

A **sigmatropic reaction** in organic chemistry is a pericyclic reaction wherein the net result is one σ -bond is changed to another σ -bond in an uncatalyzed intramolecular reaction.^[1] The name *sigmatropic* is the result of a compounding of the long-established sigma designation from single carbon-carbon bonds and the Greek word *tropos*, meaning turn. In this type of rearrangement reaction, a substituent moves from one part of a π -bonded system to another part in an intramolecular reaction with simultaneous rearrangement of the π system.^[2] True sigmatropic reactions are usually uncatalyzed, although Lewis acid catalysis is possible. Sigmatropic reactions often have transition-metal catalysts that form intermediates in analogous reactions. The most well-known of the sigmatropic rearrangements are the [3,3] Cope rearrangement, Claisen rearrangement, Carroll rearrangement, and the Fischer indole synthesis.

Woodward-Hoffman sigmatropic shift nomenclature

Sigmatropic rearrangements are concisely described by an **order term** $[i,j]$, which is defined as the **migration** of a σ -bond adjacent to one or more π systems to a new position $(i-1)$ and $(j-1)$ atoms removed from the original location of the σ -bond.^[3] When the sum of i and j is an even number, this is an indication of the involvement of a neutral, all C atom chain. An odd number is an indication of the involvement of a charged C atom or of a heteroatom lone pair replacing a CC double bond. Thus, $[1,5]$ and $[3,3]$ shifts become $[1,4]$ and $[2,3]$ shifts with heteroatoms, while preserving symmetry considerations. **Hydrogens** are omitted in the third example for clarity.

Woodward-Hoffmann Nomenclature
Reaction Order Designations

