

Electrocyclic reaction

These are pericyclic reactions (intramolecular) which under the influence of heat or light involve either the formation of a ring, with the generation of one new sigma-bond and the consumption of one pi-bond or the reverse.

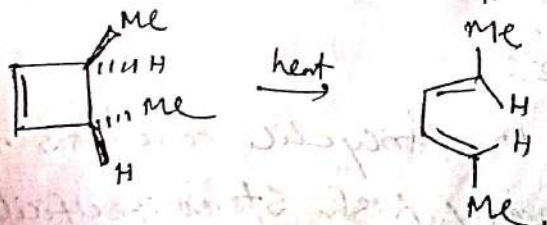
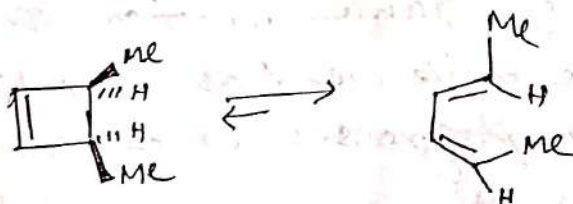
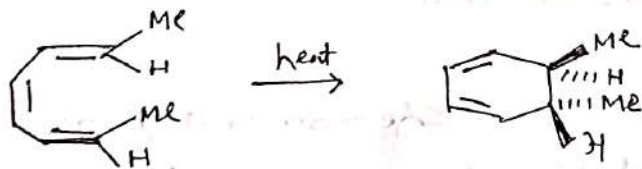
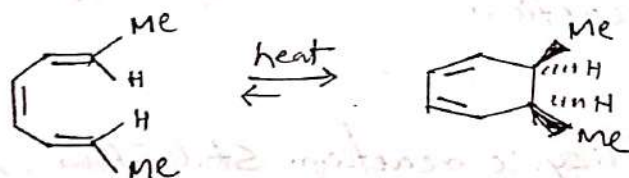


1,3,5-hexatriene

1,3-cyclohexadiene

The stereochemistry of electrocyclic reactions can be studied by using suitably substituted molecule. The reactions are thus:

1. Completely stereoselective. (A stereoselective reaction leads to the exclusive formation of one of the several possible stereoisomeric compounds. The reaction is solely concerned with the products.)



2. Electrocyclic reactions are also completely stereospecific.

3. The stereochemical outcome of an electrocyclic reaction depends on the number of double bonds in polyene and on whether the reaction is thermal or photochemical. A thermal electrocyclic reaction involving $4n+2$ electrons ($n=1,2,3,\dots$) proceeds with conrotatory motion, while the photochemical reaction involving $4n$ electrons proceeds with disrotatory motion.

A thermal reaction involving $(4n+2)$ electrons (where $n=0,1,2,\dots$) proceeds with disrotatory motion while the photochemical reaction proceeds with conrotatory motion.

4. The direction taken by an electrocyclic reaction is dependent on the relative stabilities of the ring and open chain reactants. In the case of cyclohexane, the open chain structure is favoured because of the strain in the ring, allowing the ring reaction.

* Define pericyclic reaction. State four characteristics of pericyclic reaction.

Ans

In organic chemistry, a pericyclic reaction is a type of organic reaction wherein the transition state of the molecule has a cyclic geometry, and the reaction progresses in a concerted fashion.

Characteristic:

1. Pericyclic reactions normally show a very high stereospecificity.

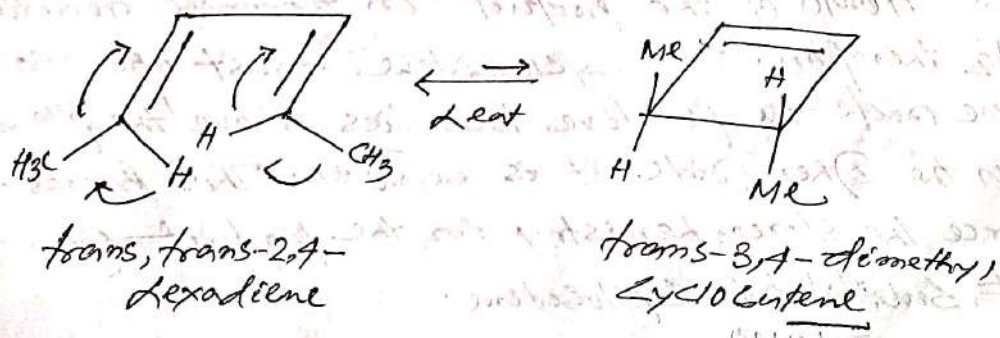
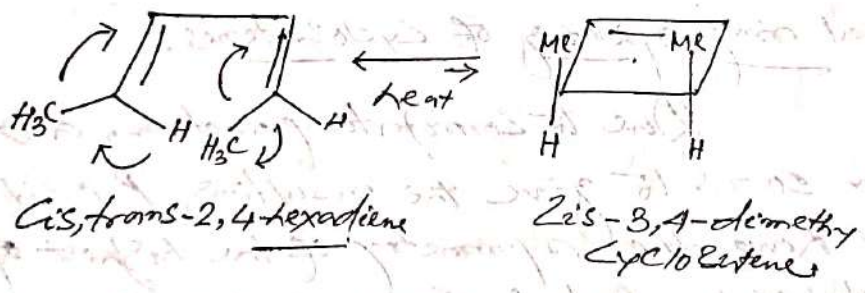
2. Pericyclic reactions can be frequently promoted by heat or light. Normally, the stereochemistry under the two sets of conditions is different.

3. Pericyclic reactions can occur in the gas phase with ~~no~~ no solvent.

4. Normally, no catalyst is needed to promote the reaction.

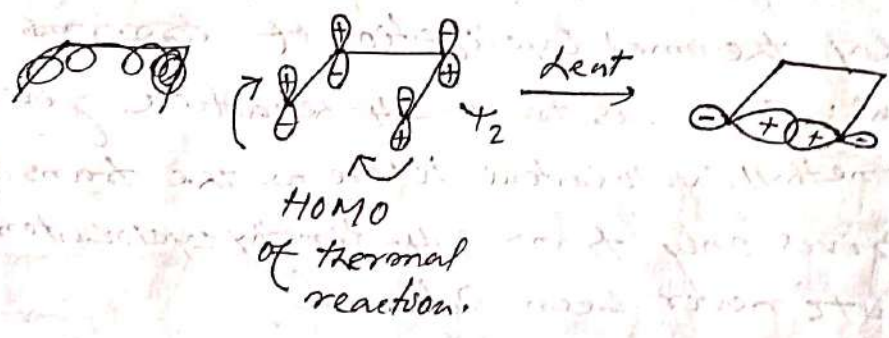
* Have that electrocyclic reactions are highly stereospecific.

Ans: Stereospecificity of this type of reaction has been proved by thermal cyclization of ~~cis,trans~~ 2,4-hexadiene. The cis,trans-2,4-hexadiene gives cis-3,4-dimethylcyclobutene whereas the trans,trans isomer gives only trans-3,4-dimethylcyclobutene. Mixture of products never been obtained.



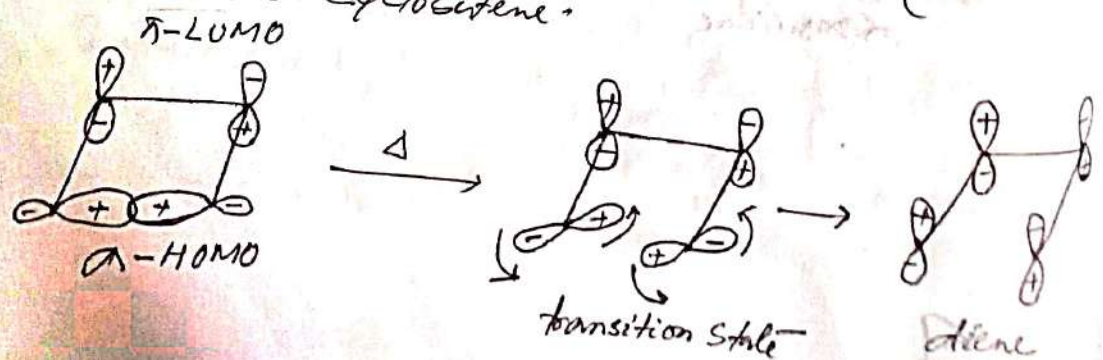
Thermal Cyclization of Butadiene (FMO approach)

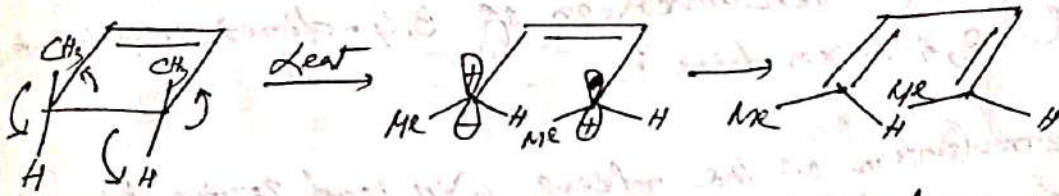
The HOMO of a conjugated diene is ψ_2 . For bond formation the overlap of lobes on C1 and C4 of the diene is required. It is only the ψ_2 orbital which brings the lobes of the same phase together for bond formation. However, the ψ_1 orbital will bring the lobes of opposite phase together and this will be repulsive and anti bonding.



Thermal ring opening of Cyclobutenes:

Due to conrotatory motion, a bond will open so as to give the resulting 'p' orbitals which will have the symmetry of the highest occupied orbital of the product. Since in the case of cyclobutene the HOMO of the product in thermal reaction is ψ_2 therefore, the cyclobutene must open so that on one side the positive lobe lies above the plane, and on the other side it is below it. This process also forms a *trans* substituted cyclohexene.



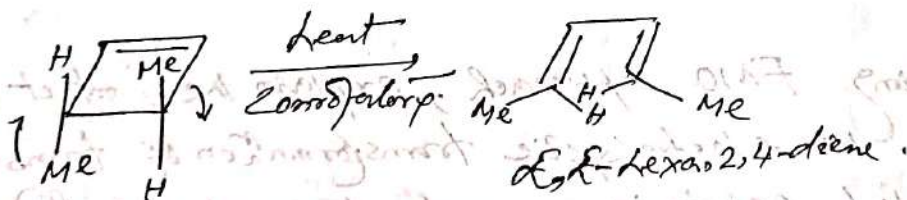


cis-3,4-dimethyl
cyclobutene

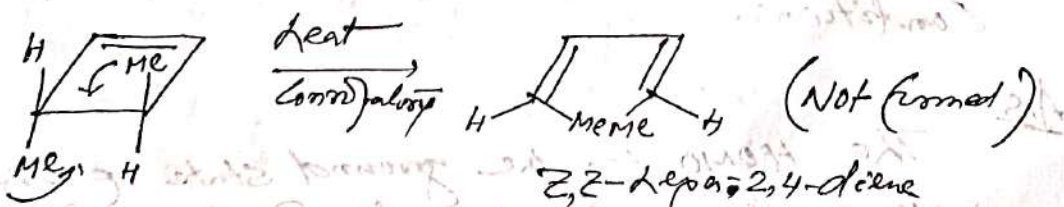
cis,trans-2,4-hexadiene

* In the thermal ring opening of trans-3,4-dimethylcyclobutene, two products can be formed by conrotatory motion, but only one is actually obtained. Which one is actually obtained and why?

Ans Trans-3,4-dimethylcyclobutene can undergo conrotatory ring opening which could in principle give two products depending on the sense of conrotation. When however, both methyl groups turn inwards a severe steric crowding would result in the formation of cis-cis-dimethyldiene. This process will raise the activation energy compared with the process of formation of trans,trans-isomer. As a result only the trans,trans-isomer is formed.



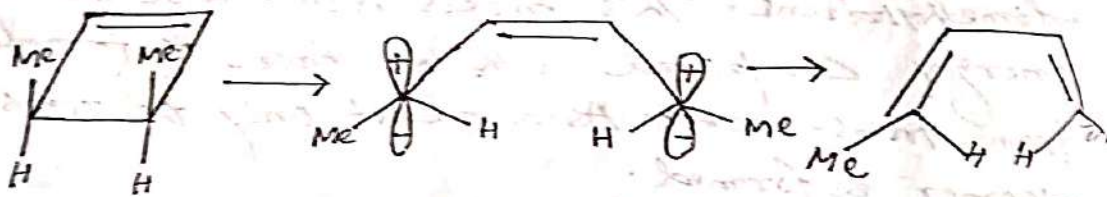
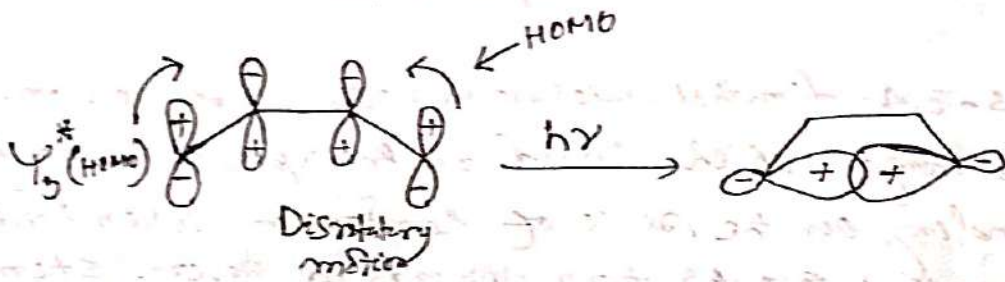
E,E-hexa-2,4-diene



Z,Z-hexa-2,4-diene

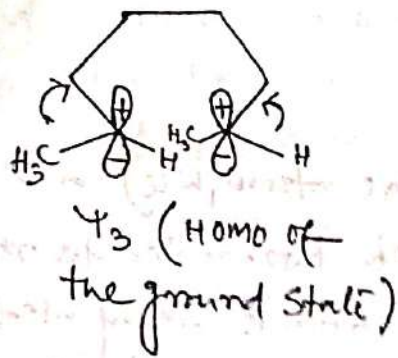
* Photochemical interconversion of 3,4-dimethylcyclohexadiene and 2,4-hexadiene:

The irradiation of the diene will lead to the promotion of an electron into the orbital of next higher energy level i.e. ψ_3 and consequently the HOMO be considered now is ψ_3 . It is now the disrotatory motion which result in bonding situation. Similarly the reverse reaction also involves a disrotatory motion which establishes the stereochemistry on substituted substrates.

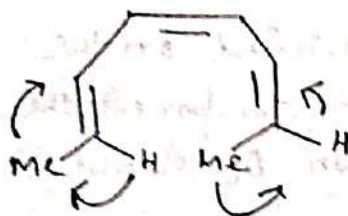
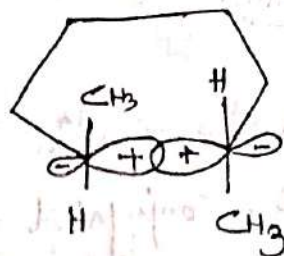


* Using FMO approach, explain the product formed by the electrocyclic transformation of trans-1,3,5-hexatriene under thermal and photochemical conditions.

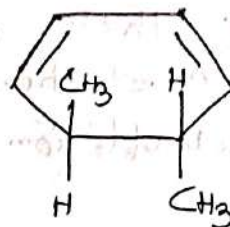
Ans The HOMO for the ground state of a hexatriene is ψ_3 and so, disrotatory motion of the orbitals leading to bonding interaction between C1 and C6 occurs and as a result of this, trans-3,4-dimethylcyclohexadiene is obtained by thermal cyclization.



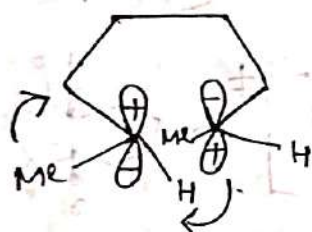
disrotatory motion



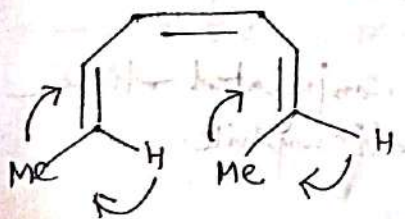
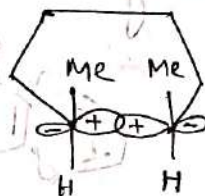
heat
disrotatory motion



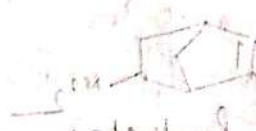
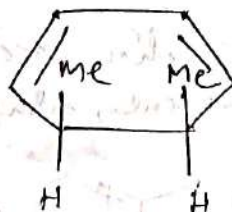
In the excited state Ψ_4^* is the HOMO of the octatriene and so conrotatory motion of the orbitals leading to bonding interaction between C-2 and C-7 occurs and as a result of this, cis-5,6-dimethyl-1,3-cyclohexadiene is obtained by photochemical cyclization.



Conrotatory motion

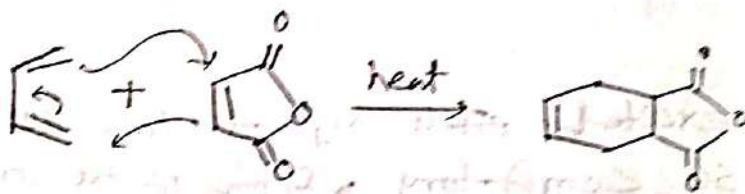


hν
Conrotatory motion

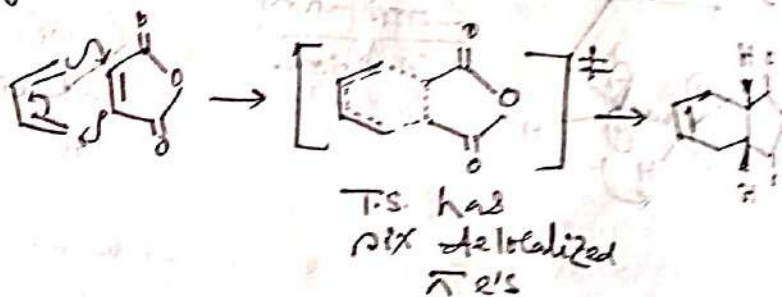


Cycloadditions

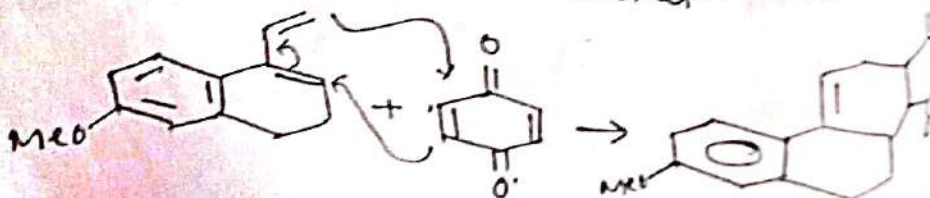
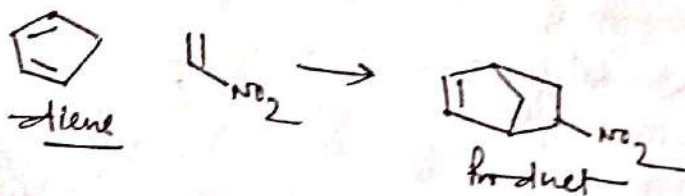
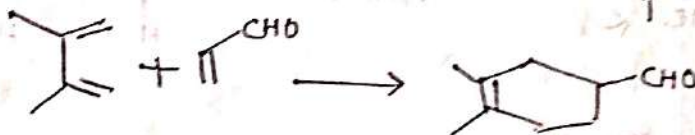
The reaction of alkenes (the dienophile) and polyenes (conjugated dienes) in which two conjugated double bonds react to form a cyclic product, with π electrons being used to form two new σ bonds are called cycloaddition reactions. These reactions are classified on the basis of π electrons involved, in each component. [4+2] cycloaddition being the well known Diels-Alder reaction.



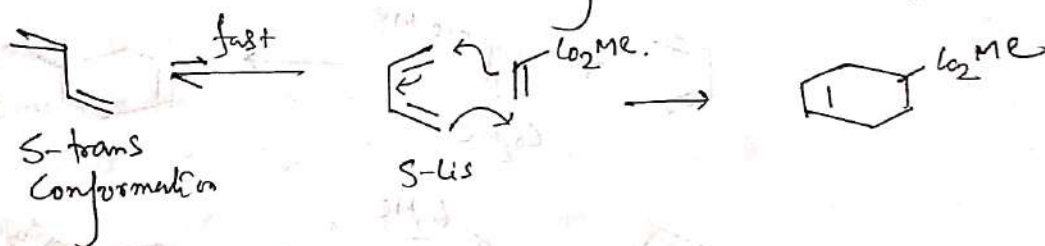
Diels-Alder goes so well because the transition state has six delocalized π 's and thus is aromatic in character, having some of the special stabilization of benzene.



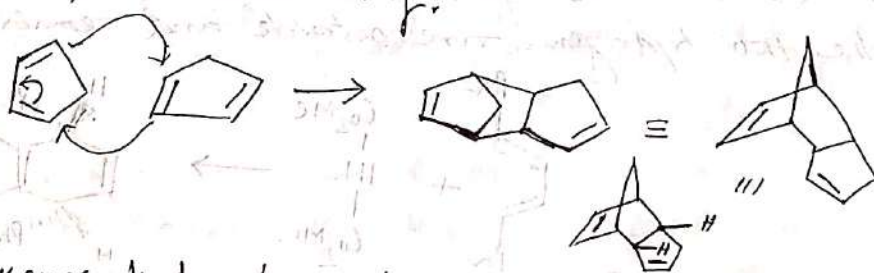
Diels-Alder reaction occurs between a conjugated diene and an alkene, usually called the dienophile.



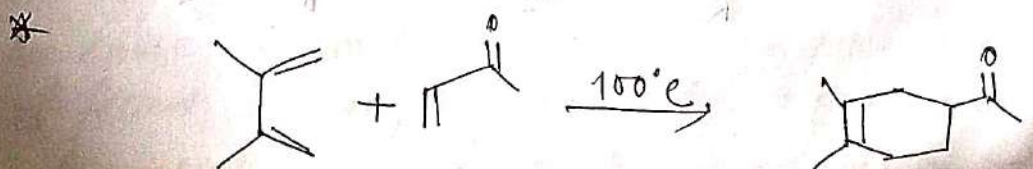
The diene component in the Diels-Alder reaction can be open-chain or cyclic and it can have many different kinds of substituents. There is only one limitation: it must be able to take up the conformation shown in the mechanism. Butadiene normally prefers the *s-trans* conformation with the two double bonds as far away from each other as possible for steric reasons. The barrier to rotation about the central σ bond is small (about 30 kJ mol^{-1} at room temperature) and rotation to the less favourable but reactive *s-cis* conformation is rapid.



Cyclic dienes that are permanently in the *s-cis* conformation are exceptionally good as Diels-Alder reaction - cyclopentadiene is a classic example - but cyclic dienes that are permanently in the *s-trans* conformation and cannot adopt the *s-cis* conformation will not do the Diels-Alder reaction at all. The two ends of these diene cannot get close enough to react with an alkene and, in any case, the product would have an impossible trans double in the new six-membered ring.

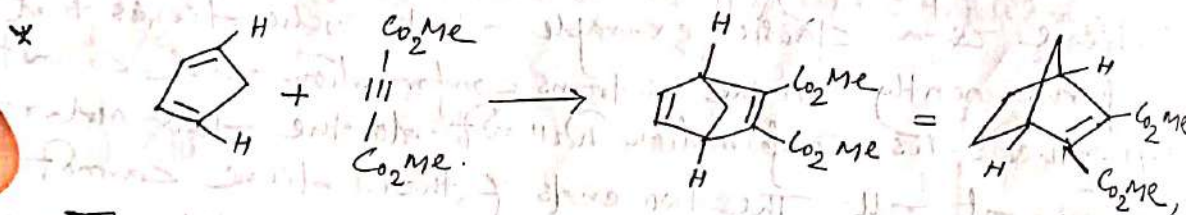
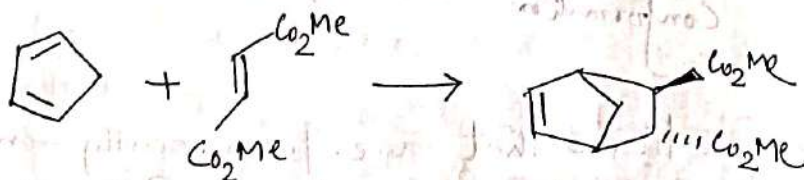
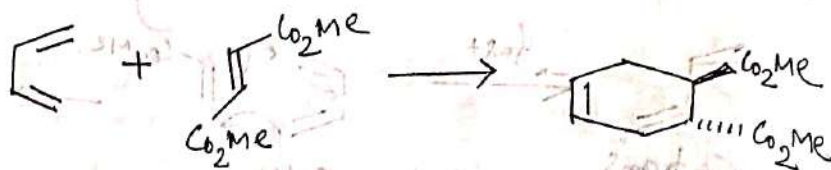
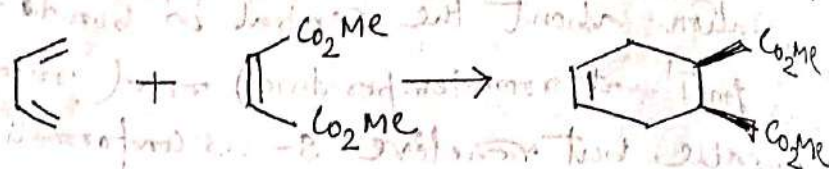


Simple alkenes that do undergo the Diels-Alder reaction include conjugated carbonyl compounds, nitro compounds, nitrile, sulfones, vinyl ether and ester.

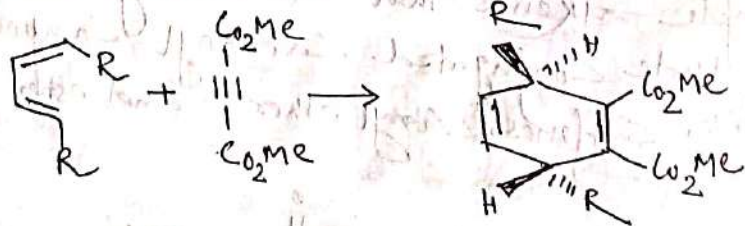
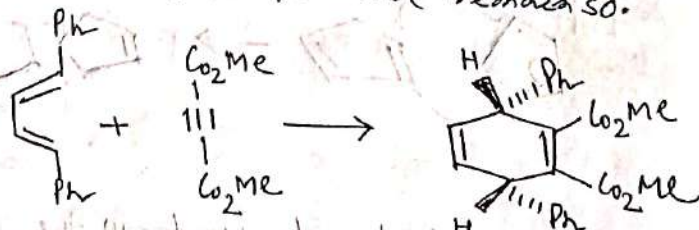


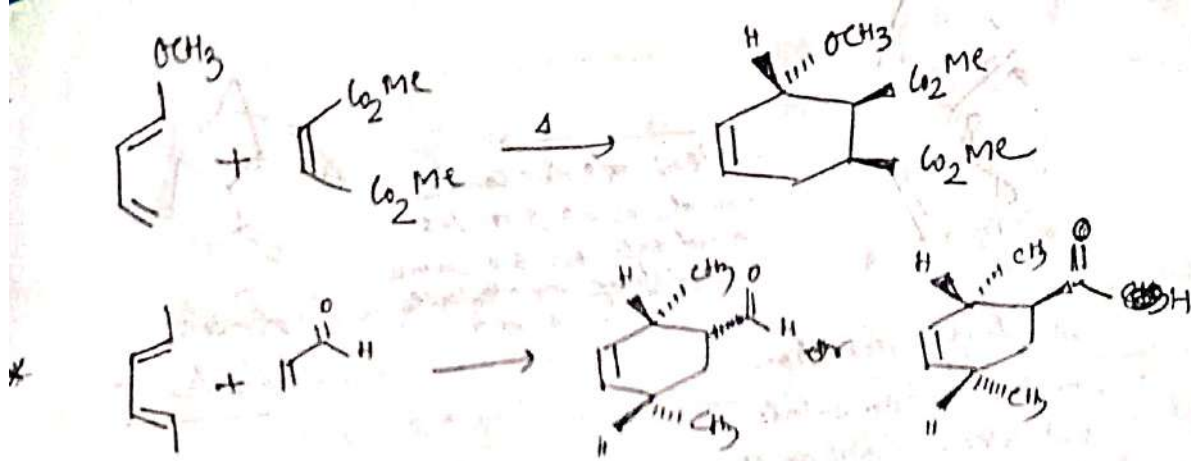
Stereochemistry:

The Diels-Alder reaction is stereospecific. If there is stereochemistry on the dienophile, then it is reproduced in the product. Thus cis and trans dienes give different diastereoisomers of the product. A reaction of maleic acid and fumaric acid provides a simple example.



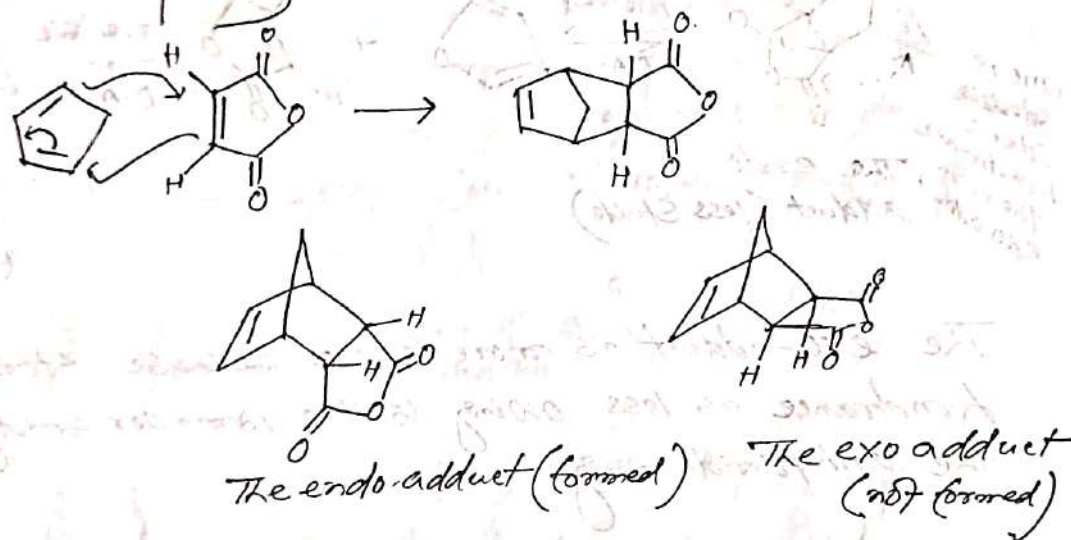
The diene has two sets of substituents - inside and outside. The inside one is the bridging CH_2 group and it has to end up on one side of the molecule while the two hydrogens are outside and remain so.





The endo rule

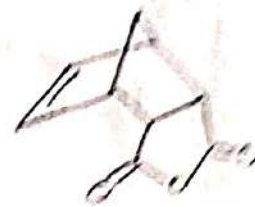
Reaction between cyclopentadiene and maleic anhydride. ~~generally gives~~ ^{there are} two possible products that obey all the rule of cycloaddition. They are the only possible diastereoisomers of the product - although it has four stereogenic centres, ~~and~~ any other diastereoisomers would be impossibly strained.



When the reaction is carried out, the product is, in fact, the endo compound. Only one diastereoisomer is formed, and it is the less stable one. The endo product is less stable than the exo product and yet it is preferred in irreversible Diels-Alder reactions - it must be the kinetic product of the reaction. It forms faster because a bonding interaction between the electron-deficient carbonyl groups of the dienophile and the developing π bond at the back of the diene lowers the energy of the transition state, leading to the endo product.



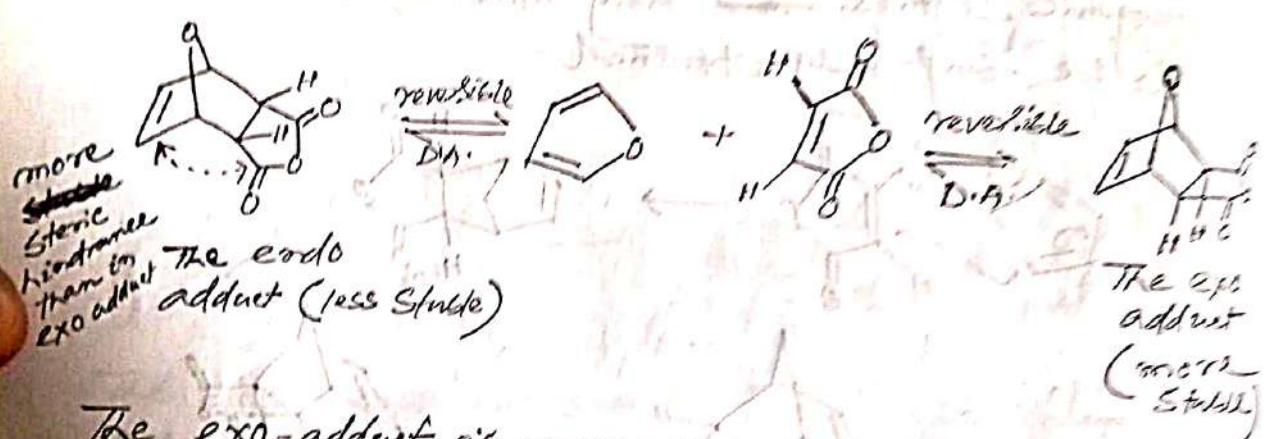
New double bond
and two groups
end up on the same
side of molecule
endo



Endo
Product

London interaction
in transition state
between carbonyl
group and back
of diene

In which the Diels-Alder reaction is reversible, and therefore under thermodynamic control, the exo form is formed instead. The best known example results in the replacement of cyclopentadiene with furan.



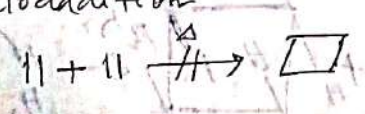
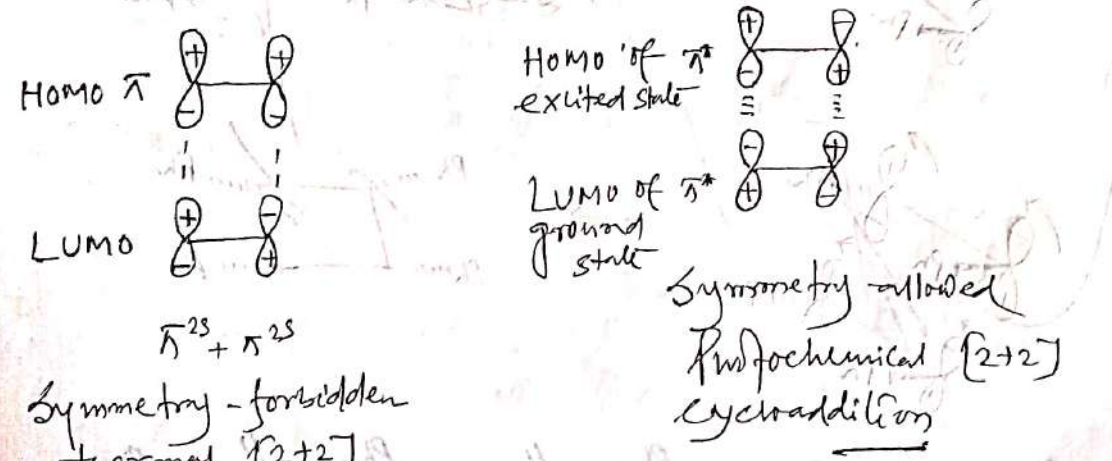
The exo-adduct is more stable because steric hindrance is less owing to the smaller bridge size of the anhydride ring.

* Thermal [2+2] Cycloaddition is uncommon but photochemical
 - Cal [2+2] Cycloaddition is well known. Explain the fact.

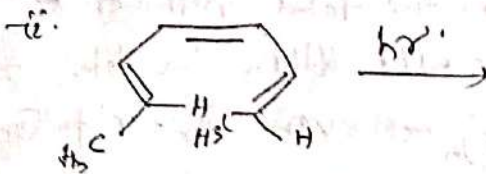
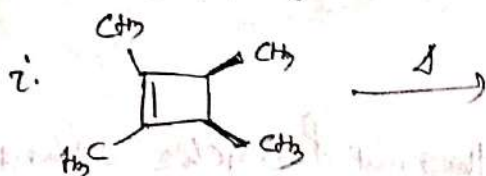
Ans

In the dimerization of ethylene, a thermal [2+2] cyclization would involve overlaps of HOMO, π of one molecule with the LUMO, π^* of the other. Now π and π^* are of opposite symmetry. If in this concerted reaction both bonds to a component are formed on the same face i.e. the process is suprafacial, the lobes of opposite phase would approach each other. This interaction which is suprafacial with respect to both components ($\pi^{2s} + \pi^{2s}$) is therefore antibonding and repulsive and the concerted reaction, does not take place.

The photochemical [2+2] cycloadditions which are suprafacial with respect to both the components ($\pi^{2s} + \pi^{2s}$) will, however, permit a previously forbidden reaction to become a symmetry allowed process. This is so, since here, one has the HOMO π^* of an excited molecule with the LUMO (also π^*) of a ground state molecule.

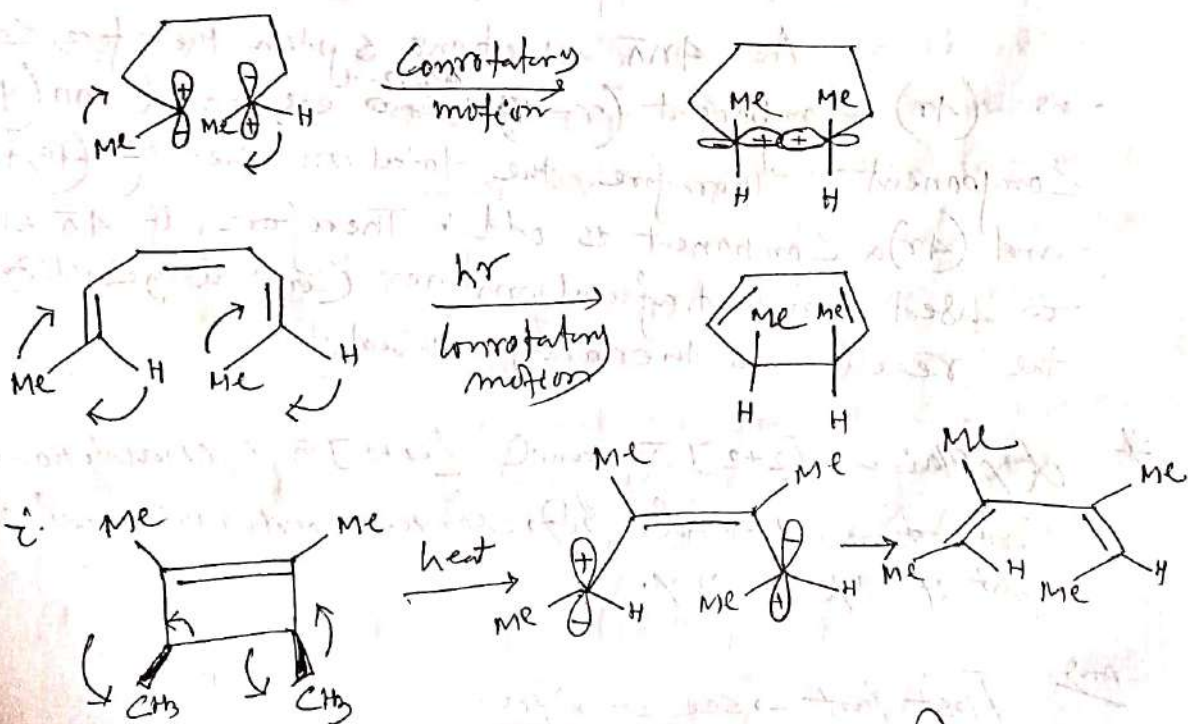


* Predict the following products with stereochemistry!



Ans

i. In the excited state ψ_4^* is the HOMO of the octatriene and so conrotatory motion of the orbitals leading to bonding interaction C-2 and C-7 occurs and as a result of this cis-5,6-dimethyl-1,3-cyclohexadiene is obtained by photochemical cyclization.



Due to conrotatory motion, a σ bond will open so as to give the resulting 'p' orbitals which will have the symmetry of the highest occupied π orbital of the product. Since for the thermal reaction, ψ_2 HOMO of the product in the thermal reaction is ψ_2 , therefore the cyclobutene must open so that two lobes are in opposite direction. The process also forces the stereochemistry.

* Write down the Woodward-Hoffmann rule for $4n$ -electron system.

Ans

A ground state thermal pericyclic change is symmetry-allowed when the total number of $(4q+2)_s$ and $(4r)_a$ component is odd. When the total number of $(4q+2)_s$ and $(4r)_a$ is even the rotation is photochemically allowed. The terms $(4q+2)$ and $(4r)$ refer to the number of interacting electrons of reacting partners and q and r may individually assume values in the series 0, 1, 2, 3 etc. Therefore, $(4q+2)$ term refers to those components of the pericyclic reaction which contain 2, 6, 10... electrons and the $(4r)$ terms to those components containing 0, 4, 8, 12... electrons. The subscripts 's' and 'a' refer to suprafacial and antarafacial interaction respectively.

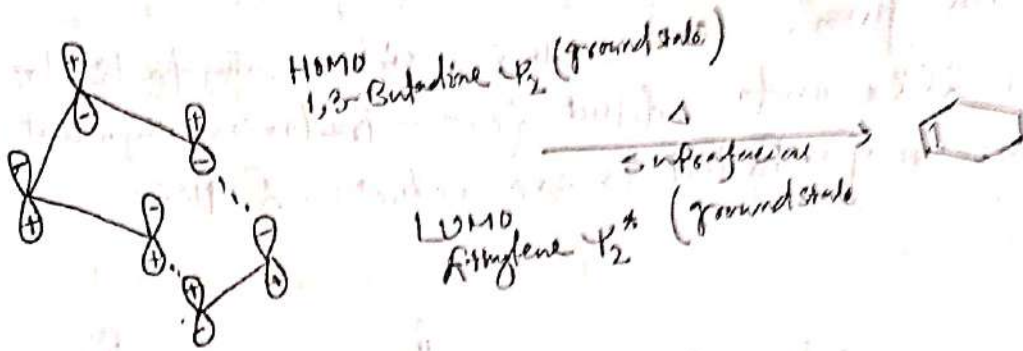
A $4n$ electron system therefore, contains a $(4r)$ component ($r = 0, 1, 2$ etc) and no $(4q+2)_s$ component. Therefore, the total number of $(4q+2)_s$ and $(4r)_a$ component is odd. Therefore, if $4n$ element is used in antarafacial manner (concerted cyclization) the reaction is thermally allowed.

* Explain $[2+2]_s$ and $[4+2]_s$ cycloaddition reactions under thermal and photochemical conditions and in the light of MO theory.

Ans

First part \rightarrow see in notes.

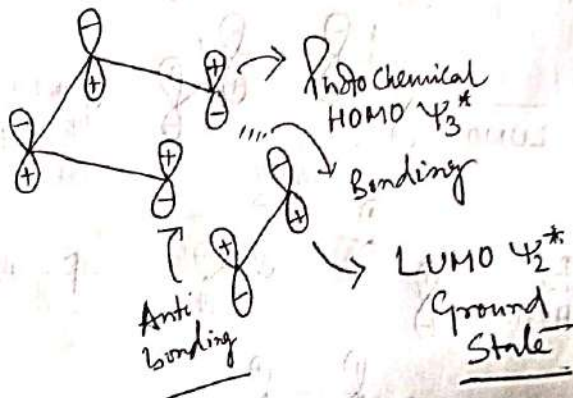
Orbital overlaps between diene ($4n$ -electron system) part and dienophile ($2n$ electron system) part in Diels-Alder cyclization can be shown as follows:



This thermally-allowed reaction involves e.g. the HOMO of 1,3-butadiene (ψ_2) with the LUMO of ethylene ψ_2^* (one could equally well use the diene LUMO and the alkene HOMO)

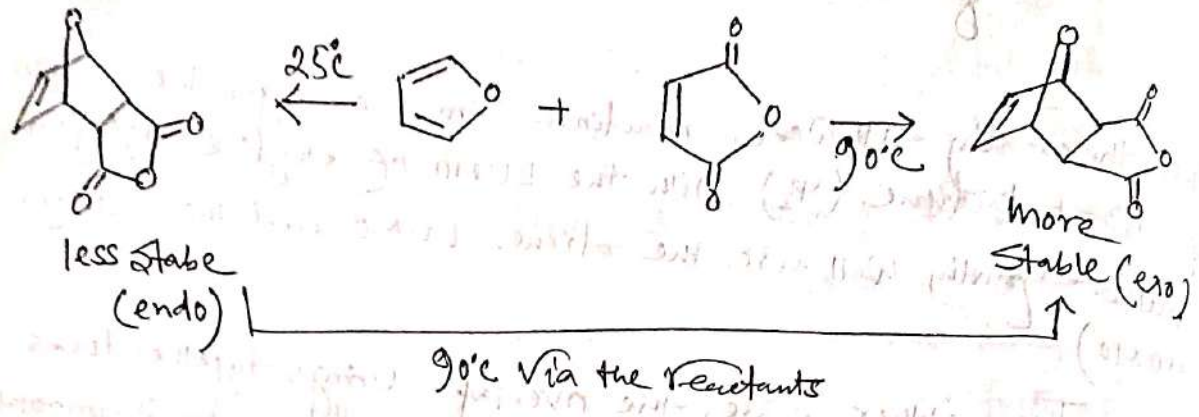
In either case, the overlap brings together lobes of the same phase and reaction takes place smoothly.

Usually the absorption of a photon will promote an electron from HOMO to LUMO. In the case of photochemical Diels-Alder reaction (which is most uncommon) the lower energy HOMO-LUMO gap is on the diene partner. Thus on absorption of light a new photochemical HOMO for the diene (ψ_3^*) is generated and new HOMO-LUMO interaction with the dienophile partner involves one antibonding overlap. Thus the new bonds cannot be formed at the same time and the photochemical Diels-Alder reaction is forbidden by orbital symmetry.



* When furan and maleic acid anhydride heated at 25°C, endo adduct forms predominantly, but at 90°C the major product is exo adduct - Explain.

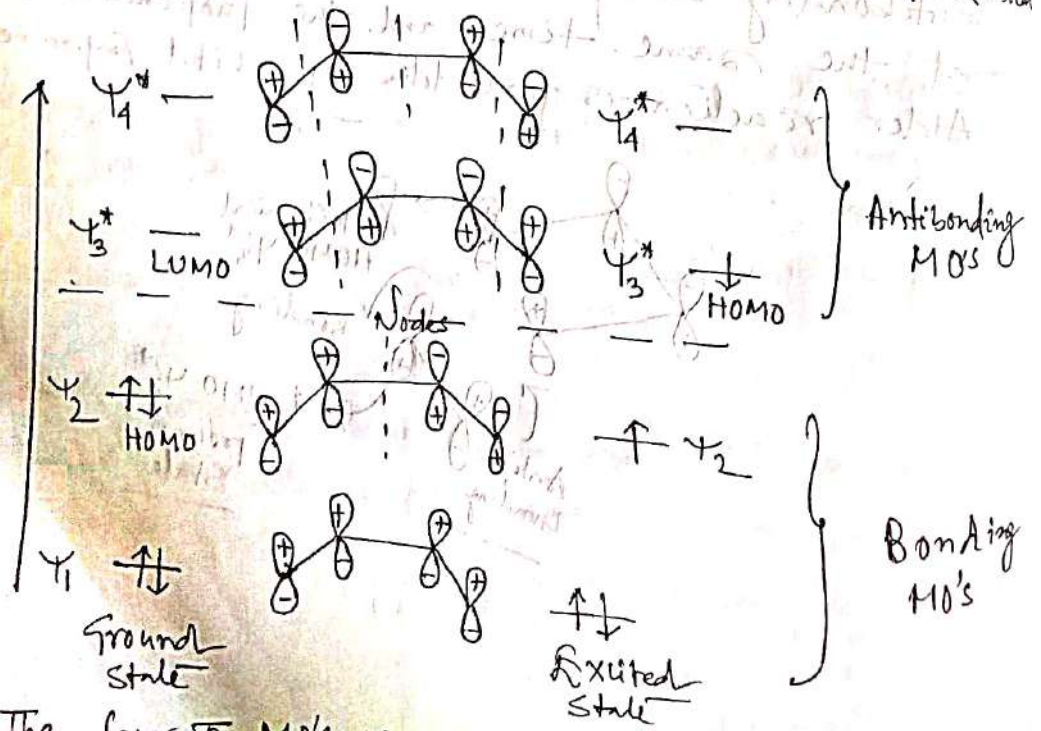
Ans



The exo product is thermodynamically more stable. The less stable endo isomer (kinetically favoured adduct) is formed faster and predominates at 25°C, the reaction is effectively irreversible. At 90°C this product is in rapid equilibrium with the reactants, consequently, the less rapidly formed, but more stable exo isomer accumulates. With time.

* Draw the MO diagram of 1,3-butadiene and indicate HOMO and LUMO under thermal and photochemical conditions.

Ans

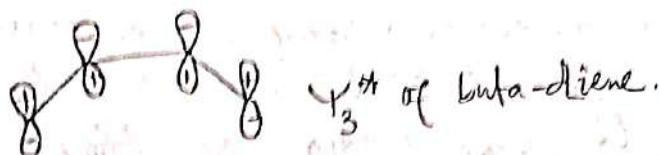


The four π MO's of 1,3-butadiene

* Draw MO picture of the LUMO of buta-1,3-diene and specify its symmetry.

Ans

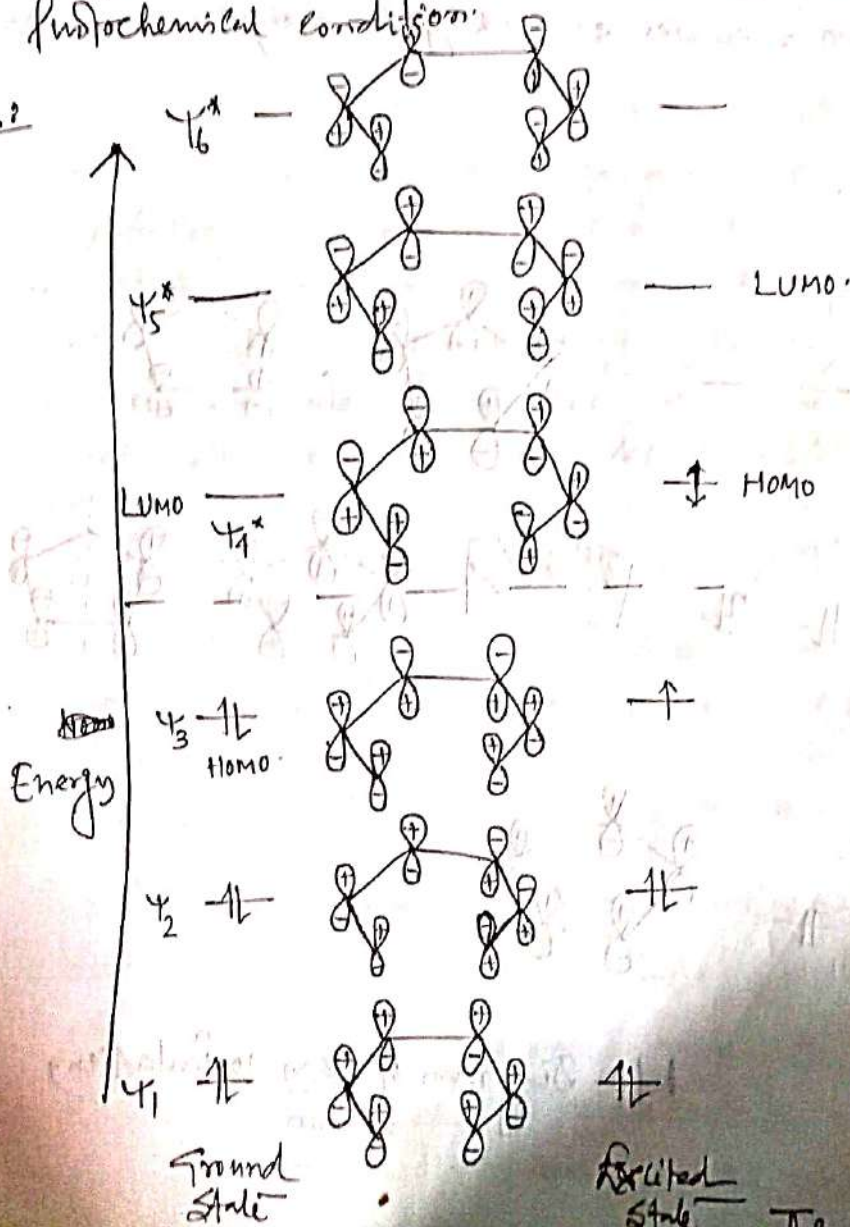
MO picture of LUMO of buta-1,3-diene is shown below:



It is ~~antisymmetric~~ asymmetric in nature - it possess a plane of symmetry.

* Draw the MO diagram of 1,3,5-hexatriene and indicate HOMO and LUMO under thermal and photochemical condition.

Ans?

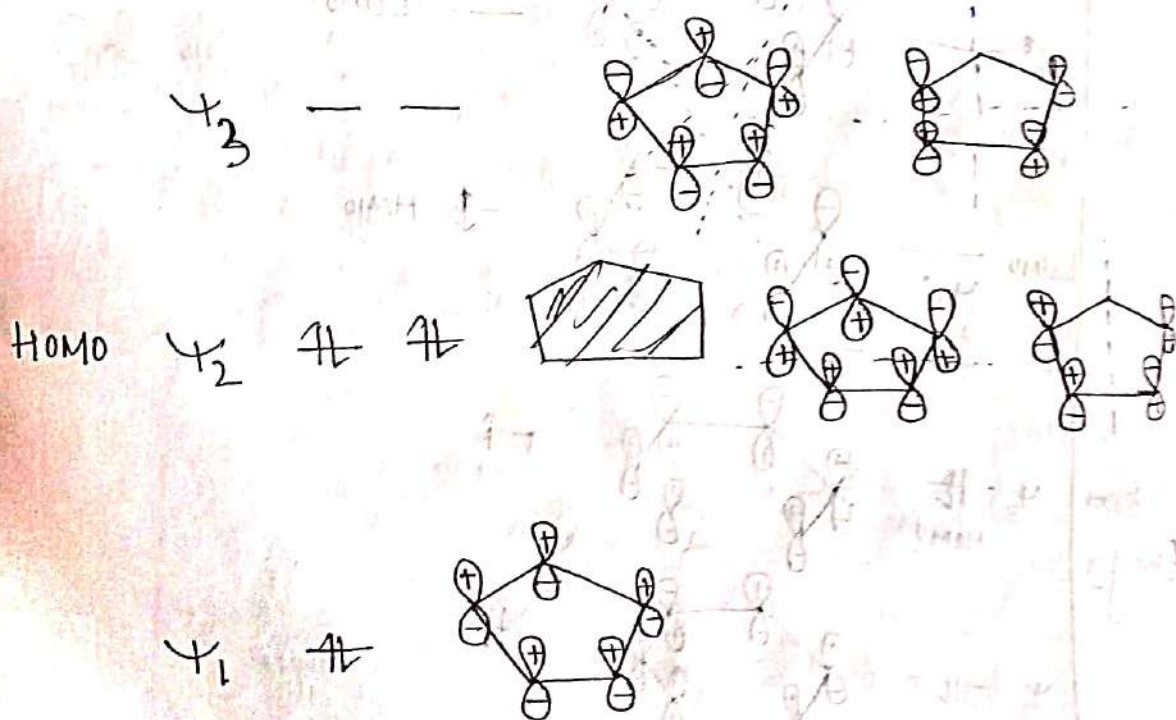


The six π molecule orbitals of 1,3,5-hexatriene

✓ Explain why HOMO and LUMO are so important in pericyclic reaction. Draw the picture of HOMO of Cyclopentadienyl anion.

Ans.

The Fuki's method concentrates on the frontier molecular orbitals, the HOMO and the LUMO. In the ground state of 1,3-butadiene ψ_2 is HOMO and ψ_3^* is the LUMO. The Fuki's FMO approach examines as to how the orbitals of HOMO or in some cases, the orbitals of HOMO of one component and the LUMO of other overlap to form new bonds. If the overlaps are favourable (bonding overlaps) then the reaction is allowed and if not favourable (antibonding overlaps) then the reaction is forbidden. Thus HOMO and LUMO decides everything in pericyclic reaction.



MO Diagram of, Cyclopentadienyl anion