

ORGANIC CHEMISTRY**Marks: 80**

- I: Aromatic Electrophilic substitution: 8 Hrs**
The arenium ion mechanism, Orientation and reactivity, energy profile diagram. The ortho / para ratio, ipso attack, orientation in other ring system, quantitative treatment of reactivity in substrates and electrophiles. Diazonium coupling, Vilsmeier reaction, Gatterman-Koch reaction.
- II: Aromatic Nucleophilic substitution: 8 Hrs**
The S_NAr , S_N1 , benzyne and $S_{RN}1$ mechanisms. Reactivity-effect of substrates structure, leaving group and attacking nucleophile. The Von Richter, Sommelet – Houser and Smiles rearrangements.
- III: Free Radical Reactions: 8 Hrs**
Types of free radical reactions, free radical substitution mechanism, mechanism at an aromatic substrate, neighboring group assistance. Reactivity for aliphatic and aromatic substrates at a bridgehead. Reactivity in attacking radicals. The effect of solvent on reactivity.
Alicyclic halogenation (NBS), oxidation of aldehyde to carboxylic acid, auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salt. Sandmeyer reaction. Free radical rearrangement. Hunsdiecker reaction.
- IV: Addition to Carbon – Carbon multiple bonds: 8 Hrs**
Mechanistic and stereochemical aspects of addition reaction 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 ring. Hydroboration. Michaelis reaction. Sharpless asymmetric epoxidation.
- V: Addition to Carbon – Hetero multiple bonds: 12 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 reaction involving enolates-aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Sotobbe reaction.
Hydrolysis of ester and amides, ammonolysis of esters.
- VI: Elimination Reactions: 10 Hrs**
The E2, E1 and E1cB mechanism and their spectrum. Orientation of double bond. Reactivity-effects of substrates structures, attacking base, the leaving group and the medium.

Mechanism and orientation in pyrolytic elimination.

VII: Magnetic Resonance Spectroscopy: 20 Hrs

A. Nuclear Magnetic Resonance Spectroscopy:

Nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shift and its measurement, factors influencing chemical shift, deshielding, spin-spin interaction, factor influencing coupling constant 'J'. Classification (ABX, AMX, ABC, A₂B₂ etc.), spin decoupling, basic ideas about instrument, NMR studies of nuclei other than proton-¹³C, ¹⁹F and ³¹P, FT NMR, advantage of FT NMR, use of NMR in medical diagnostics.

B. Electron Spin Resonance Spectroscopy:

Basic principles, zero field splitting and Kramers degeneracy, factor affecting the "g" value. Isotopic and anisotropic hyperfine coupling constant, spin Hamiltonian, spin densities and McConnell relationship, measurement techniques, applications.

C. Nuclear quadrupole resonance spectroscopy

Quadrupole nuclei, quadrupole moments, electric field gradient, coupling constant, splitting.

VIII Molecular Spectroscopy

Energy level, molecular orbital, vibronic transition, vibrational progressions and geometry of the excited states, Franck-Condon principle, electronic spectra of the polyatomic molecules. Emission spectra, radiative and nonradiative decay, internal conversion, spectra of transition metal complexes, charge-transfer spectra.