

ORGANIC CHEMISTRY**Marks: 80**

- I. Nature of bonding in organic molecules** **15 Hrs**
Delocalized chemical bonding-conjugation, cross conjugation, resonance, hyperconjugation, bonding in fullerenes, tautomerism.
Aromaticity in benzenoid and non-benzenoid compound, alternate and nonalternate hydrocarbon, Huckel rule, energy of p-molecular orbital, annulenes, antiaromaticity, Ψ -aromaticity homoaromaticity, PMO approach.
Bond weaker than covalent-addition compound, crown ether complexes and cryptands, inclusion compound, cyclodextrins, catenanes and rotaxane.
- II. Stereochemistry** **15 Hrs**
Conformational analysis of cycloalkanes, declines, effect of conformation on reactivity, conformation of sugars, steric strain due to unavoidable crowding.
Element of symmetry, chirality, molecules with more than one chiral center, thro and erythro isomer, methods of resolution, optical purity, enantiotopic and diastereotopic atoms, group of faces, stereospecific and stereoselective synthesis, asymmetric synthesis, optical activity in absence of chiral carbon (biphenyls, allenes and spiranes), chirality due to helical shape.
Stereochemistry of compound containing nitrogen, sulphur and phosphorous.
- III. Reaction mechanism: structure and reactivity** **20 Hrs**
Types of mechanism, types of mechanism, thermodynamics and kinetic requirements, kinetic thermodynamic control, Hammonds postulate, Curtin-hammett principle.
Potential energy diagram, transition state and intermediates, methods of determining mechanism, isotope effect. Hard and soft acids and bases.
Generation, structure, stability and reactivity of carbocations, carbanions, free radicals, carbenes
Effect of structure on reactivity – resonance and field effect, steric effect, quantitative treatment. The Hammett equation and linear free energy relationship, substituent and reaction constants, Taft equation.
- IV. Aliphatic nucleophilic substitution** **15 Hrs**
The SN_2 , SN_1 and SET mechanism.
The neighboring group mechanism, neighboring group participation by π and bond, anchimeric assistance.
Classical and nonclassical carbocations, phenonium ions, norboryl system, common carbocation rearrangement. Application of NMR spectroscopy in detection of carbocations.
The S_N1 mechanism
Nucleophilic substitution at an allylic, aliphatic trigonal and vinylic carbon.

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

V. Aliphatic electrophilic substitution

5Hrs

Bimolecular mechanism – S_E2 and S_E1 . The S_E1 mechanism, electrophilic substitution accompanied by doubled bond shifts. Effect of substrates, leaving group and solvent polarity

VI. Pericyclic Reactions

20 Hrs

Molecular orbital Symmetry, Frontier orbital of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl system. Classification of pericyclic reactions. Woodward Hoffmann correlation diagram, FMO and PMO approach, electrocyclic reaction – conrotatory and disrotatory motion, $4n$, $4n+2$ and allyl systems. Cycloaddition – antarafacial and suprafacial addition, $4n$ and $4n+2$ systems, $2+2$ addition of ketenes, 1,3 dipolar cycloaddition and chelotropic reactions. Sigmatropic rearrangement – Suprafacial and antarafacial shift of H, sigmatropic shift involving corban moieties, 3,3 and 5,5-sigmatropic rearrangement. Claisen, cope and aza-cope rearrangements. Fluxional isomerism. Ene reaction