GAYATRI VIDYA PARISHAD
COLLEGE FOR DEGREE AND PG COURSES (AUTONOMOUS)
Affiliated to Andhra University | | Accredited by NAAC and NBA
VISAKHAPATNAM

DEPARTMENT OF ORGANIC CHEMISTRY

M.Sc. (Final) CHEMISTRY SYLLABUS
SEMESTER-III
PAPER I - ORGANIC REACTION MECHANISMS, PERICYCLIC REACTIONS AND PHOTOCHEMISTRY
(Effective from the admitted batch of 2022-2023)

Credits: 4		**Theory: 4 Hours**
Max Marks: 100	**External: 80**	**Internal: 20**

Course Outcomes (COs)/Course Specific Outcomes (CSOs):

CO 1: Acquire the knowledge of radical reactions and mechanisms of Substitution and their importance.
CO 2: Understand the concept of mechanisms of Pericyclic reactions
CO 3: Understand the advanced reactions and mechanisms of Pericyclic reactions
CO 4: Develop interest in the areas of reactions and mechanisms of Organic Photochemistry
CO 5: Develop concepts of advanced reactions and mechanisms in Organic Photochemistry

Course learning outcome (LOs):

Upon completion of the course the students should be able to:
LO 1: Familiarize the different types of nucleophilic and radical substitution reactions
LO 2: Analyze and solve to add nucleophiles, electrophiles and free radicals to carbon-hetero atom multiple bonds
LO 3: Interpret theoretical basis of pericyclic reactions and helps them to carry out these reactions.
LO 4: Apply the concept of pericyclic reaction in synthesis of organic compounds
LO 5: Basic concepts of organic photochemical reactions
LO 6: Photochemistry of carbonyl compounds, alkenes, dienes and aromatic compounds
LO 7: To know synthetically the processes relevant organic-chemical reactions and be able to discuss the mechanism of these reactions

UNIT-I: Radical Substitution Reactions [12 Hours]

Reactivity for aliphatic substrates, reactivity at Bridgehead, Reactivity in aromatic substrates, neighbouring group assistance in free radical reactions, reactivity in the attacking radical, effect of solvent on reactivity, halogenation at an alkyl carbon and allylic carbon, hydroxylation at aromatic carbon by means of Fenton's reagent, Hunsdiecker reaction, Kolbe reaction, Reed reaction and Sandmayer reaction.

UNIT-II: Pericyclic reactions-I: [12 Hours]

Molecular orbital symmetry - frontier orbitals of ethylene - 1,3-Butadiene, 1,3,5-Hexatriene, allyl system - classification of pericylic reactions - FMO approach - Woodward-Hoffman correlation diagram method and perturbation of molecular (PMO) approach for the explanation of pericyclic reactions under thermal and photochemical conditions. **Electrocyclic Reactions:** Conrotatory and disrotatory motions, (4n) and (4n+2) - allyl systems and secondary effects.

Cycloadditions: Antarafacial and suprafacial additions, notation of cycloadditions, (4n) and (4n+2) systems with a greater emphasis on (2+2) and (4+2) - cycloadditions, and cheletropic reactions.

UNIT-III: Pericyclic reactions-II: [12 Hours]

FMO approach and perturbation of molecular (PMO) approach for the explanation of sigmatropic rearrangements under thermal and photochemical conditions - suprafacial and antarafacial shifts of H - sigmatropic shifts involving carbon moieties - retention and inversion of configurations, (3,3) and (5,5) sigmatropic rearrangements - detailed studies of Claisen (Ireland-Claisen, Overman-Claisen, Johnson-Claisen) and Cope rearrangements - aza-Cope rearrangement and fluxional tautomerism

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UNIT-IV: Organic Photochemistry-I: [12 Hours]

Photochemical energy, Frank-Condon Principle - Jablonski diagram singlet and triplet states - dissipation of photochemical energy – photosensitization – quenching - quantum efficiency and quantum yield - experimental methods of photochemistry - photochemistry of carbonyl compounds n-π, π-π* transitions - Norrish type I and Norrish type II cleavages - Paterno-Buchi reaction.

UNIT-V: Organic Photochemistry-II: [12 Hours]

Photo reduction - hydrogen abstraction - rearrangement of α,β- unsaturated ketones and cyclohexadienones - photochemistry of p-benzoquinones - photochemistry of unsaturated systems – olefins, *cis-trans*-isomerization and dimerisation - hydrogen abstractions and addition acetylenes dimerization, dienes - photochemistry of 1,3-butadiene - photochemistry of cyclohexadienes. Di-pi methane rearrangement

Photochemistry of aromatic compounds – excited state of benzene and its 1,2-, 1,3-, 1-4- additions - photofries rearrangement - photofries reactions of anilides, photosubstitution reactions of benzene derivatives.

Text Books:

1. Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, Mc.Graw Hill and Kogakush.
2. Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, Prentice Hall.
3. Pericyclic reactions by S.N. Mukharji, Mcmilan.
4. Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S. Richgardson.
5. The modern structural theory in Organic Chemistry by L.N.Ferguson, Pretice Hall.

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