SEMESTER -II

ORGANIC CHEMISTRY-II

THEORY

Programme: M.Sc. **Max.Hours : 60**
Course Code: P20/CHE/DSC/202 **Hours per week: 4**
Type of course: DSC – 6 **Max.Marks: 100**
No. of credits : 4

Course Objectives:

1. The aim of the reaction mechanism is to provide students with the tools to describe and work out reaction mechanisms of different chemical reactions and recognize neighboring group participation.
2. Pericyclic reaction is a type of organic reaction where in the transition state of the molecule has a cyclic geometry and the reaction progresses in a concerted fashion. And also deals with the Aromaticity of organic compounds.
3. The study is aimed at learning photochemical organic reactions and mechanisms like electrocyclic, radical, photo isomerization and Norisch reactions.
4. Appreciation of the relative stabilities and reactivities of the reactive intermediates and involvement of intermediates in various rearrangements.

COURSE OUTCOMES:

CO1: Discuss nucleophilic aromatic substitution reaction and benzyne mechanisms.
CO2: Explain Neighboring group participation in aliphatic Electrophilic substitution.
CO3: Discuss Ambident nucleophiles , non-classical carbocation & SET mechanism.
CO4: Explain pericyclic reactions like Electrocyclic reactions, Cycloaddition reactions and Sigmatropic reactions.
CO5: Discuss Aromatic Transition States (ATS)/Perturbation Molecular Orbitals (PMO) Approach.
CO6: Concept of Huckel –Mobius aromatic and antiaromatic transition states and Solve problems based on ATS approach
CO7: Explain the Frontier Molecular Orbital (HOMO-LUMO) approach, WoodwardHofmann selection rules for all the pericyclic reactions and solve problems based on FMO approach.
CO8: Discuss the Photochemistry of _-_* transitions with particular reference to cis- trans isomerisation and Di-Pi methane rearrangement
CO9: Discuss the Photochemistry of (n-_*) transitions with particular reference to Norrish type-I Norrish II type reactions , Paterno Bucchi reactions & photochemistry of nitrites.
CO10: Explain the generation, detection, structure, stability and reactions of carbocations, carbanions, carbenes, nitrenes and free radicals **of pericyclic reactions**: Aromatic Transition States (ATS)/Perturbation Molecular Orbitals (PMO) approach-Concept of Huckel –Mobius aromatic and antiaromatic transition states. Framing Woodward-Hofmann selection rules for all the

pericyclic reactions by ATS approach. Solving problems based on ATS approach. **Molecular orbitals**: ethylene, 1, 3-butadiene, 1, 3, 5-

Module 1: Reaction mechanism-II **(15 Hrs)**

NucleophilicAromaticsubstitution: Aromatic Nucleophilic substitution: $S_N1(Ar)$,$S_N2(Ar)$, and benzyne mechanisms; evidence for the structure of benzyne.VonRichter rearrangement..Definition and types of ambident nucleophiles.

Neighbouring group participation: Criteria for determining the participation of neighbouring group.Enhanced reaction rates, retention of configuration, isotopic labeling and cyclic intermediates. Neighbouring group participation involving Halogens, Oxygen, Sulphur, Nitrogen, Aryl, Cycloalkyl groups, σ and π-bonds. Introduction to nonclassical carbocations. **Electrophilic substitution at saturated carbon and single electron transfer reactions.** Mechanism of aliphatic electrophilic sustitution.S_E1, S_E2, and S_Ei.SET mechanism.

Module 2: Pericyclic Reactions **(15 Hrs)**

Introduction, Classification of pericyclic reactions,

Electrocyclic reactions: con rotation and dis rotation. Electrocyclic closure and opening in 4n and 4n+2 systems.

Cycloaddition reactions: suprafacial and antara facial additions in 4n and4n+2 cycloadditions.

Sigmatropic reactions: [i, j] shifts- suprafacial and antarafacial shifts, Cope and Claisen rearrangement reactions.

Approaches for the interpretation of mechanismhexatriene, allyl cation, allyl radical, pentadienyl cation, pentadienyl radical.

Frontier Molecular Orbital (HOMO-LUMO) approach-concept: Framing Woodward-Hofmann selection rules for all the pericyclic reactions by Frontier Molecular Orbital (FMO) approach. Solving problems based on FMO approach.

Conservation of orbital symmetry: (Correlation Diagrams) approach- for electrocylic and cycloadditions & cycloreversions

Module 3: Photochemistry **15 Hrs**

Photochemistry: Photochemistry of π-π* transitions: Excited states of alkenes, cis-trans isomerisation, and photo stationary state. Photochemistry of 1,3-butadiene Electrocyclisation and sigmatropic rearrangements, di-π methane rearrangement. Intermolecular reactions, photocycloadditions, photodimeriastion of simple and conjugated olefins. Addition of olefins to α, β-unsaturated carbonyl compounds. Excited states of aromatic compounds, Photoisimerisation of benzene.

Photochemistry of (n-π*) transitions: Excited states of carbonyl compounds, homolytic cleavage of α- bond, Norrish type I reactions in acyclic and cyclic ketones and strained cycloalkane diones.

Intermolecular abstraction of hydrogen: photoreduction-influence of temperature, solvent, nature of hydrogen donor and structure of the substrate.
Intramolecular abstraction of hydrogen: Norrish type II reactions in ketones, esters and 1,2 diketones, Addition to carbon-carbon multiple bonds, Paterno-Buchi reaction, Photochemistry of nitrites-Barton reaction.

Module 4: Reactive intermediates and Molecular rearrangements **15 Hrs**

Reactive Intermediates: Generation, detection, structure, stability and reactions of carbocations, carbanions, carbenes, nitrenes and free radicals.
Molecular rearrangements: Definition and classification. Molecular rearrangements involving
1) electron deficient carbon: Wagner- Meerwein, Pinacol-Pinacolone, Allylic and Wolf rearrangement.
2) electron deficient Nitrogen: Hofmann, Lossen, Curtius, Schmidt and Beckmann rearrangements
3) electron deficient Oxygen: Baeyer-Villiger oxidation. 4) Base catalysed rearrangements: Benzilic acid, Favourski , Transannular , Sommlett-Hauser and Smiles rearrangement

References:

1. Stereochemistry of Carbon compounds by Ernest L Eliel / Samuel H. Wilen
2. Stereochemistry of organic compounds – Principles and Applications by D Nasipuri
3. The third dimension in organic chemistry, by Alan Bassindale
4. Stereochemistry: Conformation and Mechanism by P S Kalsi
5. Stereochemistry by V M Potapov
6. Advanced Organic Chemistry by Jerry March
7. Mechanism and Structure in Organic Chemistry S. Mukerjee
8. Organic chemistry Vol.I and II by I.L.Finar
9. Comprehensive organic chemistry Vol.5 D.H.R.Barton and W.D..Ollis

SEMESTER -II

ORGANIC CHEMISTRY-II

MODEL THEORY QUESTION PAPER

Course Code: P20/CHE/DSC/202 **Max Time: 2½ Hrs**
Credits: 4 **Max. Marks :60**

SECTION A

I Answer the following Questions:- **4 x 10 = 40 M**

1. a) Write the mechanism involved in Von Richter Rearrangement ? **(CO1)**
   b) Give an account of different types of aliphatic electrophilic substitution reactions **(CO2)**

OR

2. a) Write notes on:
   i) SET Mechanism **(CO3)**
   ii) SN^1Ar mechanism
   b) NGP involving Halogens **(CO2)**

3. a) Frame the selection rules for sigmatropic reactions by ATS approach **(CO5)**
   b) Describe Claisen rearrangement with examples. **(CO4)**

OR

4. a) Write all the molecular orbitals of pentadienyl radical and cation, indicate their Frontier Molecular Orbitals in ground state and First Excited state **(CO7)**
   b) Write all the selection rules for electrocyclic reactions? Explain them by Huckel – Mobius method **(CO6)**

5. a) Write about photodimerisation reactions **(CO8)**
   b) Write about di-π methane rearrangement. **(CO8)**

OR\

6. a) Illustrate Norrish type 1 and type II cleavage process **(CO9)**
   b) Discuss the Photoisomerisation of benzene. **(CO8)**

7. a) Outline the mechanism of the following **(CO10)**
   i) Hofmann's rearrangement
   ii) Sommlett-Hauser rearrangement
   iii) Wagner- Meerwein rearrangement

OR

8. a) Discuss geometry, generation methods andfactors affecting stability of carbocations. **(CO10)**
   b) Outline the mechanism of Pinacol -Pinacolone rearrangement and explain the migratory aptitude involved in it **(CO10).**

II Answer any <u>FIVE</u> **5 x 4 = 20 M**

9. Write about benzyne mechanism? **(CO1)**
10. What are ambident Nucleophiles? Ilustrate their reactions with examples **(CO3).**
11. Write all the molecular orbitals of 1, 3, 5 hextriene. Indicate HOMO and LUMO under Ground state and First Excited state. **(CO7)**
12. Frame the selection rules of cycloaddition reactions based on PMO approach. **(CO5)**
13. What is Barton reaction? Explain its mechanism. **(CO9)**
14. Outline the mechanism of Paterno Buchi reaction. **(CO9)**
15. Discuss the geometry, generation methods and reactivity of carbenes. **(CO10)**
16. Outline the mechanism of Benzilic acid rearrangement. **(CO10)**