Syllabus
M.Sc. (Chemistry) Programme
(SEMESTER – II)

Organic Chemistry – II
Programme Code- (MSCCH -21)
Course Code – (MSCCH -507)

Block I: Nucleophilic Substitution

Unit 1 Aliphatic Nucleophilic Substitution

The S_N2, S_N1, mixed S_N1 and S_N2, S_N1 and SET mechanism. Neighboring group participation by π and σ bonds, anchimeric assistance. Classical and non-classical carbocations, arenium ions, norborny1 systems, common carbocation rearrangements. 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. HSAB principle. Ambident nucleophiles.

Unit 2 Aromatic Nucleophilic Substitution

The S_NAr, , S_{Ni}, benzyne and $S_{NR}i$ mechanism, Reactivity effect of substrate structure, leaving group and attacking nucleophile. The von Richter, Sommelet-Hauser and Smiles rearrangements.

Block II: Electrophilic Substitution

Unit 3 Aliphatic Electrophilic Substitution

Bimolecular mechanisms, S_E2, S_Ei, S_E1 mechanism, electrophilic substation accompanied by double bond shifts. Addition-elimination mechanism. Effect of substrates, leaving groups and the solvent polarity on the reactivity.

Unit 4 Aromatic Electrophilic Substitution

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, Villsmeir reaction, Gatterman – Koch reaction.

Unit 5 Elimination Reactions

The E2, E1, E1cB and E2C mechanisms. Orientation of the double bond. Reactivity-effects of substrate structures, attacking base, the leaving group and the medium. Mechanism an orientation in pyrolytic elimination-Saytzeff, Hoffman and Cope elimination.

Block III: Addition and free Radical Reactions

Unit 6 Addition to Carbon-Carbon Multiple Bonds

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

Unit 7 Addition to Carbon-Hetero Atom Multiple Bonds

Mechanism of metal hydride reduction of saturated and unsaturated carbony1 compounds, acid esters and nitriles. Addition of Grignard reagents, Reformatsky reaction and related reactions. Mechanism of Wittig reaction, Knoevenagel, Claisen, Mannich, Stobbe reactions. Stork enamine reaction. Concept and applications of Umpolung and sulfur ylides.

Unit 8 Free Radical Reactions

Types of free radical reactions, mechanism of free radical substitution, reactions on aromatic substrates, neighboring group assistance. Reactivity for aliphatic and aromatic substrates at a bridgehead carbon. Reactivity of the attacking radicals. The effect of solvents on reactivity. Allelic halogenations (NBS). Oxidation of aldehydes to carboxylic acids, auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts, Sandmeyer reaction. Free radical rearrangement. Hunsdiecker reaction.

Block IV Pericyclic Reactions

Unit 9 Electrocyclic Reactions

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 reactions- conrotatory and disrotatory motions, 4n, 4n+2 and allyl system.

Unit 10 Cycloadditions and Sigmatropic Reaction

Introduction, 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. Claisen, Cope and Aza-Cope rearrangements. Fluxional tautomerism, Ene reaction.

Books Suggested:

1. Advanced Organic Chemistry-Reactions, Mechanism and Structure, M. B. Smith and Jerry March, John Wiley 2001.
2. Advanced Organic Chemistry, F. A. Carey and R. J. Sundberg, Plenum Publishers.
3. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman.
4. Structure and Mechanism in Organic Chemistry, C. K. Ingold, Comell University Press.
5. Organic Chemistry, R. T. Morrison and R. N. Boyd, Prentice-Hall.
6. Principles of Organic Synthesis, R.O.C. Norman and J. M. Coxon, Blackie Academic & Professional.
7. Reaction Mechanism in Organic Chemistry, S. M. Mukherji and S. P. Singh, Macmillan.
8. Organic Reaction Mechanism by Ahluwalia and R. K. Parashar, Narosa Book Distributor Pvt. Ltd.