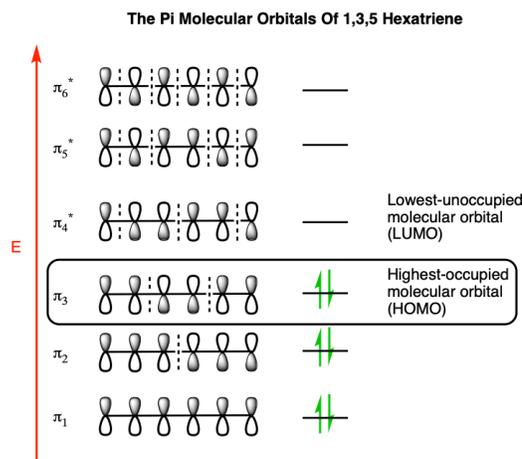


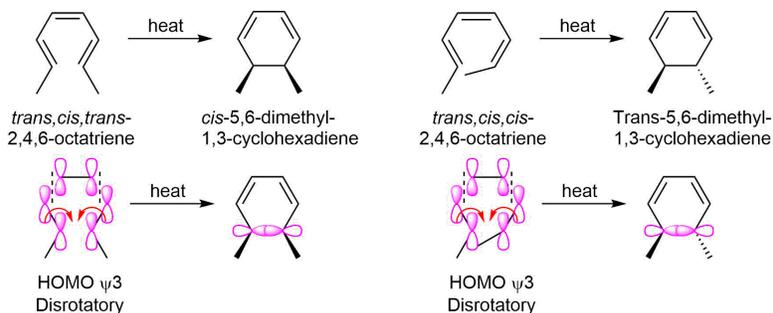
15.4: STEREOCHEMISTRY OF THERMAL ELECTROCYCLIC REACTIONS

Frontier orbital theory can be used to predict the stereochemistry of electrocyclic reactions. Electrons in the HOMO are the highest energy and therefore the most easily moved during a reaction. A molecular orbital diagram can be used to determine the orbital symmetry of a conjugated polyene's HOMO. Thermal reactions utilize the HOMO from the ground-state electron configuration of the molecular orbital diagram while photochemical reactions utilize the HOMO in the excited-state electron configuration.

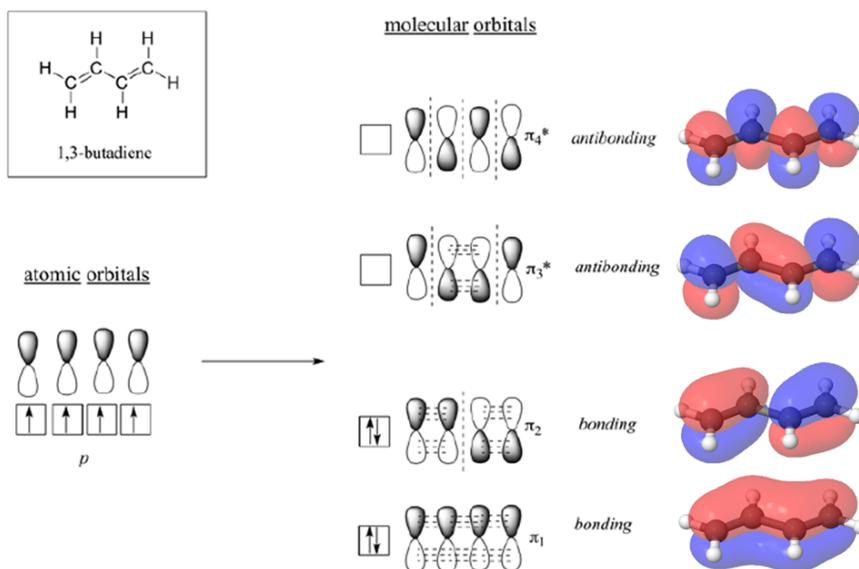
The molecular orbital of 1,3,5-hexatriene in its ground state electron configuration has ψ_3 as its HOMO. The terminal molecular orbital lobes of the HOMO with the same sign are on the same side which predicts disrotatory ring closure under thermal conditions.



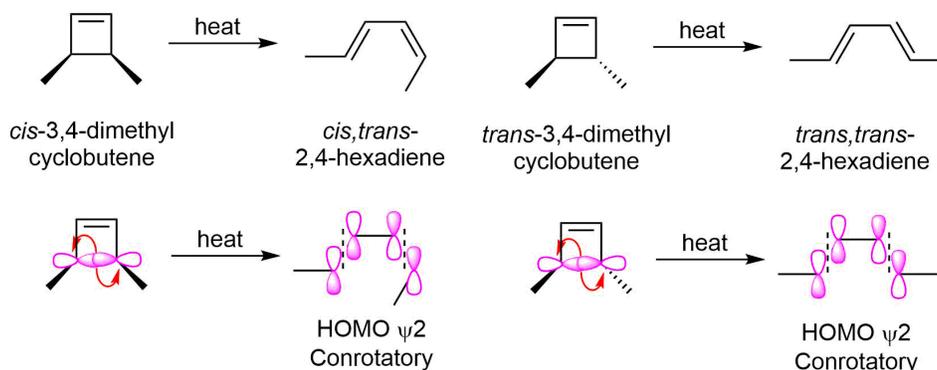
Disrotatory cyclization is observed during the electrocyclic reaction of 2,4,6-octatriene. The *trans,cis,cis*-2,4,6-octatriene isomer produces *cis*-5,6-dimethyl-1,3-cyclohexadiene as the product of thermal cyclization while the *trans,cis,cis*-2,4,6-octatriene isomer produces *trans*-5,6-dimethyl-1,3-cyclohexadiene.



The molecular orbital of a conjugated diene, such as 1,3-butadiene has ψ_2 as the HOMO in its ground state electron configuration. The terminal molecular orbital lobes of the HOMO with the same sign are on opposite sides which predicts conrotatory ring closure under thermal conditions. However, the equilibrium of the electrocyclic reaction only allows for the ring opening to be observed.



Thus heating *cis*-3,4-dimethylcyclobutene causes the conrotatory ring opening to form *cis,trans*-2,4-hexadiene. Likewise, *trans*-3,4-dimethylcyclobutene forms *trans,trans*-2,4-hexadiene when heated.



A pattern begins to form revealing a relationship between the number of double bonds in the conjugated polyene and the rotation during electrocyclic reactions. For thermal electrocyclic reactions, polyenes with an odd number of double bonds undergo disrotation and those with an even number of double bond undergo conrotation.

? EXERCISE 15.4.1

- 1) The thermal electrocyclic ring opening of *trans*-3,4-dimethylcyclobutene could form *trans,trans*-2,4-hexadiene or *cis,cis*-2,4-hexadiene. However, the *trans,trans*-2,4-hexadiene is the isomer obtained from the reaction. Explain how it is possible to get both products and why the *trans,trans*-2,4-hexadiene is preferred.
- 2) If a conjugated tetraene were to undergo a thermal electrocyclic reaction would the orbital nodes undergo con or disrotation?

Answer

- 1) Dienes undergo conrotation during thermal electrocyclic ring opening. Conrotation means the orbital nodes both rotate in the same direction either both clockwise or both counter clockwise. If the nodes both rotate counter clockwise the *trans,trans*-2,4-hexadiene isomer forms. If they both rotate clockwise the *cis,cis*-2,4-hexadiene isomer is formed. Trans double bonds are more stable than cis due to steric strain. The *trans,trans*-2,4-hexadiene is preferably formed because it is more stable.
- 2) A tetraene has an even number of double bonds so it would be expected to undergo conrotation.