Synthesis-I

[12 Hours]

Organometallic Reagents: Preparation, properties and uses of Organolithium, organomagnesium, Organozinc, Organocadmium, Organomercury, Organoindium, Organoaluminium and Organotellurium compounds.

Silicon containing Reagents: Preparation and reactions; Peterson reaction.

Boron containing Reagents: Preparation of organoboranes - Hydroboration, Reactions of Organoboranes - Isomerization, oxidation, protonolysis, carbonylation, cyanidation. Synthesis of esters, E and Z alkenes, conjugated dienes and alkynes.

Organotin Compounds: Synthesis of Organostannanes and their utility in C-C bond forming reactions. Barton decarboxylation reaction, Barton deoxygenation, Stelly-Kelly coupling reaction.

UNIT-IV: Reagents in Organic Synthesis-II

[12 Hours]

Use of the following reagents in organic synthesis and functional group transformations: Gillman's reagent, Lithium diisopropylamide (LDA), Tri-n-butyl tin hydride, Hydrosilanes, Dicyclohexyl carbodiimide (DCC), 1,3-dithiane, Trimethylsilyl iodide, Trimethyl silyl cyanide, DDQ, Selenium dioxide, Baker's yeast, Polyphosphoric acid. Chloramine-T, Aluminium *iso*-propoxide. Woodward and Prevost hydroxylation.

References

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