B.Sc. Semester-VI

GroupA / DSE-4

Organic Synthesis

II. Pericyclic Reactions

5. Sigmatropic Rearrangement (FMO Method)

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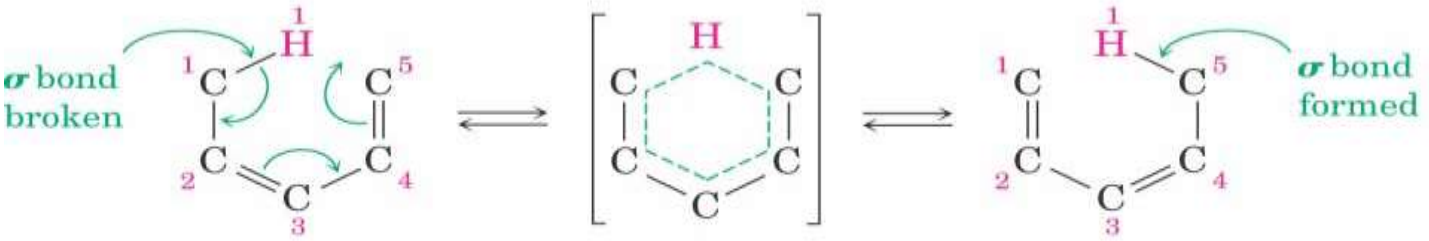
Sigmatropic Rearrangements

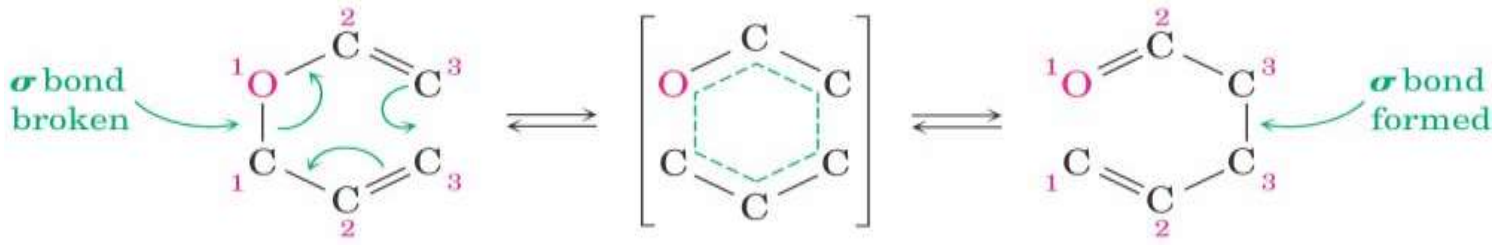
- **A σ -bonded substituent atom or group migrates across a p electron system from one position to another**
- **A σ bond is broken in the reactant, the p bonds move, and a new s bond is formed in the product**

A [1,5] rearrangement



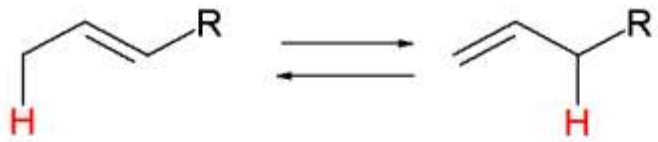
A 1,3-diene — **Cyclic transition state** — **A 1,3-diene**

A [3,3] rearrangement



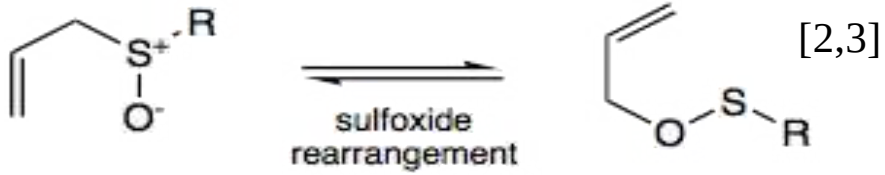
An allyl vinyl ether — **Cyclic transition state** — **An unsaturated ketone**

Sigmatropic Rearrangements



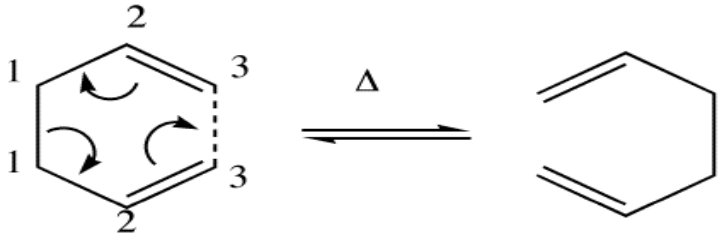
[1,3]

[1,5]



[2,3]

[1,7]



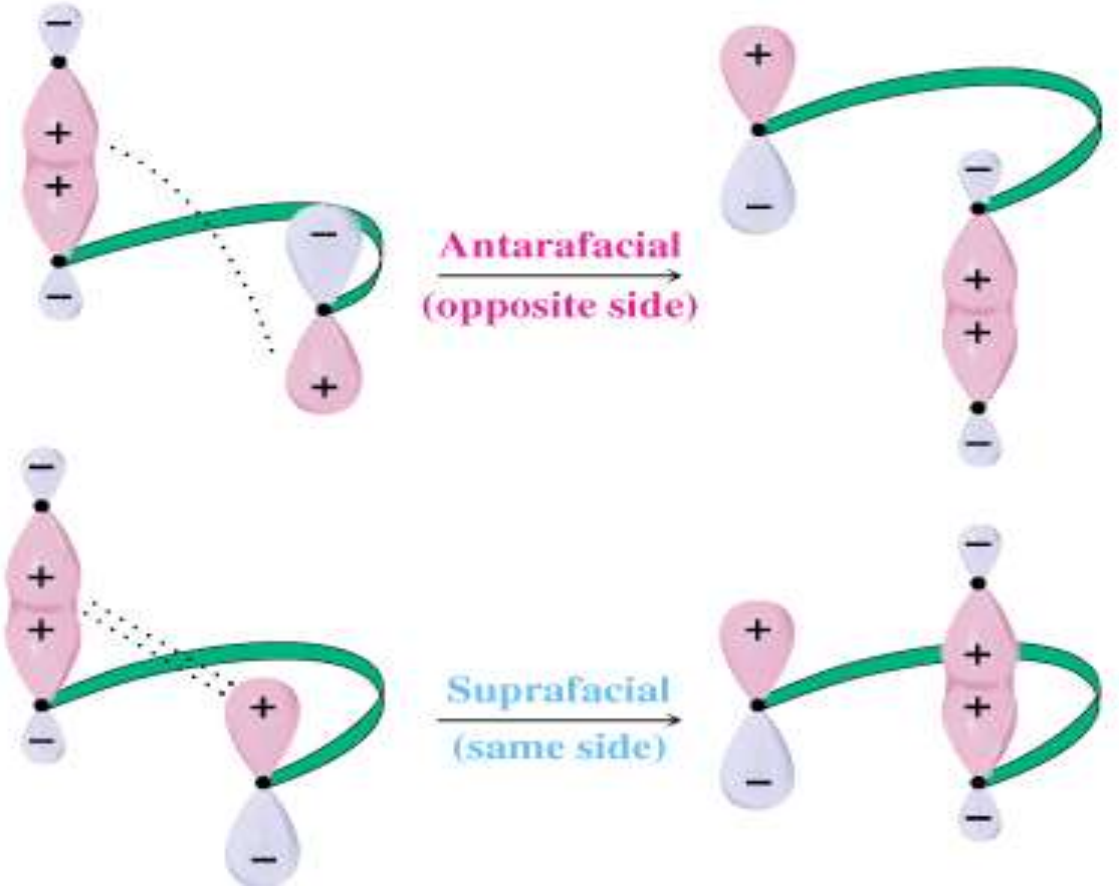
[3,3]

Sigmatropic Notation

- **Numbers in brackets refer to the two groups connected by the s 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 π system is a *suprafacial* rearrangement**
- **Migration of a group from one face of the π system to the other face is called an *antarafacial* rearrangement**

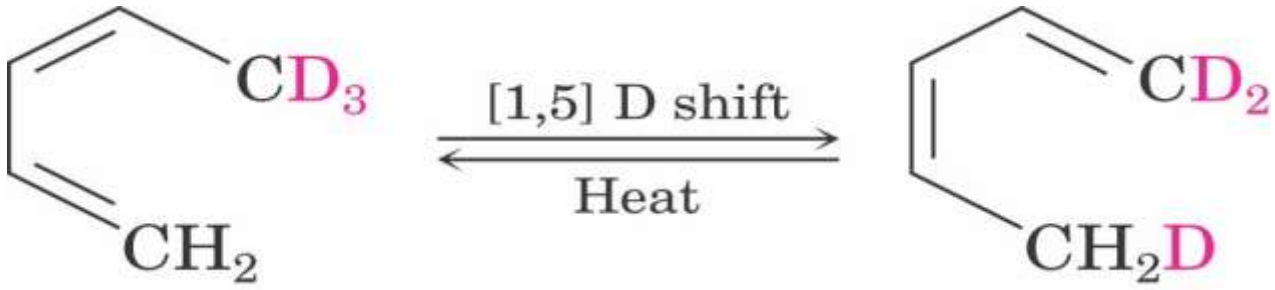


Stereochemical Rules of Sigmatropic Rearrangements

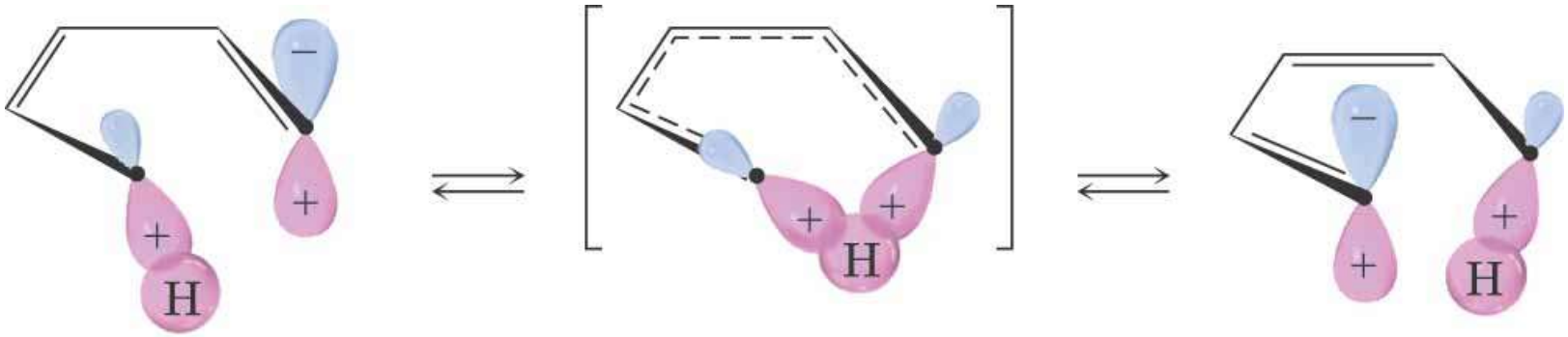
Electron Pairs	Thermal Reaction	Photochemical Reaction
Even Number	Antarafacial	Suprafacial
Odd Number	Suprafacial	Antarafacial

Example of a Sigmatropic Rearrangement

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

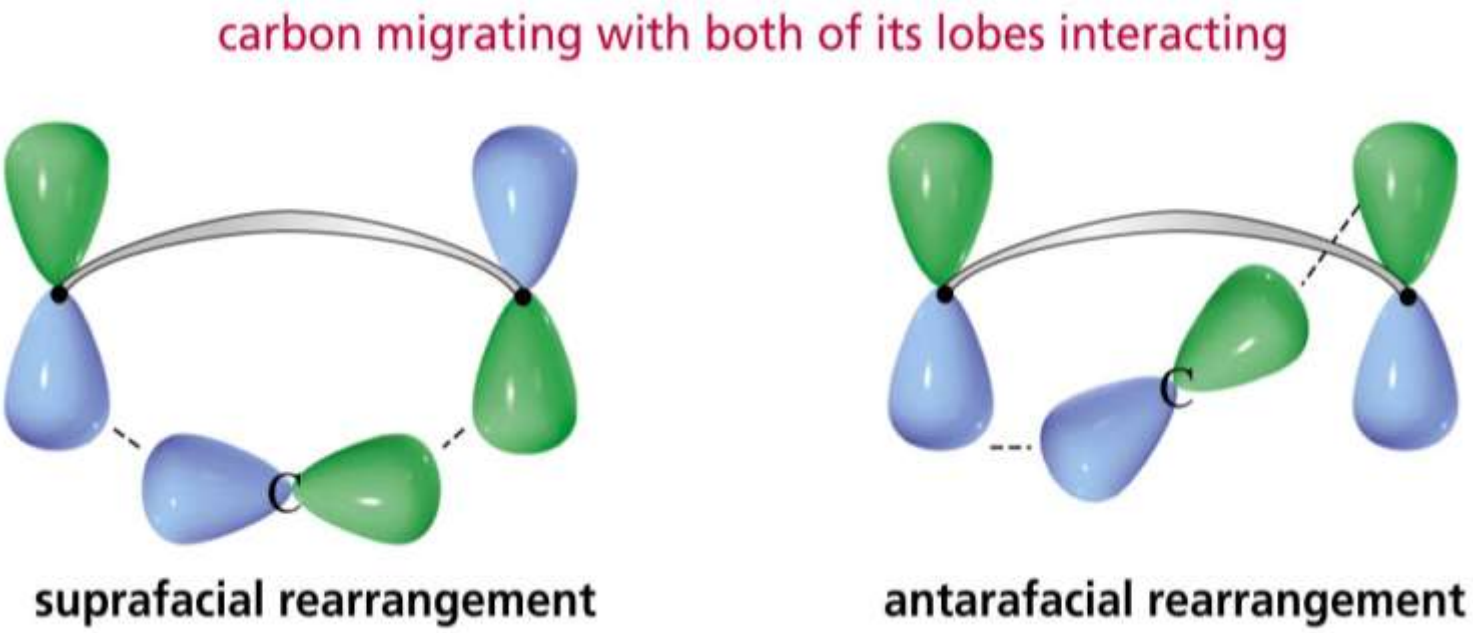


Orbital Picture of a Suprafacial [1,5] H Shift



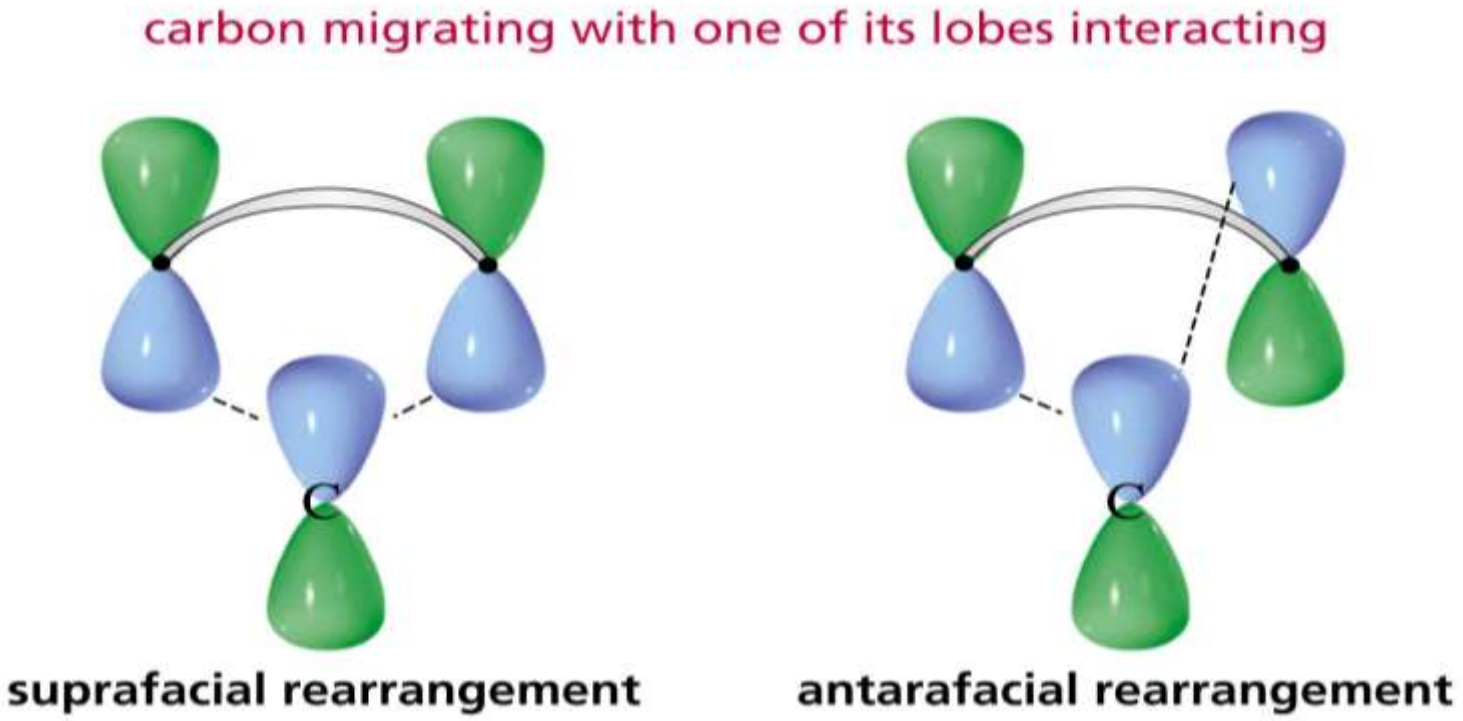
Transition state

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



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.

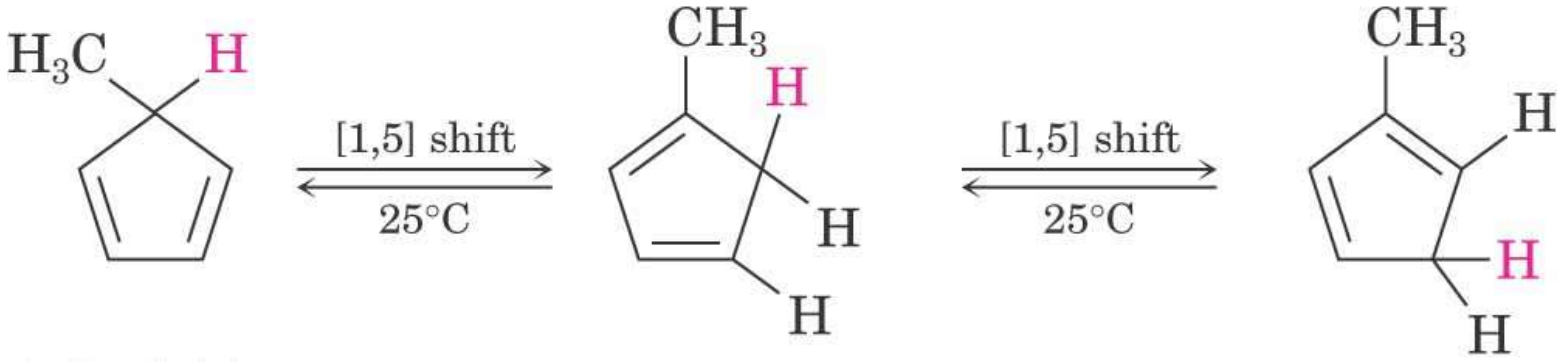
Orbital Picture of a Suprafacial and Antarafacial C Shift Using One Lobe



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

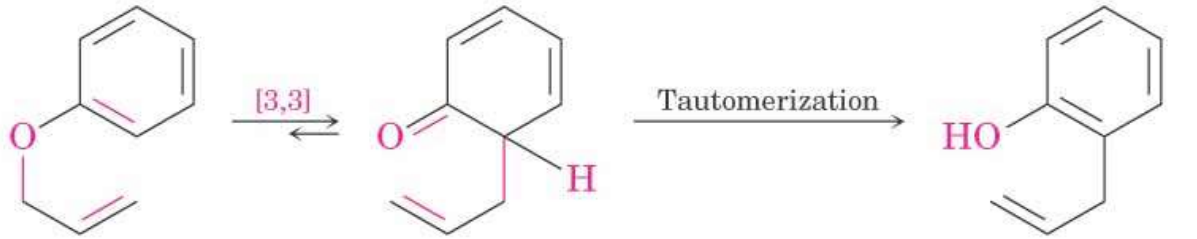
- **A [1,5] sigmatropic rearrangement involves three electron pairs (two π bonds and one σ bond)**
- **Orbital-symmetry rules predict a suprafacial reaction**
- **5-methylcyclopentadiene rapidly rearranges at room temperature**



Claisen and Cope Rearrangements are Sigmatropic

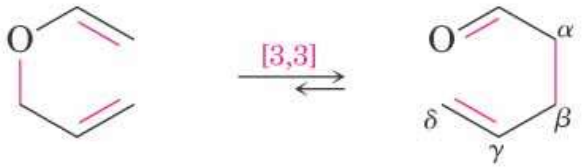
- **Cope rearrangement of 1,5-hexadiene**
- **Claisen rearrangement of an allyl aryl ether**

Claisen rearrangement



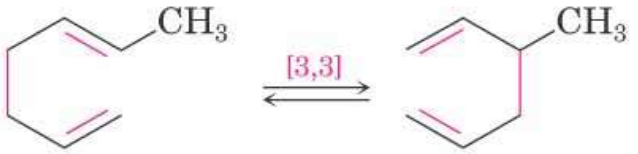
An allyl aryl ether **An *o*-allylphenol**

Claisen rearrangement



An allyl vinylic ether **A γ,δ-unsaturated carbonyl compound**

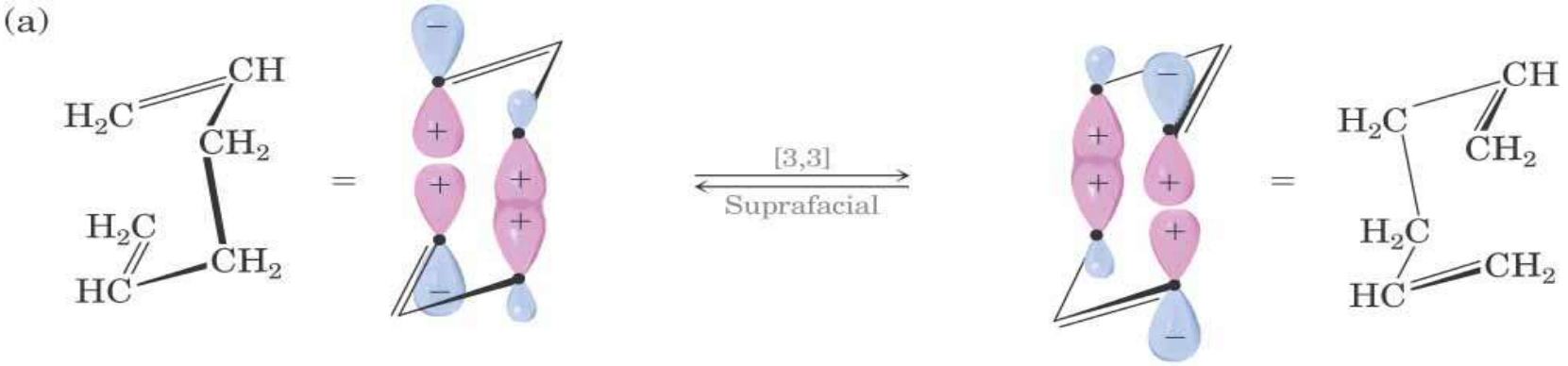
Cope rearrangement



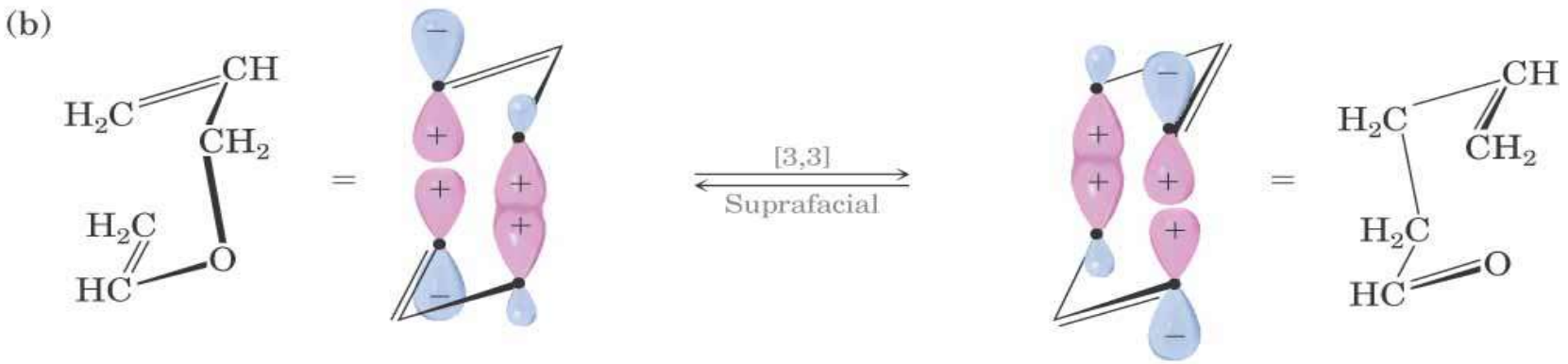
A 1,5-diene **A new 1,5-diene**

Suprafacial [3,3] Cope and Claisen Rearrangements

- **Both involve reorganization of an odd number of electron pairs (two π bonds and one σ bond)**
- **Both react by suprafacial pathways**



Cope rearrangement of a 1,5-hexadiene

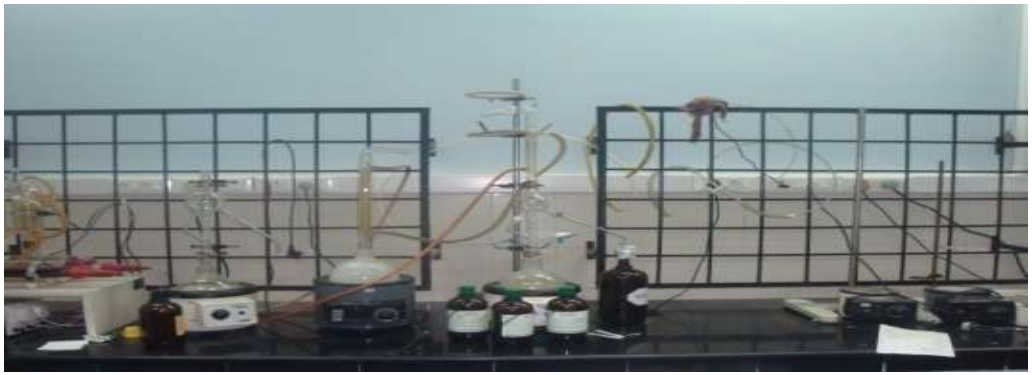


Claisen rearrangement of an allyl vinyl ether

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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