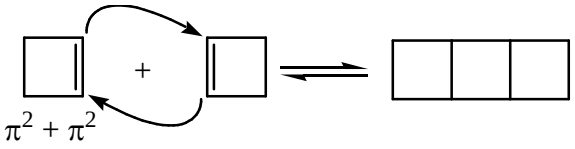
1.4: CYCLOADDITION REACTIONS

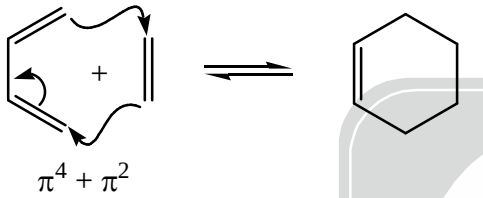
1.4.1: INTRODUCTION:

Cycloaddition reactions involve of two π systems to form ring compounds by the breaking of two π bonds and making of two σ bonds in concerted process. The reverse of cycloaddition reactions are known as retrocycloaddition reactions.

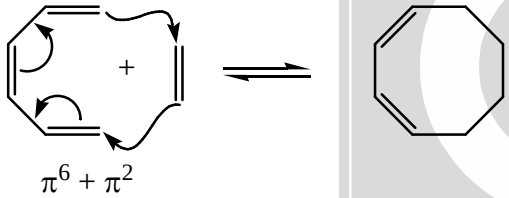
These reactions are classified according to the number of πe^- system involved in each reacting molecules. The major classes are $[\pi^2+\pi^2]$, $[\pi^4+\pi^2]$, $[\pi^6+\pi^2]$, $[\pi^8+\pi^2]$, $[\pi^6+\pi^4]$ and $[\pi^{14}+\pi^2]$. These are simply known as [2 + 2], [4 + 2], [6 + 2], [8 + 2], [6 + 4] and [14 + 2] - cycloaddition reactions.



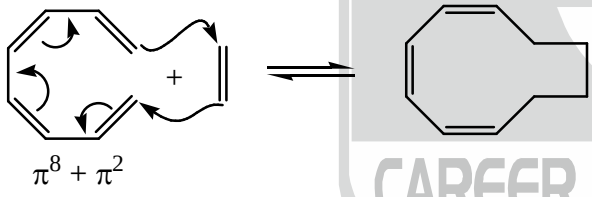
2 + 2 cycloaddition reaction



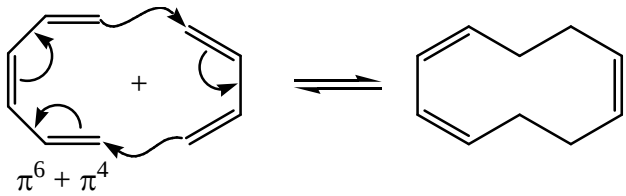
4 + 2 cycloaddition reaction



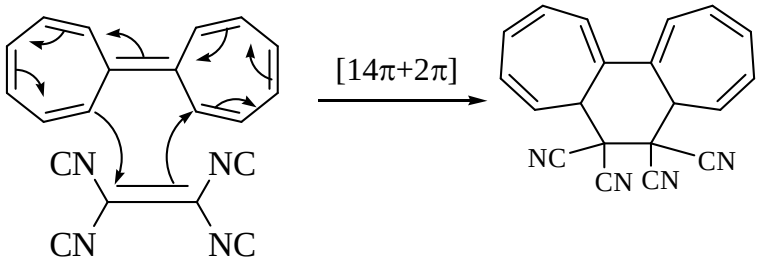
6 + 2 cycloaddition reaction



8 + 2 cycloaddition reaction



6 + 4 cycloaddition reaction



***Type of cycloaddition reactions*:**

(A) Suprafacial addition (B) Antarafacial addition

Suprafacial addition:

Suprafacial addition takes place when bonding, interaction occurs between lobes on the same face of one reactant and lobes on the same face of the other reactant. Because of the geometrical constraints of small rings, cycloaddition that form four or six membered rings must take place by suprafacial pathways.

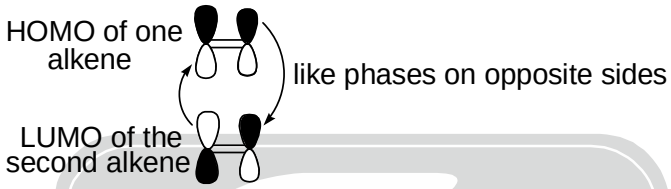
Antarafacial addition:

Antarafacial addition takes place when a bonding interaction occur between lobes on the same face of one reactant and lobes on opposite face of the other reactant.

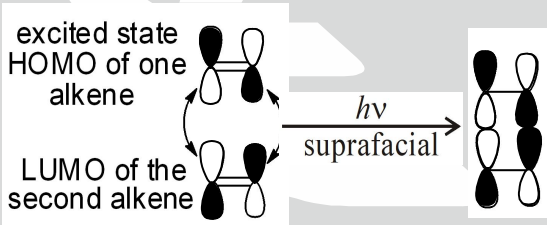
1.4.2: [2+2] CYCLOADDITION REACTION:

[2 + 2] cycloaddition does not occur under the thermal conditions, but take place photochemically.

In a thermal [2 + 2] cycloaddition, like phases of the *p*-orbitals on only one set of terminal carbons can overlap. For like phases to overlap on the other terminal carbon, the molecule must twist to allow for an antarafacial pathway. This process cannot occur to form small rings.



In a photochemical [2 + 2] cycloaddition, light energy promotes an electron from the ground state HOMO to form the excited state HOMO. Interaction of this excited state HOMO with the LUMO of the second alkene then allows for overlap of the like phases of both sets of *p*-orbitals. Two bonding interaction result and the reaction occurs by a suprafacial pathway.



Photochemical cycloaddition involving an even number of π bonds proceed by a suprafacial pathway.

In frontier orbital approach, the thermal reaction of two ethene molecules (one is HOMO and other is LUMO) is orbital symmetry forbidden process for its suprafacial- suprafacial $[\pi^2 s + \pi^2 s]$ cycloaddition but a suprafacial-antarafacial $[\pi^2 s + \pi^2 a]$ cycloaddition reaction is symmetry allowed process.

Thermal $[\pi^2 s + \pi^2 a]$ reactions usually occur in the additions of alkenes to ketenes, when alkene is in the ground state and ketene in the excited state.