Paper –II CHN-402 Organic Chemistry

I A Nature of Bonding in Organic Molecules 10 Hrs

Delocalized chemical bonding-conjugation, cross conjugation, resonance, hyperconjugation, 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, homo-aromaticity, PMO approach.

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

II Stereochemistry 15 Hrs

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, 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.

III Reaction Mechanism : Structure and Reactivity 15Hrs

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 effects. Hard and soft acids and bases.

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

Classical and nonclassical carbocations, phenonium ions, norbornyl system, common carbocation rearrangements. Application of NMR spectroscopy in the detection of carbocations.

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.

IV Aliphatic Nucleophilic Substitution 12Hrs

The S_N2, S_N1, mixed S_N1 and S_N2 and SET mechanisms.

The neighbouring group mechanism, neighbouring group participation by π and σ bonds, anchimeric assistance.

The S_Ni 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.