

2.4 FRONTIER MOLECULAR ORBITAL (FMO) METHOD

A methodology for quickly predicting whether a given pericyclic reaction is allowed by examining the symmetry of the highest occupied molecular orbital (HOMO) (in case of unimolecular reaction) and, if the reaction is bimolecular, the lowest unoccupied molecular orbital (LUMO) of the second partner.

Thus electrocyclic reaction is analysed by HOMO of the open chain partner because reaction is unimolecular reaction. The stereochemistry of an electrocyclic process is determined by the symmetry of the highest occupied molecular orbital (HOMO) of the open chain partner, regardless of which way the reaction actually runs. In thermal condition HOMO is always ground state HOMO whereas in photo chemical condition HOMO is always first excited state HOMO.

If the highest occupied molecular orbital has m symmetry, the process will be disrotatory. On the other hand if HOMO has c_2 symmetry than the process will be conrotatory (Table 2).

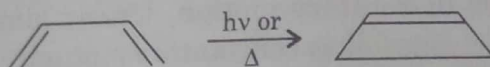
Table 2

Symmetry in HOMO	Mode of rotation
m -symmetry	Disrotatory
c_2 -symmetry	Conrotatory

Now we are in a position to consider specific examples of the application of the FMO method.

2.4.1 Cyclisation of $4n \pi$ Systems

1. **Electrocyclic ring-closure reaction given by butadiene.** 1,3-Butadiene is the first member of the conjugated polyene having $4n \pi$ electrons.



Thermal-Induced Cyclisation. When 1,3-butadiene is heated, reaction takes place from the ground state. The electrons that are used for the sigma bond formation are in the HOMO (ψ_2 in this case). Pertinent p orbitals in ground state HOMO has C_2 symmetry. For the new sigma bond to form, rotation must be conrotatory. Disrotatory motion would not place the in-phase lobes together.

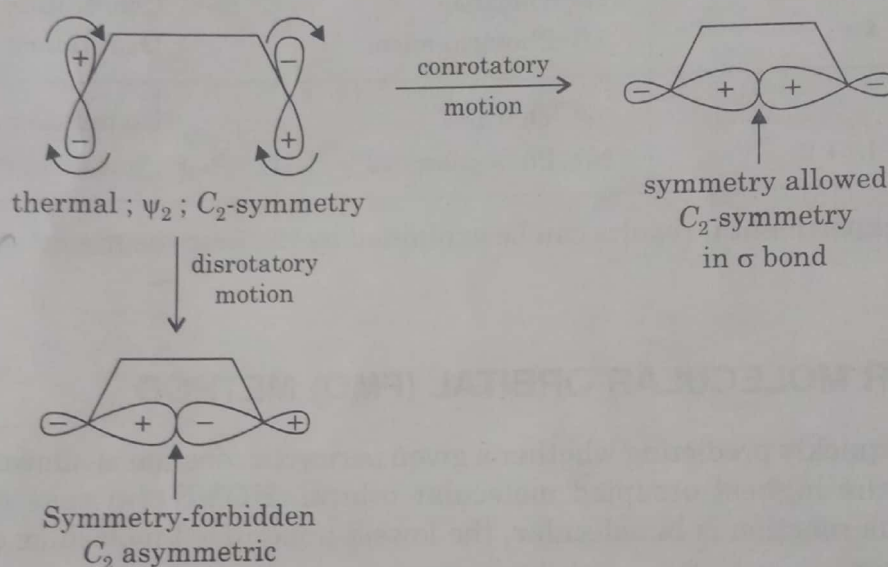
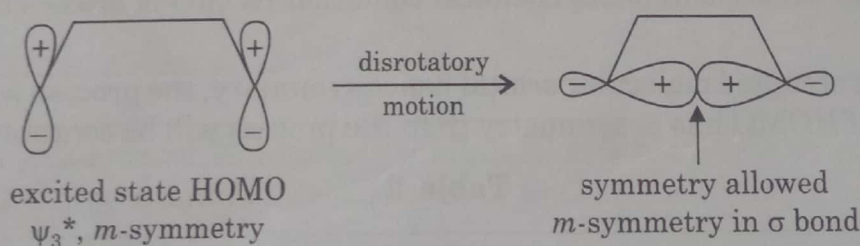
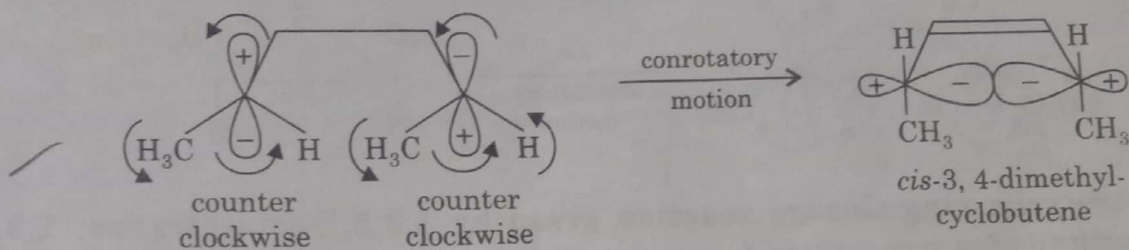
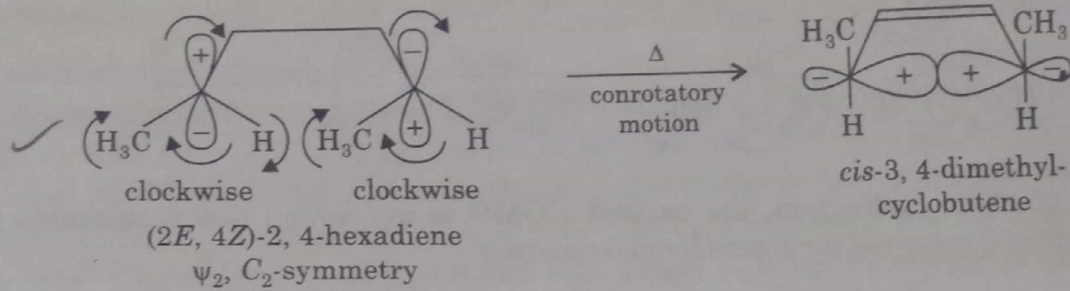


Photo-Induced cyclisation. In photo-induced cyclisation, the first excited HOMO of 1,3-butadiene is ψ_3^* which has m symmetry. For the new sigma bond to form, rotation must be disrotatory.

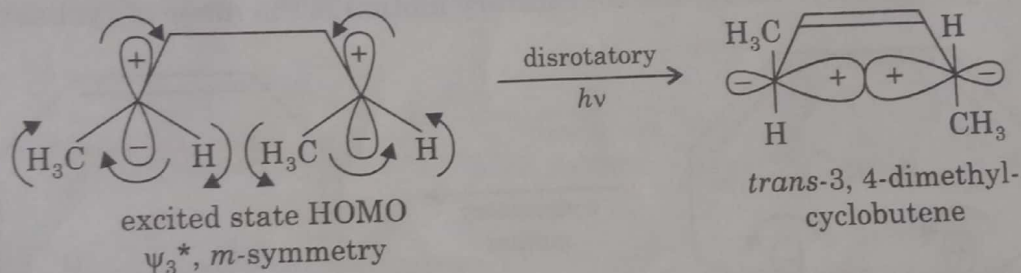


Let us return to (2*E*, 4*Z*)-2,4-hexadiene to see why the *cis*-3,4-dimethylcyclobutene results from the thermal cyclisation and the *trans*-isomer from the photo cyclisation.

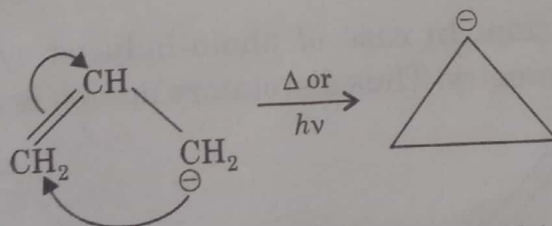
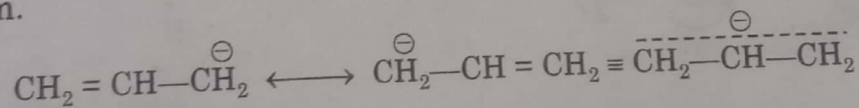
In the case of the thermal cyclisation the ground state HOMO is ψ_2 which has C_2 symmetry. Thus conrotatory motion is required for sigma bond formation. Both methyl groups rotate in the same direction, as a result they end up on the same side of the ring or *cis* is the product.



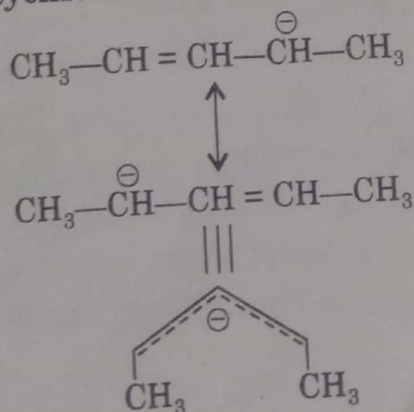
In the case of photo-cyclisation the excited state HOMO is ψ_3^* which has m -symmetry. Thus disrotatory motion is required for the σ bond formation. In disrotatory motion, one of the methyl groups, rotates up and the other rotates down. The result is that both methyl groups are *trans* in the product.

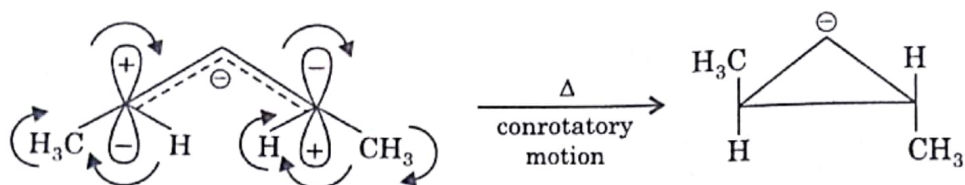


2. Electrocyclic ring-closure given by allyl carbanion. Allyl carbanion is also a $4n$ π conjugated system.

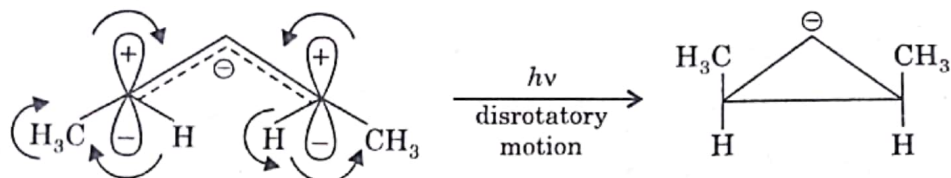


HOMO of the allyl carbanion in the ground state is ψ_2 which has c_2 symmetry. Therefore, conrotatory motion is the mode of cyclisation in the thermal condition.





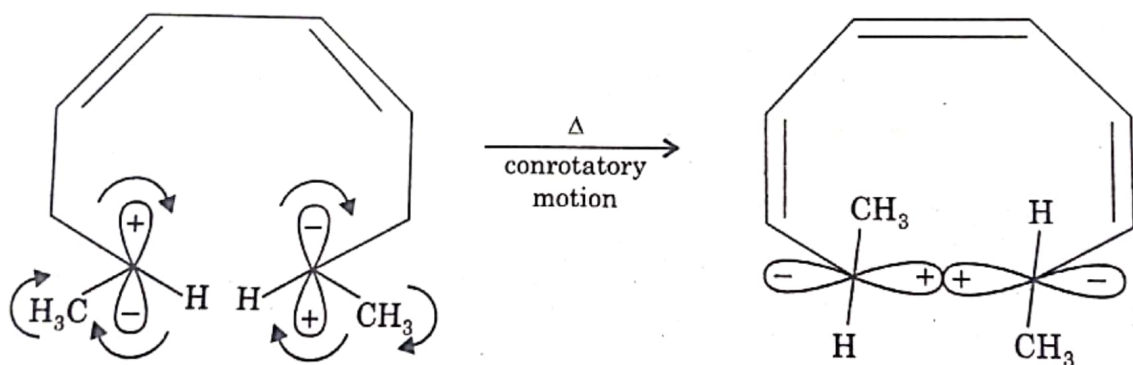
In case of photo cyclisation, the excited HOMO is ψ_3^* which has m symmetry. Thus disrotatory motion is required for sigma bond formation.



3. **Electrocyclic ring-closure reaction given by 1,3,5,7-octatetraene.** 1,3,5,7-octatetraene and its derivatives contain $4n$ π conjugated electrons.

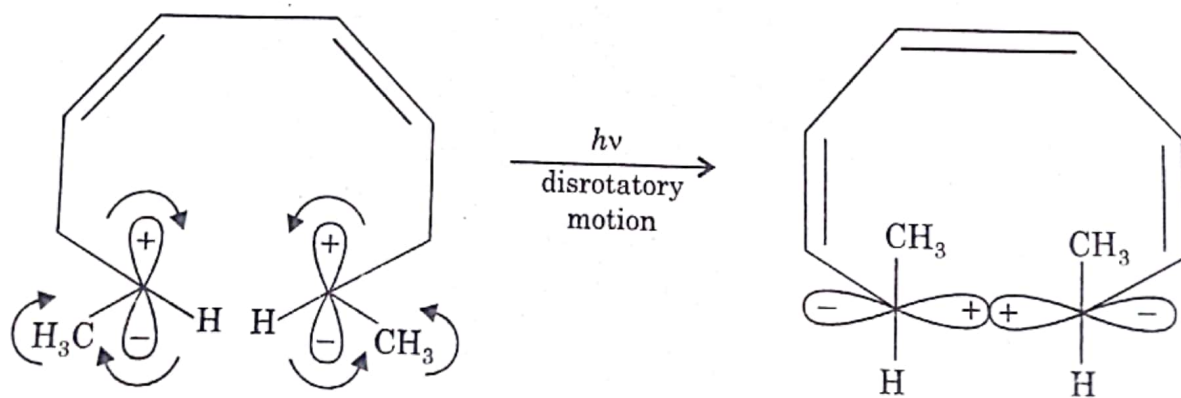
Consider the electrocyclic ring-closure of (2*E*, 4*Z*, 6*Z*, 8*E*)-2,4,6,8-decatetraene in thermal and photochemical conditions.

Thermal induced cyclisation. The tetraene is a $4n$ polyene. Its ground state HOMO is ψ_4 which has c_2 symmetry. Therefore, conrotatory motion is the mode of cyclisation.



trans-7,8-dimethyl-1,3,5-cyclotriene

Photo-Induced cyclisation. In case of photo-induced cyclisation the excited state HOMO is ψ_5^* which has m -symmetry. Thus disrotatory motion is the mode of cyclisation.

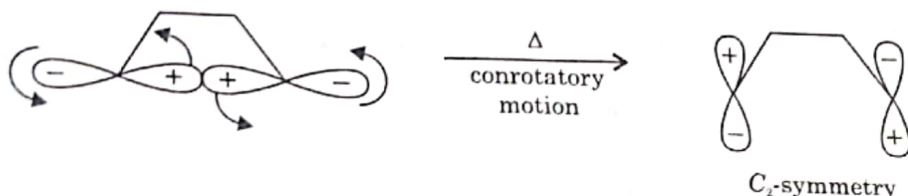


cis-7,8-dimethyl-1,3,5-cyclooctatriene

2.4.2 Electrocyclic Ring-Opening in which polyene has $4n \pi$ electrons

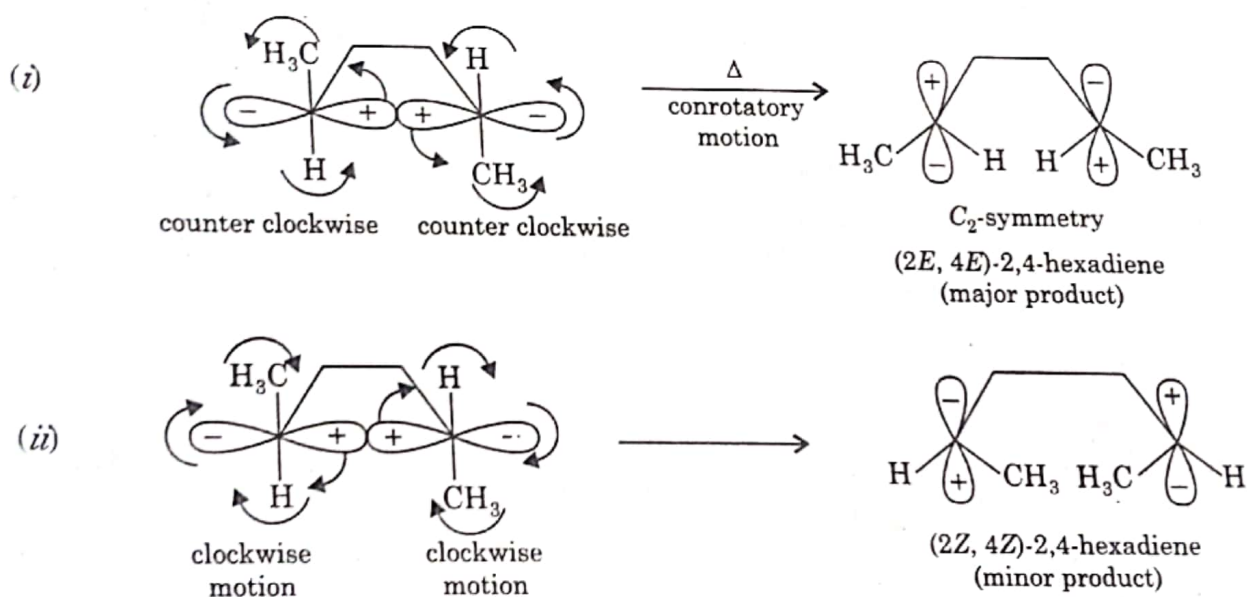
1. Conversion of cyclobutene to butadiene

A. Thermal-Induced ring opening. In the ring-opening reactions stereochemistry of the product is determined by the symmetry of the ground state HOMO of the open-chain partner. The ground state HOMO of the butadiene and its derivative will be ψ_2 which has C_2 symmetry. The cyclobutene ring must open in such a fashion that the σ bond orbitals transform into the HOMO of the product having C_2 symmetry. To get C_2 symmetry in the product HOMO, motion should be conrotatory in the ring opening of the reaction.



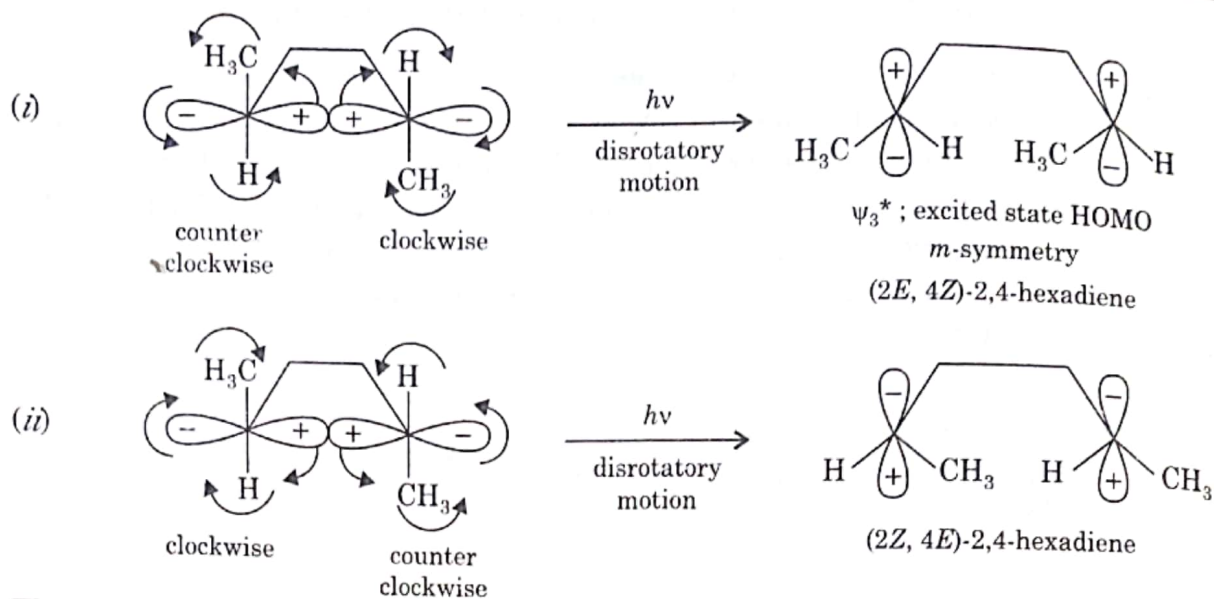
Thus if the open-chain polyene has $4n \pi$ electrons then the process is always *conrotatory* in thermal condition whether the reaction is ring-closure or ring opening.

Let us take the stereochemistry of the ring opening of *trans*-3, 4-dimethylcyclobutene. There is possibility of two modes of conrotatory motion.



Thus the thermal process is conrotatory with two products possible in the above case. The conrotation in the second case (clockwise rotation) leads to severe steric interactions between two methyl groups. This interaction is avoided in the first process (rotation is counter clockwise) in which two methyl groups move away from each other, and this is the favoured process.

B. Photo-Induced Ring Opening. The photo state HOMO of the open chain butadiene and its derivative will be ψ_3^* which has m symmetry. Thus the cyclobutene ring must be open in such a fashion that the σ bond orbitals transform into the excited state HOMO of the product having m symmetry. To get m symmetry in excited state HOMO of the product, motion should be disrotatory in the ring opening of the reaction. There is also possibility of two modes of disrotatory motion.



Thus photo-induced process is disrotatory with either possible disrotation giving same product.

Let us take the conversion of *cis*-3,4-dimethylcyclobutene into 2,4-hexadiene.

Thermal ring-opening

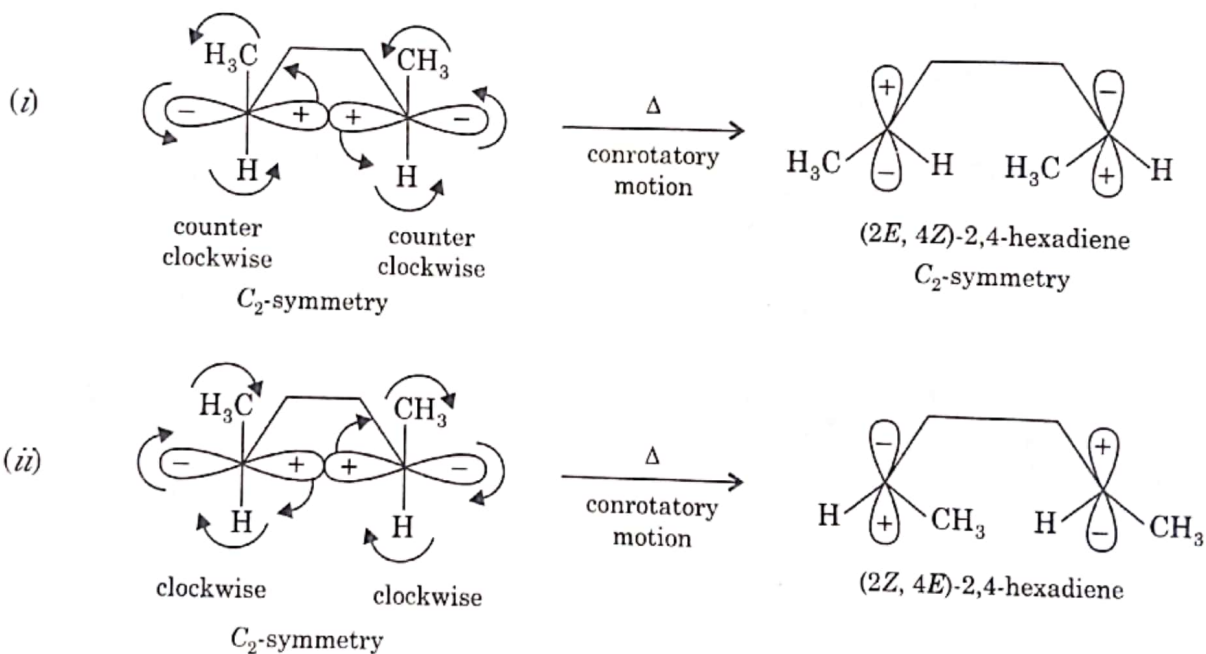
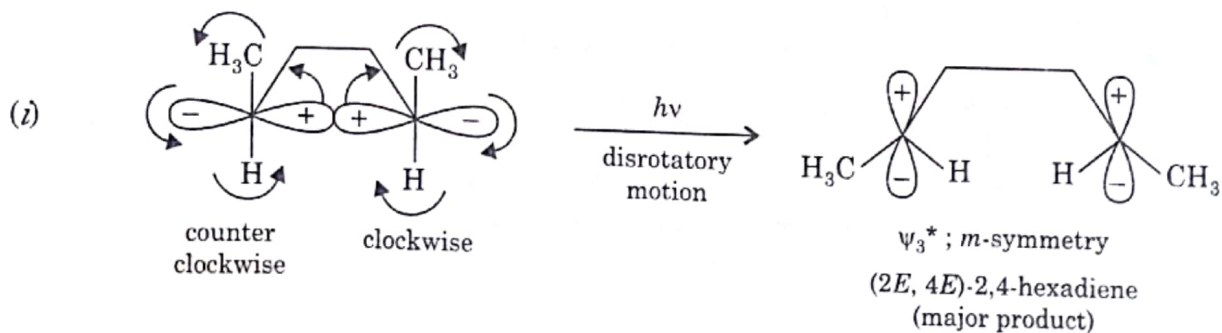
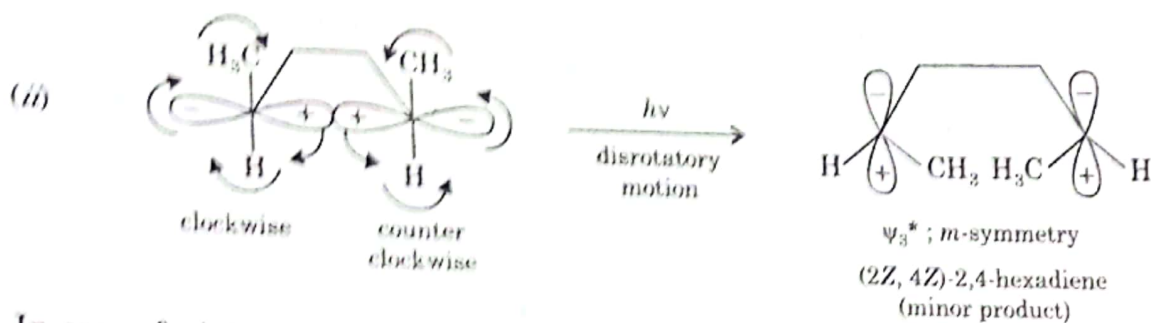


Photo-Induced ring opening



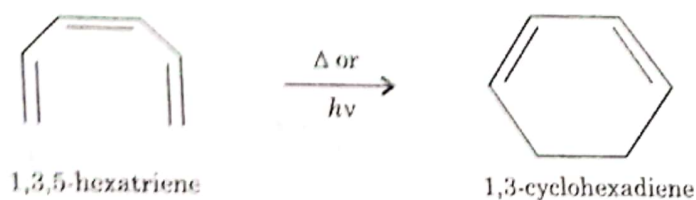


In case of *cis*-3,4-dimethylcyclobutene, the thermal process is conrotatory with either possible conrotation giving the same product. The photochemical process is disrotatory with two possible products.

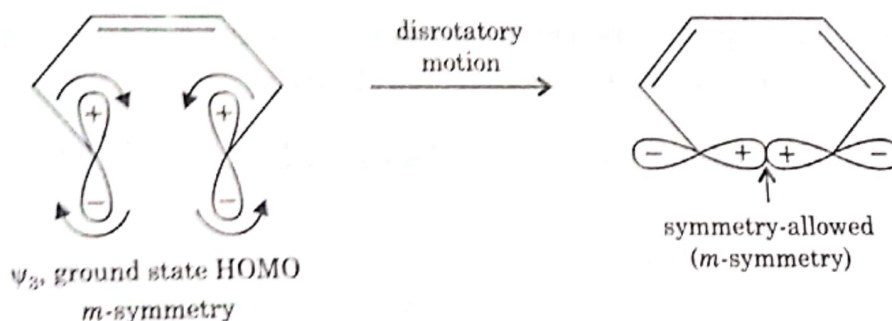
2.4.3 Cyclisation of $(4n + 2)\pi$ Systems

1. Electrocyclic ring-closure reaction given by 1,3,5-hexatriene

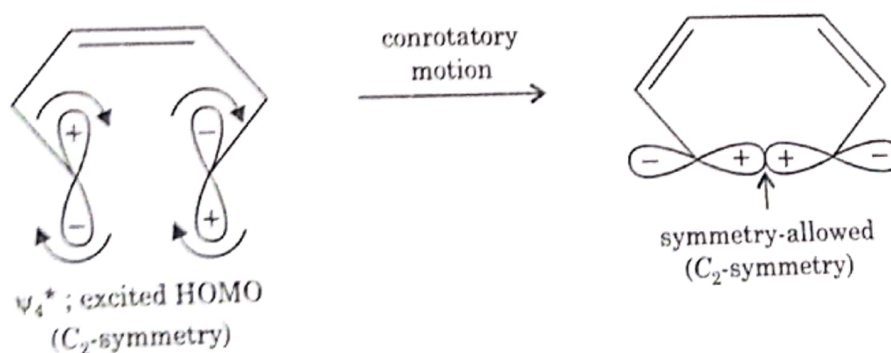
1,3,5-Hexatriene is the most common example of the polyene having $(4n + 2)\pi$ conjugated electrons.



A. **Thermal-Induced cyclisation.** ψ_3 is the ground state HOMO of 1,3,5-hexatriene which has m -symmetry. Therefore, the thermal cyclisation proceeds by disrotatory motion.

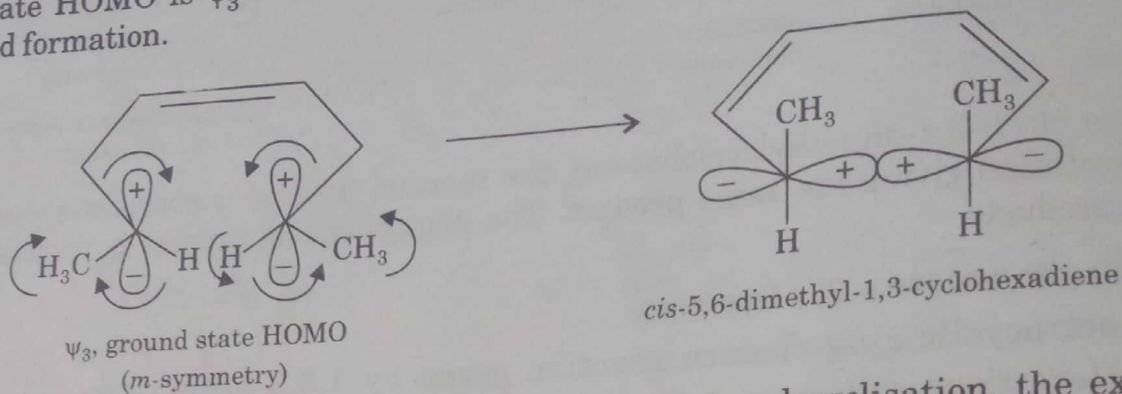


B. **Photo-Induced cyclisation.** When an electron of 1, 3, 5-hexatriene is promoted by photon absorption, ψ_4^* becomes the HOMO. This excited state HOMO has C_2 symmetry. Therefore, photo-induced cyclisation proceeds by conrotatory motion.

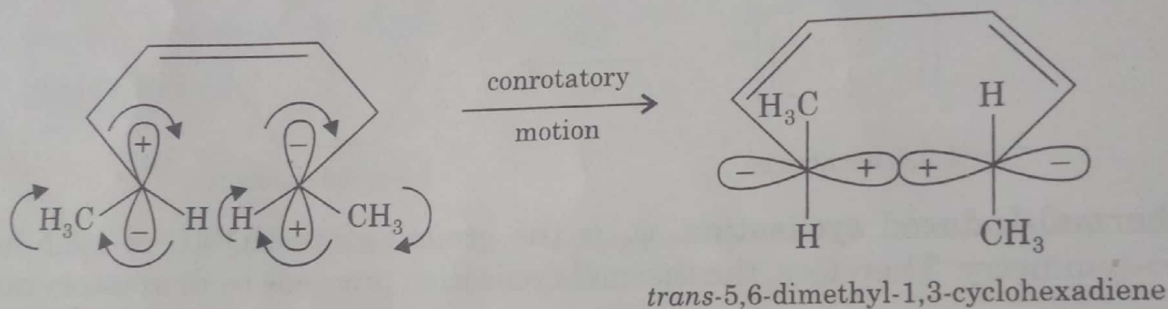


Consider the stereochemistry of the thermal and photo-induced closure of (2*E*, 4*Z*, 6*E*)-2,4,6-octatriene to 5,6-dimethyl-1,3-cyclohexadiene.

A. Thermal-Induced cyclisation. In the case of the thermal induced cyclisation, the ground state HOMO is ψ_3 which has *m* symmetry. Thus disrotatory motion is required for sigma bond formation.

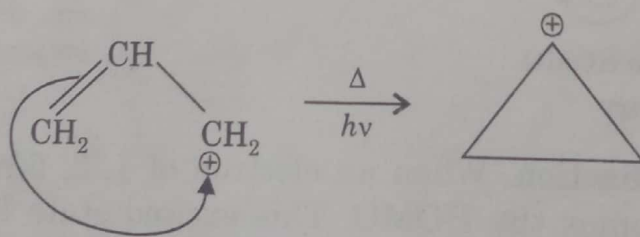
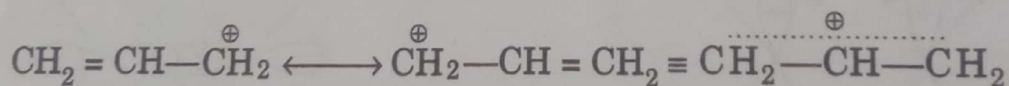


B. Photo-Induced cyclisation. In case of photo-induced cyclisation, the excited state HOMO is ψ_4^* which has C_2 symmetry. Therefore, conrotatory motion is required for sigma bond formation.

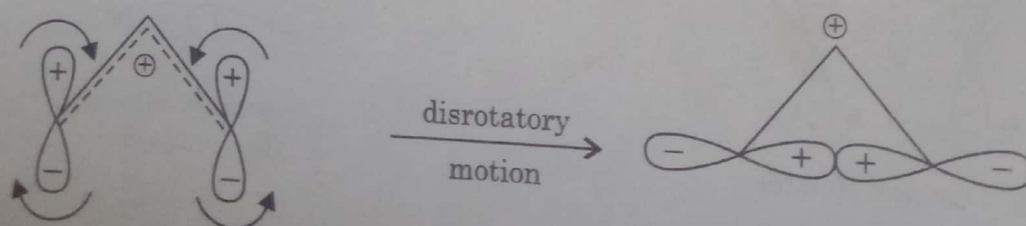


2. Electrocyclic ring-closure reaction given by allyl carbocation

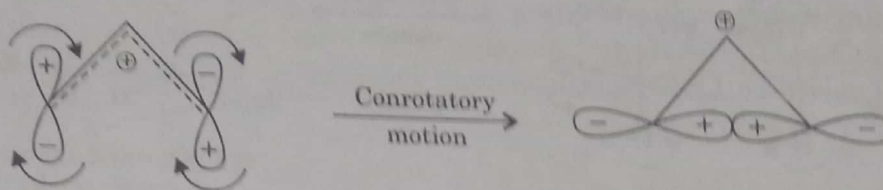
Allyl carbocation contains $(4n + 2)\pi$ conjugated electrons.



A. Thermal-Induced cyclisation. HOMO of the allyl carbocation in the ground state is ψ_1 which has *m* symmetry. Therefore, disrotatory motion is the mode of cyclisation in the thermal condition.



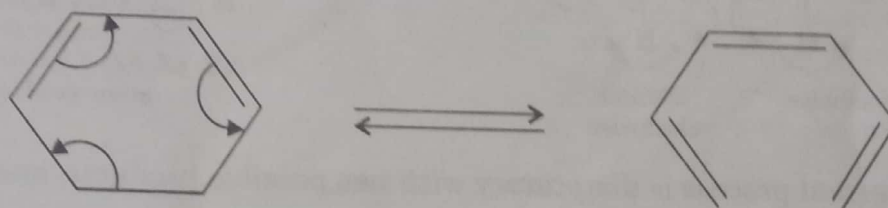
B. Photo-induced cyclisation. HOMO of the allyl carbocation in the excited state is ψ_2 which has C_2 symmetry. Thus conrotatory motion is required for σ bond formation



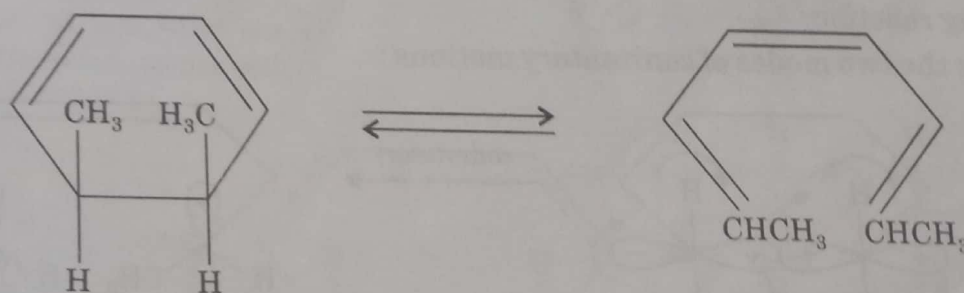
2.4.4 Electrocyclic Ring-Opening in which polyene has $(4n + 2)\pi$ electrons

1. Conversion of 1,3-cyclohexadiene to 1,3,5-hexatriene system

The most common example of this class is the conversion of 1,3-cyclohexadiene to 1,3,5-hexatriene.

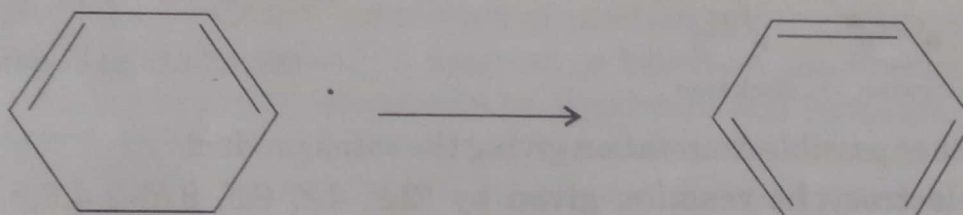


Let us take the example of the ring opening of a *cis*-5,6-dimethyl-1,3-cyclohexadiene into 2,4,6-octatriene.



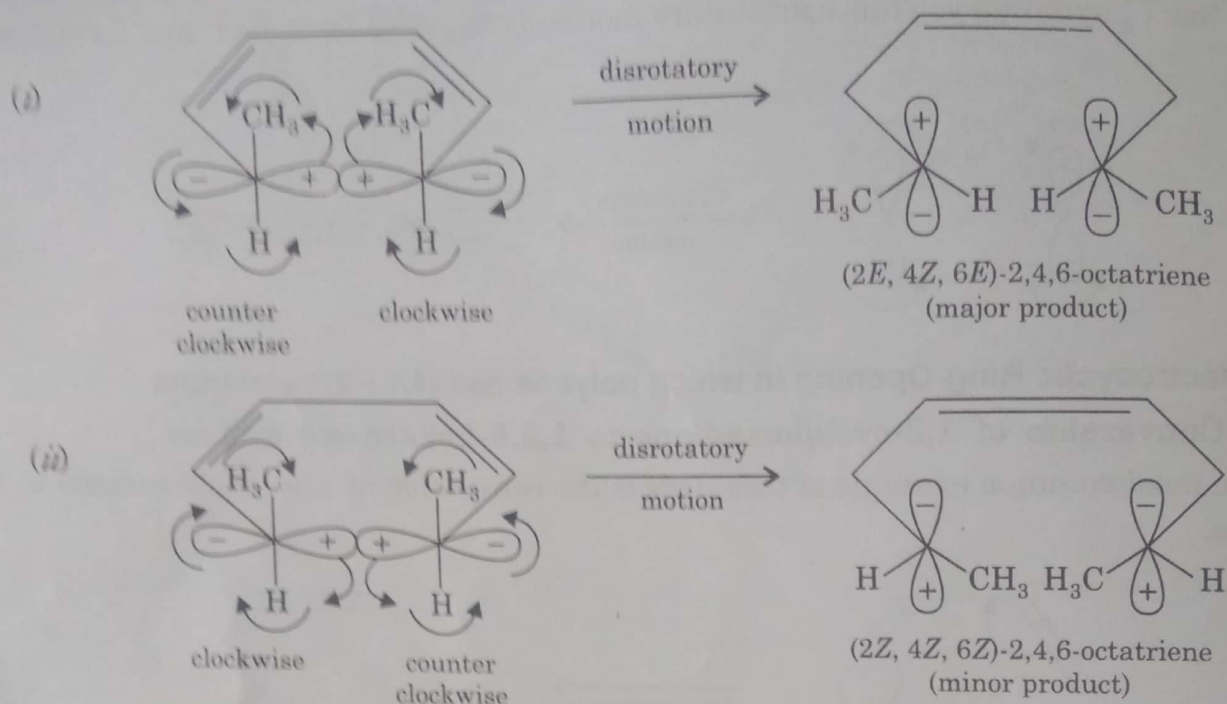
A. Thermal ring opening. As mentioned earlier that in the ring opening reactions stereochemistry of product is determined by the symmetry of the ground state HOMO of the open chain partner. The ground state HOMO of the triene will be ψ_3 which has m symmetry. The cyclohexadiene ring therefore, must open in such a fashion that σ bond orbitals transform into the ground state HOMO of the product having m symmetry. To get m -symmetry in the HOMO of the product, motion should be disrotatory in the ring opening of the reaction.

The above results can be obtained in short as follows :



Ground state HOMO is ψ_3 which has m symmetry. Therefore motion is disrotatory

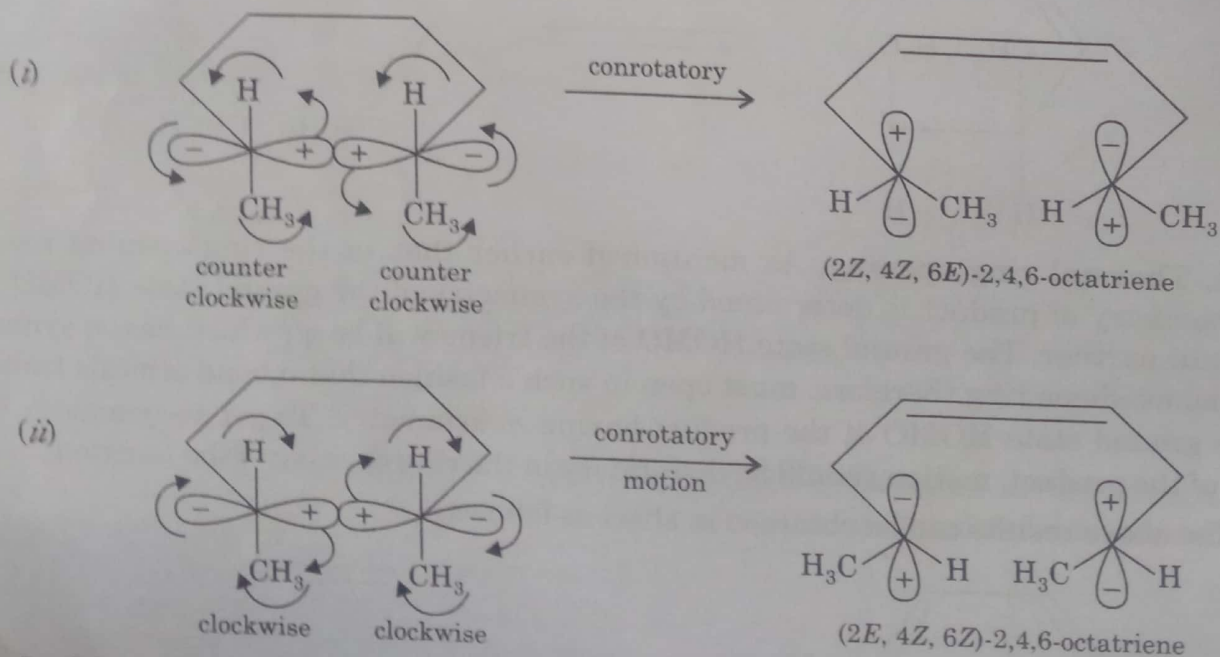
Two modes of disrotatory motions can take place as follows :



Thus the thermal process is disrotatory with two possible products, one is major and the other is minor due to the steric reasons.

B. Photo-Induced ring opening. The photo state HOMO of the triene system is ψ_4^* which has C_2 symmetry. To get C_2 symmetry in the product, motion should be conrotatory in the ring opening reaction.

Consider the two modes of conrotatory motions :



In this case either possible conrotation giving the same product.

2. Thermal electrocyclic reaction given by (2E, 4Z, 6Z, 8E)-2,4,6,8-decatetraene
The thermally induced electrocyclic reaction of (2E, 4Z, 6Z, 8E)-2,4,6,8-decatetraene is an elegant example of electrocyclic reaction.