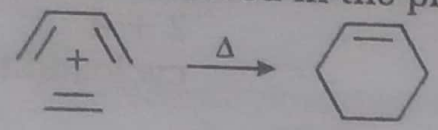
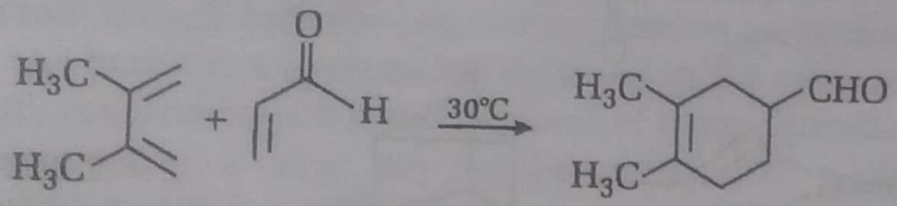
5 CYCLOADDITION REACTIONS

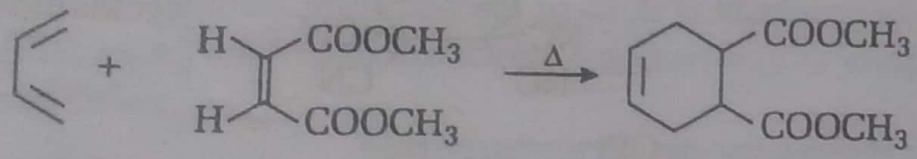
In cycloaddition reactions an olefinic system with $m\pi$ electrons adds up to a system with $n\pi$-electrons to give a cyclic partner with $(m-2)+(n-2)\pi$-electrons. In the process two σ-bonds are formed at the cost of four π-electrons. These addition reactions are called $(m+n)$ cycloadditions. They occur with high degree of stereoselectivity under thermal as well as photochemical conditions. They are referred to as $(m+n)$ or $(m+n+...)$ reactions keeping in view number of π-electrons involved in the process. Some examples are cited below :

1. 

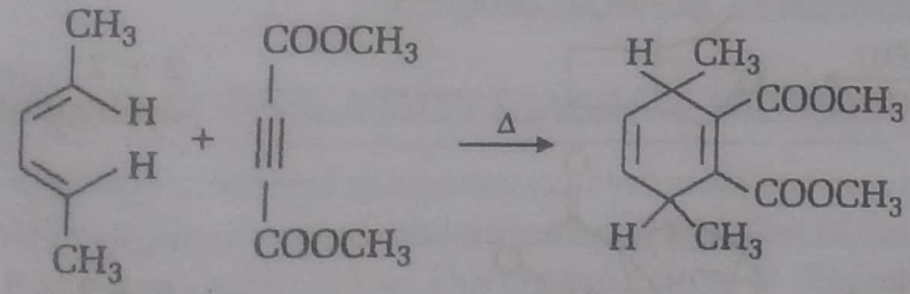
4 + 2 cycloaddition
(Diels-Alder reaction)

2. 

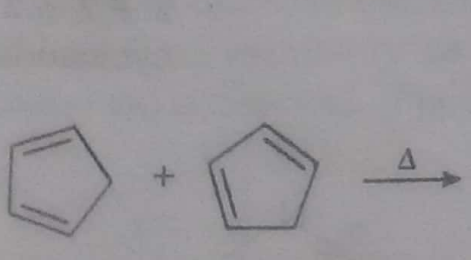
4 + 2 cycloaddition

3. 

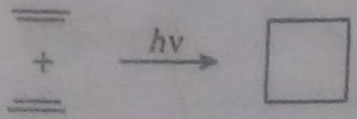
4 + 2 cycloaddition

4. 

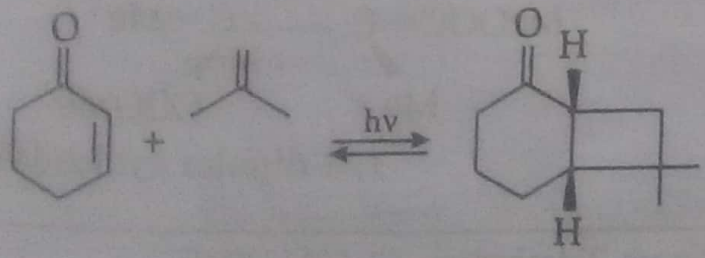
4 + 2 cycloaddition

5. 

endo-dicyclopentadiene
4 + 2 cycloaddition

6. 

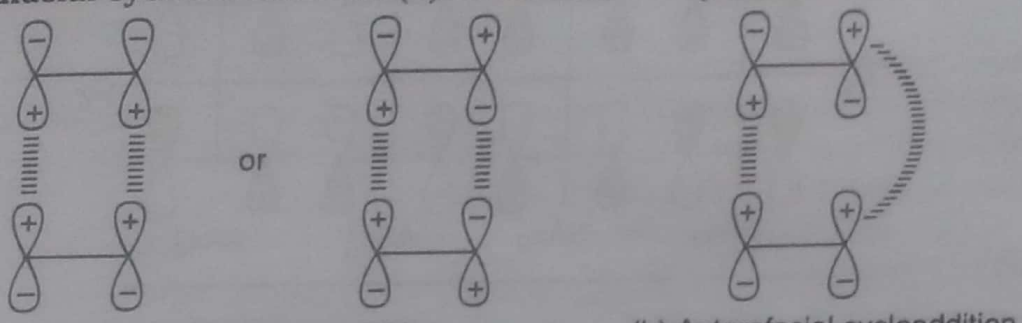
2 + 2 cycloaddition

7. 

2 + 2 cycloaddition

5.1 SUPRAFACIAL AND ANTARAFACIAL PROCESS

Because during cycloaddition, there is addition of two olefinic systems, therefore, two feasibilities are there : (a) addition may take place in such a way that lobes of same phases of one component with the lobes of same phases of other component may overlap (b) lobes of same phase of one component may overlap with the lobes of opposite faces of other component. (a) is known as **suprafacial cycloaddition** and (b) as **antarafacial cycloaddition.***



(a) Suprafacial cycloaddition (b) Antarafacial cycloaddition

Fig. 5.1.

Antarafacial processes are difficult because in them twisting of *p*-orbitals is required; though both the process are feasible on symmetry ground.

As both the π-systems are involved in the cyclo addition, it is essential to specify the modes with respect to each of them. Specification is made by placing subscript *S* or **a** after the number refering to π-component. For instance, suprafacial addition with respect to each component of Diels-Alder reaction is specified as $\pi_s^2 + \pi_s^4$ cycloaddition. Another way is simply writting it as $2s + 4s$ cycloaddition.

"PREDICTION OF FEASIBILITY"

5.2 (A) CORRELATION DIAGRAM METHOD

Control of orbital symmetry on cycloaddition can be well expressed by the simple example of suprafacial-suprafacial addition of the two ethylene molecules $(2s + 2s)$ to give cyclobutane. During the course of this reaction both mirror-plane (m), *i.e.*, vertical symmetry as well as c_2-axis of symmetry (c_2) *i.e.*, horizontal symmetry are conserved. (Fig. 5.2).

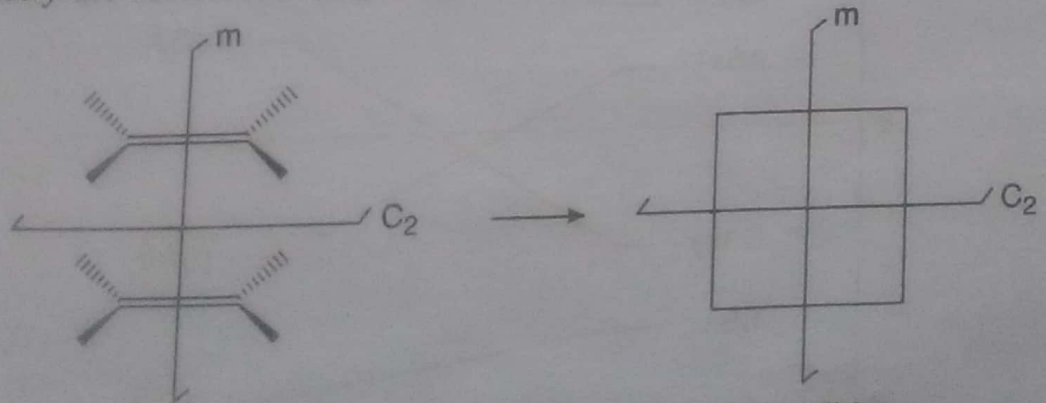


Fig. 5.2. Symmetry conservation during cycloaddition.

* R.B. Woodward and R. Hoffmann, J. Amer. Chem. Soc; 87, 2511 (1965).

In this transformation four π-orbitals of two ethylene molecules and four σ-orbitals of cyclobutane are involved. As symmetry properties of other orbitals do not undergo change, they are not taken into acount. Shape and symmetries of involved orbitals, *i.e.*, π and π* orbitals of both the ethylene molecules and σ and σ* orbitals of cyclobutane are shown in the fig. 5.3 and 5.4 given below :

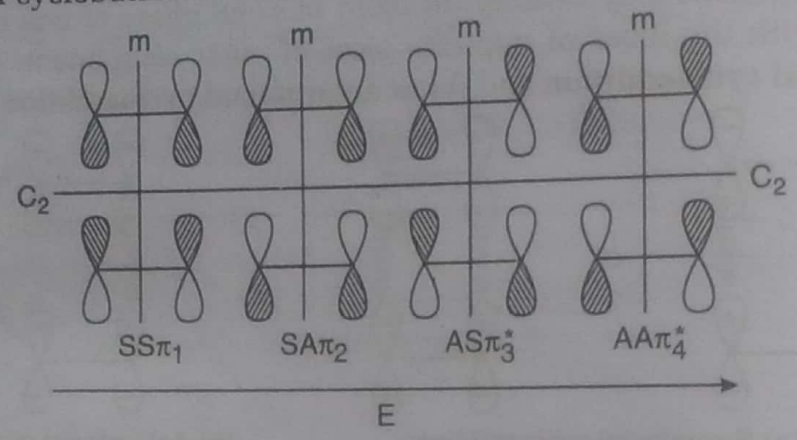


Fig. 5.3. Symmetry properties of two ethylene molecules involved in the formation of cyclobutane.

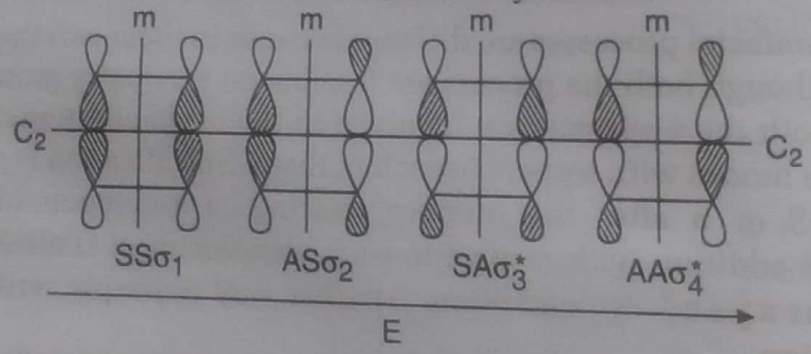


Fig. 5.4. Symmetry properties of σ-orbitals of cyclobutane.

A correlation diagram may be prepared on the basis of symmetry properties of ethylene molecules and cyclobutane that predicts feasibility of this cycloaddition (Fig. 5.5).

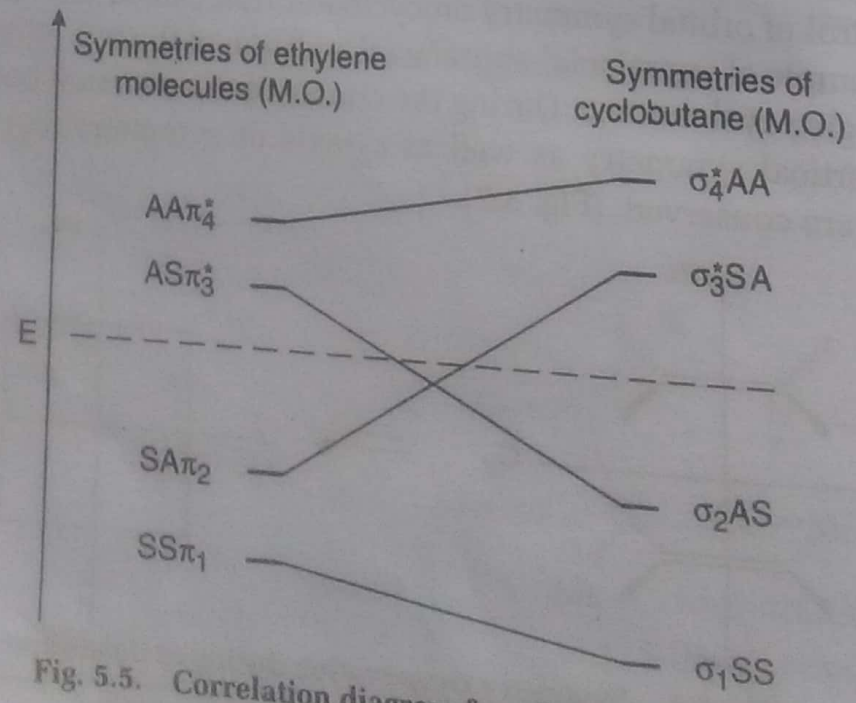


Fig. 5.5. Correlation diagram for ethylene-cyclobutane interconversion.

From the above correlation diagram it is clear that reaction is photochemically feasible because first E.S. of ethylene correlates with G.S. of cyclobutane making it symmetry allowed. On the other hand this reaction is thermally forbidden on account of the fact that G.S. of one ethylene molecule does not give G.S. of cyclobutane, therefore, ground state of two ethylene molecules can not combine to give cyclobutane while conserving symmetry of orbitals.

5.2.1 Diels-Alder Reaction

Correlation diagram may also be constructed to predict feasibility of Diels-Alder reaction which is $\pi^4 s + \pi^2 s$ cycloaddition. Results have been found in conformity with observed fact that reaction is thermally feasible. In Diels-Alder reaction only *m*-plane of symmetry is conserved. Symmetry properties and correlation diagram for Diels-Alder reaction is given below (Fig. 5.6).

Diels-Alder reaction involves ψ_1, ψ_2, ψ_3 and ψ_4 orbitals of 1, 3-butadiene and π and π^* orbitals of ethylene as reactants m.os and $\sigma_1, \sigma_2, \pi, \pi^*, \sigma_3^*, \sigma_4^*$ orbitals of cyclohexene which are product molecular orbitals. When these molecular orbitals are arranged in the increasing order of their energies alongwith their symmetries, ground state molecular orbitals of reactants correlate with the ground state molecular orbitals of their product, therefore, reaction is thermally allowed; but photochemically forbidden on account of the fact that first excited state of reactant does not correlates with first excited state of product (Fig. 5.6).

$$\psi_1^2 \pi^2 \psi_2 \psi_3 \longrightarrow\!\!\!\!\!\!\times\; \sigma_1^2 \sigma_2^2 \pi\pi^*$$

5.2.2 Cycloadditions of Benzene and its Derivatives

There are large number of cycloaddition reactions of benzene and its derivatives. Correlation diagram can be constructed to predict them which can be represented by examples of **ortho-**, **meta-** and **para**-cycloadditions of benzene and ethylene or benzene and butadiene. **Ortho-**, **meta-** and **para**-additions give different products.

5.2.2.1 Reactions between Benzene and Alkenes

These are all stereospecific with respect to alkenes. Though reaction requires excitation of benzene chromophore, but involves initial excitation of alkene. Sometimes charge transfer complex between alkene and benzene also undergoes excitation. All the three cycloadditions involve singlet excited states of benzene ring.

π-molecular orbitals of benzene and their *m*-plane symmetry is depicted in Fig. 5.8.

(a) Ortho-addition : Correlation diagram for **ortho**-addition is depicted below (Fig. 5.9).

Since, symmetry properties of reactants, *i.e.*, benzene and ethylene match with that of product in ground state reaction is thermally feasible; but photochemical *ortho* cycloaddition between benzene and ethene is unfavourable.

[*] J.M. Coxon and B. Halton, "Organic Photochemistry," Cambridge University Press (1986).

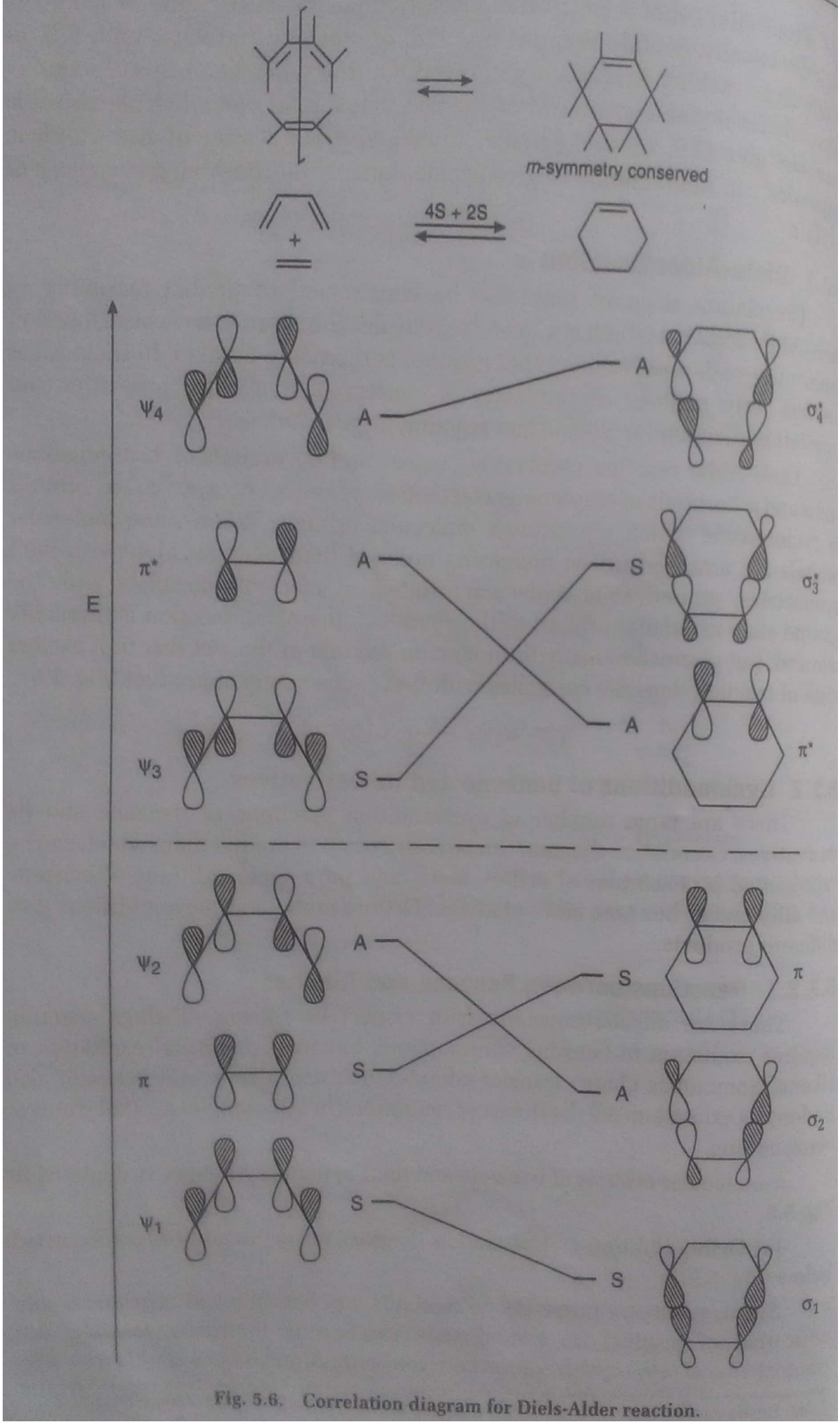
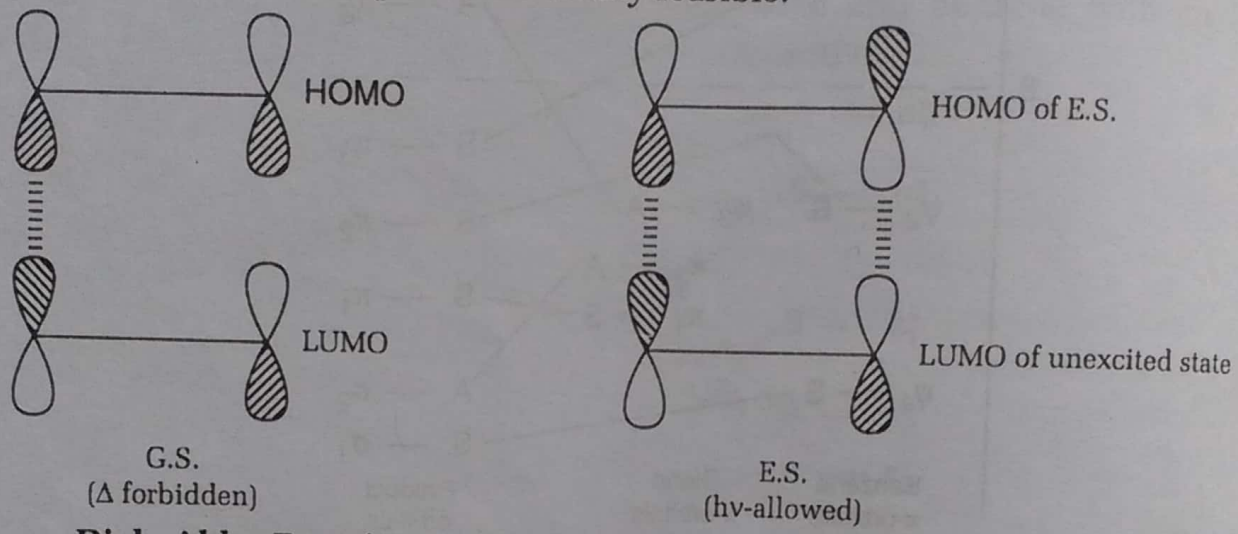


Fig. 5.6. Correlation diagram for Diels-Alder reaction.

5.3 FRONTIER MOLECULAR ORBITAL (FMO) METHOD

Frontier molecular orbital (FMO) approach to predict course of cycloaddition reaction takes into account the symmetry properties of HOMO of one reactant and LVMO of other reactant. Reaction is favourable when signs of cofficient of HOMO and LVMO are same. Cycloaddition of ethylene is

$2s+2s$ reaction which involves interaction of HOMO of one molecule of ethylene and LVMO of other molecule of reactant (ethylene) to yield the product cyclobutane. Because, in ground state signs of HOMO and LVMO of two ethylene molecules are not same, therefore, reaction is thermally forbidden. Upon irradiation one electron from the HOMO of one ethylene molecule is promoted from bonding to antibonding orbital which now becomes HOMO and sings lobes of HOMO of one molecule of ethylene and LUMO of another molecule become same reaction becomes photochemically feasible.



Diels-Alder Reaction : In the manner similar to cycloaddition of ethylene Diels-Alder reaction can be analysed which involves π-molecular orbitals of butadiene and ethylene.

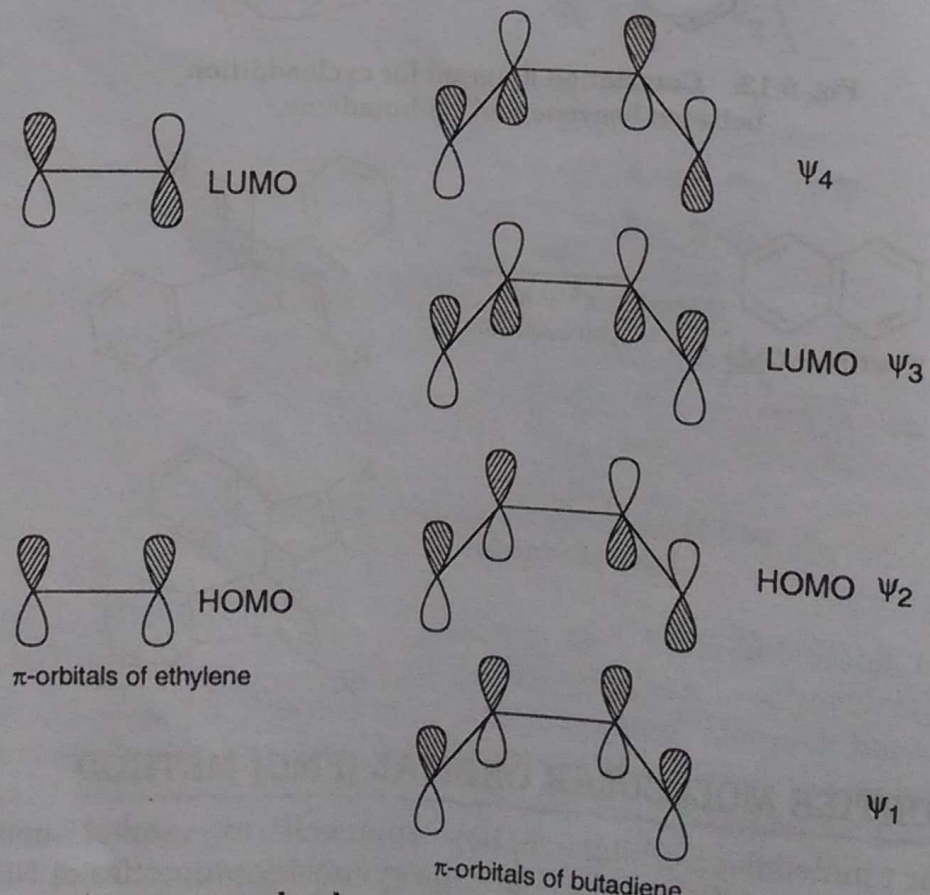
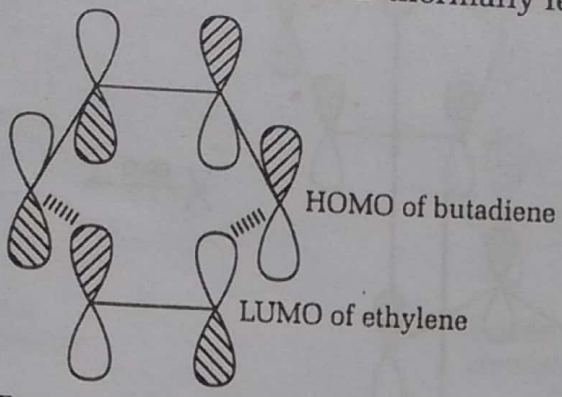


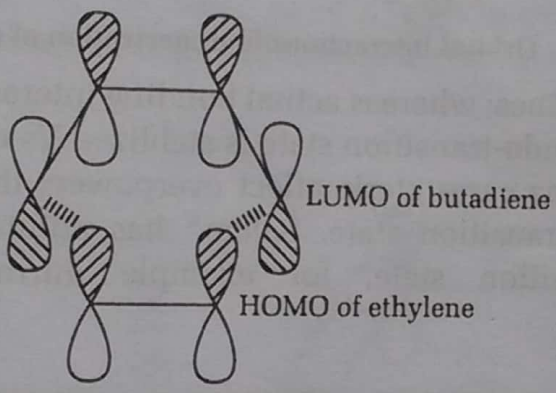
Fig. 5.14. π-molecular orbitals of ethylene and butadiene.

Signs of 1, 4-lobes of butadiene HOMO and ethylene LUMO are same, therefore, they interact and make the reaction thermally feasible.



Reaction thermally feasible

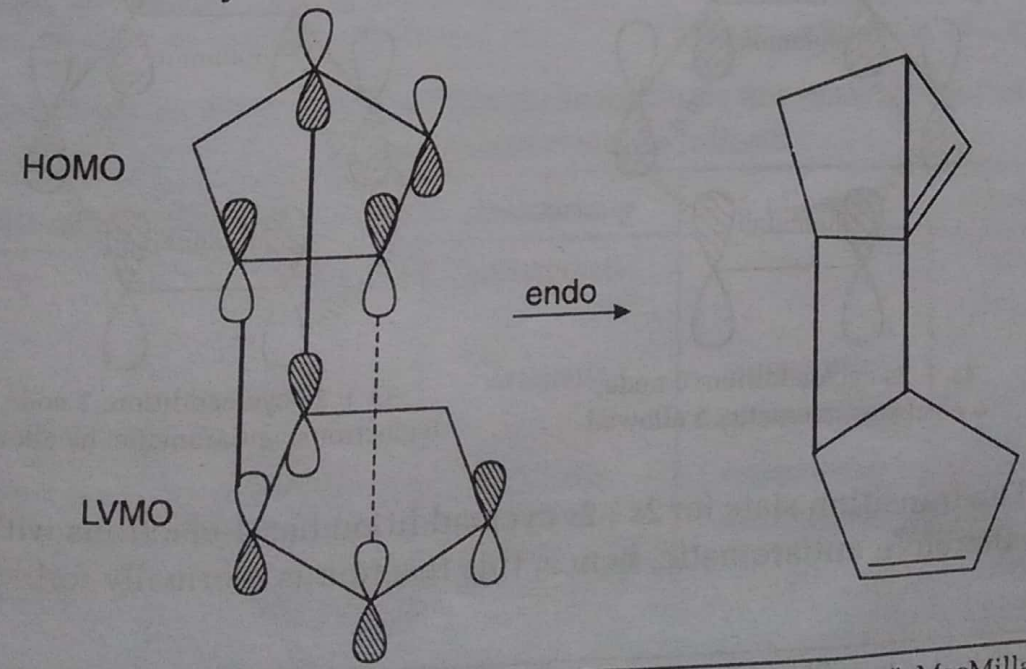
Same conclusion is drawn if we consider HOMO of ethylene and LUMO of butadiene.



Reaction thermally feasible

Upon imadation with U.V. light such interaction is not feasible, therefore, reaction is photochemically forbidden.

Another important example of application of FMO method on Diels-Alder reaction is dimerization of cyclopentadiene to yield dicyclopentadiene. In this case **endo** isomer is formed rather than **exo** although **exo** isomer is thermodynamically more stable. Reason behind this is that in case of **endo** isomer favourable secondary interactions are there between diene and dienophile*



* Chemistry" MacMillan India

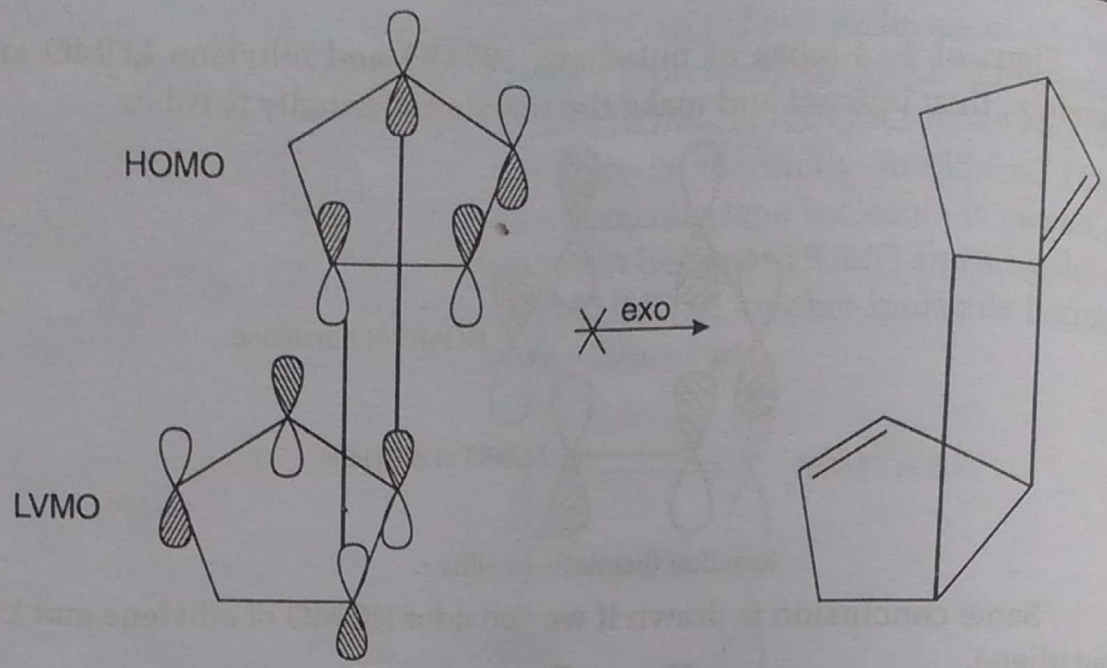
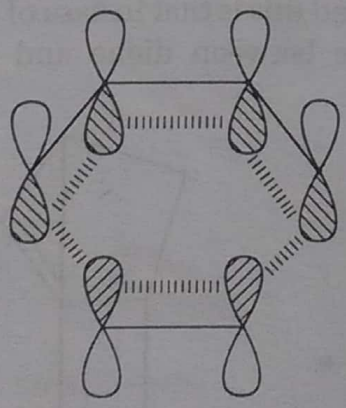


Fig. 5.15. Orbital interactions in dimerization of cyclopentadiene.

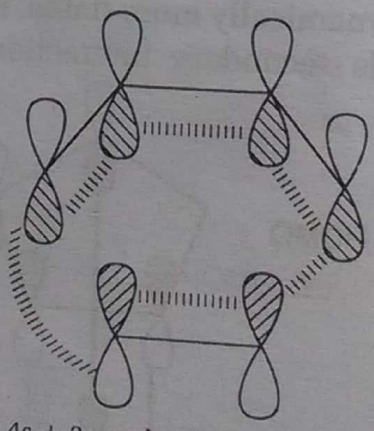
[shown by broken lines; whereas actual bonding interactions are shown by thick lines (Fig. 5.15)]. **Endo**-transition state is stablized Vs **exo**, therefore **endo**-attack is favoured. In some cases steric effect overpowers this effect and favours the formation of **exo**-transition state. Salem* has pointed out the possibility of symmetrical transition state, for example during the dimerization of cyclopentadiene.

5.4 PERTURBATIONAL MOLECULAR ORBITAL (PMO) METHOD

Cycloaddition reactions can also be predicted through PMO-method. If a given process is allowed can be determined through transition state. $\pi^4 s + \pi^2 s$ cycloaddition, *i.e.*, Diels-Alder reaction is allowed because the transition state is Hückel's type and is isoconjugate with benzene (a Hückel type system).



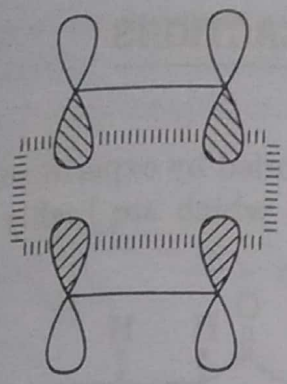
4s + 2s cycloaddition; 0 node, 6 electrons, aromatic, Δ allowed



4s + 2a cycloaddition; 1 node, 6 electrons, antiaromatic, hν allowed

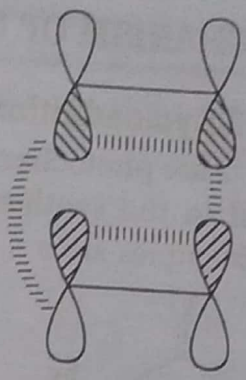
The transition state for $2s + 2s$ cycloaddition has 4-electrons with zero node and is therefore antiaromatic, hence, this reaction is thermally forbidden.

* L. Salem, J. Amer. Chem. Soc; **90**, 543, 553 (1968).



(2s + 2s)

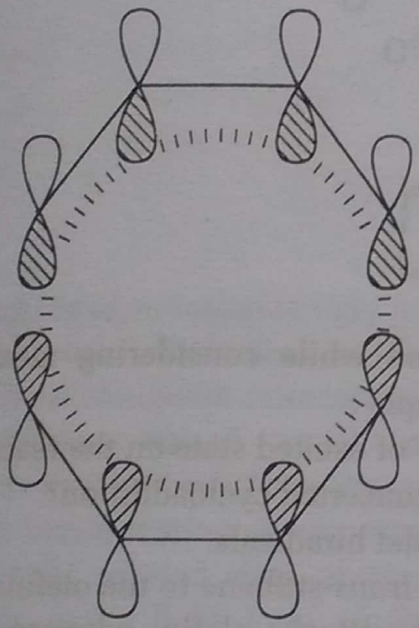
0 node, 4 electrons,
antiaromatic, hν-allowed



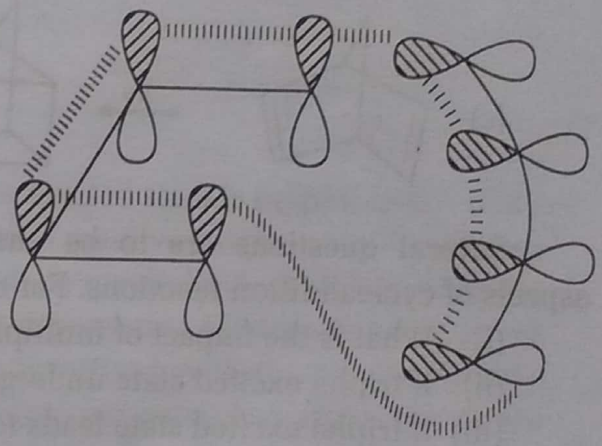
(2s + 2a)

1-node, 4 electrons,
aromatic, Δ-allowed

In the similar manner $\pi^4 s + \pi^4 s$ cycloaddition is expected to be thermally forbidden as transition state is isoconjugate with cyclooctatetraene (Hückel antiaromatic system). On the other hand $\pi^4 s + \pi^4 a$ cycloaddition takes place under thermal conditions through aromatic transtion state.



π^4s + π^4s cycloaddition; 0 node, 8 electrons,
antiaromatic T.S., thermally disallowed



π^4s + π^4a cycloaddition; 1 node,
8 electrons, aromatic T.S., Δ-allowed

Conclusions drawn from all the three methods are same. Selection rules (for PMO-method) arrived at can be summarized as follows :

$m + n$ electrons	Number of nodes	Aromaticity	Δ allowed	$h\nu$ allowed
$4q$	o or even	antiaromatic	—	supra-supra antara-antara
$4q$	odd	aromatic	supra-supra antara-antara	—
$4q + 2$	o or even	aromatic	supra-supra antara-antara	—
$4q + 2$	odd	antiaromatic	—	supra-supra antara-antara

q is an integer.