

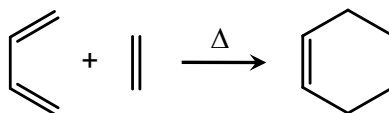
Pericyclic Reactions

Pericyclic reactions involve a concerted (one-step) mechanism and a cyclic transition state, involving a simultaneous change in π and σ bonds.

Cycloaddition:

A reaction in which two π -containing molecules come together to form two new σ -bonds and a new cycle.

Example: Diels-Alder.



Allowed and Forbidden Pericyclic Reactions

Woodward-Hoffmann rules dictate which pericyclic reactions are “allowed”—have molecular orbital interactions that make them possible—and which are “forbidden”.

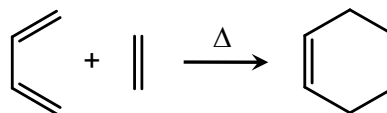
Woodward-Hoffman rules for cycloaddition:

Total number of π -electron pairs:

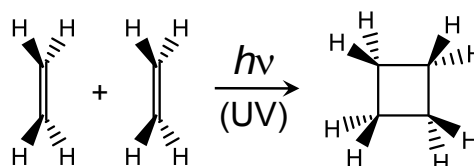
odd Thermally allowed, photochemically forbidden.

even Photochemically allowed, thermally forbidden.

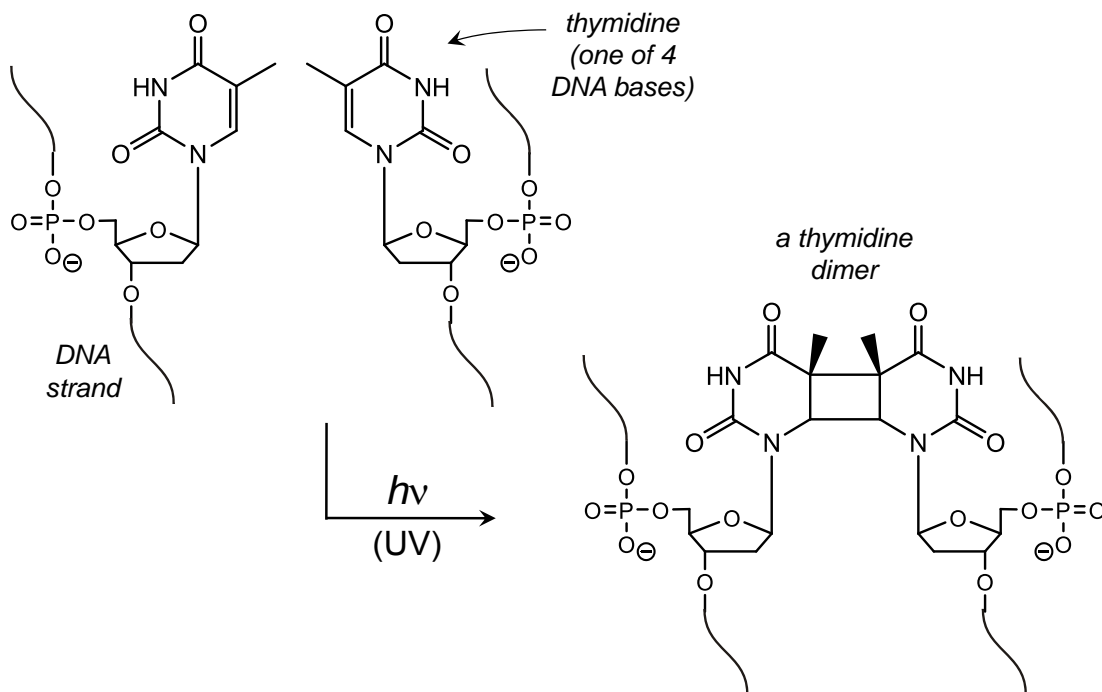
So [4+2] cycloaddition only requires heat,



but [2+2] requires light.



[2 + 2] Cycloadditions Damage DNA, Lead to Melanoma

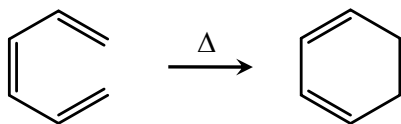


Electrocyclic Ring Opening and Closing

Electrocyclic reactions either form a ring from an acyclic starting material, or open an existing ring into an acyclic product.

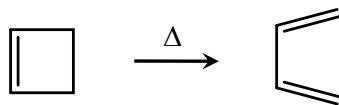
Ring Closing:

An sp^3 - sp^3 bond is made.



Ring Opening:

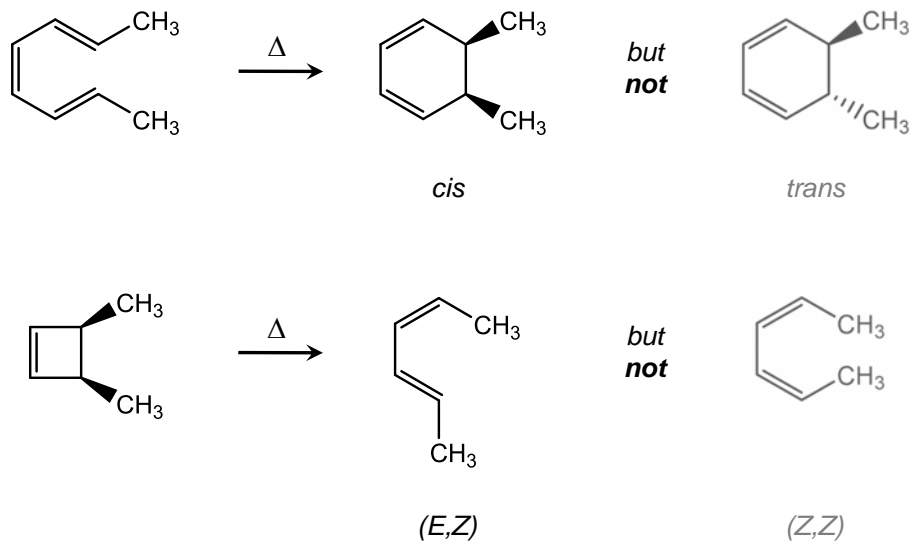
An sp^3 - sp^3 bond is broken.



- All electrocyclic ring reactions are allowed.
- Electrocyclic reactions are, in principle, reversible. In practice, thermodynamics typically favors one direction over the other.

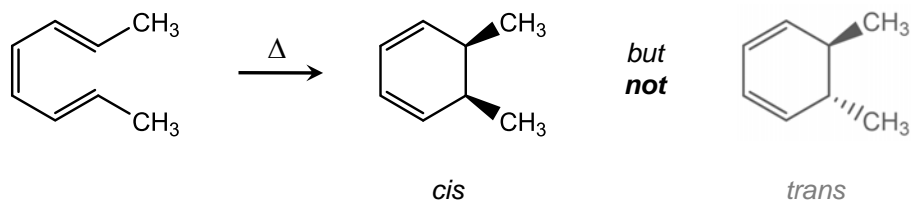
Electrocyclic Reactions Are Diastereoselective

Examples:

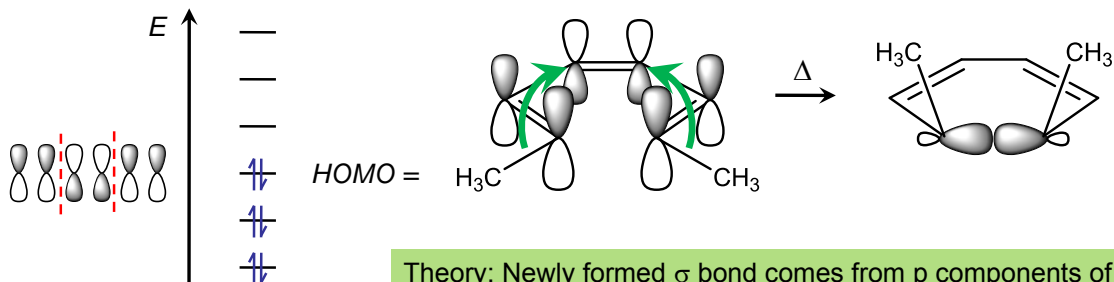


Selectivity of Electrocyclic Ring Closure

Electrocyclic ring closure is controlled by the highest occupied molecular orbital (HOMO) of the conjugated π starting material.



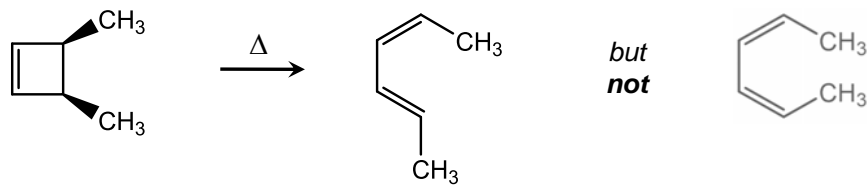
Molecular orbital diagram:



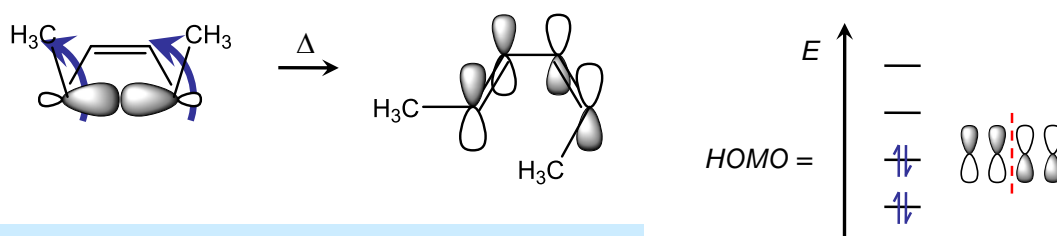
Theory: Newly formed σ bond comes from p components of HOMO; groups twist in opposite directions (**disrotatory**).

Selectivity of Electrocyclic Ring Opening

Electrocyclic ring opening is controlled by the highest occupied molecular orbital (HOMO) of the conjugated π product.



Molecular orbital diagram:



Theory: Breaking σ bond becomes p components of HOMO; groups twist in same direction (**conrotatory**).

Woodward-Hoffman Rules for Electrocyclic Reactions

Total number of reacting electron pairs:	Thermal reaction pattern:	Photochemical reaction pattern:
<i>odd</i>	disrotatory	conrotatory
<i>even</i>	conrotatory	disrotatory