Bachelors with Chemistry as Major
4th Semester

Title of the course: Stereochemistry and Reaction Mechanism

Course Code: CHM422J3**Credits:** Theory-4, Tutorials-2

Theory (4 credits: 60 Hours) **Max. Marks**: 100, **Min Marks:** 36

Course Objectives:

To impart advanced knowledge ofstereochemistry and stereochemical implications of mechanisms based on addition to double bonds, carbonyl groups, pericyclic and rearrangement reactions.

Learning outcomes:

Students will be expected to gain knowledge about basic concept of symmetry and chirality in the molecules, their spatial arrangement, properties and reactivity of stereoisomers, importance of the configuration of chiral organic compounds which will be useful in pharmaceutical industry where chemistsworkson stereoselective synthesis of compounds. The students will also gain knowledge about reaction mechanism and stereochemistry involved in formation of products. The knowledge about controlling the stereochemical pathways of the reaction is very useful in pharmaceutical industry.The broad spectrum of pericyclic reactions involved in organic synthesis, mechanism and applications

UNIT I: Stereochemistry (15 hours)

Chirality, Chirality of organic molecules with one chiral centre. Chirality of biphenyls, allenes, spiranes, Helical chirality. Chirality in molecules with more than one chiral center, optical purity, and methods of resolution. Homotopic, enantiotopic, and diastereotopic atoms, groups, and faces. Stereoselective and stereospecific synthesis (Specify with two examples of each). Enantioselectivity and Diastereoselectivity.
Configurations, conformations and stability of mono, di and trisubstitutedcyclohexanes, cyclohexenes, cyclohexanones, and decalins.Effect of conformation on reactivity.

UNIT II: Reactions at α and βTo Carbonyl Group (15 hours)

Nucleophilic additions to carbonyls and stereochemical aspects through various models (Cram, Cram chelation) for acyclic systems. Stereochemical control in addition of nucleophiles to cyclic carbonyl compounds. Formation and stability of enolates and enamines. Mechanism and stereochemical aspects of Aldol reactions (Controlling aldol reactions, intramolecular Aldol reaction and Cross Aldol condensation). Addition of Phosphorus and sulfur ylids. Wittig-Horner reaction. Michael addition.

UNIT III: Addition and Elimination Reactions (15 hours)

Stereochemical implications of addition reactions of acyclic and cyclic systems. Heterogeneous and homogeneous hydrogenation of double bonds and aromatic rings. Hydroboration of alkene, Electrophilic and nucleophilic epoxidation of alkene.Regioselectivity of epoxide ring opening. Sharpless asymmetric epoxidation. Addition to dienes.

Mechanism, stereochemistry and regio-chemistry of Elimination reactions in cyclic systems.

UNIT IV: Pericyclic Reactions (15 hours)

Introduction, Types of Pericyclic Reactions, Molecular Orbitals of Ethene, 1, 3-Butadiene and 1,3,5 Hexatriene. Frontier Molecular Orbitals (FMO).

Cycloaddition Reactions: Introduction, [2 + 2] and [4 + 2] Cycloaddition Reactions, Woodward-Hoffmann Rules for Cycloaddition Reactions, 1, 3-Dipolar Cycloadditions

Electrocyclic Reactions: Introduction, Cyclisations and stereochemistry of [4n] and [4n+2] Systems, Conrotatory and Disrotatory Motions, Ring Opening of 4n and [4n+2] Systems, Woodward-Hoffmann Rule for Electrocyclic Reactions

Sigmatropic Rearrangement: Introduction and Classification, Mechanism of Sigmatropic Rearrangement, Suprafacial and Antrafacial processes. Examples of [1,3]-, [1,5]-, and [1,7]-Sigmatropic rearrangements.

Books Recommended:

1. Stereochemistry of Organic Compounds: Principles and Applications. D. Nasipuri, 3rd Edition 2018.
2. Stereochemistry: Conformation and Mechanism. P. S. Kalsi, New Age International, 2008.
3. March's Advanced Organic Chemistry Reactions, Mechanism and Structure, 6thEd., Smith, M.B. (Wiley-2014)
4. Organic Chemistry 8thEd. - F. A. Carey and Robert M. Giuliano (McGraw Hill-2012).
5. Organic Chemistry - 2ndEd., J. Hornback. (Brooks/Cole- 2006).
6. Organic Chemistry, 5th Ed., John McMurry. (Brooks/Cole-2000).
7. Advanced Organic Chemistry, 5thEd., F.A Carey & R.J Sundberg (Springer-2007).
8. Organic Chemistry, 2ndEd., Jonathan Clayden (OUP-2016).
9. Organic Chemistry, 11thEd., Solomons, T.W.G., (Wiley-2015).
10. Organic chemistry, Morrison, Boyd and Bhattacharya. 7th Ed. Pearson-2013.
11. Pericyclic Reactions, Ian Fleming, 1998, Oxford University Press

Tutorials (2 credits: 60 Hours) Max. Marks: 50, Min Marks: 18

1. Understand stereochemistry using Ball and Stick models.
2. Creating models of different compounds using Ball and Stick models.
3. Animations involving different steps of mechanism in substitution and addition reactions and effect of steric hinderance on stereochemical outcome of the reaction.
4. Molecular modelling using various software's like Jmol, BIOVIA Draw, ChemDraw etc.
5. Problem based exercises on reaction mechanism.

Books Recommended:

1. Mendham, J. *Vogel's Quantitative Chemical Analysis*, Pearson, 2009.
2. Comprehensive Practical Organic Chemistry: Qualitative analysis Ahluwalia, V.K. &Sunita Dhingra; Universities Press, India, 2004.
3. Advanced Practical Organic Chemistry; N. K. Vishnoi; 3rdEdn; Vikas Publishing, 2009.
4. Organic Chemistry, 2ndEd., Jonathan Clayden, 2016.