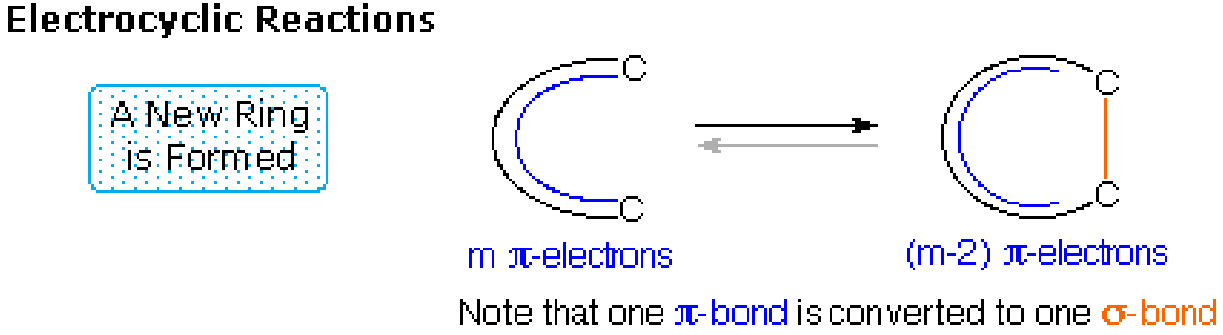
Pericyclic Reaction

Pericyclic Reactions: Electrocyclic Reaction

1. Electrocyclic ring closing
2. Electrocyclic ring opening

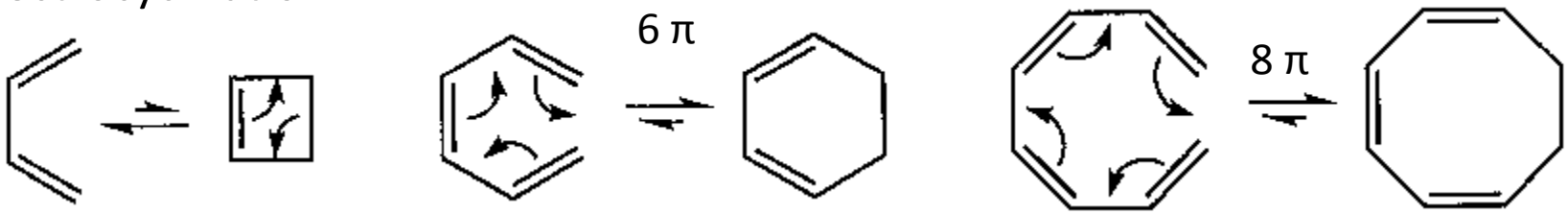
Electrocyclic ring closing reaction is characterized by

a. The **formation of a ring** from an **open chain** conjugated system
b. Via a **new σ-bond** at both end of the conjugated π-component
c. with a **reduction in the length** of the conjugated system

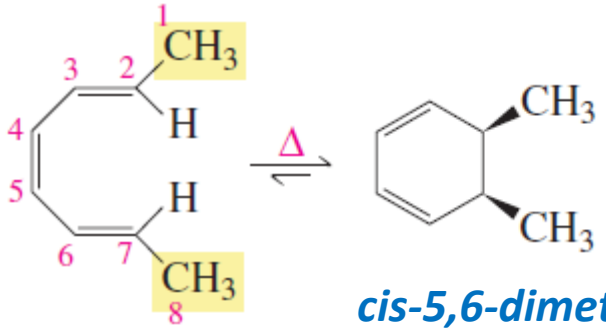


Electrocyclic ring opening reaction has opposite characteristics of Electrocyclic ring closing reaction

4 π-electrocyclization

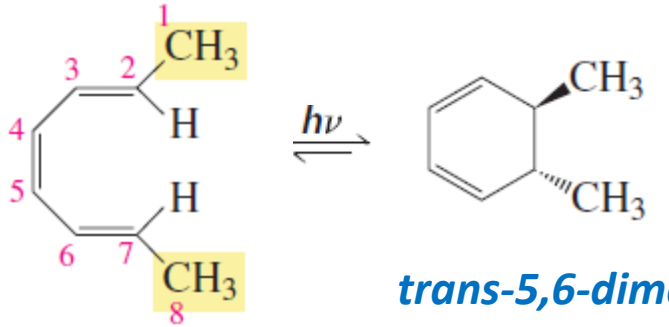


Pericyclic Reactions: Electrocyclic Reaction



(2*E*,4*Z*,6*E*)-octatriene

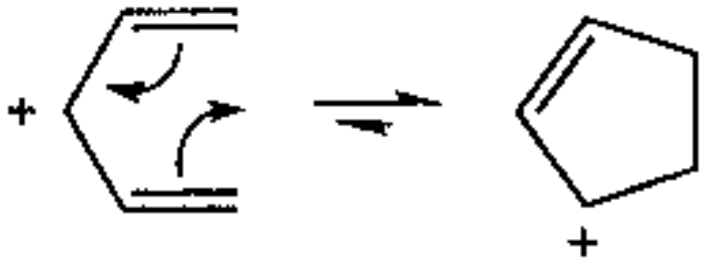
cis-5,6-dimethyl-1,3-cyclohexadiene



(2*E*,4*Z*,6*E*)-octatriene

trans-5,6-dimethyl-1,3-cyclohexadiene

How to describe this electrocyclic reaction?

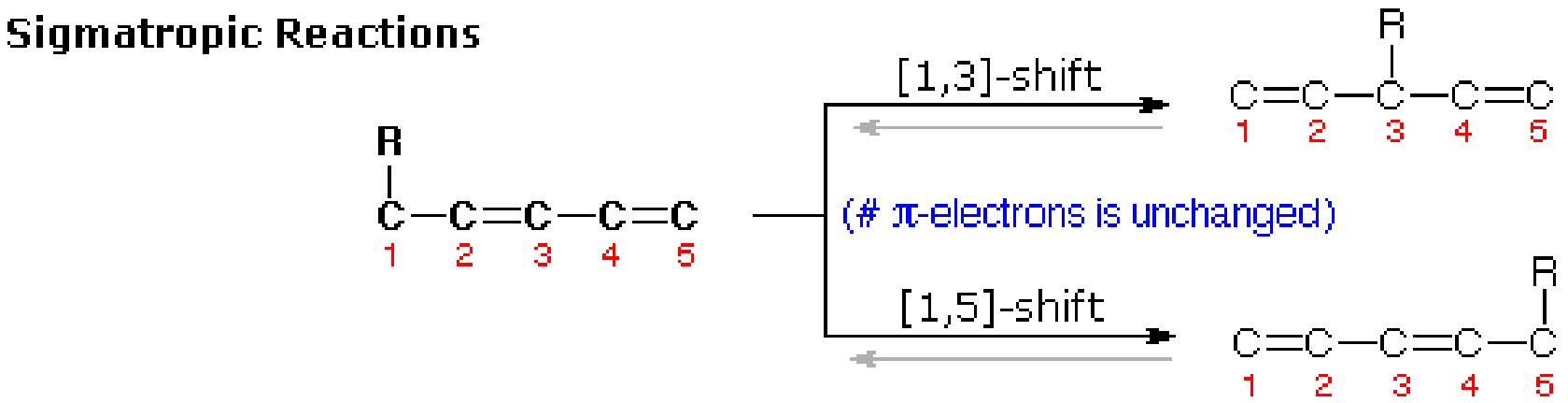


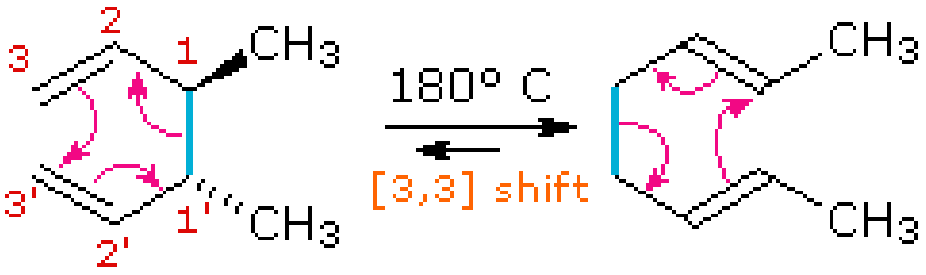
What is the main difference between cycloaddition and electrocyclic reaction?

Pericyclic Reactions: Sigmatropic Reaction

Sigmatropic reaction is

a. A **unimolecular isomerization** reaction
b. That involves movement of a **σ-bond** from one position to another in the conjugated π-component
c. with a **concomitant movement of** π-bond





[3,3] sigmatropic rearrangement

Pericyclic Reactions: Sigmatropic Reaction

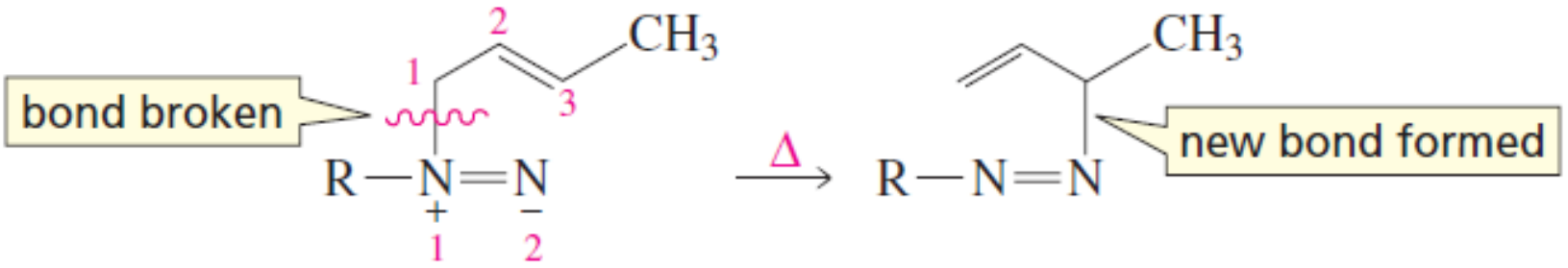
How to describe a given sigmatropic reaction ?

First, mentally break the **σ-**bond in the reactant and give a number **1** label to the each atom that were attached by the bond.

Then look at the new **σ-**bond in the product.

Count the number of atoms in each of the fragments that connect the broken **σ-**bond and the new **σ-**bond.

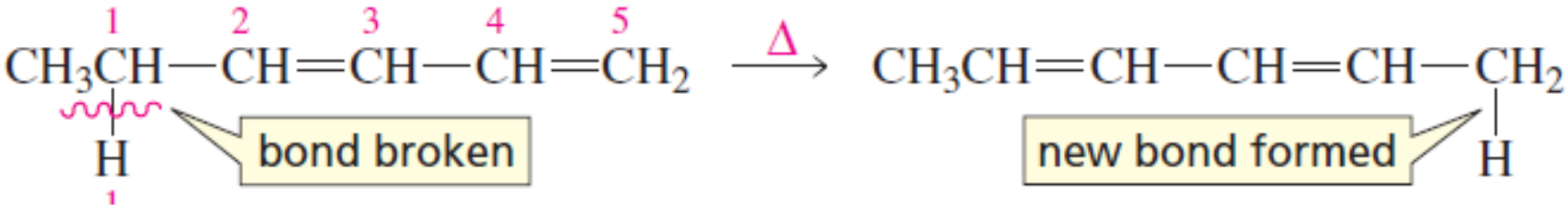
The two numbers are put in brackets with the smaller number stated first.



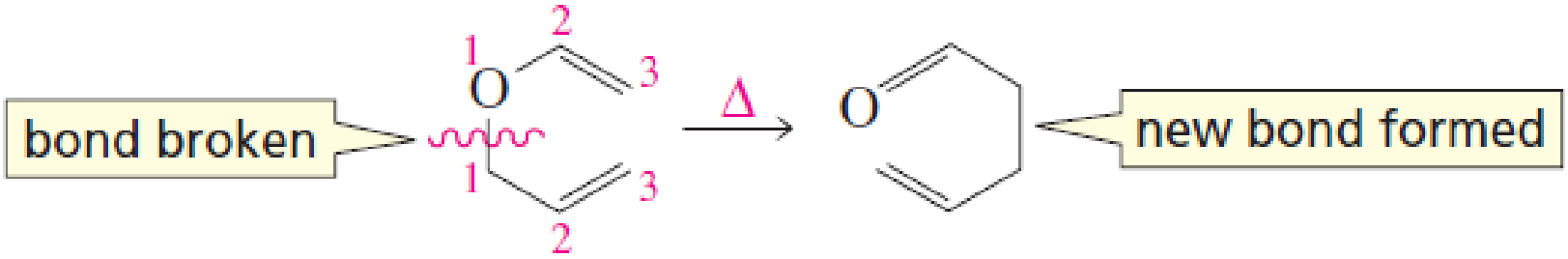
[2,3] sigmatropic rearrangement, generally lowest number comes first

Pericyclic Reactions: Sigmatropic Reaction

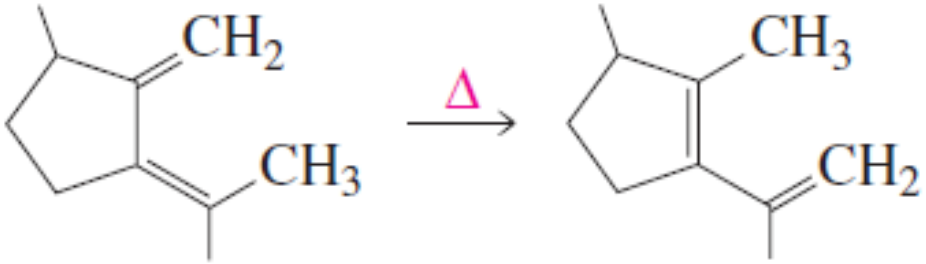
[1,5] sigmatropic rearrangement



[3,3] sigmatropic rearrangement



What kind of sigmatropic reaction is it?



[1,5] sigmatropic reaction

Pericyclic Reactions: Sigmatropic Reaction

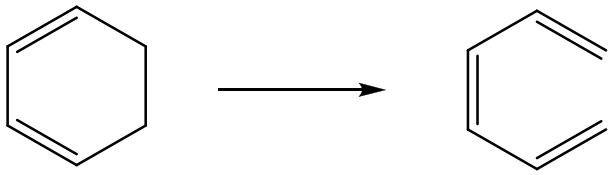
Main difference between cycloaddition and sigmatropic rearrangement

Cycloaddition	Sigmatropic
Involves two components	Involves one components

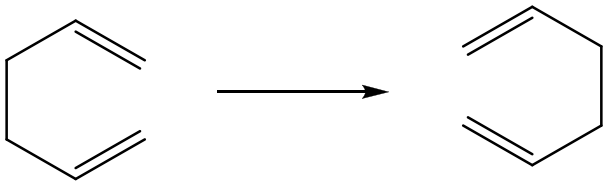
Difference between electrocyclic reaction and sigmatropic rearrangement

Electrocyclic	Sigmatropic
Involves one components	Involves one components
π-bond breakes; **σ**-bond formed	**σ**-bond breaks and **σ**-bond formed

What type of pericyclic reactions are these?

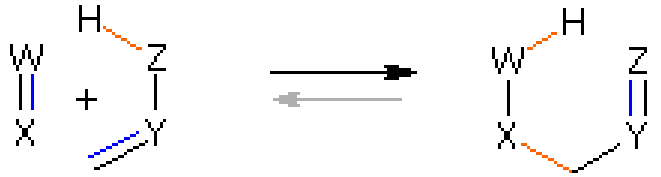


Electrocyclic reaction



Sigmatropic reaction

Pericyclic Reactions: Group Transfer Reaction



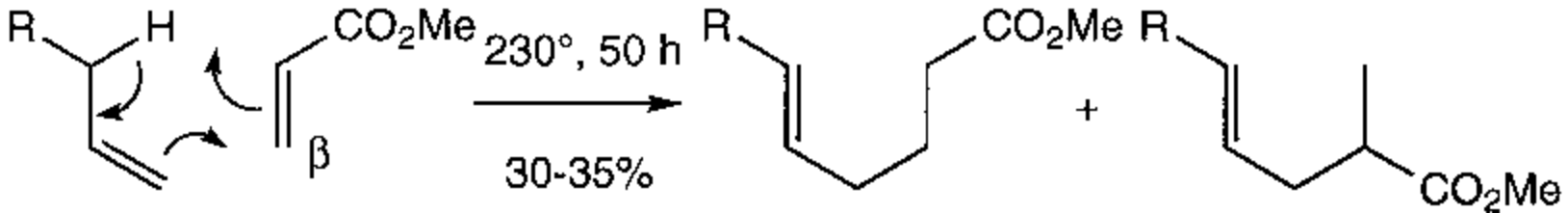
Note that a π-bond is converted to a σ-bond, but no rings are formed or broken.

Two component reaction but no cycle is formed; **not a cycloaddition**

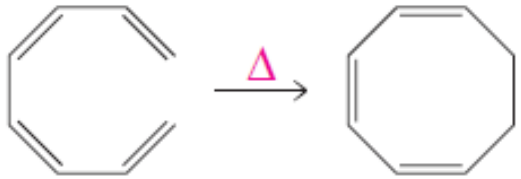
As it is two component reaction, so **distinguished from electrocyclic and sigmatropic reaction**

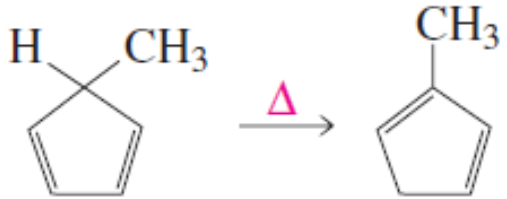
A group or atom is transferred from one π-system to another π-system

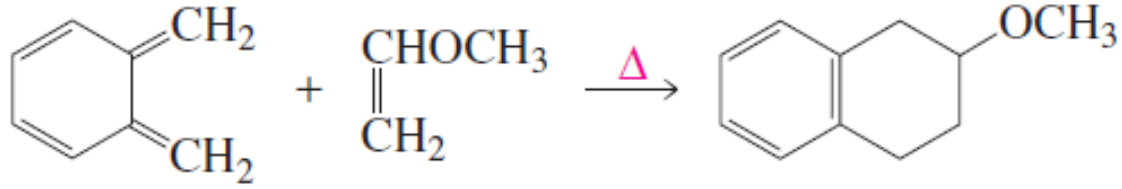
Group transfer reaction is a pericyclic reaction where an atom or group is transferred from one component to another

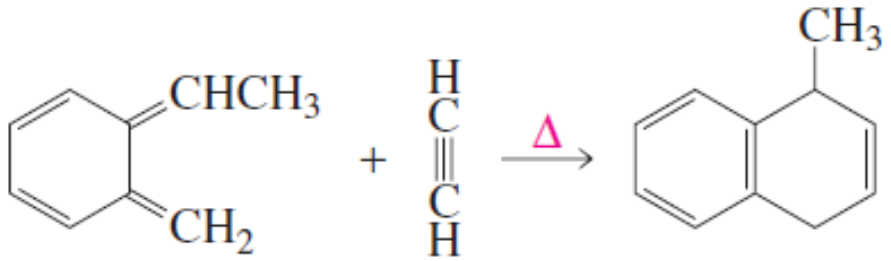


Pericyclic Reactions

a. 

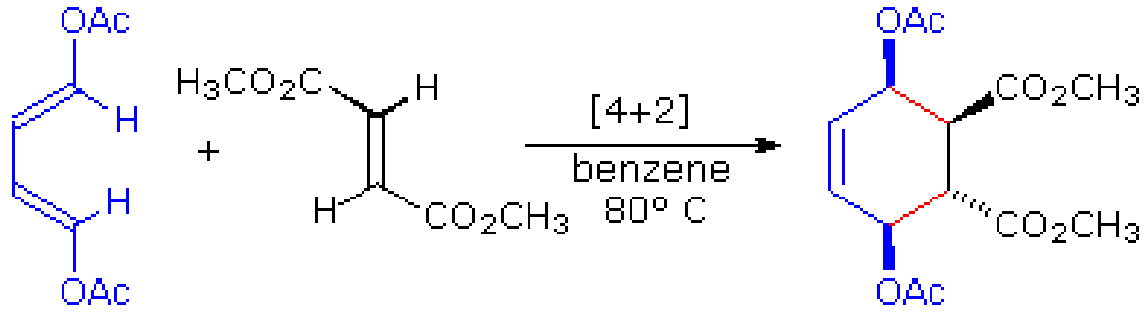
b. 

c. 

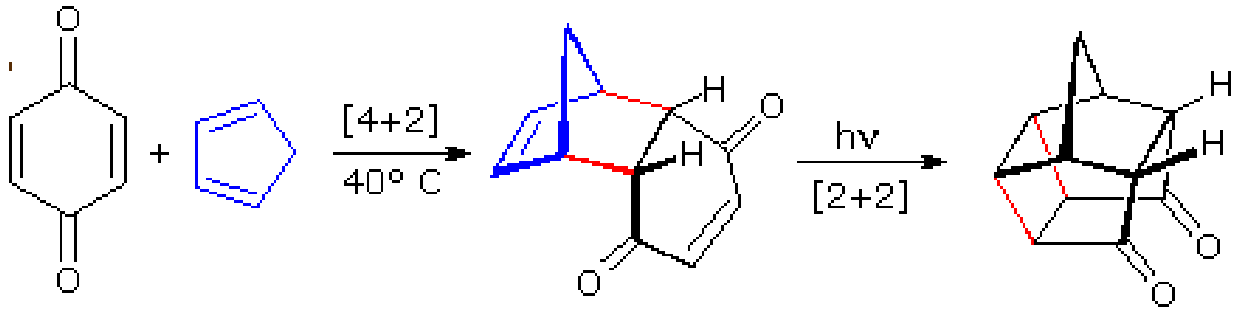
d. 

e. 

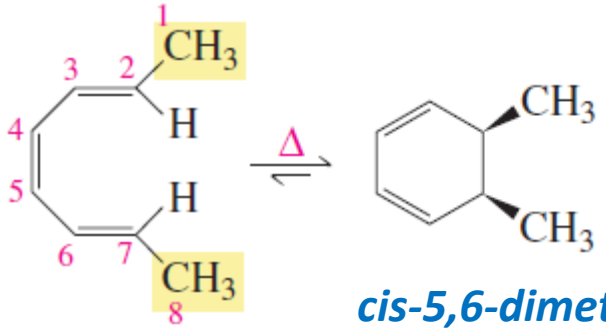
Pericyclic Reactions: Reactivity and Selectivity



Why only one isomer?

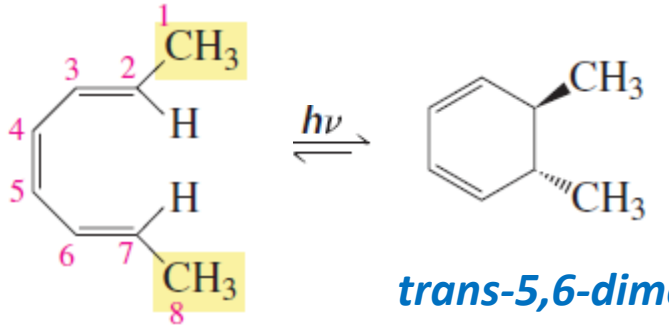


Why [2+2] cycloaddition requires photochemical condition?



(2*E*,4*Z*,6*E*)-octatriene

***cis*-5,6-dimethyl-1,3-cyclohexadiene**



(2*E*,4*Z*,6*E*)-octatriene

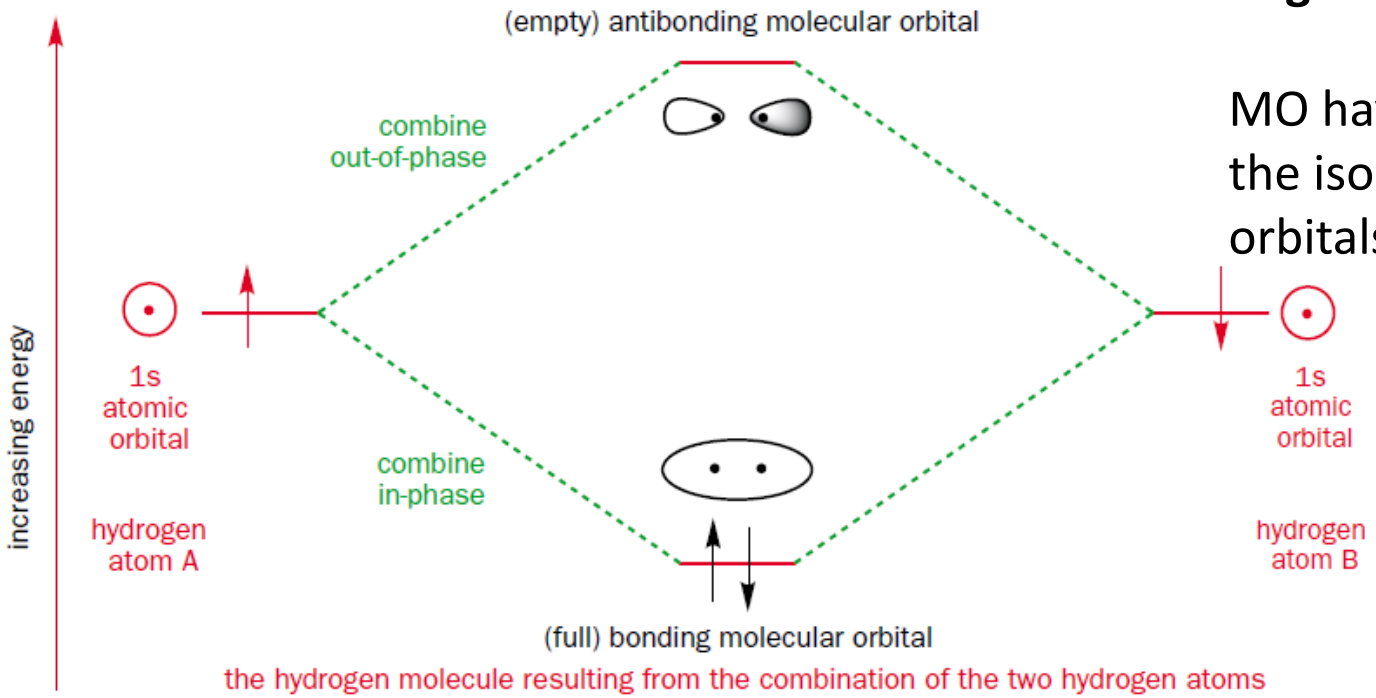
***trans*-5,6-dimethyl-1,3-cyclohexadiene**

Why stereoselectivity changes with changes in reaction condition?

Pericyclic Reactions: Frontier Molecular Orbital (FMO) Theory

Molecular Orbital: Atomic orbitals of atoms can combine and overlap to give more complex Orbitals that is called molecular orbital

two atomic orbitals that results in out-of-phase interaction of orbitals is called **Antibonding MO**



MO having same energy as the isolated interacting atomic orbitals Nonb**onding MO**

Two orbitals on adjacent atoms that forms in-phase interaction between the atoms is called **Bonding MO**

Pericyclic Reactions: Frontier Molecular Orbital (FMO) Theory

What is /are Frontier Molecular Orbital ?

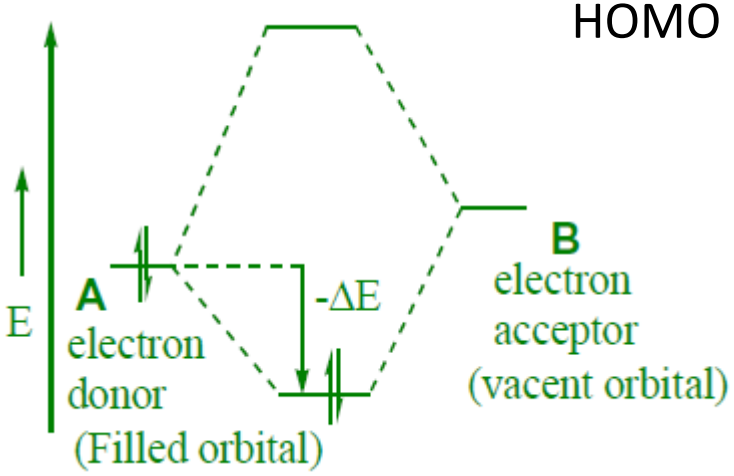
Tow molecules interact with each other means two molecular orbital interacts

Molecular orbitals that interacts are HOMO and LUMO

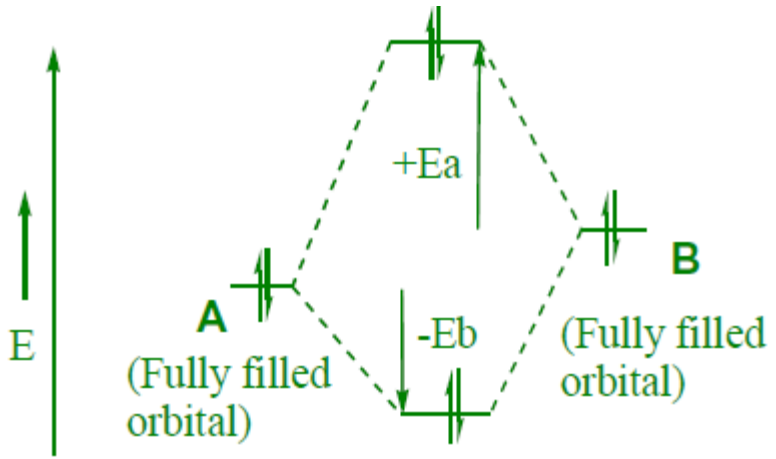
HOMO and LUMO are called Frontier Molecular Orbitals

What does the Frontier Molecular Orbital theory says ?

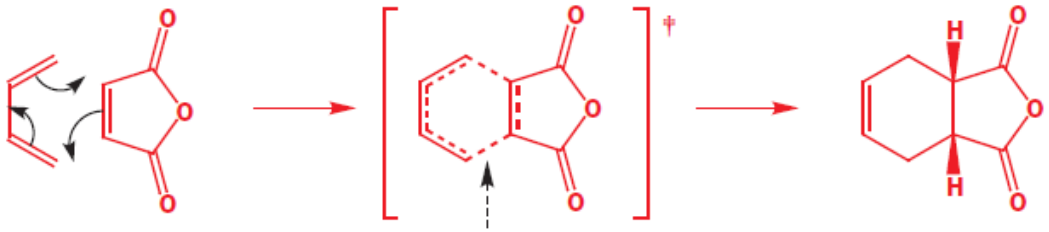
HOMO of one molecule interact with LUMO of another



Why HOMO-HOMO or LUMO-LUMO interaction are not feasible ?



Pericyclic Reactions: π-Molecular Orbital

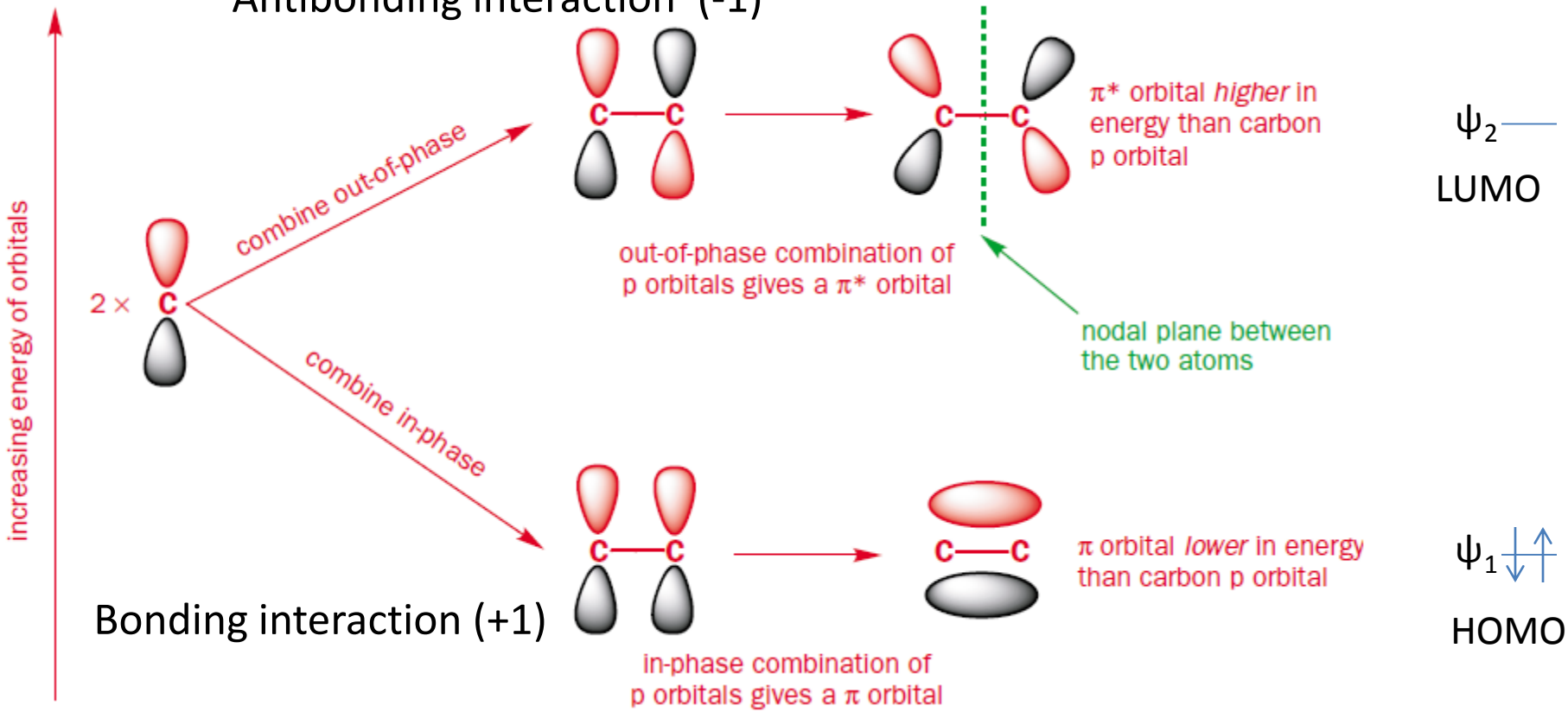


here the different phases of the p orbital are labelled positive and negative – this can be confusing and so is best avoided

here the different phases of the p orbital are shown by shading one half and not the other

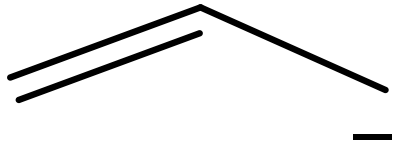
Pericyclic reaction involves the interaction between pi-molecular orbital of one or more component

Antibonding interaction (-1)



Bonding interaction (+1)

Pericyclic Reactions: π-Molecular Orbital



Provide the molecular orbitals of allyl anion

Pericyclic Reactions: π-Molecular Orbital

1. Find out no of p-atomic orbital (say n) in the conjugated system (**only p-oribtal not the no of carbon or no of electron**)

2. Total number of π-molecular orbital will be the same as the number of p-atomic orbital

3. If n_p is even, $n_{BMO} = n_p/2$ BMO: bonding molecular orbital
$n_{AMO} = n_p/2$ AMO: anti-bonding molecular orbital
$n_{NMO} = 0$ NMO: non-bonding molecular orbital

4. If n_p is odd, $n_{BMO} = (n_p-1)/2$
$n_{AMO} = (n_p-1)/2$
$n_{NMO} = 1$

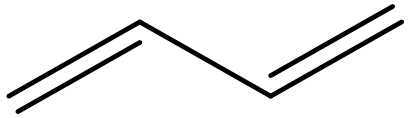
5. If the wavefunction of π-molecular orbital are symbolized as ψ_n (n = 1,2,3,4….), the number of node of ψ_n will be (n-1).

6. Nodes are arranged symmetrically with respect to the center of π-electron system

7. Electrons in each MO are placed according to Aufbau Principle, Hund's rule and Pauli exclusion principle

Pericyclic Reactions: π-Molecular Orbital

Draw the molecular orbitals of 1,3-butadiene



Looking forward

Pericyclic Reaction:
Reactivity and Selectivity

Course material will be uploaded **after 17:00** h on **every Friday** @

http://www.iitg.ac.in/ckjana/ckjana/Teaching.html