FIRST YEAR

SEMESTER I
PAPER - 1
ORGANIC CHEMISTRY – I

OBJECTIVES:

To make the students learn and understand the concept of stereochemistry, conformational analysis and their application in the determination of reaction mechanism. To understand the mechanism of nucleophilic and electrophilic substitution reactions. To learn the importance of kinetics in organic reactions.

OUTCOMES:

The student will be able to

- *Describe the concept of Stereochemistry*
- *Illustrate the importance of Conformation*
- *Analyze the mechanism of Aliphatic and Aromatic Substitution reactions*
- *Acquire knowledge on the various concepts of reaction kinetics and mechanism*

UNIT-I: STEREOCHEMISTRY

Optical activity and chirality, classification of chiral molecules as asymmetric and dissymmetric. Topicity – Homotopic, enantiotopic and diastereotopic ligands and faces. A brief study of dissymmetry of allenes, biphenyls, spiro compounds, trans-cyclooctene and molecules with helical structures. Absolute configuration - R, S notation of biphenyls and allenes. Fischer projection. Inter conversion of Sawhorse, Newman and Fischer projections. Erythro and threo nomenclature, E and Z nomenclature - Asymmetric synthesis - Cram's rule. Stereospecific and stereoselective reactions.

UNIT-II: CONFORMATIONAL ANALYSIS

Conformational analysis of disubstituted cyclohexane and their stereochemical features (geometrical and optical isomerism (if shown) by these derivatives). Conformation and reactivity of substituted cyclohexanol (oxidation and acylation), cyclohexanone (reduction) and cyclohexane carboxylic acid derivatives (esterification and hydrolysis). Conformation and stereochemistry of cis and trans-decalin and 9 - methyldecalin.

UNIT-III: ALIPHATIC SUBSTITUTION REACTIONS

Nucleophilic substitution reactions: SN1, SN2 and SNi mechanisms - Neighbouring group participation – Reactivity - structural and solvent effects - substitution in norbornyl and bridgehead systems - substitution at allylic and vinylic carbons - substitution by ambident nucleophiles - substitution at carbon doubly bonded to oxygen and nitrogen - alkylation and acylation of amines, halogen exchange, Von-Braun reaction, alkylation and acylation of active methylene carbon compounds, hydrolysis of esters, Claisen and Dieckmann condensation.

Electrophilic substitution reactions: SE1, SE2 and SEi mechanism, double bond shift - Reactivity. Migration of double bond, keto-enol interconversion, Stork- Enamine reaction, halogenation of aldehydes and ketones and decarboxylation of aliphatic acids.

UNIT-IV: AROMATIC SUBSTITUTION REACTIONS

Electrophilic substitution reactions: The arenium ion mechanism. Orientation and reactivity (ortho, meta and para directing groups). Typical reactions including Reimer - Tiemann reaction, Vilsmeyer - Hack, Gattermann, Gattermann - Koch reaction and Kolbe reaction. Synthesis of di and tri substituted benzene (symmetrical tribromo benzene, 2-amino-5-methyl phenol, 3-nitro-4-bromobenzoic acid, 3, 4- dibromonitrobenzene and 1, 2, 3 - trimethylbenzene) starting from benzene or any monosubstituted benzene.

Nucleophilic substitution reactions: Mechanisms: SNAr and Benzyne mechanisms. Methods for the generation of benzyne intermediate and reactions of aryne intermediate. Nucleophilic substitution involving diazonium ions. Aromatic nucleophilic substitution of activated halides, Ziegler alkylation and Chichibabin reaction.

UNIT – V QUANTITATIVE TREATMENT OF ORGANIC REACTIONS

Kinetic and Non-kinetic methods of determining reaction mechanisms. Isotope effects. Effect of structure on reactivity: Hammett and Taft equation. Partial rate factor. Significance of □ and □□□Simple problems

Recommended Books

1. Jerry March, Advanced organic chemistry, 4th edition, John wiley and sons, New York, 1992.

2. S. H. Pine, Organic chemistry, 5th edition, Mcgraw Hill international edition chemistry series, New York, 1987.