MANGALORE UNIVERSITY

Department of Chemistry

MSc ORGANIC CHEMISTRY

OC S 504: Organic Photochemistry & Pericyclic Reactions

COURSE OUTCOME:

- Students will gain knowledge on principles of photochemistry and diverse types of photochemical reactions of various classes of organic molecules with multiple examples, photochemistry of vision, photodegradation of polymers, photochemical cell, energy conversion and storage, photocatalysis, photocleavage of waste,
- They learn photo-oxidation and reduction reactions.
- Students will understand the photochemical reactions of various three, four, five, six and seven membered simple and fused heterocyclic compounds with one or more heteroatoms, various fiveand six membered simple and fused heterocyclic compounds.
- Students will learn the concepts of pericyclic reactions, diverse types of electrocyclic, cycloaddition and sigmatropic reactions with multiple examples.

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

Bonding and antibonding orbital, σ and π orbitals, σ* and π* orbitals, singlet and triplet states, relative energies and excited states, Chemistry of excited states of organic molecules, Jablonski diagram and quantum yield, Photodissociation, Photoreduction, Photochemical isomerisation, Photocyclisation and related reactions. Norrish Type-I and Type-II reactions, Di-pi methane rearrangement, Optical pumping, Barton reaction and Photo Fries rearrangement, Paterno-Buchi reaction, Photochemistry of alkenes, benzenes, Yang cyclisation. Photochemistry of vision. photodegradation of polymers. Introduction to Photochemical cells, energy conversion and storage. Photocatalysis: Photocleavage of waste which are environmentally hazardous by using TiO2, Photooxidation and photoreduction reactions.

UNIT-II: **[12 Hours]**

Photochemistry of Heterocycles: Photo-oxidation of pyrroles, photochemical reactions of pyrazoles, 1,2,3 and 1,2,4-triazoles, 1,2,3-triazines, 1,3,4-oxadiazoles, mono and disubstituted tetrazoles. Photochemistry of pyridazines and pyrimidines. Photochemistry of five membered heterocycles-with one heteroatom-Pyrrole, Furan and Thiophene; with two hetero atoms-Thiazole, Oxazole, isoxazole and Pyrazole. Photochemistry of six and seven membered heterocycles-Pyridine, Pyrones, Pyridazine and Pyrazine. Fused heterocycles-Benzothiophene. Synthesis of Pyrazine from azirine derivatives. Photochemical reactions of Pyrazine.

UNIT-III: **[12 Hours]**

Pericyclic Reactions: Introduction, Characteristics and classification of pericyclic reactions-Electrocyclic, cycloaddition & cycloreversions and sigmatropic reactions. Aromatic

Transition States (ATS)/Perturbation Molecular Orbitals (PMO) approach for the interpretation of mechanism of pericyclic reactions. Molecular orbital symmetry, Frontier orbitals of ethylene,1,3-butadiene, 1,3,5-hexatriene and allyl systems. Woodward-Hoffmann correlation diagram and FMO approach.

Electrocyclic Reactions: Introduction, Con-rotatory and dis-rotatory Process, 4n and 4n+2systems. Reactions of cations and anions, formation and cyclisation of dipolar molecules. **Cycloaddition reaction:** Suprafacial and Antrafacial addition, notation of cycloadditions,2+2 and 4+2 systems, 2+2 additions of ketones, secondary effects of substitutes on the rates of cycioadditions and chelotropic reactions. 1,3-dipolar cycloaddition reactions and their applications in the synthesis of five membered heterocycles, nitrile oxid and sydnones. **Sigmatropic reactions:** FMO approach and perturbation of molecular (PMO) approach for the explanation of sigmatropic rearrangements under thermal and photochemical conditions. Suprafacial and Antrafacial shift of H, [1,3] [1,5] [1,7] and [3,3]-sigmatropic shifts. Walk, Claisen, Cope, Oxy-Cope and Aza-Cope rearrangements.

References:

1. Organic Photochemistry- Vol I & II- O.L. Chapman (Marcel Decker).
2. Organic Chemistry- Vol 1-3 - Mukherji Singh and Kapoor (Wiley Eastern).
3. Organic Reaction Mechanisms-V.K. Ahluwalia & R.K. Parashar (Narosa) 2006.
4. Advanced Organic Chemistry-Reaction Mechanisms, Reinhard Bruckner (Academic), 2005.
5. Pericyclic reactions, S.M Mukherji (McMillan) 1979.
6. J. A. Joule and G. F. Smith: Heterocyclic Chemistry, Cambridge University press (1972).
A. R. Katritzky and C. J. Rees: Comprehensive Heterocyclic Chemistry, Pergamon (1984).
7. D. H.R. Barton and W. D. Ollis: Comprehensive Organic Chemistry, Vol 14, Heterocyclic Compounds, Pergamon (1979).
8. A. R. Katritzky: Advances in Heterocyclic Chemistry, Vol 15-25, Academic (1971-81).