

P.B.SIDDHARTHA COLLEGE OF ARTS & SCIENCE
DEPARTMENT OF CHEMISTRY
M.Sc – CHEMISTRY (ORGANIC CHEMISTRY)
III SEMESTER

Paper Code & Title: 22CH3E1: ORGANIC REACTION MECHANISM

No. of hours per week: 04
Total marks: 100

Total credits: 04
(Internal: 30 M & External: 70M)

Course: Organic Reaction Mechanism (code 22CH3E1)		
S.No	COURSE OUTCOMES	PO'S
	The student will be able to	
1	Acquire sound knowledge of oxidations, reductions, molecular rearrangements, pericyclic reactions and photo chemistry.	2
2	Understand the concepts involved in oxidations, reductions, molecular rearrangements, pericyclic reactions and photo chemistry.	1,7
3	Apply the conceptual knowledge gained in oxidations, reductions, molecular rearrangements, pericyclic reactions and photo chemistry in chosen fields.	1,5,6
4	Analyse and categorise the various types oxidations, reductions, molecular rearrangements, pericyclic reactions and photo chemistry in a given reactions.	1,7,4

UNIT-I

Oxidations

Definition and types of Oxidations, oxidations with ruthenium tetroxide, NBS, iodobenzene diacetate, Ti(III) nitrate, Chromium (VI) oxidants, Lead tetra acetate, SeO₂, MnO₂, Ag₂CO₃, Oppenauer oxidation, perhydroxylation using KMnO₄, OsO₄, HIO₄, oxidation with iodine silver carboxylate (Woodward and Prevost conditions), Definition & mechanism of epoxidation by peracids.

UNIT-II

Reductions

Definition and types of reductions, reduction by dissolving metals - Reduction with metal and liquid ammonia (Birch Reduction of aromatic compounds), Reduction with metal acid - Clemensons reduction, Reduction by hydride transfer reagents, Aluminium alkoxide - Meerwein-Ponndorf-Verley Reduction, LiAlH₄, NaBH₄, Diisobutylaluminium hydride (DIBAL), Sodium cyanoborohydride, trialkylborohydrides, Reduction with diimide, Wolff-Kishner reduction.

UNIT-III

Molecular Rearrangements

Migration to electron deficient carbon atom. Pinacole-Pinacolone rearrangement, Wagner-Meerwein rearrangement, Dienone-Phenol rearrangement, Benzil-Benzilic acid rearrangement, Favorski rearrangement, Arndt Eistert rearrangement, Sommelet – Hauser rearrangement.

Migration to electron deficient hetero atom: Wolf, Hofmann, Curtius, Lossen, Schmidt, Beckmann rearrangement, Baeyer-Villiger rearrangement, Stevens, Neber rearrangements. Fries, Fischer-Hepp, Orton, Bamberger, Dakin, Cumene Hydroperoxide rearrangement.

UNIT-IV

Pericyclic Reactions – I:

Definition, classification of pericyclic reactions, Molecular Orbital energy level diagrams, electronic configuration in ground and first excited states of Ethylene, 1,3-Butadiene, 1,3,5-Hexatriene, allyl system, stereo chemical notations – suprafacial, antarafacial, conrotatory and disrotatory modes, Woodward and Hoffmann selection rules.

Electrocyclic reactions: Mechanism, Stereochemistry of $(4n)$ and $(4n+2)$ π systems. PMO, FMO and correlation methods.

Cyclo additions: Mechanism, stereochemistry of $(2+2)$ and $(4+2)\pi$ systems, PMO, FMO and correlation methods.

Sigmatropic rearrangements: Classification, mechanism for FMO and PMO approach under thermal and photo chemical conditions. (Detailed treatment of Claisen, Cope rearrangements fluxional molecules, aza-cope rearrangements).

UNIT-V

Photochemistry:

Photochemical processes: Energy transfer, sensitization and quenching. Singlet and triplet states and their reactivity. Photochemistry of olefins – conjugated olefins, Aromatic compounds – isomerisation – additions. Photochemistry of carbonyl compounds – Norrish type I and II reactions – Paterno – Buchi Reaction.

Photoreduction, Photochemical rearrangements – PhotoFries rearrangement, Di- π -methane rearrangement.

Reactions of unactivated C – H bonds: The Hoffmann Löffler Freytag reaction, Barton reaction, photolysis of organic nitrites, photolysis of N – nitrosoamides.

References:

1. Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, Prentice Hall.
2. Reaction mechanism in organic chemistry. 3rd edition, S.M. Mukherji & Singh.
3. Advanced Organic Chemistry-Reactions, Mechanisms and Structure, Jerry March, John Wiley and sons, 6th edition.
4. Advanced Organic Chemistry, F.A. Carey and R.J. Sundberg, Plenum.
5. Modern methods of organic synthesis, Cambridge University press, 3rd edition, W. Carruthers.
6. Organic Reaction Mechanisms, V.K. Ahluwalia, 4th edition, Narosa.
7. Reactions, rearrangements and reagents. S.N. Sanyal, 4th edition.
8. Organic Photo chemistry and Pericyclic reactions' M.G. Arora Anmol Publications Pvt. Ltd.
9. Fundamentals of Photochemistry by K.K. Rohatgi – Mukherjee New Age international publishers.