MC-02
ORGANIC CHEMISTRY

(Question will be set from each unit/section with internal choice)

Marks - 100 **120 Hrs. (4Hrs/Week)**

Units	Topics
I	1. **Nature of Bonding in Organic Molecules** Delocalized chemical bonding-conjugation, cross conjugation, resonance, hyper conjugation, bonding in fullerenes, tautomerism. Aromaticity in benzenoid and non-benzenoid compounds, alternant and non-alternant hydrocarbons, Huckel's rule, energy level of π-molecular orbitals, annulenes, anti-aromaticity, ψ-aromaticity, homoaromaticity PMO approach. Bonds weaker than covalent - addition compounds, crown ether complexes and cryptands, inclusion compounds, cyclodextrins, catenanes and rotaxanes.
	2. **Stereochemistry** **15 Hrs.** Conformational analysis of cycloalkanes, declaims, effect of conformation on reactivity, conformation of sugars, steric strain due to unavoidable crowding. Elements of symmetry, chirality, molecules with more than one chiral centre, threo and erythro isomers, methods of resolution, optical purity, enantiotopic and diastereotopic atoms, groups and faces, stereospecific and stereoselective synthesis. Asymmetric synthesis. Optical activity in the absence of chiral carbon (biphenyls, allenes and spiranes), chirality due to helical shape. Stereochemistry of the compounds containing nitrogen, sulphur and phosphorus.
II	**Reaction Mechanism: Structure and Reactivity** **12 Hrs.** Types of mechanisms, types of reactions, thermodynamic and kinetic requirements, kinetic and thermodynamic control, Hammond's postulate, Curtin-Hammett principle. Potential energy diagrams, transition states and intermediates, methods of determining-mechanisms, isotope effect. Hard and soft acids and bases. Generation, structure, stability and reactivity of carbocations, carbanions, free radicals, carbenes and nitrenes. Effect of structure on reactivity - resonance and field effects, steric effect, quantitative treatment. The Hammett equation and linear free energy relationship, substituent and reaction constants. Taft equation.
	Free Radical Reactions **8 Hrs.** Type 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 diazonimum salts. Sandmeyer reaction. Free readical rearrangement. Hunsdiecker reaction.
III	**Aliphatic nucleophilic Substitution** **6 Hrs.** The S_N2, S_N1, mixed S_N1 and S_N2 and SET mechanism. The neighbouring group mechanism, neighbouring group participation by π and σ bonds, anchimeric assistance. Classical and nonclassical carbocations, phenonium ions, norbornyl system, common carbocation rearrangements. Application of NMR spectroscopy in the detection of carbocations.

The S_N1 mechanism.

Nucleophilic substitution at an allylic, aliphatic trigonal and a vinylic carbon.

Reactivity effects of substrate structure, attacking nucleophile, leaving group and reaction medium, phase transfer catalysis and ultrasound, ambident nucleophile, regioselectivity.

Aliphatic Electrophilic Substitution **5 Hrs.**

Biomolecular mechanisms - S_E2 and S_E1 the S_E1 mechanism, electrophilic substitution accompanied by double bond shifts. Effect of substrates, leaving group and the solvent polarity on the reactivity.

Aromatic Electrophilic Substitution **6 Hrs.**

The arenium ion mechanism, orientation and reactivity, energy profile diagrams. The orthopara ratio, ipso attack, orientation in other ring systems. Quantitative treatment of reactivity in substrates and electrophiles. Diazonium coupling, Vilsmeir reaction, Gattermann-Koch reaction.

Aromatic Nucleophilic Substitution **5 Hrs.**

The S_NAr, S_N1, benzyne and $S_{RN}1$ mechanisms. Reactivity - effect of substrate structure, leaving group and attacking nucleophile. The von Richter, Sommelet Hauser, and Smiles rearrangements.

IV **Addition to carbon-Carbon multiple Bonds** **7 Hrs.**

mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, regio and chemoselectivity, orientation and reactivity. Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenation of aromatic rings. Hydroboration. Michael reaction. Sharpless asymmetric epoxidation.

Addition to Carbon-Hetero multiple Bonds **12 Hrs.**

Mechanism of metal hybrid reduction of saturated an 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 reaction involving enolates - Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe reactions.

Hydrolysis of esters and amides, ammonolysis of esters.

Elimination Reactions **5 Hrs.**

The E2, E1 and E1 cB 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.

V **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 reaction - 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 cheleotropic reactions.

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