

**M.Sc. Semester-IV  
Core Course-9 (CC-9)  
Synthetic Organic Chemistry**



**II. Pericyclic Reactions  
5. Sigmatropic Rearrangement  
(FMO Method)**



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## II Pericyclic Reactions 20 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1, 3, 5-hexatriene, allyl system, Classification of pericyclic reactions. FMO approach, Woodward-Hoffman correlation diagram method and PMO approach for pericyclic reaction under thermal and photochemical conditions.

Electrocyclic reactions: Conrotatory and disrotatory motion,  $4n$  and  $(4n+2)$  systems, Cycloaddition reaction:  $[2+2]$  and  $[4+2]$  cycloaddition reaction, Cycloaddition of ketones, Secondary effects in  $[4+2]$  cycloaddition. Stereochemical effects on rate of cycloaddition reaction, Diels-Alder reaction, 1,3-dipolar cycloaddition, Chelotropic reaction, The Nazarov reaction.

Sigmatropic rearrangement: Suprafacial and antarafacial shift involving H and carbon-moieties, Peripatetic cyclopropane bridge, Retention and inversion of configuration,  $[3,3]$ -,  $[1,5]$ -,  $[2,3]$ -,  $[4,5]$ -,  $[5,5]$ -, and  $[9,9]$ -Sigmatropic rearrangements, Claisen rearrangements (including Aza-Claisen, Ireland-Claisen), Cope rearrangements (including Oxy-Cope, Aza-Cope), Sommelet-Hauser rearrangements, Group transfer reaction, Ene reaction, Mislow - Evans rearrangement, Walk rearrangement.

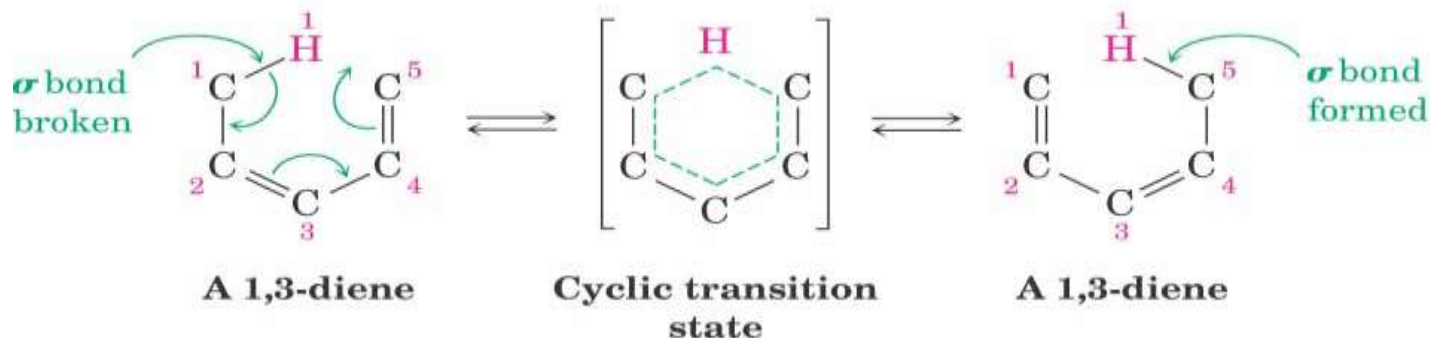
### Coverage:

1. Sigmatropic Rearrangement: Suprafacial and Antarafacial Shift Involving H and carbon-moieties
2. Claisen Rearrangement
3. Cope Rearrangement

# Sigmatropic Rearrangements

- A  $\sigma$ -bonded substituent atom or group migrates across a p electron system from one position to another
- A  $\sigma$  bond is broken in the reactant, the p bonds move, and a new  $\sigma$  bond is formed in the product

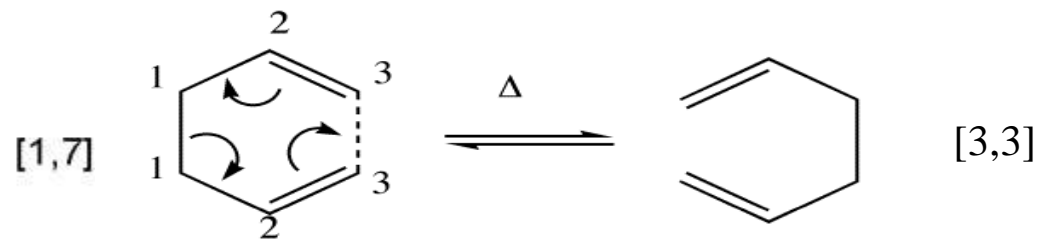
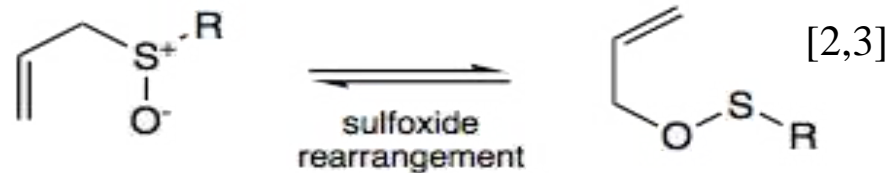
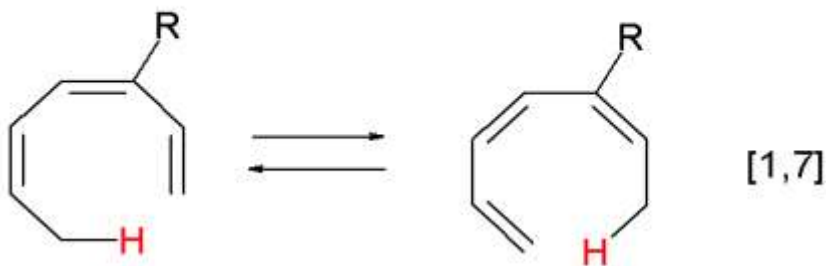
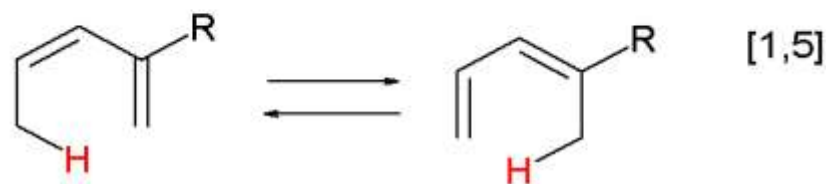
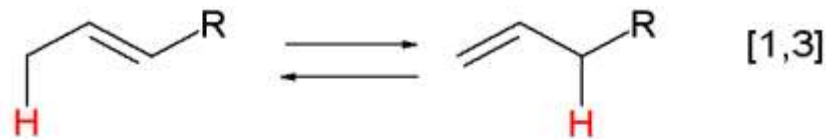
## A [1,5] rearrangement



## A [3,3] rearrangement



# Sigmatropic Rearrangements

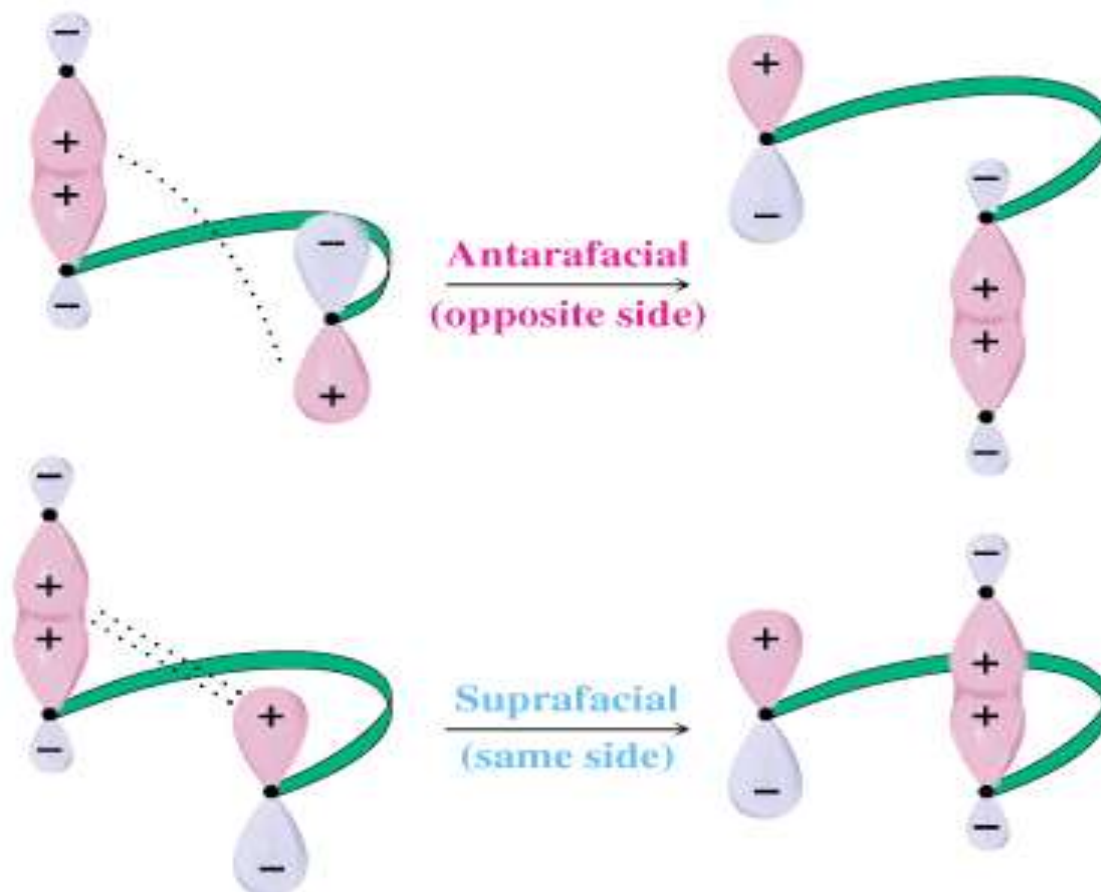


## Sigmatropic Notation

- Numbers in brackets refer to the two groups connected by the  $\sigma$  bond and designate the positions in those groups *to which migration occurs*
- In a [1,5] sigmatropic rearrangement of a diene migration occurs to position 1 of the H group (the only possibility) and to position 5 of the pentadienyl group
- In a [3,3] Claisen rearrangement migration occurs to position 3 of the allyl group and also to position 3 of the vinylic ether

# Sigmatropic Stereospecificity: Suprafacial and Antarafacial Migration

- Migration of a group across the same face of the  $\pi$  system is a *suprafacial* rearrangement
- Migration of a group from one face of the  $\pi$  system to the other face is called an *antarafacial* rearrangement

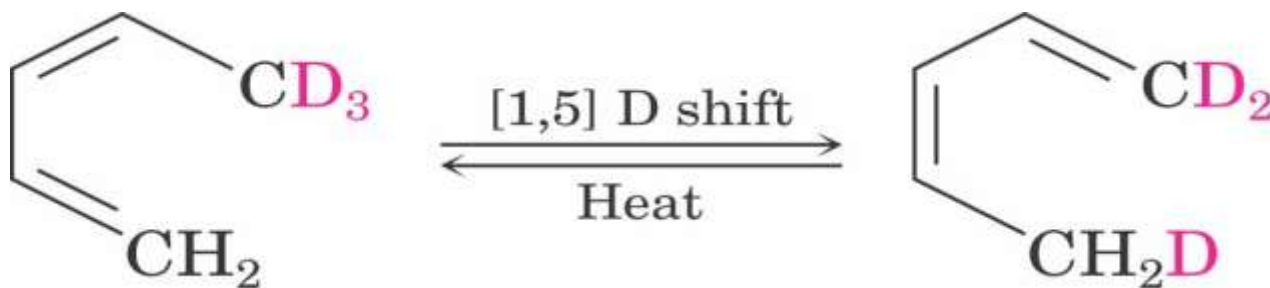


## Stereochemical Rules of Sigmatropic Rearrangements

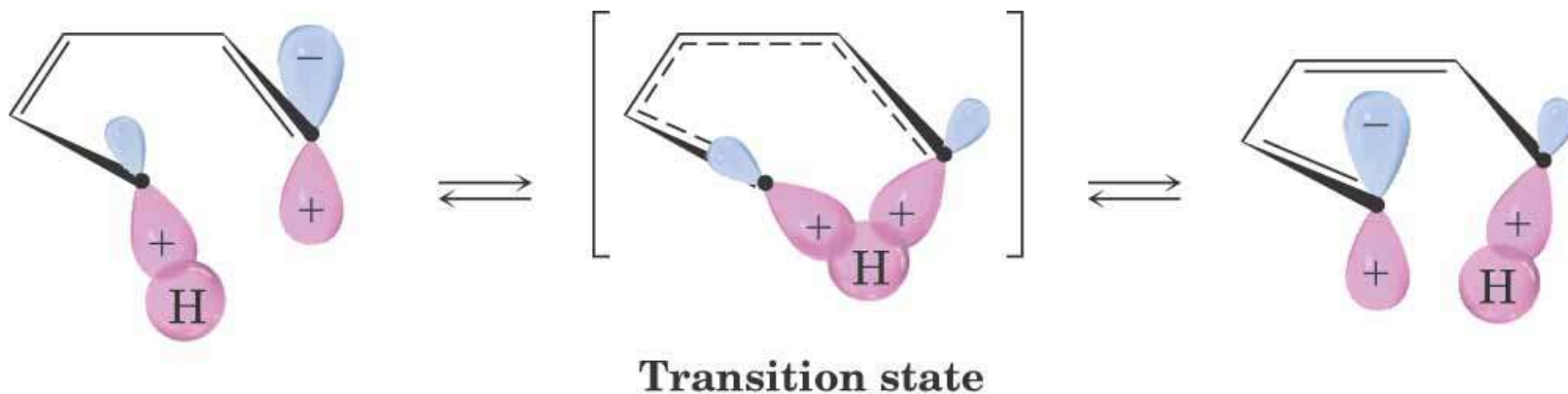
Electron Pairs	Thermal Reaction	Photochemical Reaction
Even Number	Antarafacial	Suprafacial
Odd Number	Suprafacial	Antarafacial

### Example of a Sigmatropic Rearrangement

- Heating 5,5,5-trideuterio-(1,3Z)-pentadiene causes scrambling of deuterium between positions 1 and 5



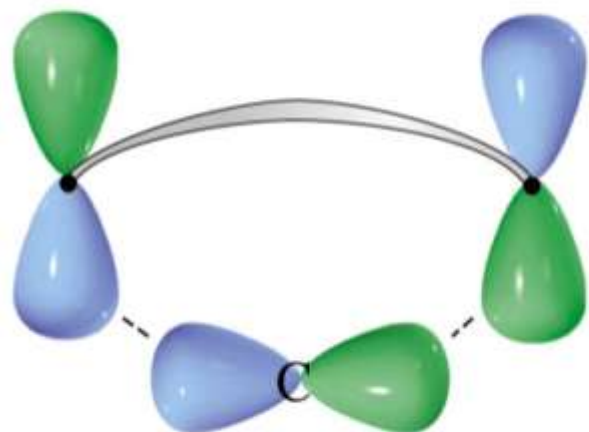
## Orbital Picture of a Suprafacial [1,5] H Shift



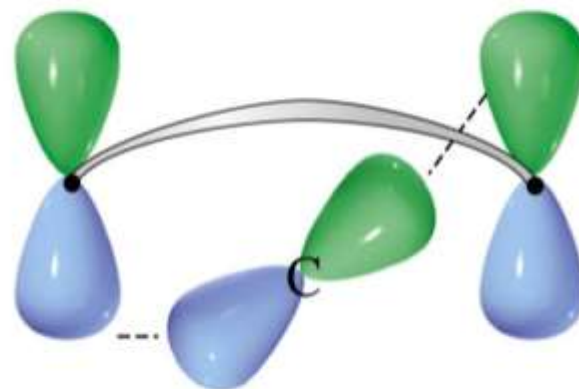


## Orbital Picture of a Suprafacial and Antarafacial C Shift Using Both Lobes

carbon migrating with both of its lobes interacting



suprafacial rearrangement

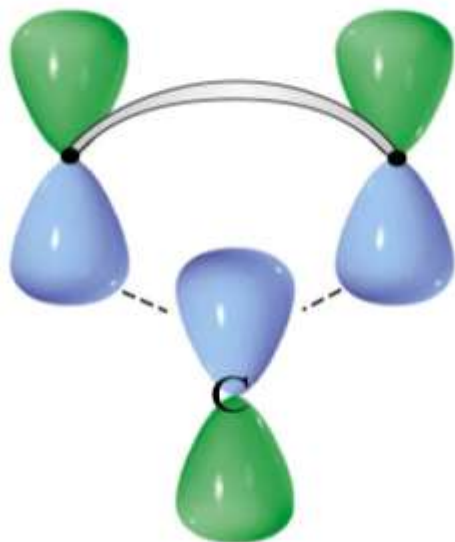


antarafacial rearrangement

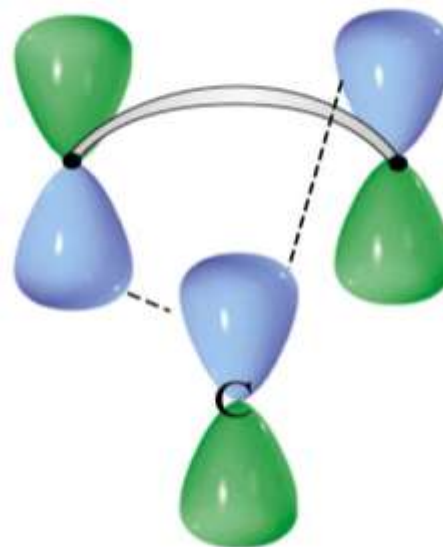
When carbon uses both lobes to migrate in a sigmatropic rearrangement, it must migrate **antarafacially when an odd number of electron pairs are involved in the migration (symmetric HOMO)** and **suprafacially when an even number of electron pairs are involved in the migration (antisymmetric HOMO)**. This type of migration results in inversion of configuration at the migrating carbon.

# Orbital Picture of a Suprafacial and Antarafacial C Shift Using One Lobe

carbon migrating with one of its lobes interacting



suprafacial rearrangement

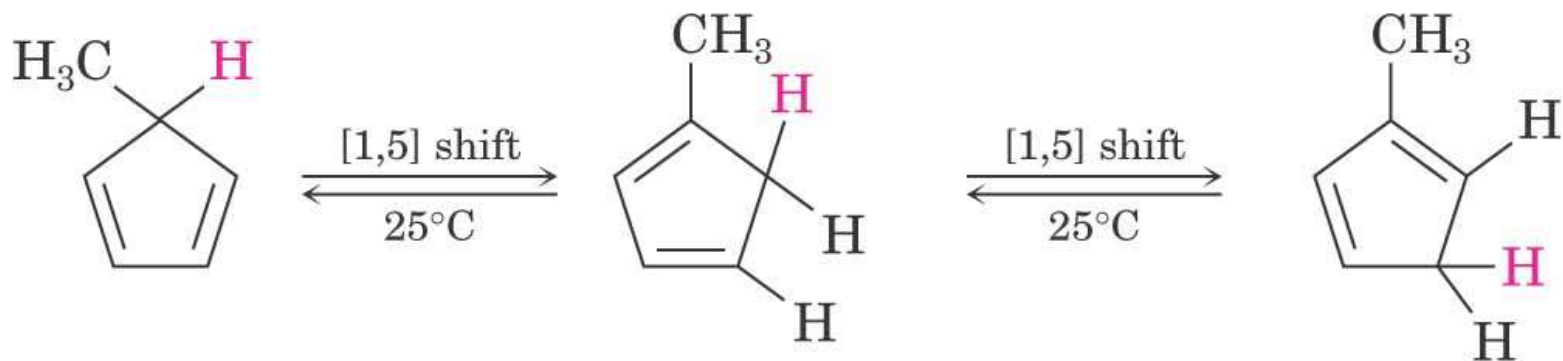


antarafacial rearrangement

When carbon uses only one lobe to migrate in a sigmatropic rearrangement, it must migrate **suprafacially when an odd number of electron pairs are involved in the migration (symmetric HOMO)** and **antarafacially when an even number of electron pairs are involved in the migration (antisymmetric HOMO)**. This type of migration results in retention of configuration at the migrating carbon.

## Other Example of a Sigmatropic Rearrangement

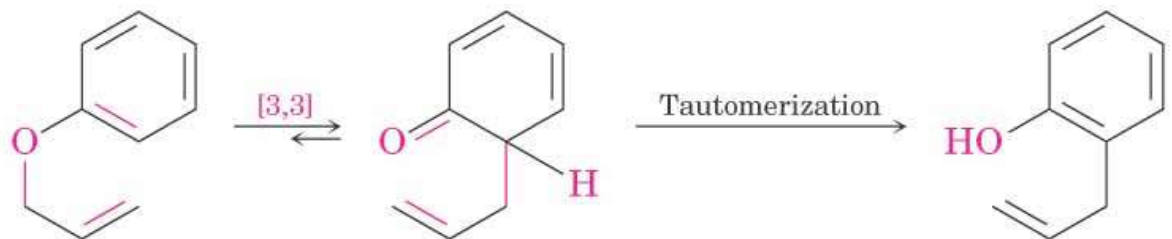
- A [1,5] sigmatropic rearrangement involves three electron pairs (two  $\pi$  bonds and one  $\sigma$  bond)
- Orbital-symmetry rules predict a suprafacial reaction
- 5-methylcyclopentadiene rapidly rearranges at room temperature



# Claisen and Cope Rearrangements are Sigmatropic

- Cope rearrangement of 1,5-hexadiene
- Claisen rearrangement of an allyl aryl ether

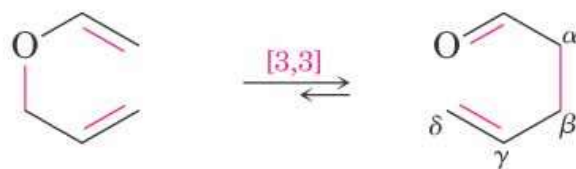
Claisen rearrangement



An allyl aryl ether

An *o*-allylphenol

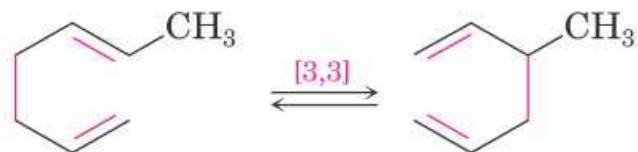
Claisen rearrangement



An allyl vinylic ether

A  $\gamma,\delta$ -unsaturated carbonyl compound

Cope rearrangement

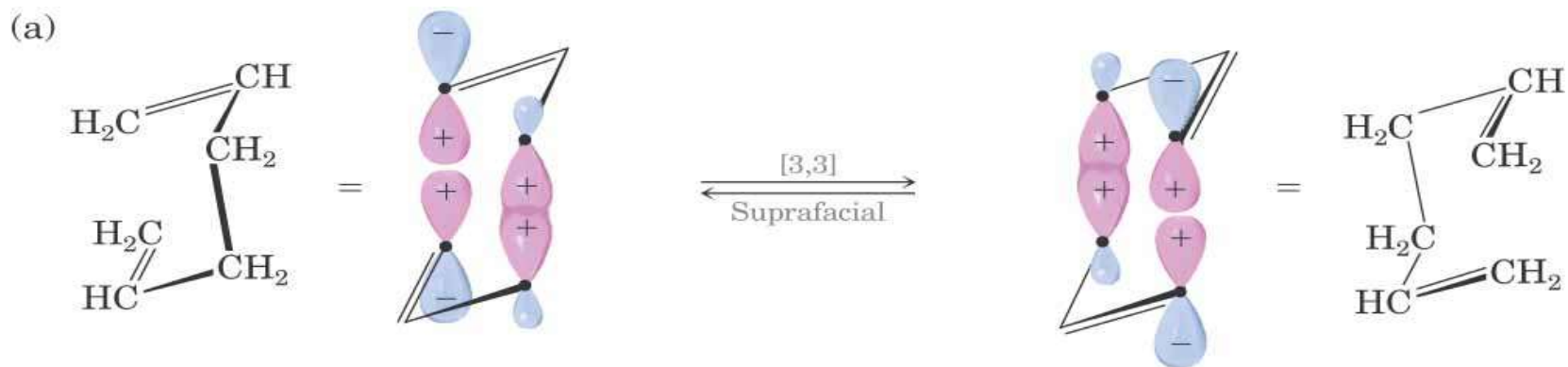


A 1,5-diene

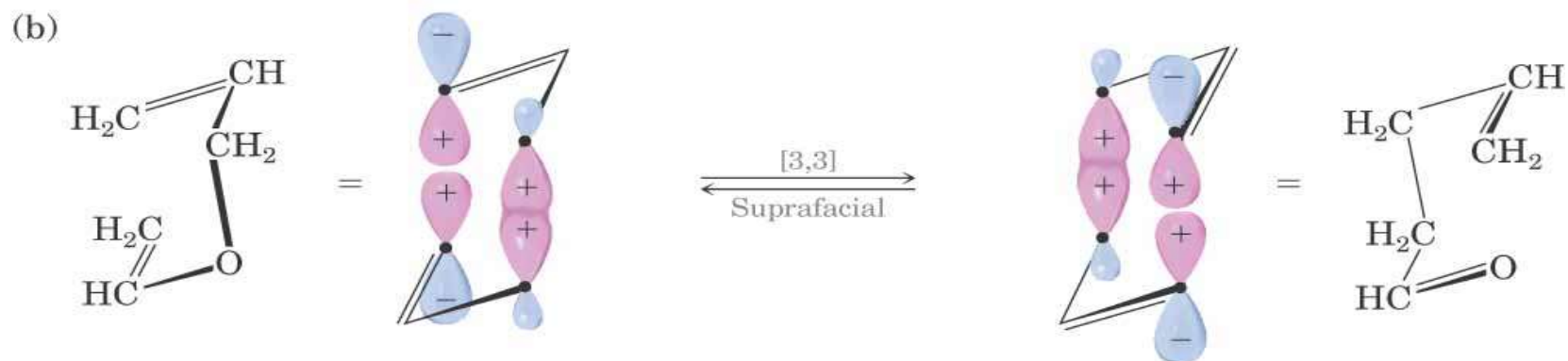
A new 1,5-diene

# Suprafacial [3,3] Cope and Claisen Rearrangements

- Both involve reorganization of an odd number of electron pairs (two  $\pi$  bonds and one  $\sigma$  bond)
- Both react by suprafacial pathways



Cope rearrangement of a 1,5-hexadiene



Claisen rearrangement of an allyl vinyl ether

## Selection Rules for Pericyclic Reactions

Electron state	Electron pairs	Stereochemistry
Ground state (thermal)	Even number	Antara-con
	Odd number	Supra-dis
Excited state (photochemical)	Even number	Supra-dis
	Odd number	Antara-con

# Thank You



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