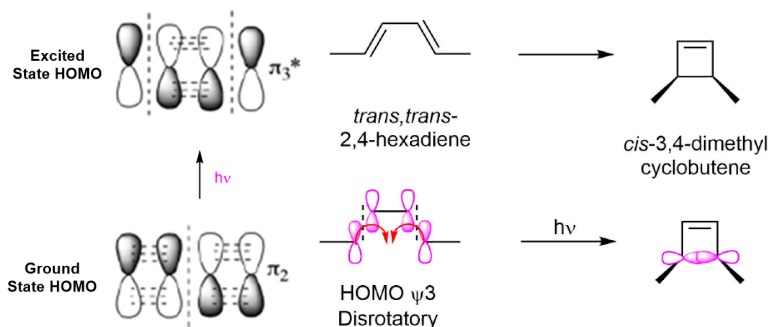
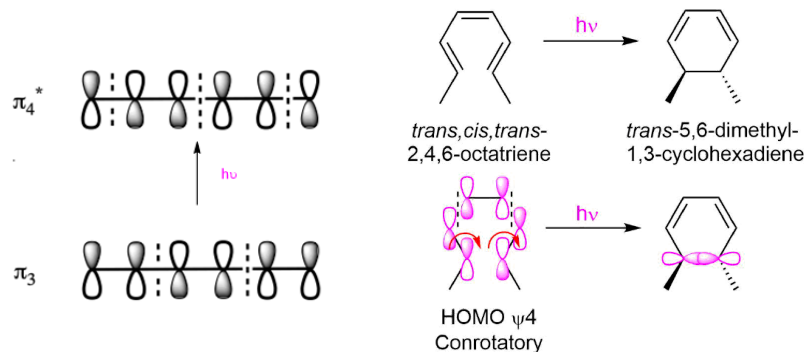


## 15.5: PHOTOCHEMICAL ELECTROCYCLIC REACTIONS

As discussed in **Section 30.1**, irradiation of a conjugated polyene with ultraviolet light causes an electron from the ground-state HOMO to be excited to the ground state LUMO. This creates a new higher energy HOMO in an electron configuration called the excited state. Electron excitation changes the symmetry of the new HOMO which has a corresponding effect on the reaction stereochemistry. Under photochemical reaction conditions conjugated dienes undergo disrotatory cyclization whereas under thermal conditions they undergo conrotatory cyclization. Likewise, conjugated trienes undergo conrotatory photochemical cyclization while undergoing disrotatory thermal cyclization. For example, *trans,trans*-2,4-hexadiene undergoes conrotatory photochemical cyclization to form *cis*-3,4-dimethylcyclobutene.



The conjugated triene, *trans,cis,trans*-2,4,6-octatriene undergoes conrotation to form *trans*-5,6-dimethyl-1,3-cyclohexadiene during photochemical cyclization.



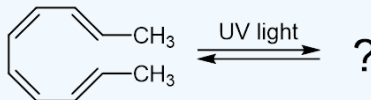
### GENERALIZED STATEMENT OF WOODWARD-HOFFMANN RULES FOR ELECTROCYCLIC REACTIONS

Thermal and photochemical electrocyclic reactions always produce the opposite stereochemistry products due to the difference in symmetries in their HOMO frontier orbitals. This idea can be combined with the trend of even and odd polyenes to provide simple rules to predict the stereochemistry of electrocyclic reactions.

Number of Double Bonds	Thermal	Photochemical
Odd	Disrotatory	Conrotatory
Even	Conrotatory	Disrotatory

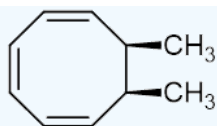
#### ? EXERCISE 15.5.1

Would the following electrocyclic reaction be con or disrotatory? Please draw the expected product.



#### Answer

An even number of double bonds in photochemical conditions predicts a disrotatory reaction.



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