

**Paper Name : Organic Chemistry (Theory)**

**Course Code CH 402**

**Credits : 04**

**Learning Hours : 60**

The objective of this syllabus is to provide a comprehensive understanding of various reactive intermediates including carbocations, carbanions, free radicals, carbenes, nitrenes, and arynes, focusing on their generation, structure, stability, and reactions. Additionally, the syllabus aims to introduce fundamental concepts such as Huckel's rule and aromaticity, covering aromatic, anti-aromatic, and non-aromatic systems, with detailed analysis using Frost circle diagrams for cyclobutadiene and benzene. Further, the objective includes elucidating nucleophilic substitution reactions (S<sub>N</sub>1 and S<sub>N</sub>2) and their mechanisms, stereochemistry, leaving group effects, and reaction mediums, as well as electrophilic substitution reactions (S<sub>E</sub>1 and S<sub>E</sub>2) with their corresponding mechanisms and stereochemistry. Moreover, the syllabus aims to cover addition reactions of alkenes and alkynes, elimination reactions (E1 and E2) including Zaitsev's rule and various rearrangement reactions such as carbon-carbon, carbon-nitrogen, and carbon-oxygen rearrangements, providing insights into their mechanisms, reactions, and applications in organic synthesis.

**By the end of the course, the students will be able to:**

- ❖ Understand the generation, structure, stability, and reactions of carbocations, carbanions, free radicals, carbenes, nitrenes, and arynes, enabling the identification and analysis of these reactive intermediates in organic reactions.
- ❖ Gain proficiency in applying Huckel's rule and understanding the concept of aromaticity, distinguishing between aromatic, anti-aromatic, and non-aromatic systems, and utilizing Frost circle diagrams for cyclobutadiene and benzene to analyze their aromaticity.
- ❖ Acquire knowledge of nucleophilic substitution reactions (S<sub>N</sub>1 and S<sub>N</sub>2) including their mechanisms, stereochemistry, leaving group effects, and the influence of reaction mediums, facilitating the understanding and prediction of substitution reactions in organic synthesis.
- ❖ Master the mechanisms and stereochemistry of electrophilic substitution reactions (S<sub>E</sub>1 and S<sub>E</sub>2), enabling the interpretation and prediction of substitution reactions involving electrophilic reagents.
- ❖ Develop proficiency in understanding and predicting addition reactions of alkenes and alkynes, as well as elimination reactions (E1 and E2), including Zaitsev's rule, dehydration of alcohols,

dehydrohalogenation of haloalkanes, and Hoffman elimination, for application in organic synthesis.

- ❖ Gain a comprehensive understanding of various rearrangement reactions, including carbon-carbon, carbon-nitrogen, and carbon-oxygen rearrangements, their mechanisms, reactions, and applications in organic synthesis, enabling the design and execution of complex synthetic pathways.

### **DETAILED SYLLABUS**

<b>Unit 1 (A).</b>	<b>Reactive Intermediate</b>	<b>(14 Marks)</b>
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- Generation, Structure, Stability and Reactions of:

- Carbocations
- Carbanions
- Free radicals
- Carbenes
- Nitrenes
- Arynes

<b>(B).</b>	<b>Aromaticity</b>
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- Introduction
- Huckel's rule and concept of aromaticity
- Types of aromaticity- Aromatic, Anti-aromatic, non-aromatic.
- Frost circle diagram for cyclobutadiene, benzene.
- Resonance and chemical stabilization-aromatic character based on NMR criteria, Huckel's molecular orbital (HMO) method, MO of simple organic systems such as ethene, allyl and butadiene.
- Aromaticity in benzenoid and non-benzenoid compounds and charged rings, annulenes, fulvenes, azulenes, antiaromaticity and homoaromaticity.

<b>Unit 2</b>	<b>Types of Organic Reactions</b>	<b>(14 Marks)</b>
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- **Nucleophilic substitution reactions:** The  $S_N1$  and  $S_N2$  reactions and their mechanisms and Stereochemistry, Leaving group effect and reaction medium.

- **Electrophilic substitution reactions:** SE1 and SE2 reactions, their mechanism and stereochemistry.
- **Addition reactions:** Addition reactions of alkenes and alkynes.
- **Elimination reactions:** E1 and E2 mechanism, Zaitsev's rule, Dehydration ( $-H_2O$ ) of alcohols, Dehydrohalogenation ( $-HX$ ) of haloalkanes, Hoffman elimination.
- Neighbouring group Participation in Nucleophilic substitution: O ( $COO^-$ ,  $-OH$ ), N ( $NH_2$ ,  $NHR$ ,  $NR_2$ ), S ( $SH$ ,  $SR$ ), and halogen as Neighbouring group donor

### Unit 3

### Rearrangement Reactions

(14 Marks)

- Mechanism to Nucleophilic, Electrophilic, and Free radical molecular rearrangements. Their reaction, mechanism and applications
  - **Carbon-Carbon rearrangements**
    - ❖ Pinacol- Pinacolone rearrangement.
    - ❖ Wagner-Meerwein rearrangement.
    - ❖ Tiffeneau-Demjanov rearrangement.
    - ❖ Favorskii rearrangement.
    - ❖ Wolff rearrangement.
    - ❖ Benzil Benzilic acid rearrangement.
    - ❖ Neber rearrangement.
    - ❖ Benzidine rearrangement.
  - **Carbon- Nitrogen rearrangements**
    - ❖ Hoffmann rearrangement.
    - ❖ Curtius rearrangement.
    - ❖ Lossen rearrangement.
    - ❖ Schmidt rearrangement
    - ❖ Beckmann rearrangements.
  - **Carbon-Oxygen rearrangements**
    - ❖ Bayer-Villiger rearrangement.
    - ❖ Dakin rearrangement.

❖ Wittig rearrangement.

**Unit 4**

**Stereochemistry**

**(14 Marks)**

Planar and helical Chirality: Configurational nomenclature: Planar chiral ANSA compounds and trans cyclooctene. Helical chiral compounds. Enantioselective Synthesis — Epoxidation of allyl alcohols (Sharpless epoxidation), Enantioselectivity through Hydroboration-Oxidation, Enantioselectivity through use of Phase transfer catalysts, Reduction of ketones with chiral hydride donors. Asymmetric resolution: Dynamic resolution, Dynamic kinetic resolution, and Dynamic Thermodynamic resolution.

**References**

1. Advanced Organic Chemistry, Reactions Mechanisms and Structure, J. March, 6<sup>th</sup> Edition, John Wiley.
2. Carbenes, nitrenes and arynes, T.L. Gilchrist and C.W. Rees.
3. Reaction Mechanism in Organic Chemistry by S. M. Mukherji and S. P. Singh
4. Organic Chemistry; Morrison, R. N. & Boyd, R. N.; Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
5. Organic Chemistry (Volume 1); Finar, I. L.; Dorling Kindersley (India) Pvt. Ltd. (Pearson Education)
6. A Text Book of Organic Chemistry; ArunBahl and B.S. Bahl; Sultan Chand & Sons, New Delhi.
7. Organic Chemistry Second Edition — Mehta and Mehta; PHI Learning Pvt. Ltd.