

29.0: Chapter Overview

Learning Objectives

- Define pericyclic reactions as concerted processes involving cyclic movement of electrons.
- Explain the Woodward-Hoffmann Rules for predicting outcomes based on molecular orbital symmetry.
- Outline subclasses like cycloadditions, electrocyclic reactions, and sigmatropic rearrangements.
- Describe how pericyclic reactions proceed through cyclic transition states and molecular orbitals.
- Provide key examples like Diels-Alder, electrocyclic ring closures, and Claisen rearrangements.
- Discuss how pericyclic reactions are used in synthesis of complex molecules and materials.

Pericyclic reactions represent a fascinating class of organic reactions characterized by the concerted movement of electrons around a cyclic array of atoms. These reactions involve a cyclic transition state where bonding changes occur with the involvement of π electrons. The term "pericyclic" stems from the Greek roots "peri," meaning around, and "cyclo," referring to cycle or ring, encapsulating the cyclic nature of these reactions.

Key features of pericyclic reactions include their stereospecificity, concertedness, and often high regio- and stereochemical control. They are governed by orbital symmetry rules, primarily the Woodward-Hoffmann rules, which provide a theoretical framework for predicting the outcome of these reactions based on the symmetry properties of the molecular orbitals involved.

Pericyclic reactions encompass several important subclasses, including:

1. **Cycloadditions:** In cycloaddition reactions, two or more unsaturated molecules combine to form a cyclic product. Diels-Alder reaction is a classic example, where a conjugated diene reacts with a dienophile to form a cyclohexene ring.
2. **Electrocyclic Reactions:** These reactions involve the reorganization of π electrons in a conjugated system to form a cyclic compound. Examples include the ring-opening and ring-closing reactions of cyclobutene and cyclohexadiene systems.
3. **Sigmatropic Rearrangements:** Sigmatropic rearrangements involve the migration of a σ -bond (a single bond) along a conjugated system. The Claisen rearrangement and the Cope rearrangement are prominent examples of sigmatropic shifts.
4. **[2+2] Cycloadditions:** These reactions involve the formation of a four-membered ring from two unsaturated reactants.

Pericyclic reactions find wide applications in organic synthesis due to their efficiency, selectivity, and the ability to form multiple bonds stereospecifically in a single step. Moreover, their predictable nature based on orbital symmetry principles makes them valuable tools for designing complex molecular architectures. Understanding and mastering pericyclic reactions are essential for synthetic chemists aiming to construct intricate organic molecules efficiently and with precision.

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