

Paper-VIII CHN502 Organic Chemistry

I Free Radical Reactions

12Hrs

Types of free radical reactions, free radical substitution mechanism, mechanism at an aromatic substrate, neighbouring group assistance. Reactivity for aliphatic and aromatic substrates at a bridgehead. Reactivity in the attacking radicals. The effect of solvents on reactivity.

Allylic halogenation (NBS), oxidation of aldehydes to carboxylic acids, auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts. Sandmeyer reaction. Free radical rearrangement. Hunsdiecker reaction.

II Addition to Carbon- Hetero Multiple Bonds

15 Hrs

Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Addition of Grignard reagents, organozinc and organolithium reagents to carbonyl and unsaturated carbonyl compounds. Wittig reaction.

Mechanism of condensation reactions involving enolates — Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe reactions.

Hydrolysis of esters and amides, ammonolysis of esters.

III Pericyclic Reactions

20 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl system. Classification of pericyclic reactions. Woodward—Hoffmann correlation diagrams. FMO and PMO approach. Electrocyclic reactions — conrotatory and disrotatory motions, $4n$, $4n+2$ and allyl systems. Cycloadditions — antarafacial and suprafacial additions, $4n$ and $4n+2$ systems, 2+2 addition of ketenes, 1,3 dipolar cycloadditions and cheletropic reactions.

IV A Sigmatropic rearrangements

5Hrs

Sigmatropic rearrangements — suprafacial and antarafacial shifts of H, sigmatropic shifts involving carbon moieties, 3,3- and 5,5- sigmatropic rearrangements. Claisen, Cope and aza-Cope rearrangements. Fluxional tautomerism. Ene reaction.

B Elimination Reactions

8 Hrs

The E2, E1 and E1cB mechanisms and their spectrum. Orientation of the double bond. Reactivity - effects of substrate structures, attacking base, the leaving group and the medium.

Mechanism and orientation in pyrolytic elimination.