

Study Notes on Pericyclic Reactions



Pericyclic reactions

A pericyclic reaction follows a concerted type mechanism and proceeds through a cyclic transition state. These reactions take place in the presence of either light or heat.

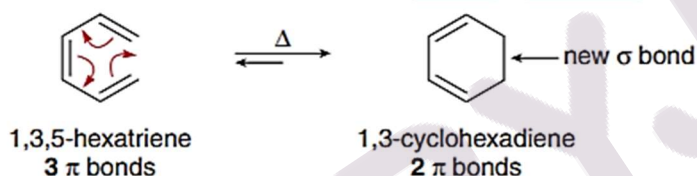
and are completely stereospecific i.e. a single stereoisomer of the reactant will form a single stereoisomer of the product.

Pericyclic reactions are of two types: electrocyclic reactions and cycloadditions.

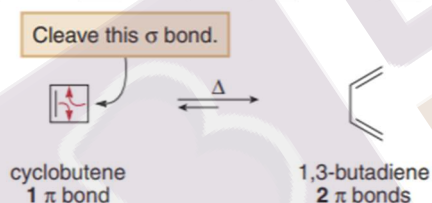
Electrocyclic reaction:

It is a reversible reaction which involves ring closure or ring opening.

- In a ring closure electrocyclic reaction, there is formation of a cyclic product which contains one more σ bond and one fewer π bond than the reactant.

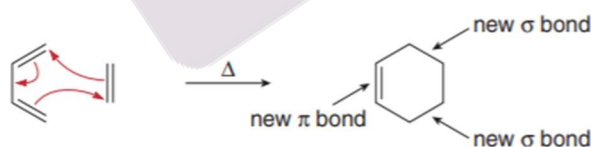


- In a ring-opening electrocyclic reaction, a σ bond of a cyclic reactant is cleaved to form a conjugated product having more than one π bond.



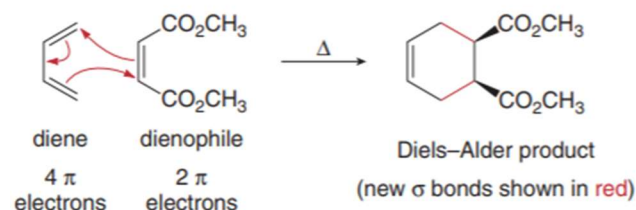
Cycloaddition reaction:

A cycloaddition is an intermolecular reaction in which compounds having π bonds form a cyclic product with two new σ bonds.



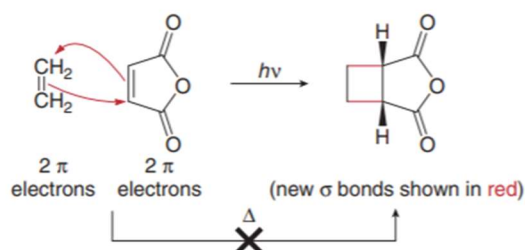
Diels–Alder reaction: It is a thermal $[4 + 2]$ cycloaddition that occurs between a diene with four π electrons and a dienophile with two π electrons.

Note : (4 and 2 refers to the number of π electrons)



Photochemical reaction : It is a $[2 + 2]$ cycloaddition that occurs between two alkenes, each having two π electrons and results in the formation of cyclobutane.

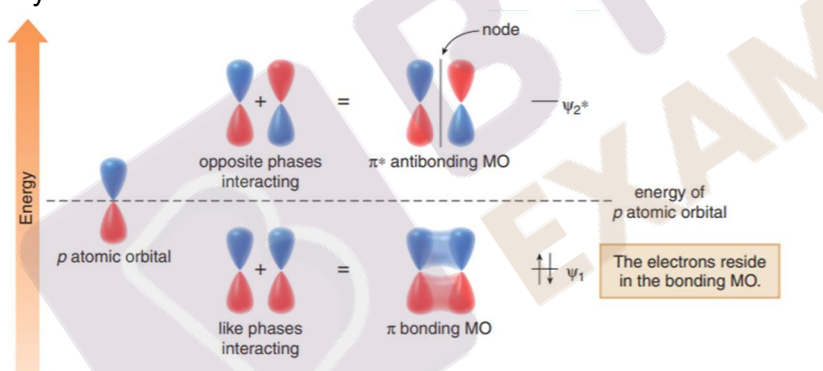
Note :Thermal $[2 + 2]$ cycloadditions do not take place



Molecular Orbitals

MO theory considers bonds as the mathematical combination of atomic orbitals that forms a new set of orbitals called molecular orbitals (MOs).

Ethylene π molecular orbitals



Two p orbitals can combine in two different ways and result in the formation a π bonding molecular orbital (designated as ψ_1) and a π^* antibonding molecular orbital (designated as ψ_2^*)

Advantages of Pericyclic reactions :

- Less probability of formation of unwanted side products since these reactions are unaffected by the influence of solvent or any reagent).
- The reaction is highly stereospecific in nature because of concerted orbital symmetry
- Variety of applications in biosynthesis.
- This reaction is also a non-conventional energy source e.g. the conversion of cyclobutane to two ethylene molecules is accompanied by the release of heat.

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