PERICYCLIC REACTION

Introduction

Pericyclic reactions are reactions that occur by a concerted cyclic shift of electrons. This defination states two key elements. First, a pericyclic reaction is concerted i.e reactant bonds are broken and product bonds are formed simultaneously without intermediates. Selond a pericyclic reaction involves a cyclic shift of electrons. The word pericyclic means around the circle.

The Diels-Alder reaction and S_N2 reaction are both concerted reaction but only the Diels-Alder reaction occurs by a cyclic electron shift. Hence the D.A. rxn is a pericyclic reaction, but the S_N2 reaction is not.

$$R\text{-}Cl \xrightarrow[S_N2]{HO^{\ominus}} R\text{-}OH + Cl^{\ominus}$$

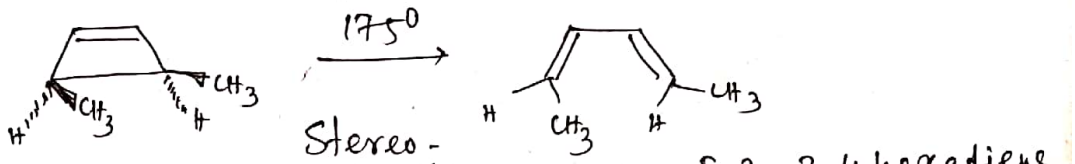
Types of Pericyclic reaction :-

This chapter is concerned with three major types of pericyclic reaction, although there are others.

① Electrocyclic reaction :-

An intramolecular reaction of an acyclic π-electron system in which a ring is formed with a new σ-bond and also the reverse that means ring breaking rxn with the cyclic shift of electrons.

a) 

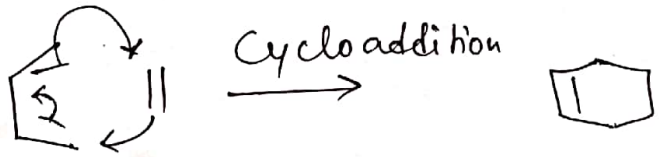
b) 

cis- Stereo-specific E,Z-2,4 hexadiene

trans- ⟶ E,E-isomer.

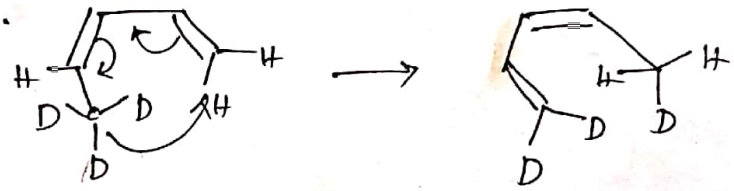
② Cycloaddition

A reaction of two separate π-electron systems in which a ring is formed with two new σ-bonds, and product has two fewer π-bonds than the reactants.

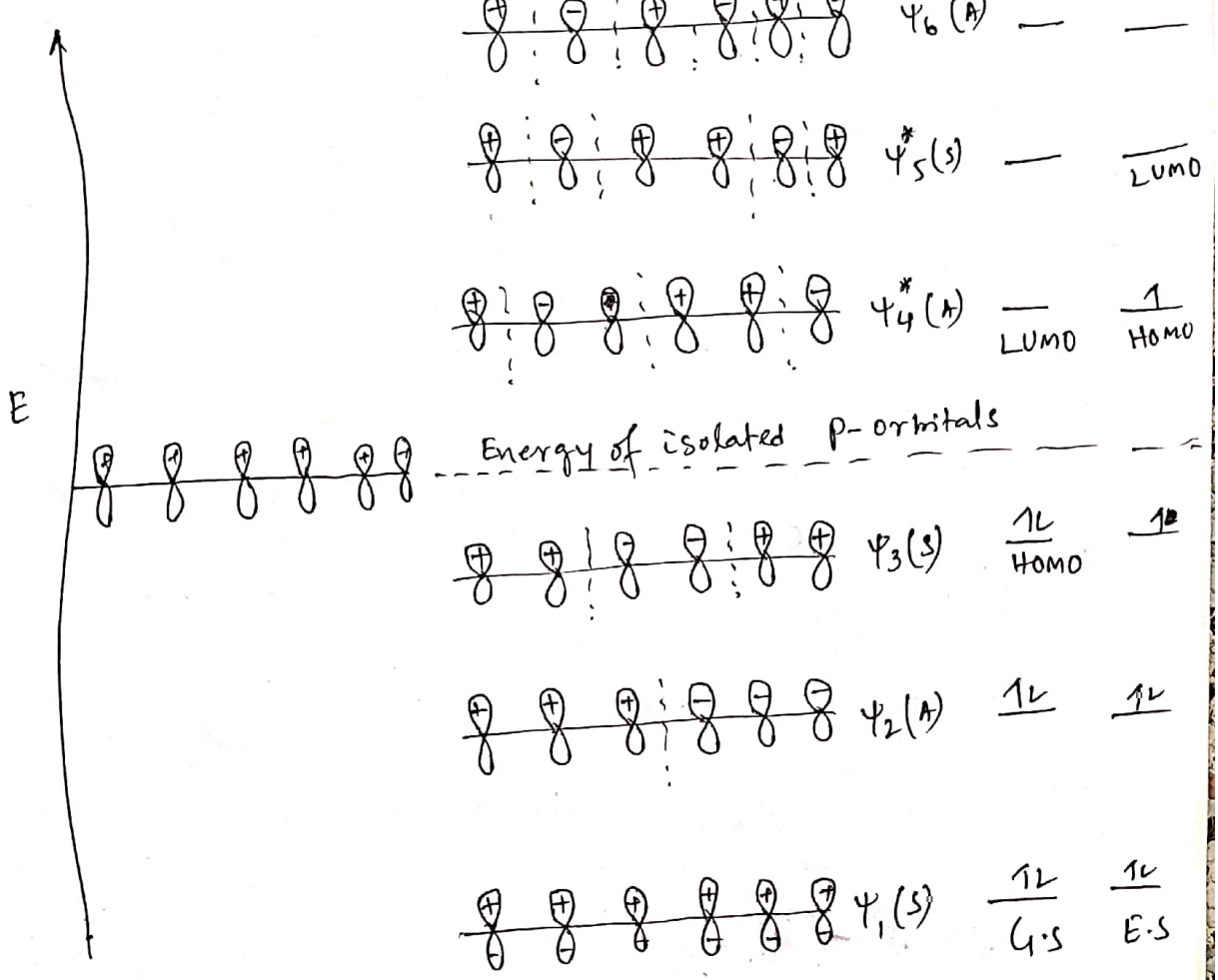


③ Sigmatropic reaction :-

A reaction in which an allylic σ-bond at one end of a π-electron system appears to migrate to the other end of the π-electron system. The π-bonds change position in the process, and their total number is unchange.



4. 1,3,5- Hexatriene



Electrocyclic Reaction :-

Bond formation in most organic compounds occurs through progressive overlap of orbitals.

There are two type of rotation fashion
(i) Conrotation fashion (ii) Disrotation fashion

Conrotation :- The motion in which terminal c atoms rotate either clockwise or counter clockwise is called the conrotatory mode. It is designated by the symbol '$\curvearrowright\curvearrowright$' or '$\curvearrowleft\curvearrowleft$'.

Disrotation :-

The motion in which terminal 'c' atoms rotate in the opposite sense during ring closer or ring opening process is called disrotatory mode. It is designated by the symbol 'D', or ↶↷.

On heating or light absorption, the two p-orbitals on the end of the π system must overlap such a fashion that the overlap occurs in same phase i.e the wave peak of one carbon must overlap with the wave peak on the other or a wave trough must overlap with a trough. If a peak were to overlap with a trough, the electron waves would cancel and no bond would form. Former path is called Symmetry allowed path and later one is Symmetry forbidden path.

The molecular orbital containing the π-electron of highest energy i.e. HOMO will take part in a Electrocyclic reaction.

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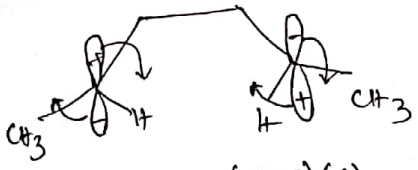
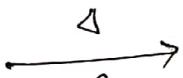
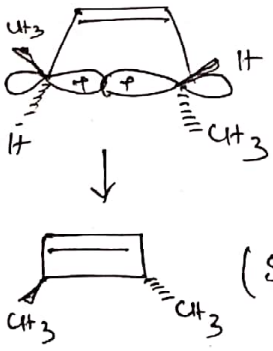


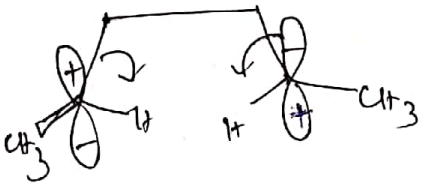
Ψ_2 (HOMO) (A)

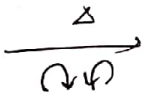


Conrotation

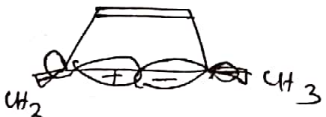


(Symmetry allowed path)





disrotation

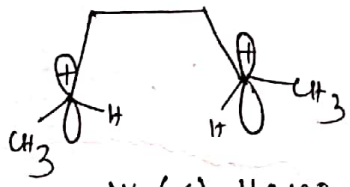


(Symmetry forbidden path)

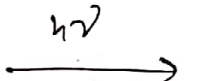
no pdt.

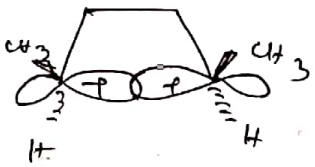
Thus the orbital symmetry — that determines whether the rxn is $\curvearrowright\curvearrowright$ or $\curvearrowright\curvearrowleft$ is the key of the rxn.

(*)



Ψ_3 (S) HOMO



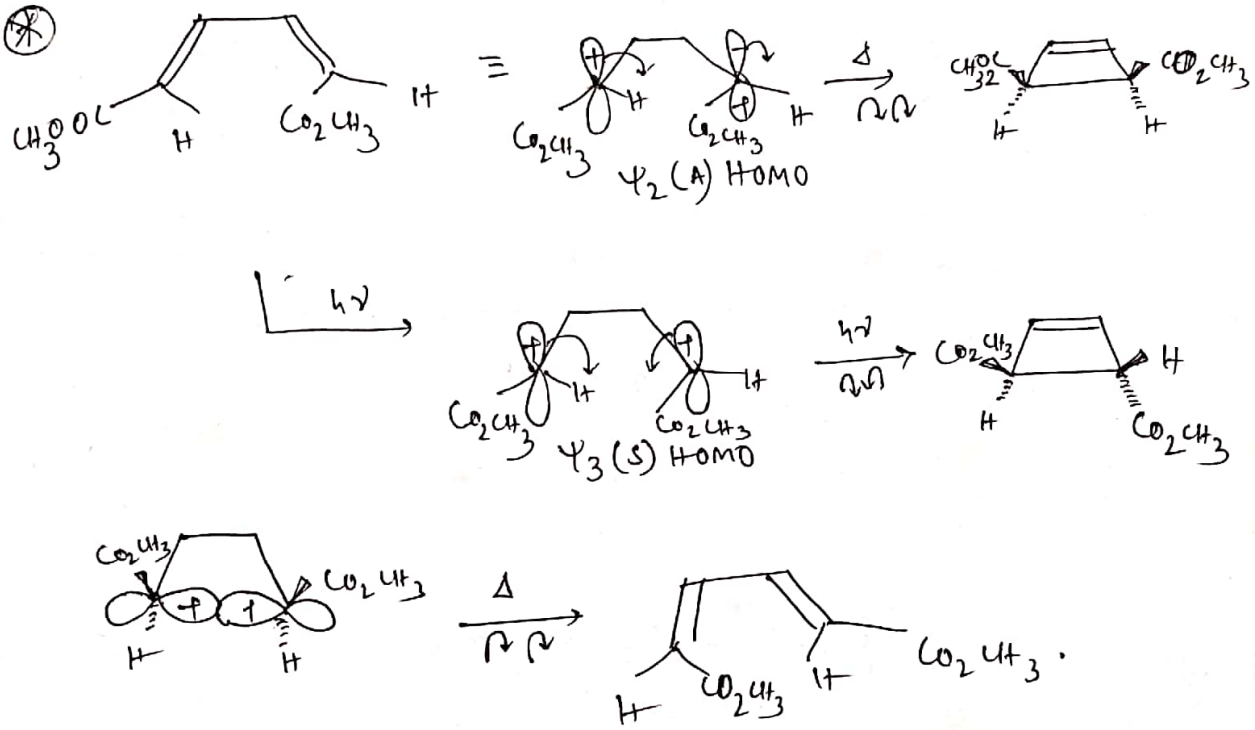


SELECTION RULE

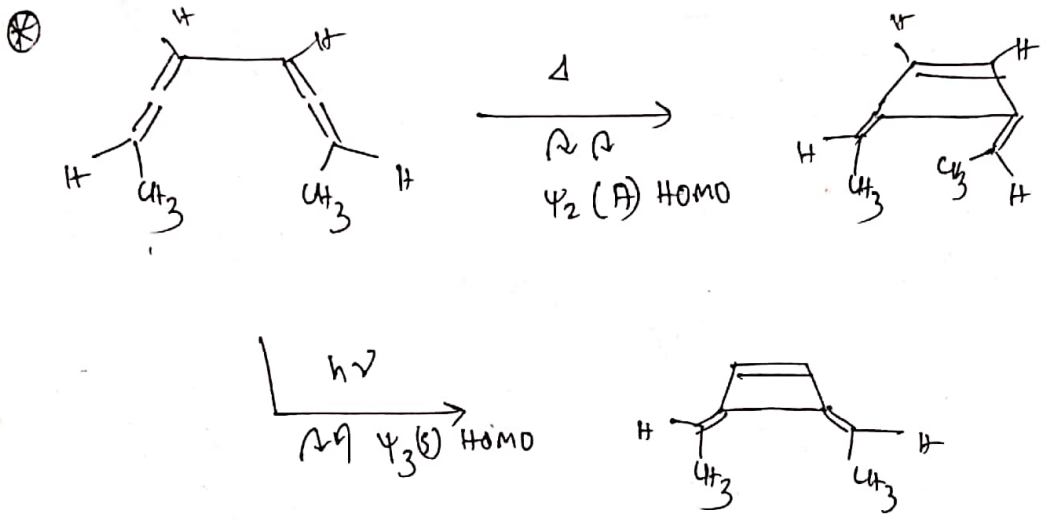
No. of electrons	Symmetry	mode of activation	Symmetry allowed path
$4n$ $n = 1, 2 \cdots$	A (HOMO)	Δ	$\curvearrowright\curvearrowright$
	S (HOMO)	$h\nu$	$\curvearrowright\curvearrowleft$
$(4n+2)$ $n = 1, 2 \cdots$	S (HOMO)	Δ	$\curvearrowright\curvearrowleft$
	A (HOMO)	$h\nu$	$\curvearrowright\curvearrowright$

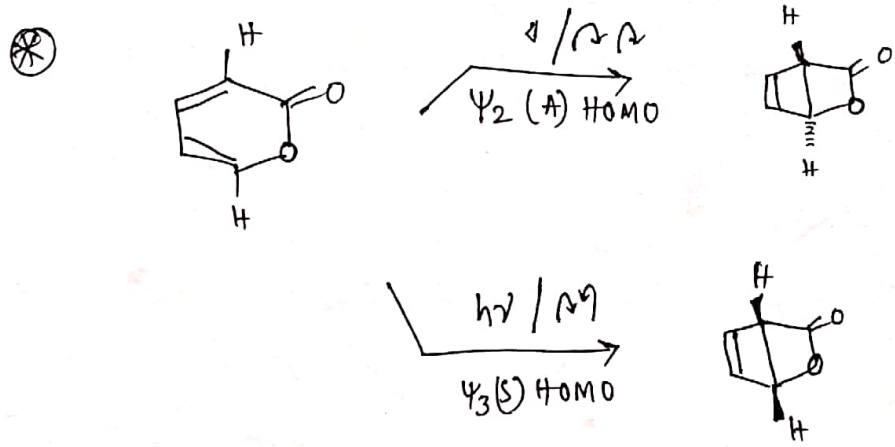
will be restricted.

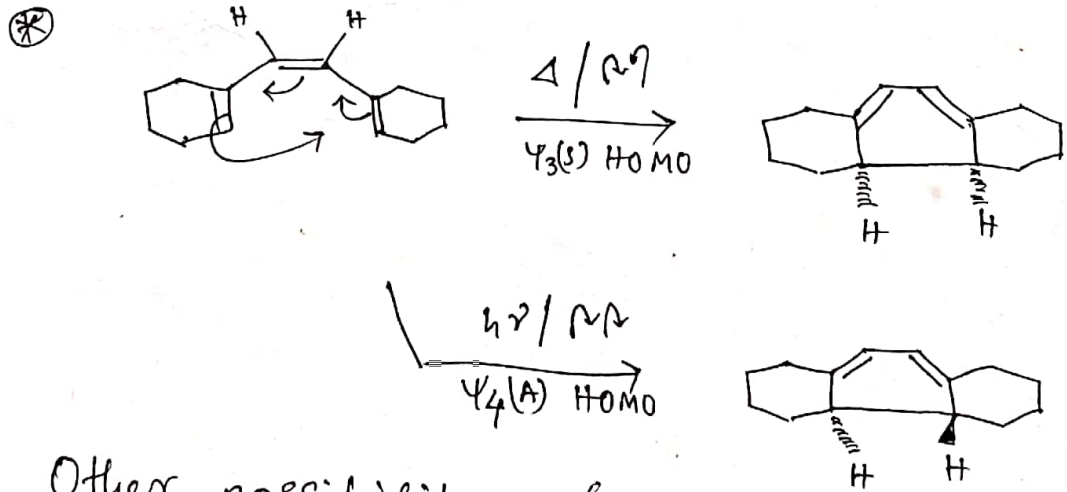
Some Example of electrocyclic rxn



In polyene system the electron density is higher at the two terminal carbon atom. So the rxn occurs at the two terminal carbon side. Again the orbital co-efficient value is also higher in 1 & 8 position.

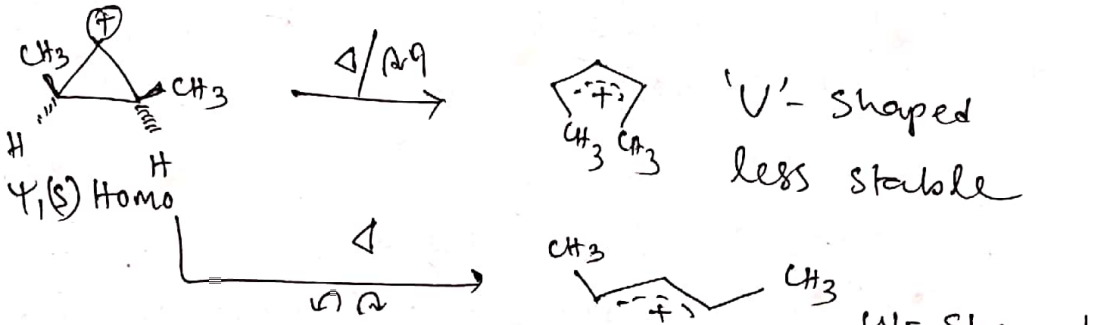


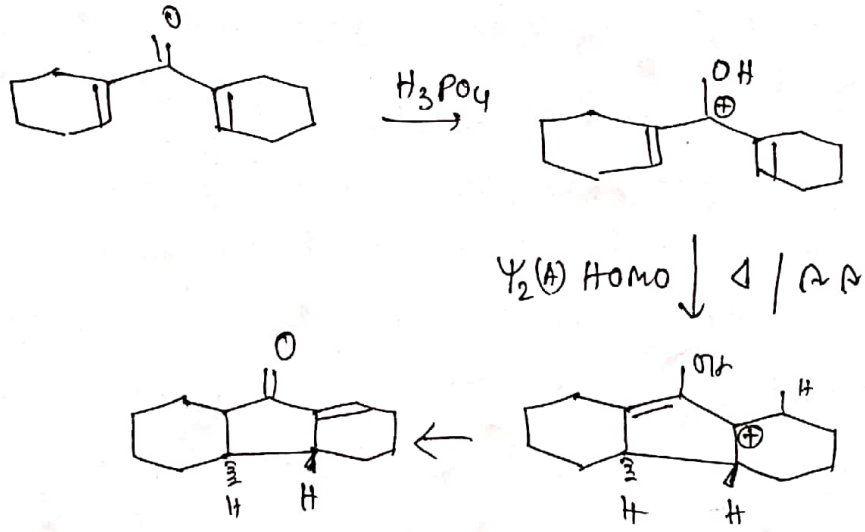


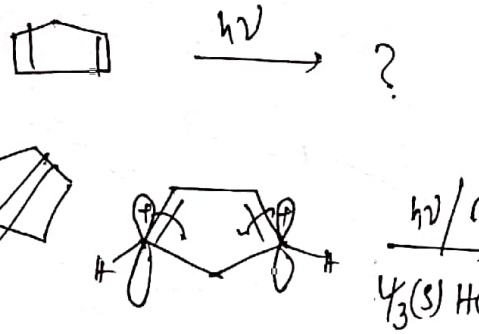


Other possibility of modes i.e for ψ_3 ↷↶ and for ψ_4 ↶↶ of this rxn will give

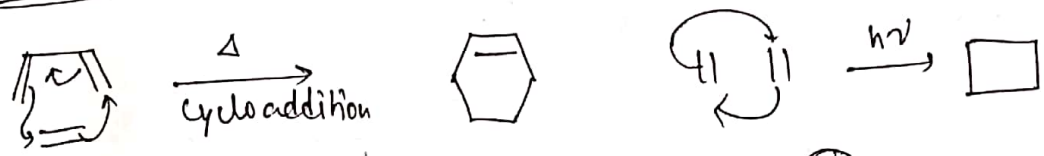
(*) There is another facet to the stereochemistry in substituted cyclopropyl system. For a cis 2, 3-dimethyl cyclopropyl cation, for example, two different disrotatory modes are possible, leading to conformationally distinct allyl cations.



(*) 

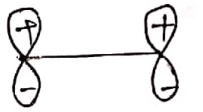
(*) 

Cyclo addition Reaction



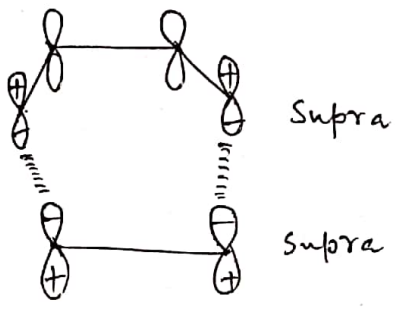
(A) (B)

The reaction in (A) is a [4+2] cyclo addition because the rxn involves four electrons from ~~diene~~ one reacting compound and two electrons from the other. The rxn in (B) is a [2+2] Cycloaddition. A cyclo addition may in principle occur either across the same face or across opposite faces of the plane in each reacting component. If the rxn occurs across, the same face of a π system the rxn is said to be Supra-facial(s) with respect to that π-system. If the rxn occurs at opposite faces of a π system, it is said to be antra-facial(a).

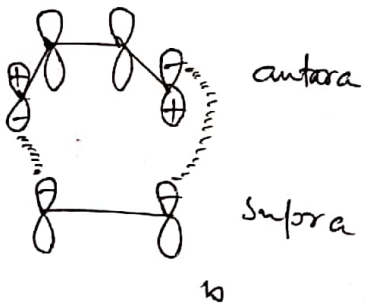


Suprafacial

Anterarafacial



a



b

a) [4s+2s] or $\pi_s^4 + \pi_s^2$ i.e Supra-supra addition

b) [4a+2s] or $\pi_a^4 + \pi_s^2$ i.e antara-supra

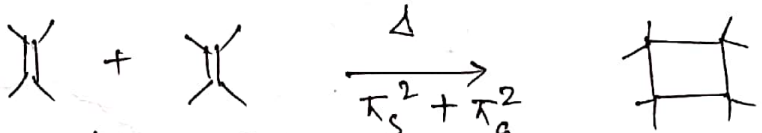
Bonding overlap begins when the HOMO of one component interacts with LUMO of the other. It does not matter whether we consider the HOMO from 4π-electron component and the LUMO from 2π-electron component, or vice-versa. The important point is that the two frontier MO's involved in the interaction must have matching phases if bonding overlap is to be achieved.

Selection rule

No. of electrons	Mode of activation	Allowed path
$4n$	Δ	s-a / a-s
	$h\nu$	s-s / a-a
$4n+2$	Δ	s-s / a-a
	$h\nu$	s-a / a-s

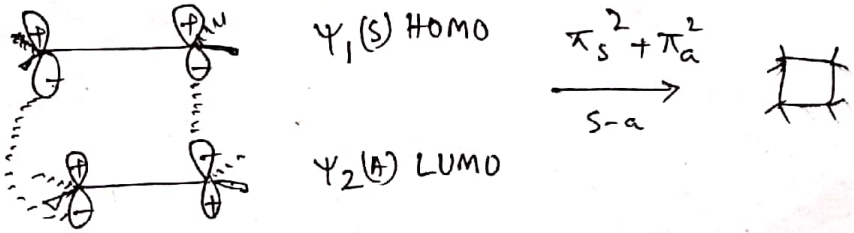
Example :-

(1)

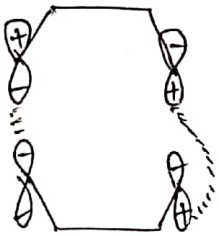


Ψ_1 (HOMO)S $\quad$ Ψ_2(A) LUMO $\quad$ allowed path.

Frontier orbital interaction



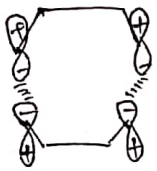
(3)



$\Psi_2(A)$ HOMO

$\Psi_3(S)$ LUMO

$\xrightarrow{\Delta}$ $\pi_s^4 + \pi_a^4$ Bonding pdt. (allowed path)



$\Psi_3(S)$ HOMO

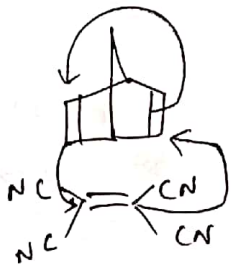
$\Psi_3(S)$ LUMO

Ψ_4

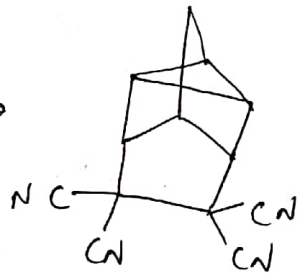
$\xrightarrow{h\nu}$ $\pi_s^4 + \pi_s^4$ Bonding pdt. (allowed path).

(4)

(Norbordiene) $\equiv$



$\xrightarrow{\Delta}$



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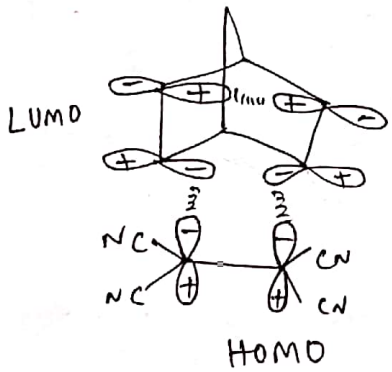
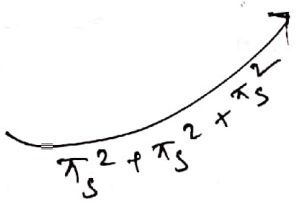


LUMO



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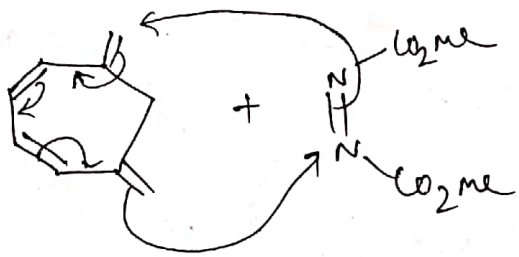
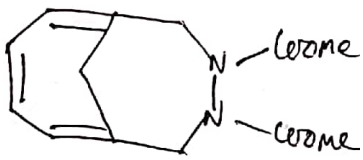


$\xrightarrow{\Delta}$



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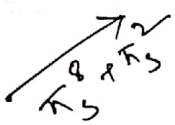
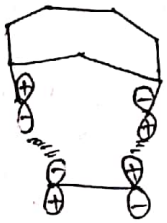
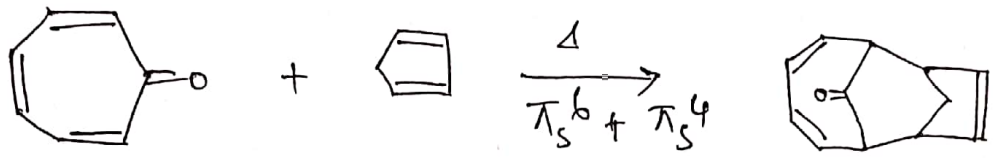




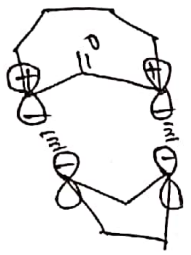
Ψ_4(HOMO) A

$\Psi_2(A)$ LUMO

(6)

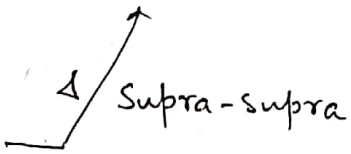


F-O-I



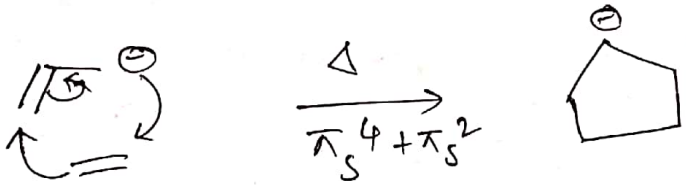
Ψ_3(AS) HOMO

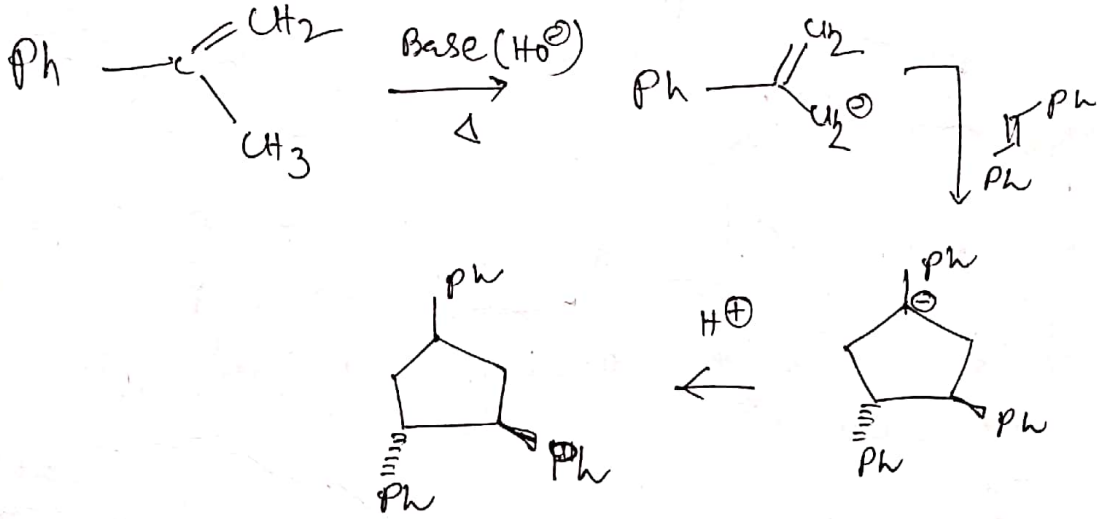
Ψ_3(S) LUMO



Supra-supra

(7)





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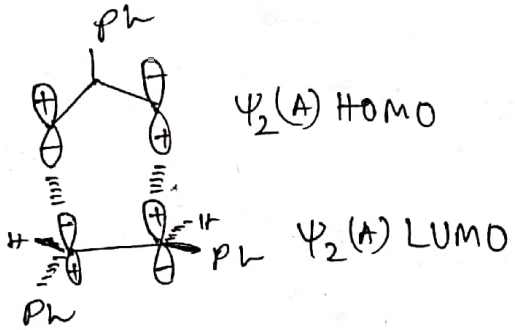
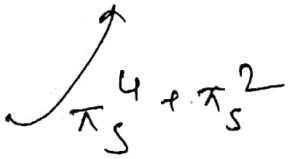
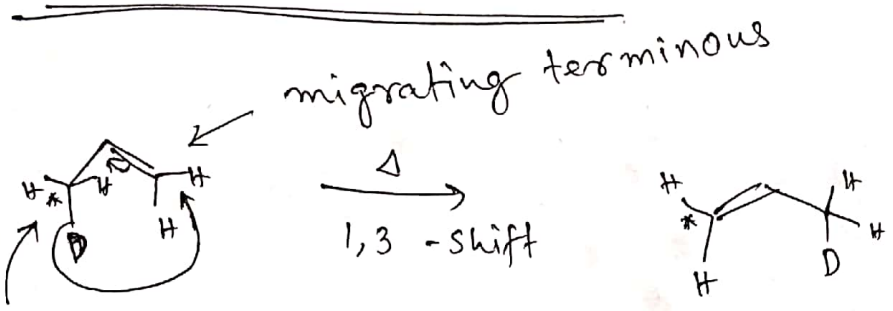


Ψ_2(A) HOMO

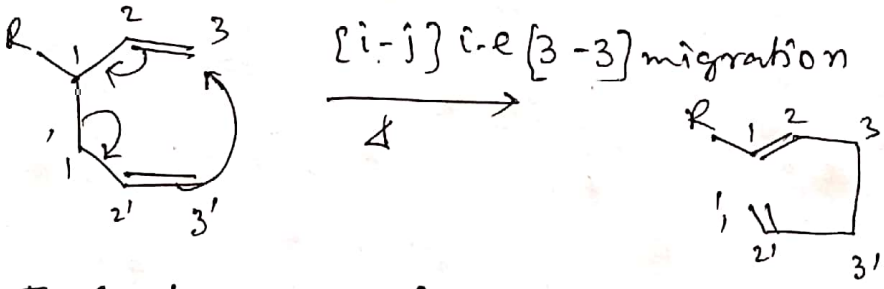
Ψ_2(A) LUMO



SIGMATROPIC REACTION

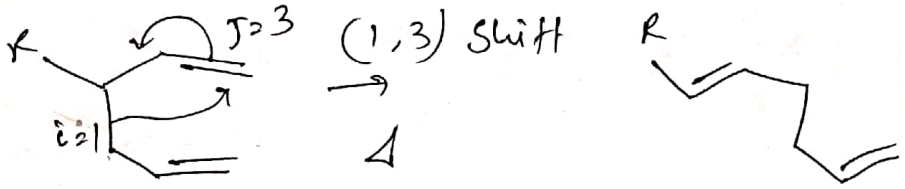


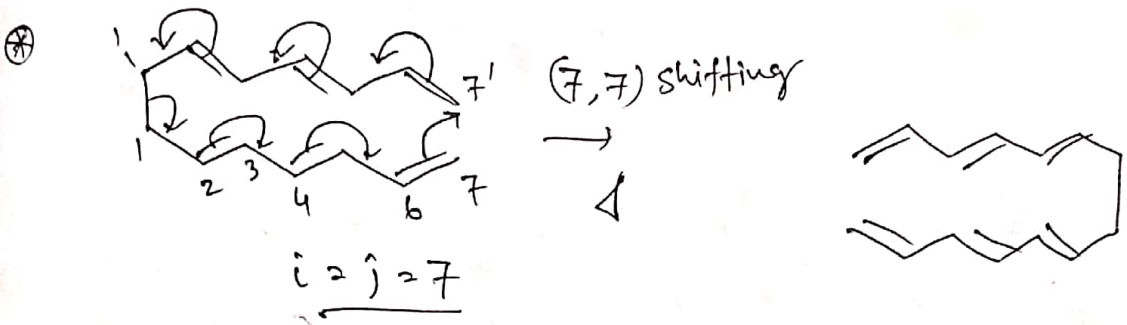
Sigmatropic reaction can be defined as migration of a allylic σ- bond or an atom or group ($-\overset{R_1}{\underset{R_3}{\overset{|}{\underset{|}{C}}}}R_2$) along with sigma bond from a migrating origine to the terminous of a conjugated polyene system. The order [i, j] specifies the number of atoms in the migrating fragment and the number of atoms in the π - system that are directly involved in the bonding changes.

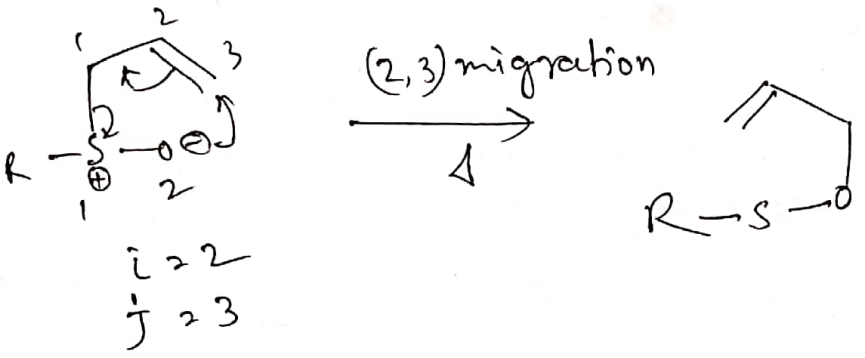


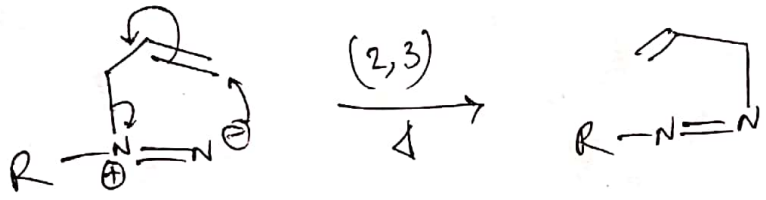
In π - system, no of atoms involved = 3
i.e j = 3

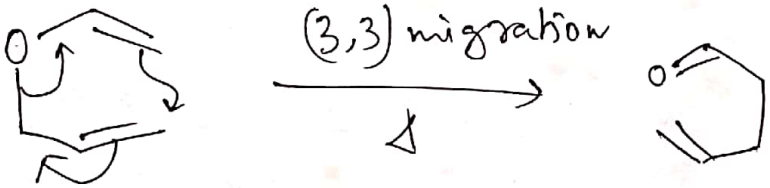
In migrating fragment, no of atoms involved = 3 i.e i = 3.

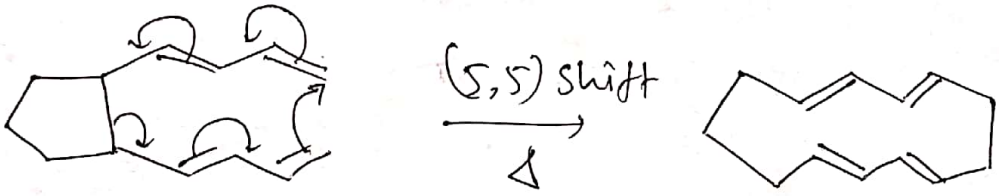












STEREOCHEMISTRY

If the migrating group remains associated with the same face of the conjugated π-system throughout the process, the migration is termed Suprafacial.