

BOOKS

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry, Jonathan Clayden Nick Greeves Stuart Warren, 2th Edition
- 4) Organic Chemistry, John E. McMurry, 8th. Edition
- 5) Reaksiyon Mekanizmaları: Metin Balcı, 2. Baskı.

1. Pericyclic Reactions

1.1 Introduction

1.2 Characteristic of Pericyclic Reactions

1.3 Types of Pericyclic Reactions

1.3.1 Electrocyclic Reactions

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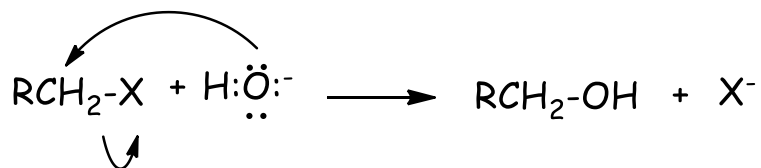
1.3.3 Sigmatropic Reactions

1. Pericyclic Reactions

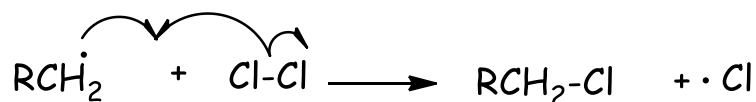
1.1 Introduction

In organic chemistry, it is possible to group reactions into three groups.

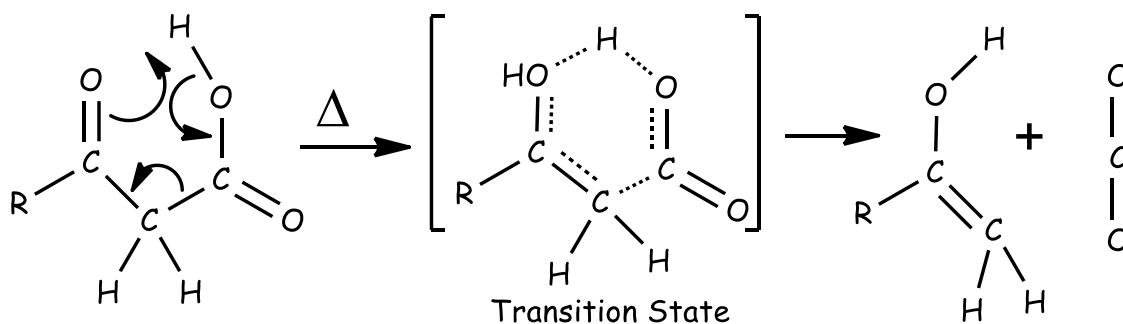
1. Polar reactions



2. Radical reactions



3. Pericyclic reactions



A pericyclic reaction, a reaction that occurs as a result of reorganizing the electrons in the reactant(s)

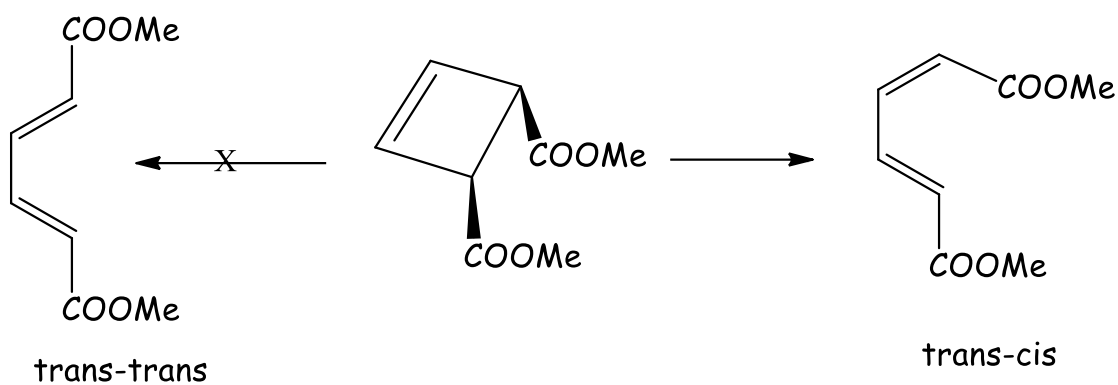
1.2 Characteristic of Pericyclic Reactions

- ✓ The polarity of the solvent generally has no effect on the reaction rate and product distribution.
- ✓ They are single-step reactions.
- ✓ No intermediate occur
- ✓ The transition state is cyclic.
- ✓ Pericyclic reactions require light or heat
- ✓ They are completely stereospecific
- ✓ Pericyclic reactions are concerted reactions
- ✓ Changes in the number of pi and sigma bonds distinguish pericyclic reactions from each other.

	Change in the number of σ bonds	Change in the number of π bonds
Cycloaddition	+2	-2
Electrocyclic	+1	-1
Sigmatropic	0	0

- ✓ Pericyclic reactivity can be understood in terms of frontier molecular orbital (FMO) theory and the outcome of reactions can be predicted using the Woodward-Hoffmann rules.
- ✓ **Woodward-Hoffmann rules:** A pericyclic reaction can take place only if the symmetries of the reactant MOs are the same as the symmetries of the product MOs.
- ✓ During a pericyclic reaction, orbitals in the same phase overlap and make a bond
- ✓ There is no bond with the overlap of the orbitals in different phases.
- ✓ If the *symmetries* of both reactant and product orbitals match up, the reaction is said to be ***symmetry-allowed***.
- ✓ If the *symmetries* of reactant and product orbitals don't correlate, the reaction is ***symmetry-disallowed***.

For example



In order to overlap the two end orbitals of the HOMO to form the new σ -bond, they can be turned in two different directions:

- ✓ Conrotatory Orbital Rotation
- ✓ Disrotatory Orbital Rotation

Only the symmetry of the HOMO is important in determining the course of the reaction

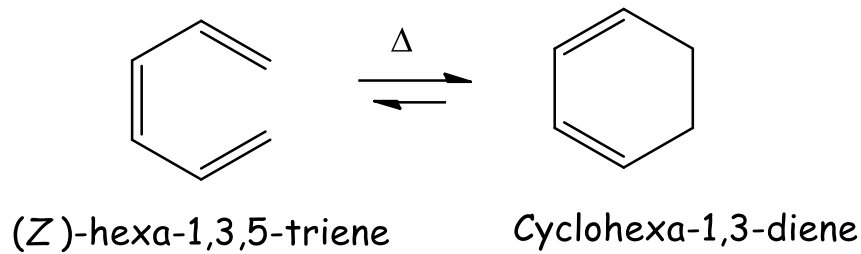
1.3 Types of Pericyclic Reactions

1. Electrocyclic Reactions: Intramolecular ring closure and openings
2. Cycloadditions: The Diels-Alder reaction, a [4+2] cycloaddition

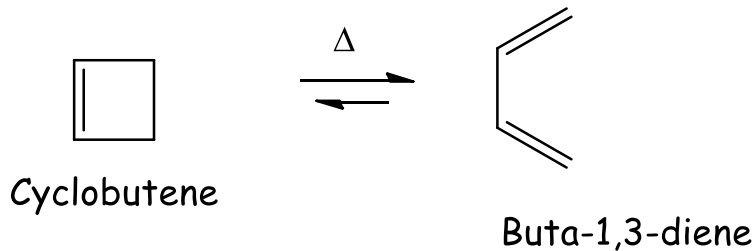
3. Sigmatropic rearrangement

1.3.1 Electrocyclic Reactions

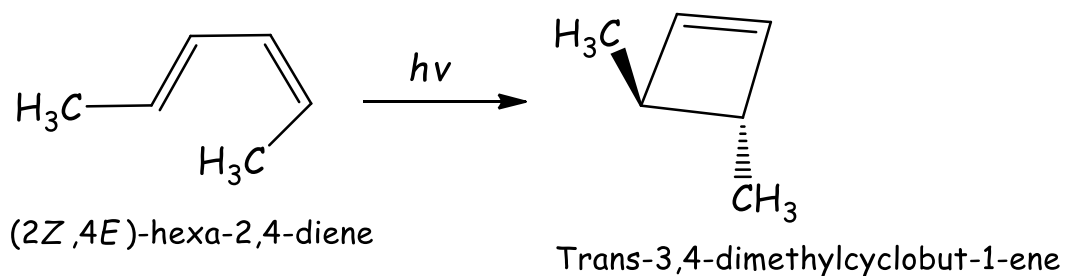
- ✓ An intramolecular reaction
- ✓ A cyclic compound is formed

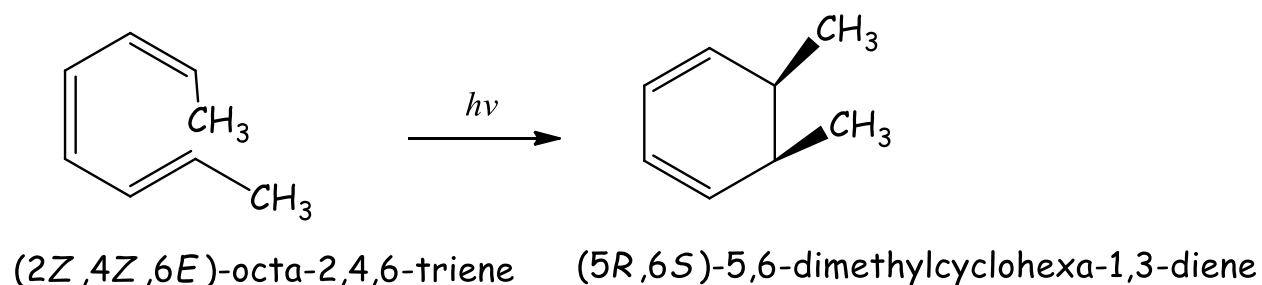
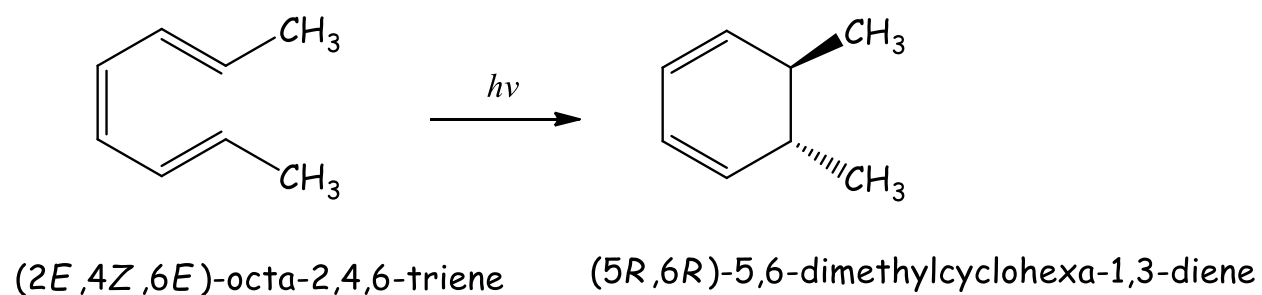
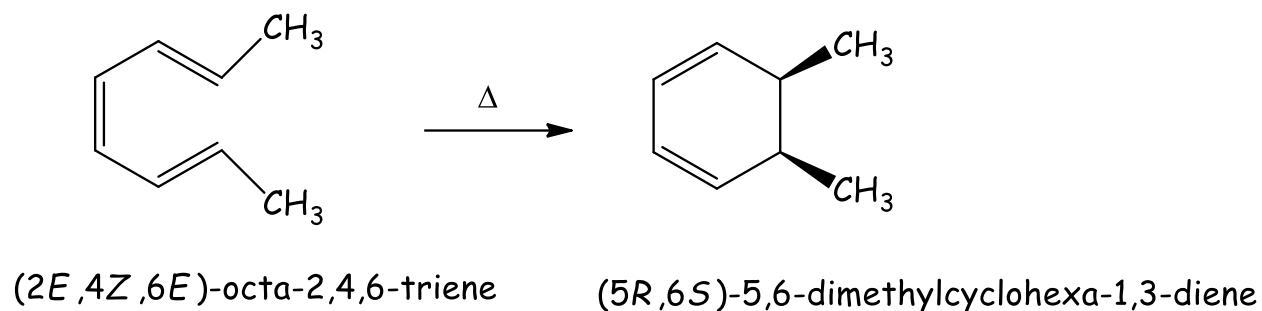
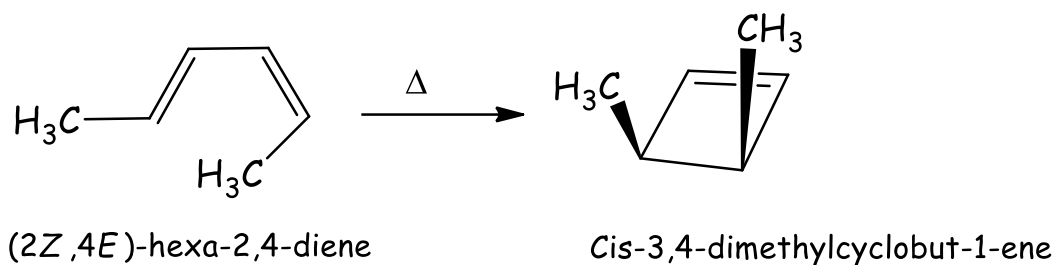


Electrocyclic reactions are reversible



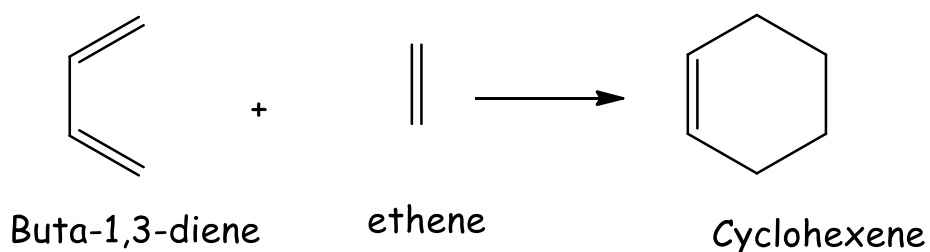
Examples:





1.3.2 Cycloaddition Reactions

- ✓ Two different p bond-containing molecules react to form a cyclic compound



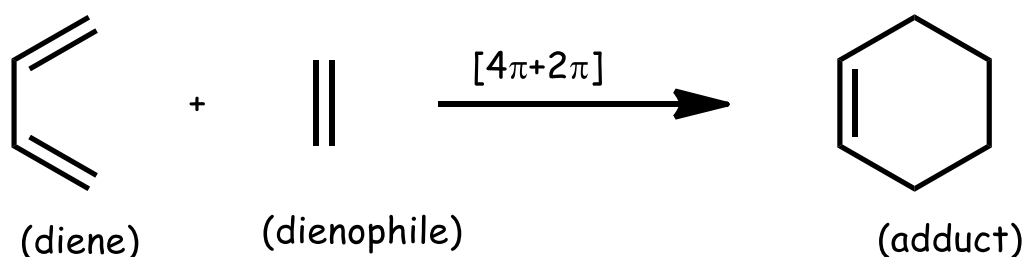
- ✓ Reactions are classified according to the number of π -bonds present in the reactants and directly involved in the reaction.
- ✓ Cycloaddition reactions can be either thermally allowed or prohibited, as well as photochemical allowed or prohibited, as in electrocyclic reactions.
- ✓ Three important classes of cycloaddition reactions
 - (i) Diels-Alder reaction: [4+2] Cycloaddition
 - (ii) [2+2] Cycloaddition
 - (iii) [1,3]-Dipolar cycloaddition
- ✓ σ -Bonds formation can happen in two ways:

- ✓ Suprafacial cycloadditions
- ✓ Antarafacial cycloadditions

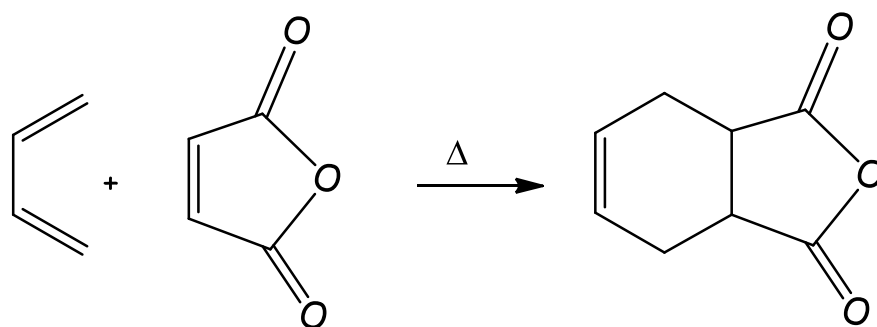
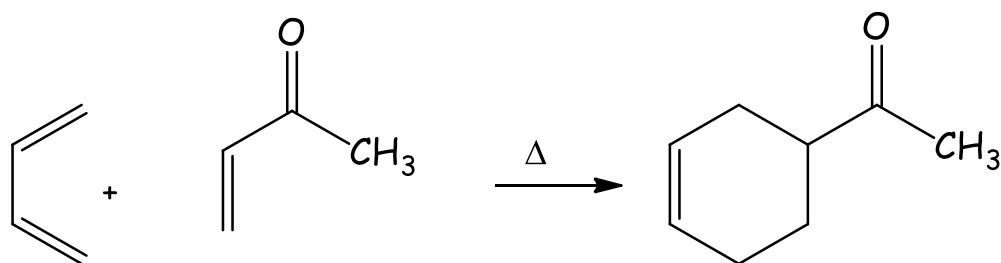
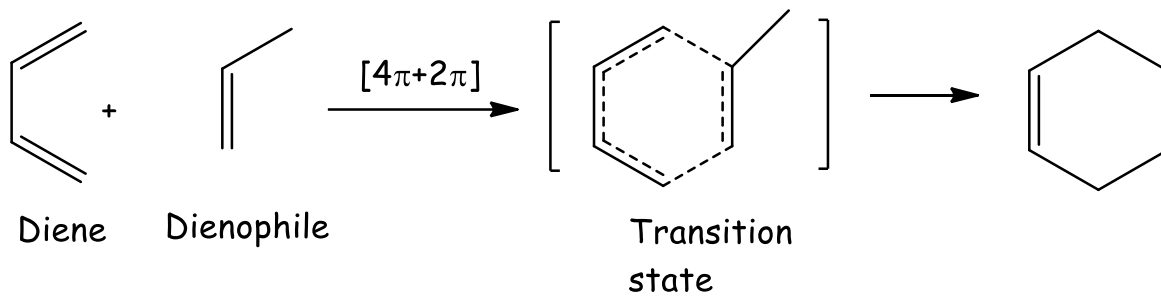
1.3.2.1 Diels-Alder Reaction

The Diels-Alder cycloaddition reaction is a pericyclic process that takes place between a diene (four π electrons) and a dienophile (two π electrons) to yield a cyclohexene product.

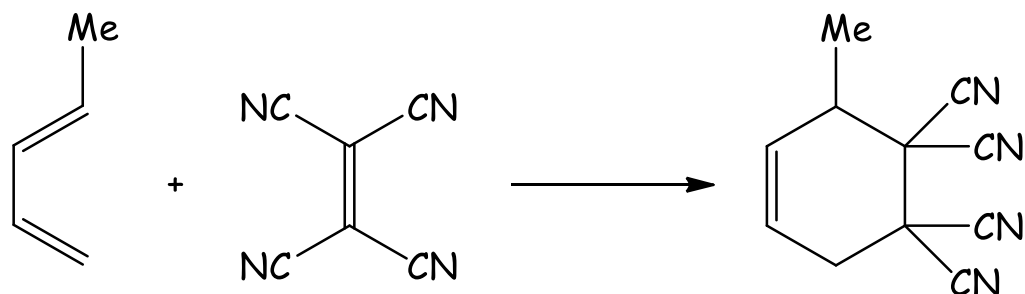
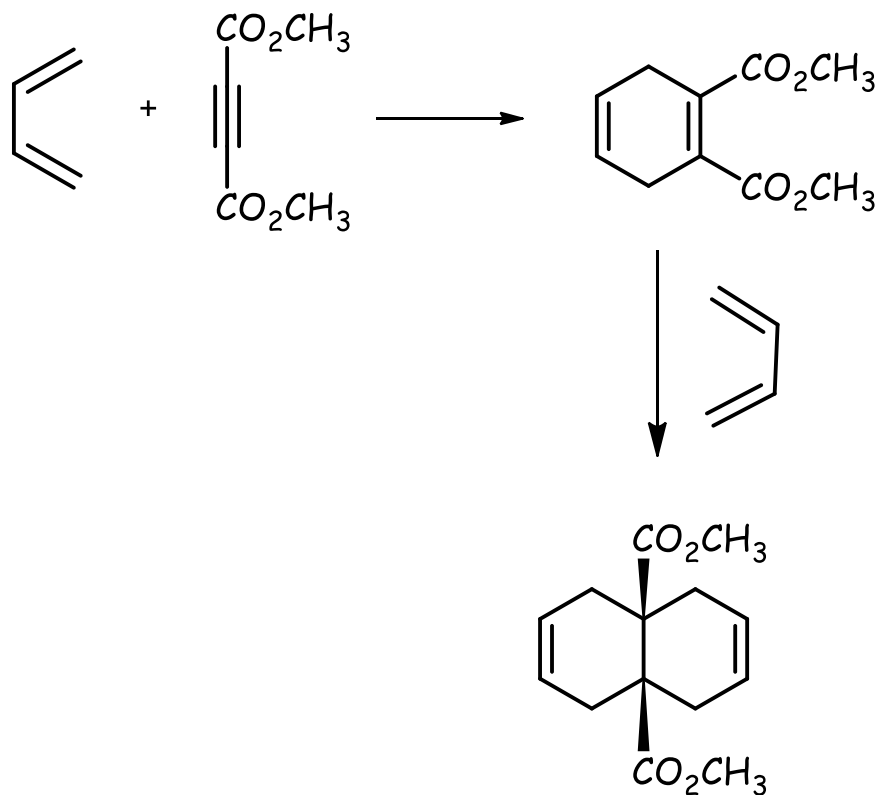
The resulting reaction is a cyclization reaction



Many thousands of examples of Diels-Alder reactions are known.



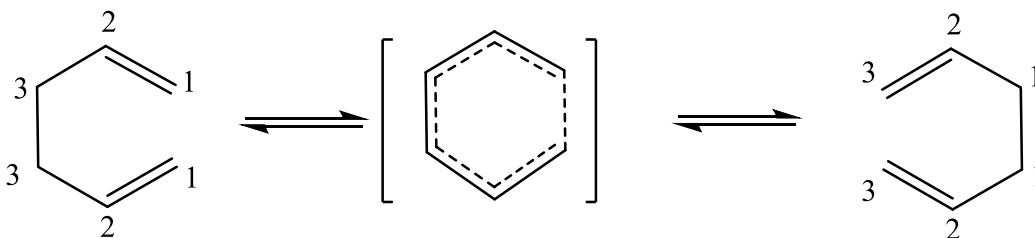
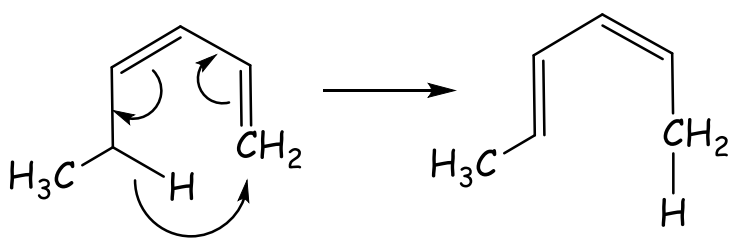
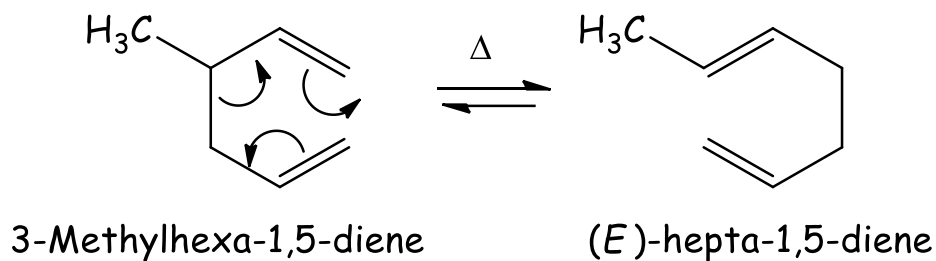
Maleic anhydride



1.3.3 Sigmatropic Reactions

- ✓ Sigmatropic rearrangements are also unimolecular pericyclic reactions.

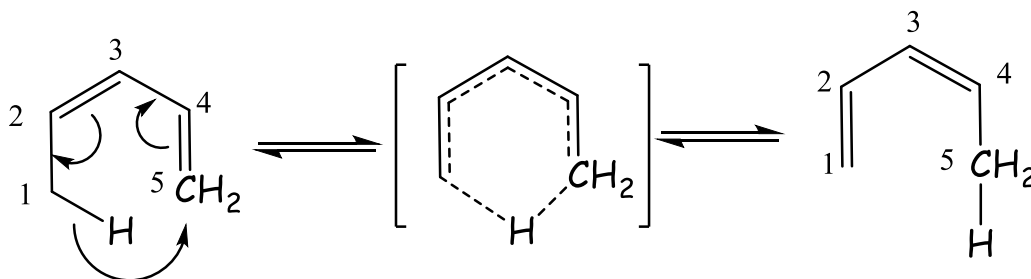
- ✓ A σ -bonded substituent, atom or group migrates across a π electron system from one position to another
- ✓ A σ bond is broken in the reactant, a new σ bond is formed in the product, and the π bonds rearrange
- ✓ Sigmatropic reactions; they work under thermal and photochemical conditions and do not require any catalyst.



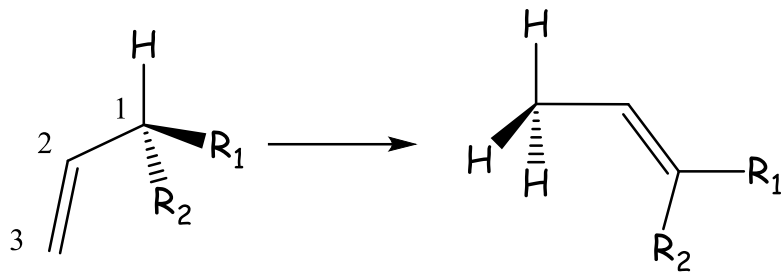
Different types of sigmatropic rearrangement reactions are

- [2,3] sigmatropic rearrangement
- [3,3] sigmatropic rearrangement
- [1,3] sigmatropic rearrangement
- [1,5] sigmatropic rearrangement
- [1,7] sigmatropic rearrangement

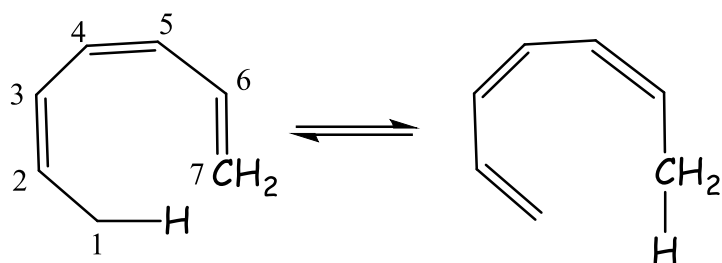
[1,5] sigmatropic rearrangement



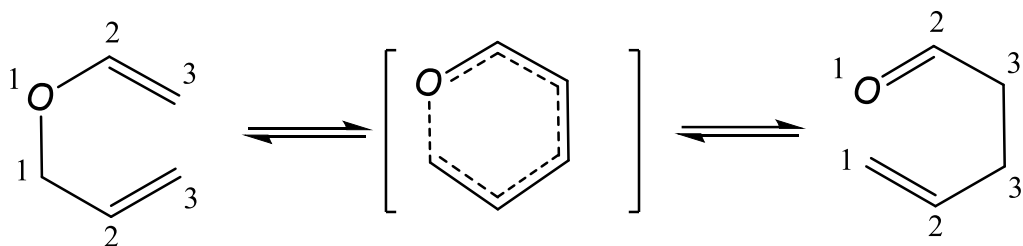
[1,3] Hydrogen Shift



[1,7] Hydrogen Shift



[3,3] Claisen rearrangement



[3,3] Cope rearrangement

