

Module I

(14 hours)

Nature of Bonding in Organic Molecules:

Delocalised chemical bonding conjugation, cross conjugation, resonance, hyperconjugation, bonding in fullerenes, tautomerism.

Aromaticity in benzenoid and nonbenzenoid compounds, alternant and non-alternant hydrocarbons.

Huckels rule, energy level of π - molecular orbitals, annulenes, antiaromaticity, Ψ -aromaticity, homo-aromaticity, PMO approach.

Bonds weaker than covalent, addition compounds, crown ether complexes and cryptands, inclusion compounds (cyclodextrins, catenanes and rotaxanes).

Stereochemistry:

Conformational analysis of cycloalkanes, decalins, effect of conformation on reactivity, conformation of sugars, steric strain due to unavoidable crowding.

Elements of symmetry, chirality, molecules with more than one chiral center, threo and erythro isomers, methods of resolution.

Optical purity, enantiotropic and diastereotopic atoms, groups and faces, stereospecific and stereoselective synthesis.

Optical activity in the absence of chiral carbon (biphenyls, allenes and spiranes), chirality due to helical shape.

Module II

(12 hours)

Reaction Mechanism (Structure, Reactivity and Rearrangements):

Generation, structure, stability and reactivity of carbocations, carbanions, free radicals, carbenes and nitrenes.

Types of mechanisms: S_N2 , S_N1 , mixed S_N1 and S_N2 and SET, S_E1 .

Kinetic and thermodynamic control, Hammond's postulate, Curtin-Hammett principle, potential energy diagrams, transition states and intermediates.

Methods of determining reaction mechanisms, isotope effects.

Hard and soft acids and bases concept and its application in organic synthesis.

Effect of structure on reactivity: resonance and field effects, steric effect.

Quantitative treatment, Hammett equation and linear free energy relationships, substituent and reaction constants, Taft equation.

The NGP mechanism, NGP by π and σ bonds, anchimeric assistance.

Classical and nonclassical carbocations, phenonium ions, norbornyl systems, common carbocation rearrangements.

The S_N1 mechanism, S_N at an allylic, aliphatic trigonal and a vinyl carbon.

Reactivity effects of substrate structure, attacking nucleophile, leaving group and reaction medium, phase transfer catalysis and ultra sound, ambient nucleophile and regioselectivity.

Module III

(14 hours)

Aromatic Electrophilic Substitution Reactions:

The arenium ion mechanism, orientation and reactivity, energy profile diagrams, the ortho/para ratio, ipso attack, orientation in other ring systems, quantitative treatment of reactivity in substrates and electrophiles, diazonium coupling, Vilsmeier reaction, Gattermann-Koch reaction.

The S_NAr , S_N1 , benzyne $S_{RN}1$ mechanisms, reactivity effect of substrate structure, leaving group and attacking nucleophile.

The von Richter, Sommelet-Hauser and Smiles rearrangements.

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

Text Books:

1. March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Michael B. Smith, 7th Edition, Wiley, 2013.
2. Advanced Organic Chemistry Part A: Structure and Mechanisms, Carey, Francis A., Sundberg, Richard J, Fifth Edition, Springer International Edition, 2007.

Reference Books:

1. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Sixth Edition, John Wiley & Sons, Inc., New York, 1985.
2. Structure and mechanism in organic chemistry, von C. K. Ingold. Cornell Univ. Press, Ithaca. 1953
3. Organic Chemistry, R. T. Morison and R. N. Boyd, Sixth Edition, Prentice-Hall, 1992.
4. Modern Organic Reactions, H. O. House, Benjamin-Cummings Publishing Co., Subs. of Addison Wesley Longman, US; 2nd edn, 1972..
5. Principles of Organic Synthesis, R. O. C. Norman and J.M.Coxon, Third Edition, Blackie Academic and Professional, 1993.
6. Pericyclic Reactions: A Mechanistic Study. S. M. Mukherji Macmillan India Press, New Delhi, , 1979.
7. Reaction Mechanism in Organic Chemistry, S. M. Mukherji and S. P. Singh, Third Edition Macmillan India Press, New Delhi, 1976.
8. Stereochemistry of Organic Compounds. D. Nasipuri, Third Edition, New Age International, 2014.
9. Stereochemistry of Organic Compounds. P.S.Kalsi, Eighth Edition, New Age International, 2015.
10. Organic Synthesis: Clayden J., Greeves N, Warren S, and Wothers, Second Edition Oxford University Press, 2000.