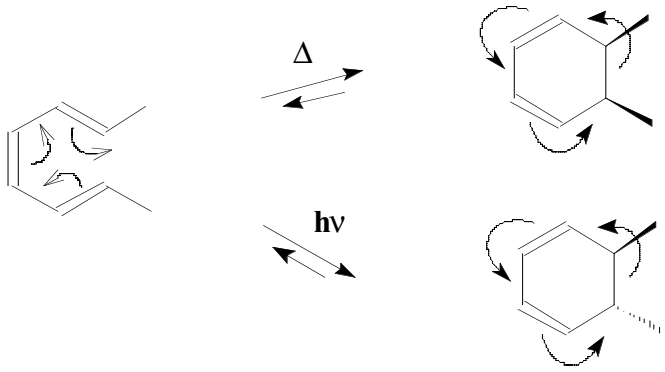
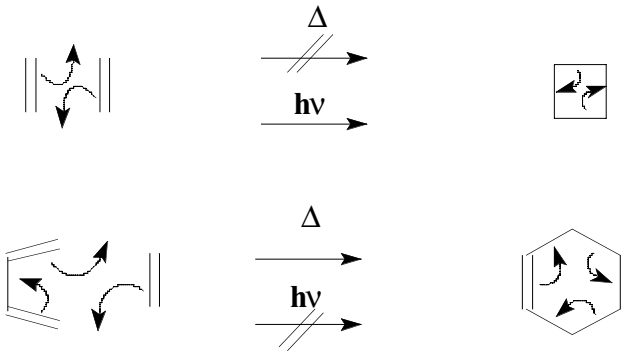
PERICYCLIC REACTIONS

Concerted reactions with cyclic transition states

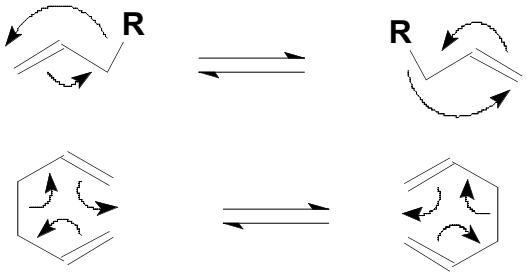
1. Electrocyclic reactions



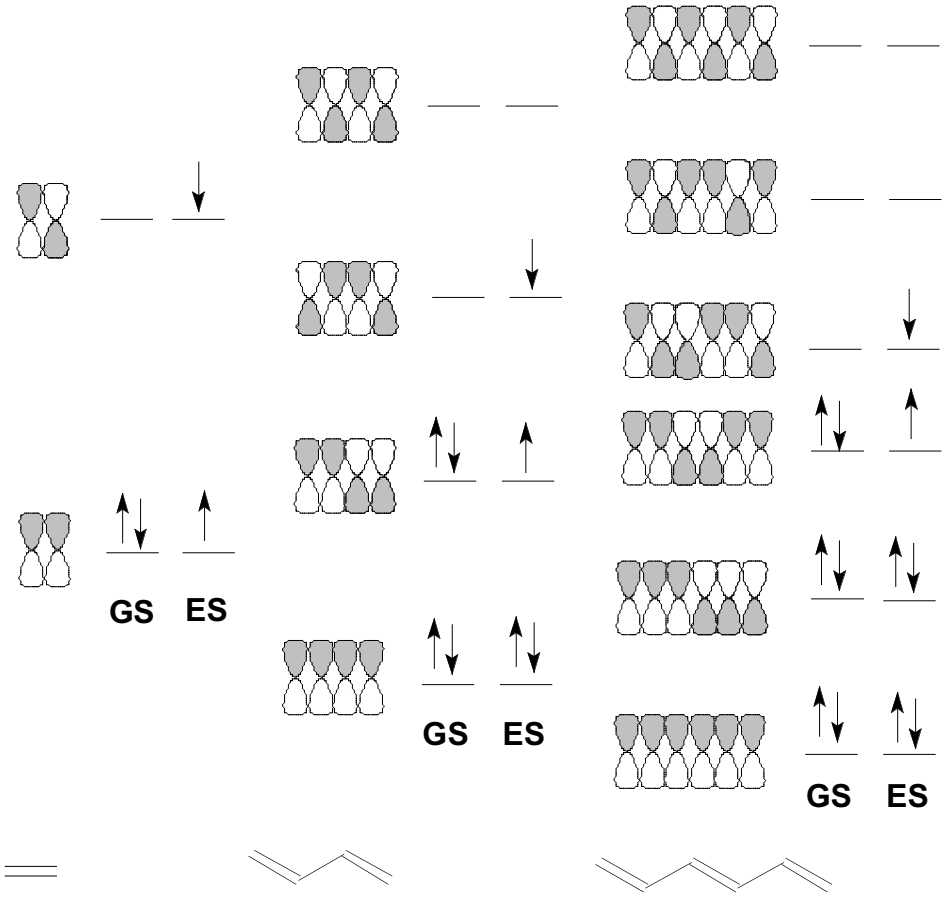
2. Cycloaddition reactions



3. Sigmatropic rearrangements



MOLECULAR ORBITALS
(A review)



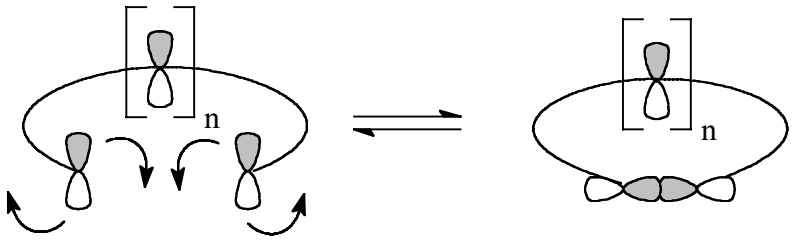
HOMO = Highest Occupied Molecular Orbital
LUMO = Lowest Unoccupied Molecula Orbital

SYMMETRIC = Symmetry operation does not change lobe signs
ANTISYMMETRIC = Symmetry operation inverts lobe signs

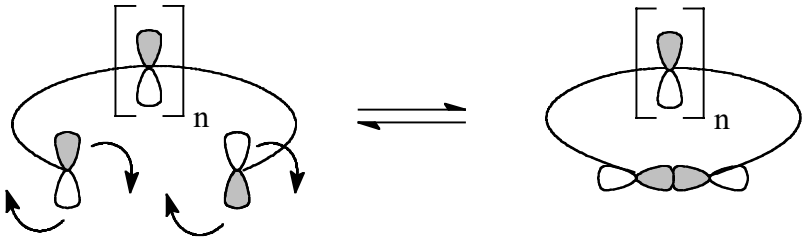
Generic energy level ordering: σ, π, π^*, σ^* (for π-type orbitals the more nodes, the higher the energy)

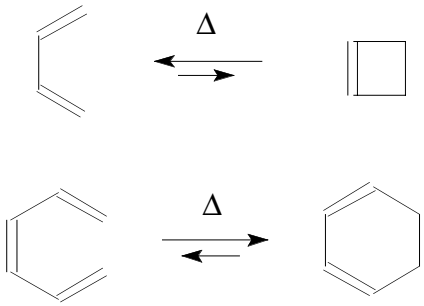
ELECTROCYCLIC REACTIONS

Disrotatory (one clockwise and one couterclockwise)



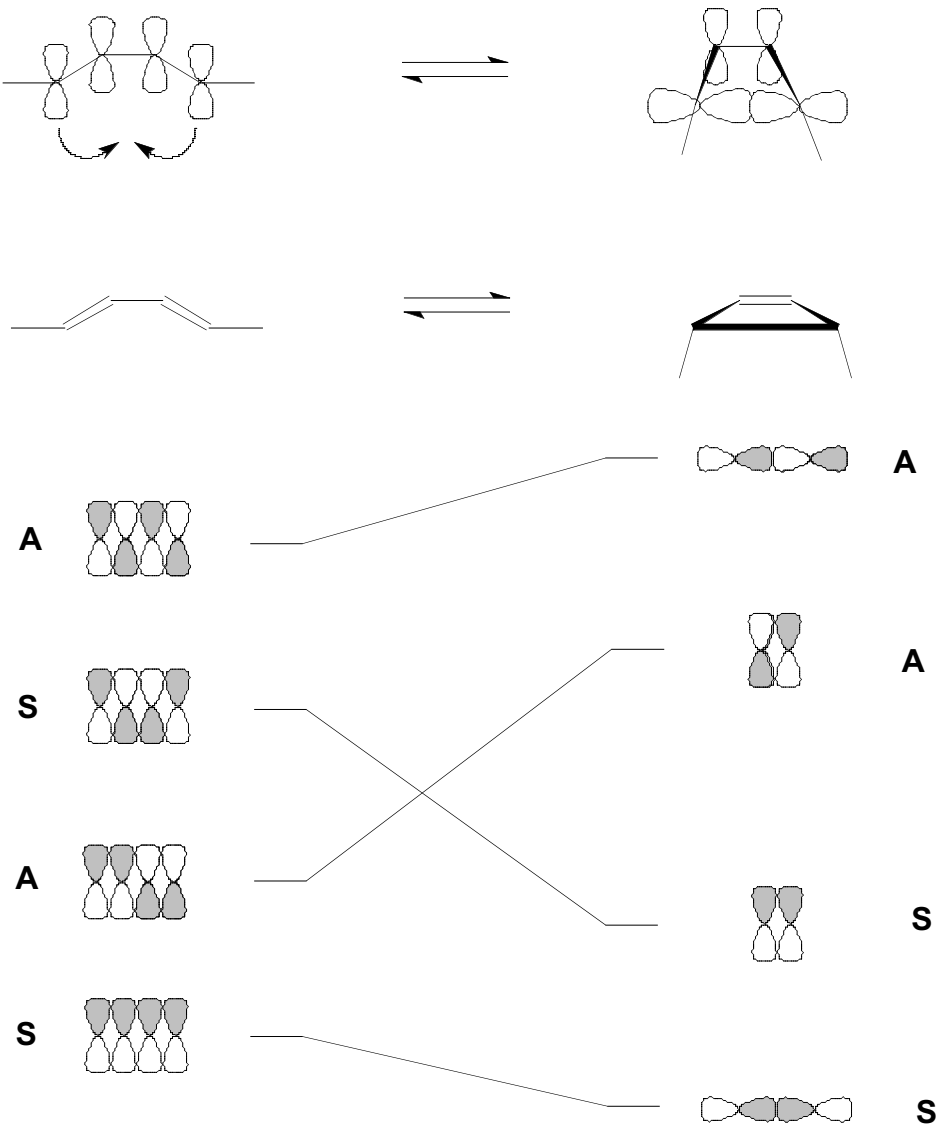
Conrotatory (both clockwise or both couterclockwise)





ELECTROCYCLIC REACTIONS

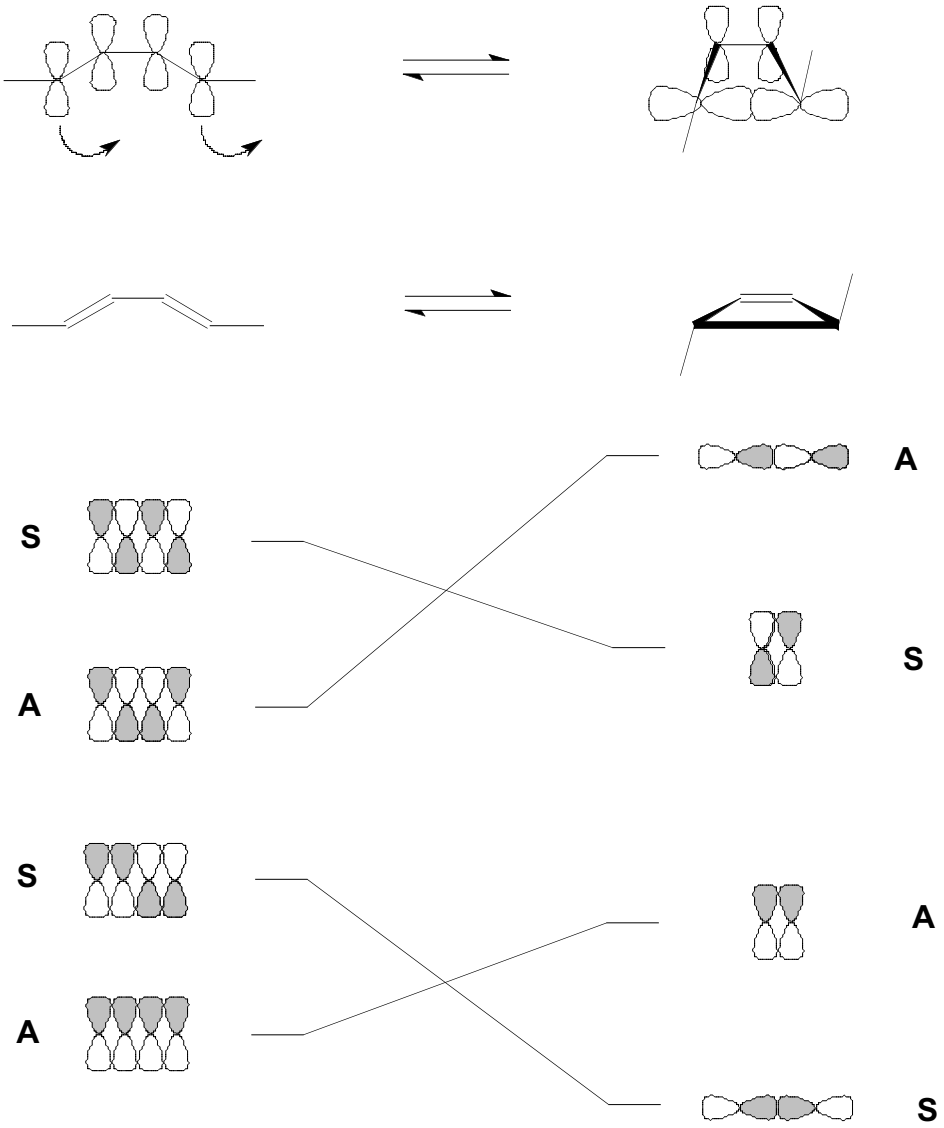
1a. Disrotatory ring closure/opening (4 electrons)



thermally disallowed; photochemically allowed

ELECTROCYCLIC REACTIONS

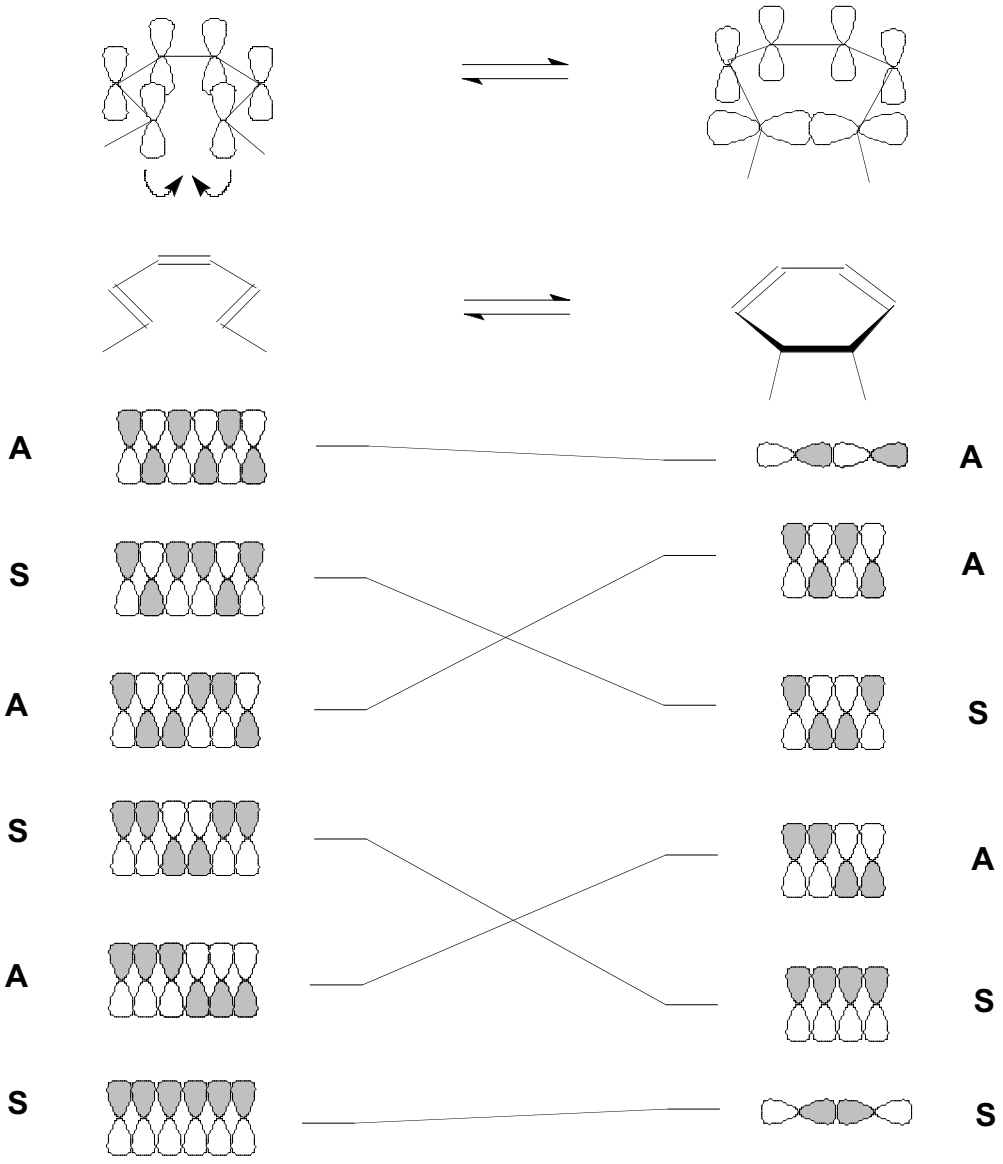
1b. Conrotatory ring closure/opening (4 electrons)



thermally allowed; photochemically disallowed

ELECTROCYCLIC REACTIONS

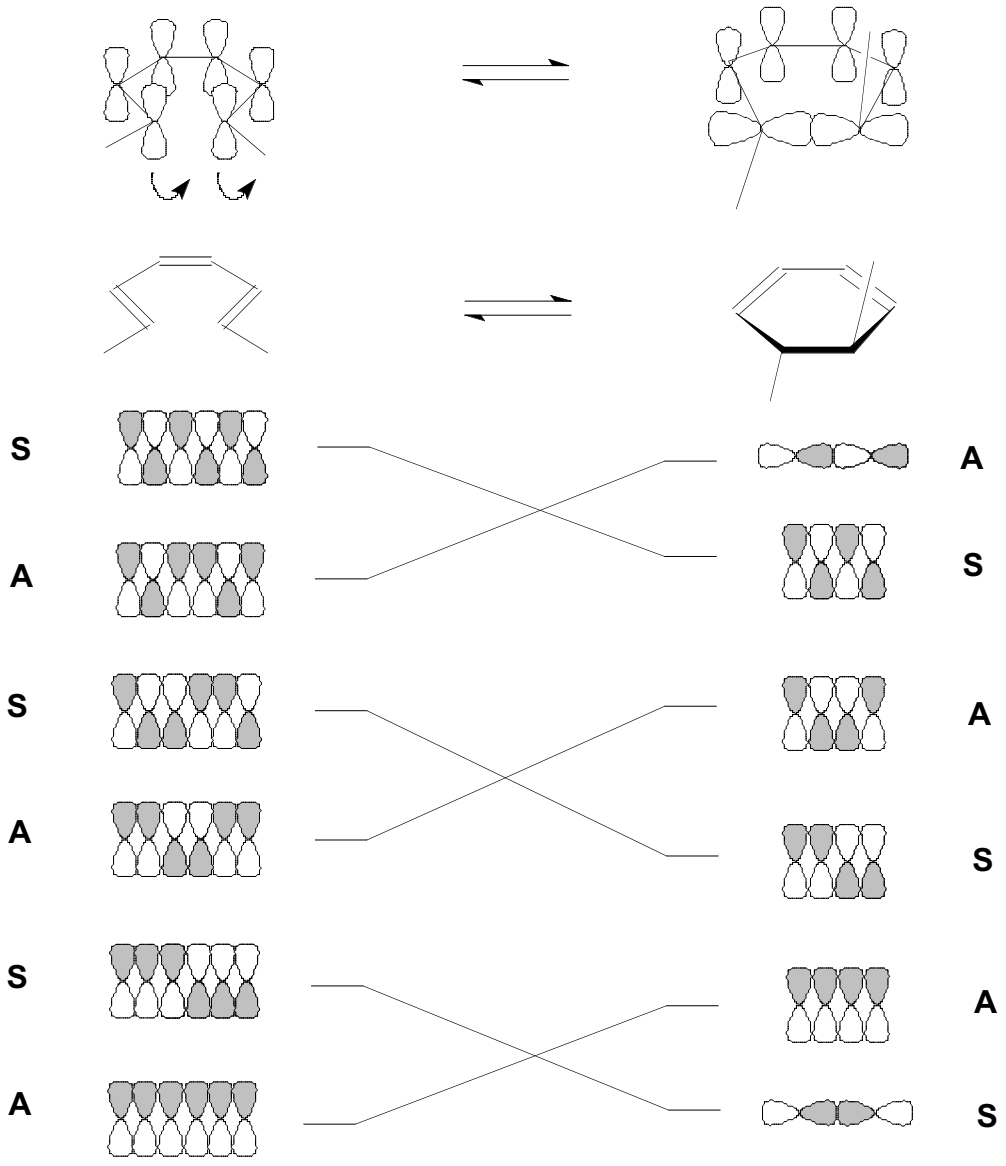
2a. Disrotatory ring closure/opening (6 electrons)



thermally allowed; photochemically disallowed

ELECTROCYCLIC REACTIONS

2b. Conrotatory ring closure/opening (6 electrons)



thermally disallowed; photochemically allowed

ELECTROCYCLIC REACTIONS

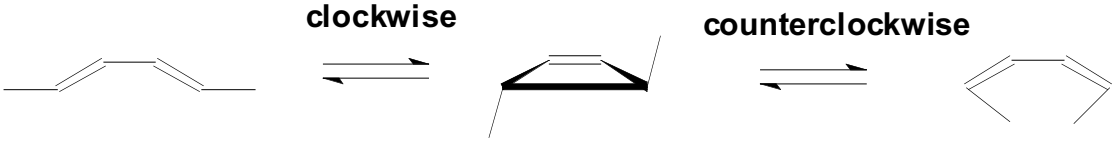
Electrocyclic reactions are controlled by the symmetry of the HOMO of the polyene.

Electron pairs	Thermal	Photochemical
even number	conrotatory	disrotatory
odd number	disrotatory	conrotatory

Note:

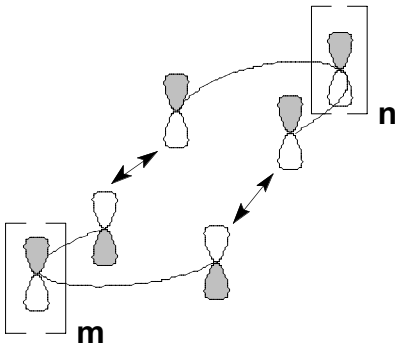
If there is a choice, the sterically favored sense of rotation is going to dominate, see for example:

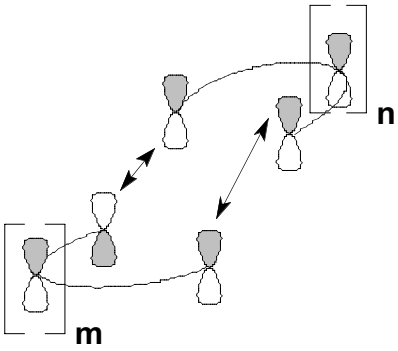
Thermally allowed conrotatory opening



CYCLOADDITION REACTIONS

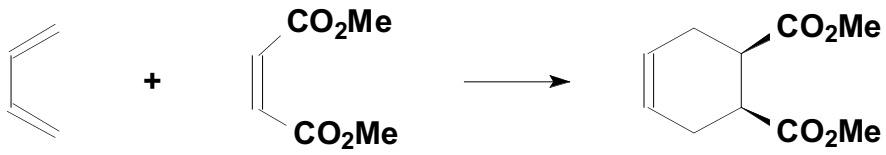
suprafacial/suprafacial **antarafacial/suprafacial**





suprafacial **antarafacial**

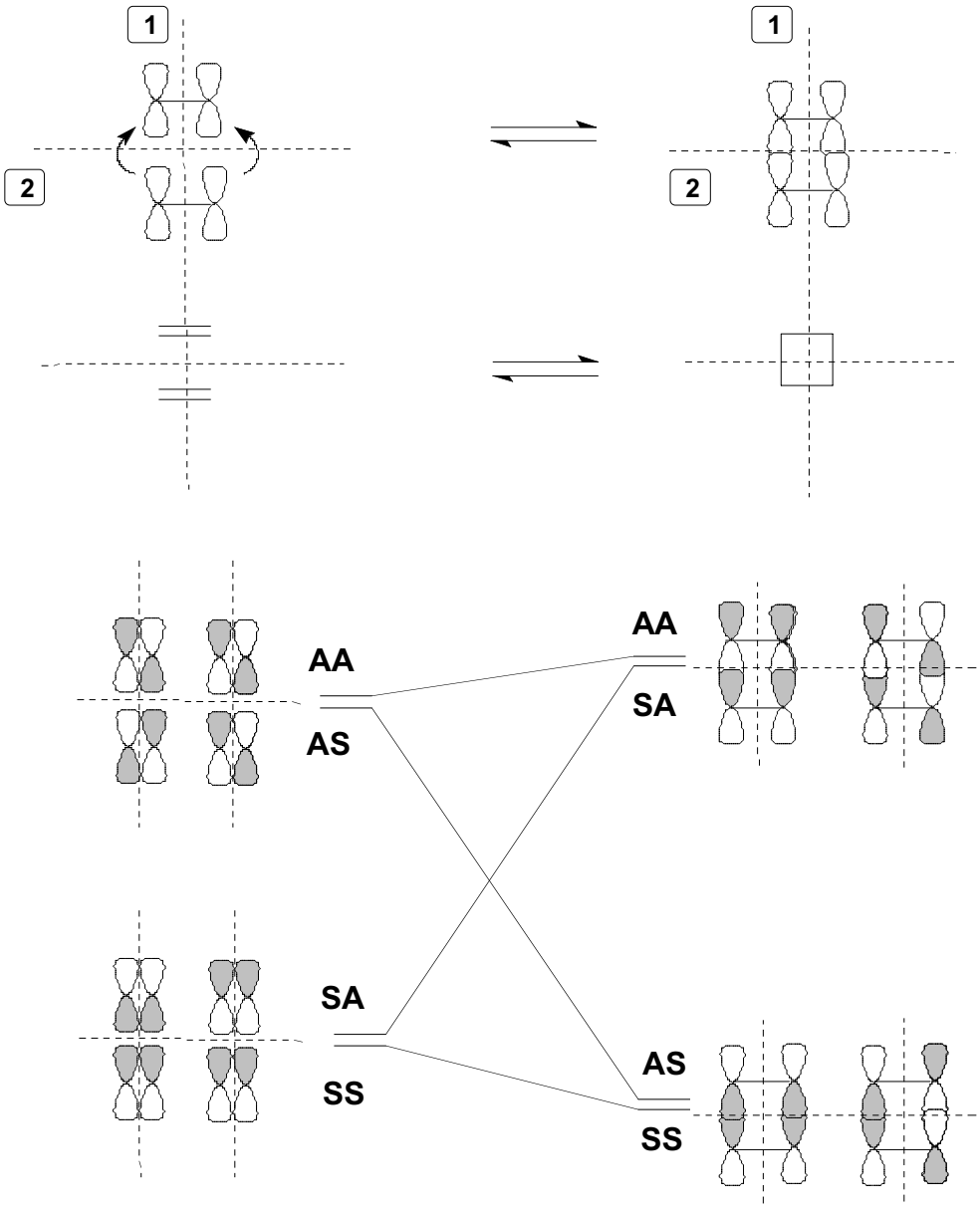
Example: [2+4] thermal cycloaddition (Diels-Alder reaction)



diene (cisoid) **dienophile (cis)** **adduct (cis)**

CYCLOADDITION REACTIONS

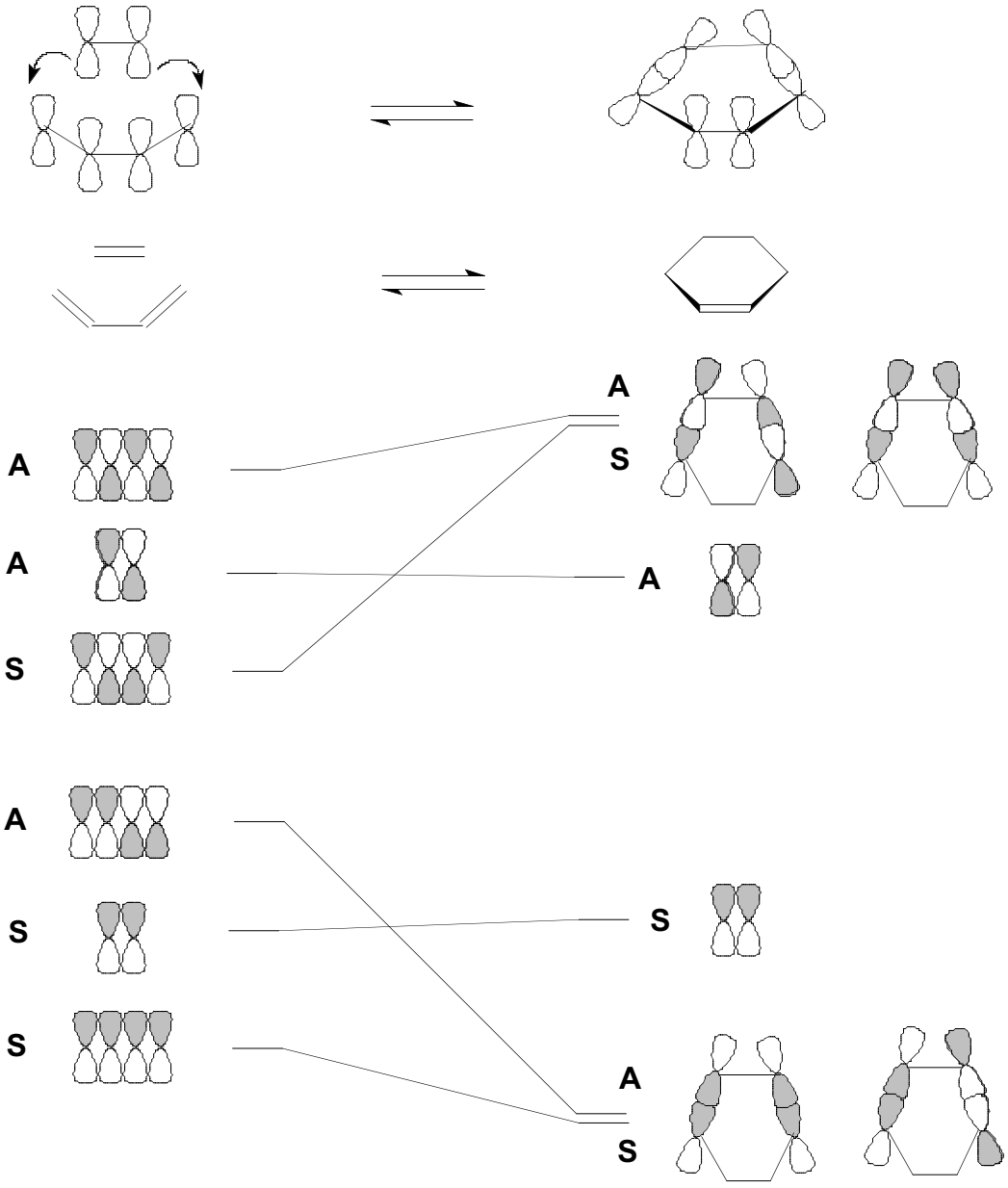
1. Suprafacial [2+2] cycloaddition (4 electrons)



thermally disallowed; photochemically allowed

CYCLOADDITION REACTIONS

2. Suprafacial [4+2] cycloaddition (6 electrons)



thermally allowed; photochemically disallowed

CYCLOADDITION REACTIONS

Cycloadditon reactions are controlled by the symmetries of the HOMO of one component and the LUMO of the other component (they must match).

Electron pairs	Thermal	Photochemical
even number	antarafacial	suprafacial
odd number	suprafacial	antarafacial

Note:

Antarafacial additions may not be possible for geometric reasons.

Stereochemical issues:

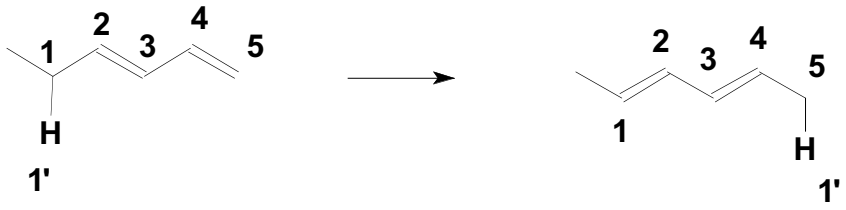
cis/trans products (stereochemistry of starting materials)

exo/endo products (secondary HOMO-LUMO interactions)

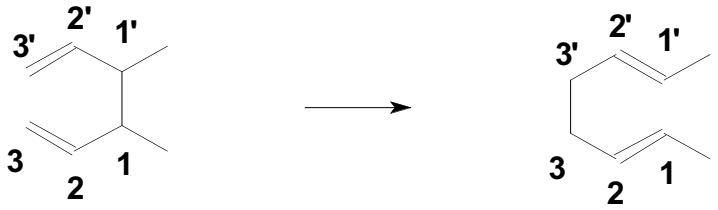
regioselectivity (controlled by the relative size of orbital lobes)

SIGMATROPIC REARRANGEMENTS

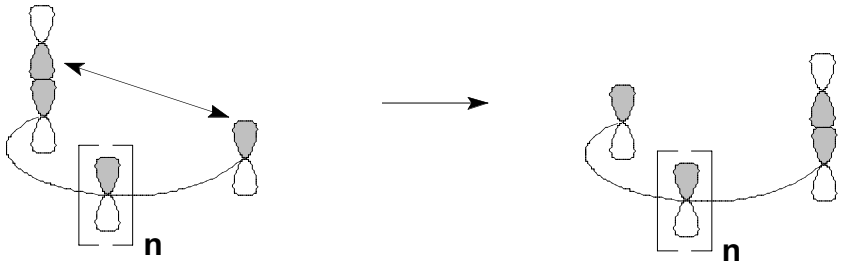
[1,n] shifts, for example [1,5]



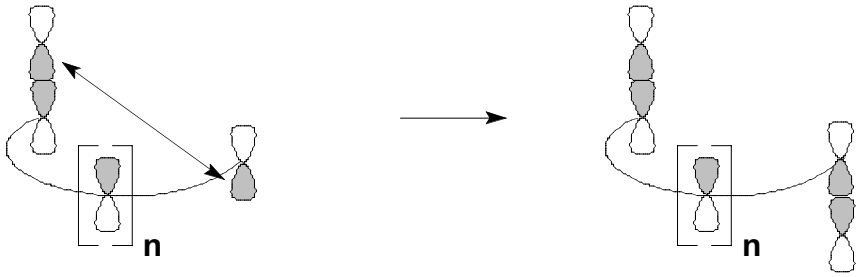
[n,m] shifts, for example [3,3] (Cope rearrangement)



Suprafacial (suprafacial/suprafacial)



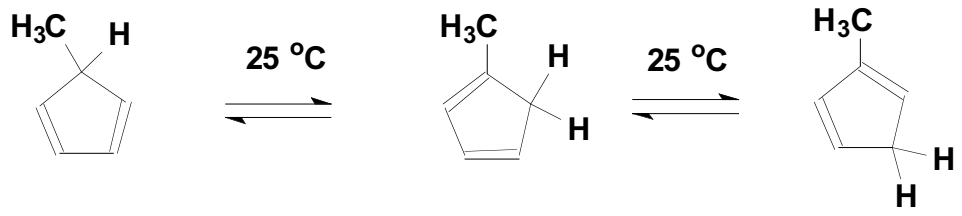
Antarafacial (antarafacial/suprafacial)



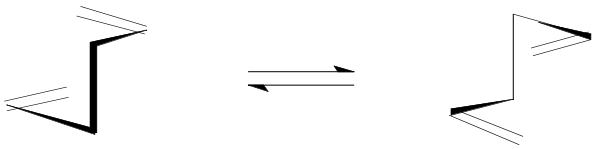
SIGMATROPIC REARRANGEMENTS

Common examples of thermal shifts

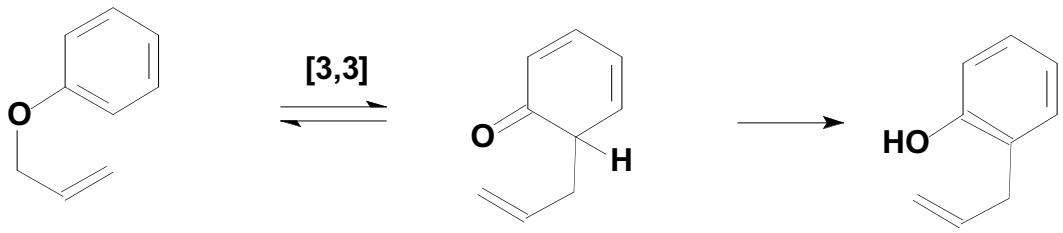
1. [1,5] hydrogen shift



2. Cope rearrangement



3. Claisen rearrangement



SIGMATROPIC REARRANGEMENTS

The same symmetry rules as for cycloadditions

Electron pairs	Thermal	Photochemical
even number	antarafacial	suprafacial
odd number	suprafacial	antarafacial

Note:

Antarafacial sigmatropic rearrangements may not be possible for geometric reasons, especially for "short" π systems

SUMMARY OF SYMMETRY RULES FOR PERICYCLIC REACTIONS

Electron state	Electron Pairs	Stereochemistry
ground state	even number	antara-con
	odd number	supra-dis
excited state	even number	supra-dis
	odd number	antara-con

A General Procedure for Determination of What's Allowed

Note: The orbitals used here are "basis" orbitals (not any specific molecular orbitals).

1. **Draw the reaction scheme and show with arrows the "electron flow".**
2. **Draw all basis orbitals participating in the reaction (σ and π).**
3. **Connect with lines on the same face (side) all orbital lobes forming continuous π networks or σ bonds.**
4. **Give the connected lobes the same sign (color).**
5. **Indicate the newly made bonds with arrows, following the stereochemistry you want to explore.**
6. **Count the number of electrons, and the number of sign inversions in the "cycle" of connected orbitals.**
7. **Use the table below to determine whether the reaction is allowed or disallowed.**

For thermal reactions

# of electrons in the cycle	odd # of sign inversions	even # of sign inversions
4n	allowed	disallowed
4n + 2	disallowed	allowed (aromatic)

For photochemical reactions the rules are reversed