

CH H 462: ADVANCED ORGANIC CHEMISTRY

Course Outcome

- Students will gain an understanding of all details of aromatic electrophilic and nucleophilic substitution reactions.
- Learn about various free radical reactions and elimination reactions including pyrolytic eliminations.
- Gain an understanding of formation and hydrolysis of esters.
- Study the all types of addition to carbon-carbon and carbon-heteroatom multiple bonds.
- Know the reaction mechanism and synthetic uses of organic named reactions.

UNIT-I

[12 Hours]

Aromatic Electrophilic and Nucleophilic Substitution Reactions: Mechanism of aromatic electrophilic substitution reactions-nitration, halogenation, sulfonation, Friedel-Crafts alkylation and acylation, orientation and reactivity, energy profile diagram. The ortho/para ratio, ipso attack, orientation in other ring systems. Mechanism of Vilsmeier-Haack reaction, Mannich reaction, Diazonium coupling, Pechmann reaction and Fries rearrangement. Mechanisms of aromatic nucleophilic substitution reactions - S_NAr , S_N1 & arylne mechanism. Von-Richter rearrangement, Sommelet-Hauser rearrangement, Smiles rearrangement.

UNIT-II

[12 Hours]

Free Radical Reactions: Mechanisms of free radical substitution reactions & neighbouring group assistance. Reactivity for the aliphatic and aromatic substances at a bridgehead. Reactivity of attacking radical. Effect of solvent on reactivity. Auto-oxidation, coupling of alkynes. Arylation of aromatic compounds by diazonium salts. Sandmeyer & Hunsdiecker reactions.

Elimination Reactions: Discussions of $E1$, $E2$ and $E1cB$ mechanisms. Orientation during elimination reactions. Saytzeff and Hofmann rules. Reactivity-effects of substrate structures, attacking base, leaving group and solvent medium.

Pyrolytic Eliminations: Mechanisms of pyrolysis of acetates. Xanthate pyrolysis-Chugaev reaction, Hofmann degradation and Cope elimination.

UNIT-III

[12 Hours]

Formation and Hydrolysis of Esters: Plurality of mechanism. Mechanism of esterification reactions. Ester hydrolysis- $A_{AC}2$, $B_{AC}2$, $B_{AL}1$, $B_{AL}2$, $A_{AC}1$ & $A_{AL}1$ mechanisms. Trans-esterification.

Addition to Carbon-Carbon Multiple Bonds: Addition reactions involving electrophiles, nucleophiles and free radicals. Cyclic mechanisms. Orientation and stereochemistry. Addition of halogens, hydrogen halides, oxygen-epoxidation, carboxylic acids and amines. Michael addition, Addition to cyclopropanes.

Addition to Carbon-Hetero Multiple Bonds: Electrophilic, nucleophilic and free radical additions to $C=O$ and $C=N$ systems. Addition of Grignard reagents. Reformatsky reaction, aldol condensation, Knoevenagel condensation, Perkin reaction and Wittig reactions.

UNIT-IV

[12 Hours]

Organic Name Reactions: Reactions, Mechanisms and synthetic uses of the following: Stobbe condensation, Darzen condensation, Gattermann-Koch reaction, Duff reaction, Chichibabin reaction, Benzoin condensation, Claisen-Schmidt condensation, Claisen reaction, Stork Enamine reactions, Sharpless asymmetric epoxidation, Suzuki coupling, Heck reaction, Ullmann reaction, Bucherer reaction, Shapiro reaction, Mitsunobu reaction, Stephen reaction.

References

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