ACHARYA NAGARJUNA UNIVERSITY DEPARTMENT OF CHEMISTRY M.Sc. ORGANIC CHEMISTRY :: SEMESTER-III

PAPER-II: ORGANIC SYNTHESIS & REACTION MECHANISMS-I (R22OC32)

(For the students admitted from the A.Y. 2022-2023 onwards)

Max. Marks: 100

Learning Objectives:

(Internal-30M & External-70M)

SYLLABUS

- \checkmark To learn about the basics of tools required for determining reaction mechanisms.
- \checkmark To develop simple skills in writing mechanism of organic reactions.
- ✓ To understand different radical reactions involving additions, substitutions, and decompositions and their mechanisms.
- ✓ To learn different approaches and reagents of various oxidation and reduction processes in organic synthesis and also their mechanisms.
- \checkmark To learn terminology and selectivity in asymmetric synthesis and also apply the approaches in organic synthetic reactions.

UNIT-I

Methods for Reaction Mechanism by Kinetic & Non-Kinetic studies

Kinetic studies: Kinetics of reaction, Energy profile diagram, Intermediate versus transition state, Reaction rate and rate limiting step.

Non-Kinetic studies Identification of products, testing possible intermediates, trapping of intermediates, Cross over experiments, Isotopic labeling.

UNIT-II

Free Radicals

Free radicals and their reactions-Introduction to radical reactions, Addition of halogens, Hydrogen halides. Substitution reactions- Halogenation, Aromatic substitution, Sandmayer reaction, Autooxidation, Decomposition of dialkyl and diacyl peroxides.

UNIT-III

Oxidations

Introduction: Different Oxidative processes.

Hydrocarbon: Alkenes, aromatic rings saturated C-H groups (activated and unactivated), Alcohols, diols, aldehydes, Ketones, Carboxylic acids, Amines, hydrazines, sulphides. Oxidations with ruthenium tetroxide iodobenzene diaccetate and Tl(III) nitrate, Lead tetra acetate, SeO₂, MnO₂ Ag₂CO₃, peracids.

Oxidation of C=C perhydroxylation using KMnO₄, OsO₄, peracids.

UNIT-IV

Reductions

Introduction: Reductive process Hydrocarbons: Alkanes, alkenes, alkynes, and aromatic rings Carbonyl compounds-aldehydes, ketones, acids and their derivatives. Nitro, nitroso, azo and oxime group Hydrogenolysis. Catalytic hydrogenations, Reduction by dissolving metals, Reduction with metal and acid. Reduction with metal in liquid ammonia (Birch reduction). Reduction by hydride transfer reagents Aluminium alkoxide, LiAlH4, NaBH4, Diisobutyl

aluminium hydrides–Sodium cyano borohydride, tryalkyl borohydirdes-Reduction with diimide.

14H

10H

10H

14H

UNIT-V

Asymmetric Synthesis-I

Terminology: Topocity in molecules Homotopic, stereo Heterotopic (enantiotopic and diastereotopic) groups and faces- symmetry, substitution and addition criteria. Prochirality nomenclature: Pro-R, Pro-S, Re, and Si.

Selectivity in synthesis: Stereo specific reactions (substrate stereoselectivity). Conditions Stereo selective reactions (product stereoselectivity): Enantio selectivity and diastereoselectivity.:

Analytical Methods: % Enantiomer excess, optical purity, % diastereomeric excess.

Reference Books:

- 1) Mechanism and structure in Organic Chemistry " E.S.Could Henry Holt and Co, Newyork.
- 2) Advances in Organic Reaction mechanism and structure J. March (McGrew Hill).
- 3) Aguide Book to Mechanism in Organic Chemistry" by P.Sykes.
- 4) Synthetic approaches in organic chemistry by R.K.Bansal (Narosa Publications).
- 5) Some modern methods of synthesis by Carruthers (Cambridge).
- 6) Asymmetric synthesis by Nogradi.
- 7) Asymmetric organic reactions by it) Morrison and HS Moscher.
- 8) Stereo differentiating reactions by Izumi.

Learning Outcomes:

- ✓ Students can understand the fundamental tools required for the determination of reaction mechanisms.
- \checkmark Students can able to apply the reagents and approaches for various synthetic reactions involving oxidations and reductions
- ✓ The knowledge on asymmetric synthesis provides a platform for carryout various stereo chemical reactions wherever necessary to apply towards research.
- \checkmark Students can understand the reduction by dissolving metals, reduction with metal and acid.
- \checkmark Students can understand the terminology, selectivity in synthesis and analytical methods.

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