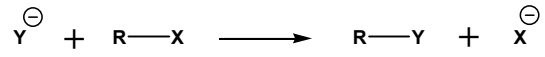
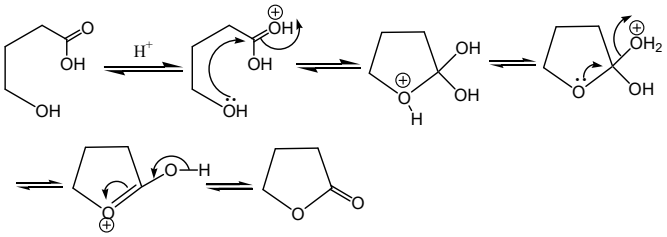
Pericyclic Reactions

Three Classes of Organic Reactions

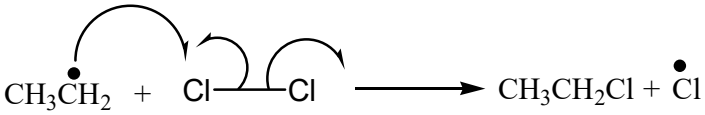
Polar reactions



R = aliphatic as well as aromatic



Radical reactions

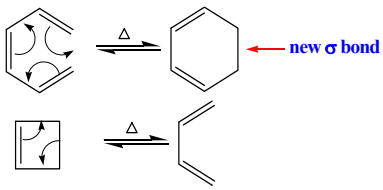


Pericyclic reactions

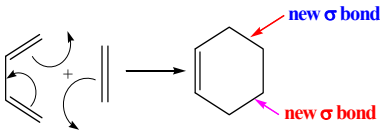
This reaction occurs as a result of a cyclic reorganization of electrons

Three most common types of pericyclic reactions

Elcetrocyclic reactions

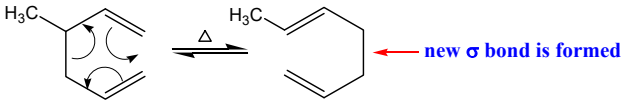


Cycloaddition reactions

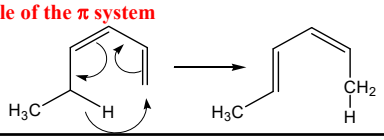


Diels-Alder reaction

Sigmatropic reactions



σ bond is broken in the middle of the π system



σ bond broken at the end of the π-system

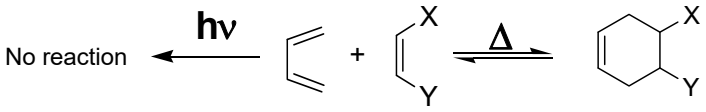
Certain common features of pericyclic reactions

- **They are all concerted reactions, electron reorganization takes place in single step. Therefore, there is one TS and no intermediates**
- **As the reactions are concerted, they are highly stereospecific**
- **The reactions are generally not effected by *catalysts* or by a change in *solvent***

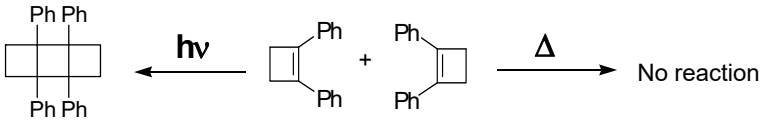
Product configuration depends on
- Configuration of the reactant
- The number of double bonds in the reactant
- Whether the reaction is photochemical or thermal

Some pericyclic reactions are induced thermally or photochemically

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

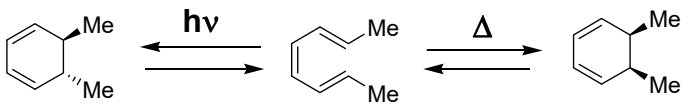


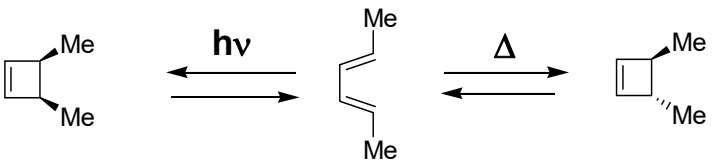
[2+2]-cycloaddition



Some pericyclic reactions are induced thermally and photochemically

Electrocyclic reaction





Conservation of Orbital Symmetry Theory

R. B. Woodward and Roald Hoffmann (1965)

In phase orbitals overlap during the course of a pericyclic reaction

Based on Frontier Molecular orbital theory (1954, Fukui)

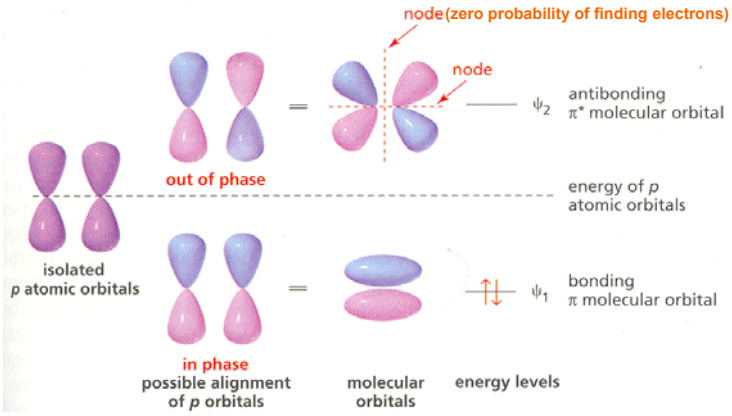
(HOMO, LUMO)

- The occupied orbitals of different molecules repel each other.
- Positive charges of one molecule attract the negative charges of the other.
- The occupied orbitals of one molecule and the unoccupied orbitals of the other (especially the HOMO and LUMO) interact with each other causing attraction.

Molecular orbital symmetry controls

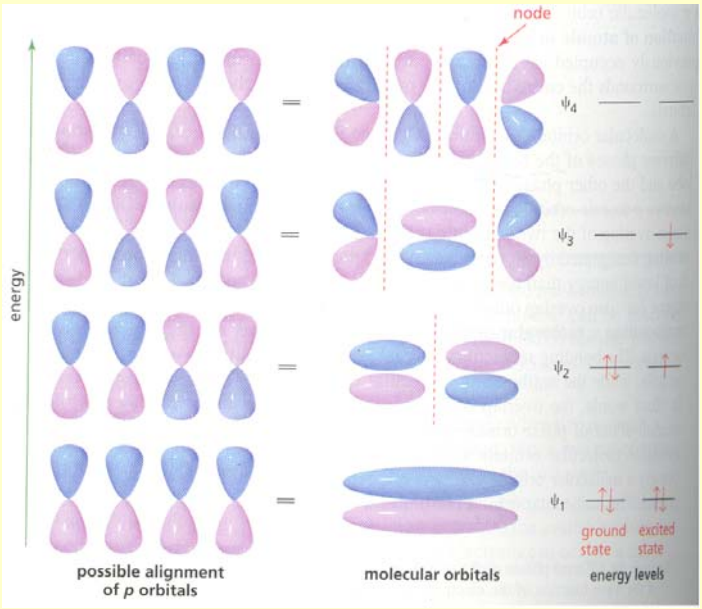
- Weather or not compound undergoes a reaction under particular conditions
- What product will be formed

A molecular orbital description (ethene)



- Overlap of in-phase *p* orbitals gives a bonding π molecular orbital that is lower in energy than the *p* atomic orbitals.
- Overlap of out-of-phase *p* atomic orbitals gives an antibonding π molecular orbital that is higher in energy than the *p* atomic orbitals.

1,3-butadiene



Asymmetric

Nodes are more than no. of bonding interactions

Symmetric

Asymmetric

bonding interactions are more than no. of nodes

Symmetric

Four *p* atomic orbitals overlap to give the four π molecular orbitals

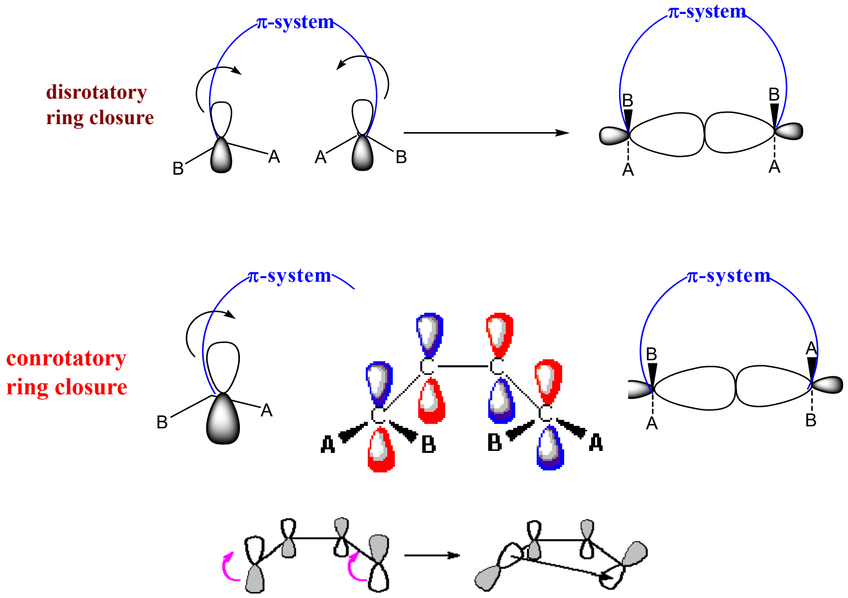
Electrocyclic Reactions

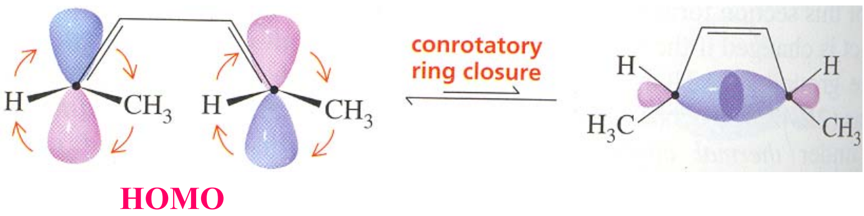
These reactions are defined as involving the cyclization of an n *pi*-electron system to an (n-2)*pi* + 2sigma-electron system or the reverse process.

$$n(\pi) \rightleftharpoons n\text{-}2\ (\pi) + 2\ (\sigma)$$

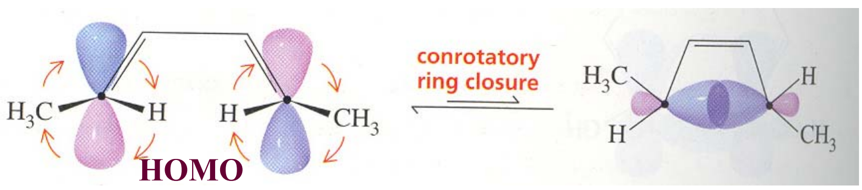
- **The reactions are reversible.**
- **Observance of ring opening and ring closure depends upon the thermodynamic stability of the open and closed forms.**

Two distinct modes are possible….

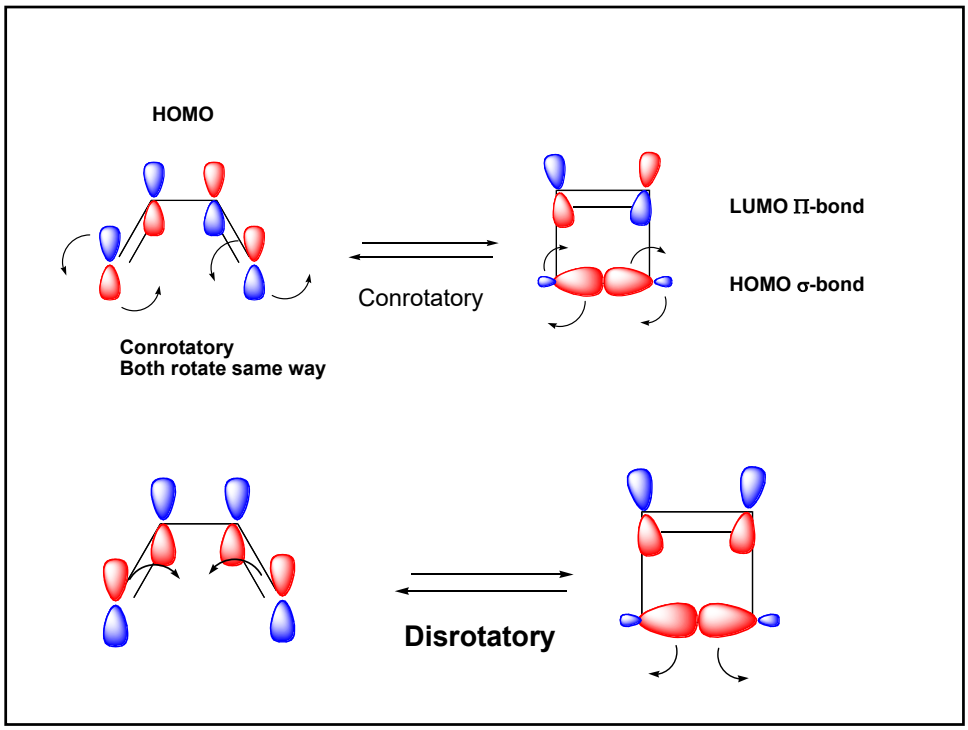


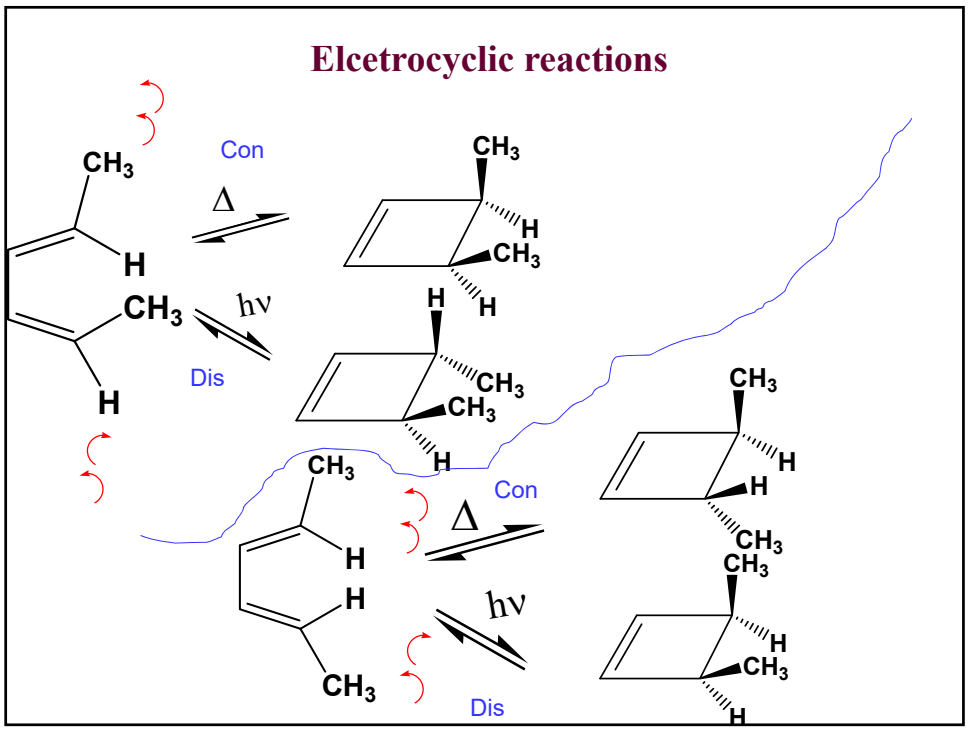


(2E,4Z)-hexadiene



(2E,4E)-hexadiene


HOMO
Conrotatory
Conrotatory
Both rotate same way
LUMO Π-bond
HOMO σ-bond
Disrotatory


Elcetrocyclic reactions
Con
Δ
hν
Dis
Con
Δ
hν
Dis

Selection rules for electrocyclic reactions

Woodward-Hoffmann rules


No. of π-electrons	Thermally allowed, photochemically forbidden	Thermally forbidden, photochemically allowed
4n	Conrotatory	Disrotatory
4n+2	Disrotatory	Conrotatory

n = integer