

15.3: ELECTROCYCLIC REACTIONS

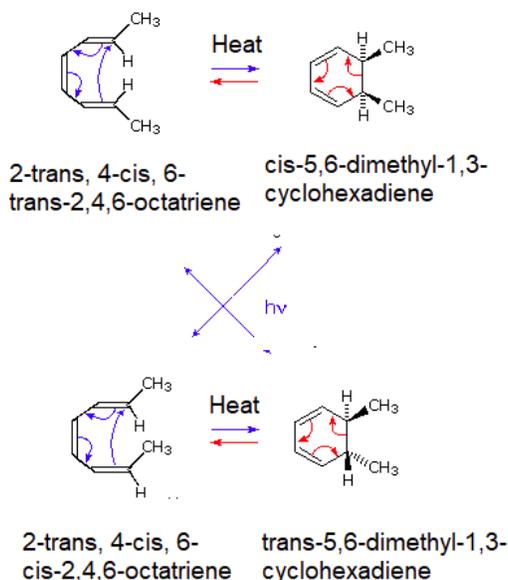
An electrocyclic reaction is the concerted cyclization of a conjugated π -electron system by converting one π -bond to a ring forming σ -bond. The key sigma bond must be formed at the terminus of a pi system. These reactions classified by the number of pi electrons involved. Thus, 4 pi reactions form 4 membered rings, as in a conjugated diene can be converted into a cyclobutene. Also, 6 pi reactions form 6 membered rings as in a conjugated triene can be converted into a cyclohexadiene. These reactions are often reversible with the reverse reaction may be called *electrocyclic ring opening*. Although more pi electrons can be used, the 4 pi and 6 pi variants are by far the most common and are illustrated below with the key sigma bond highlighted in magenta.



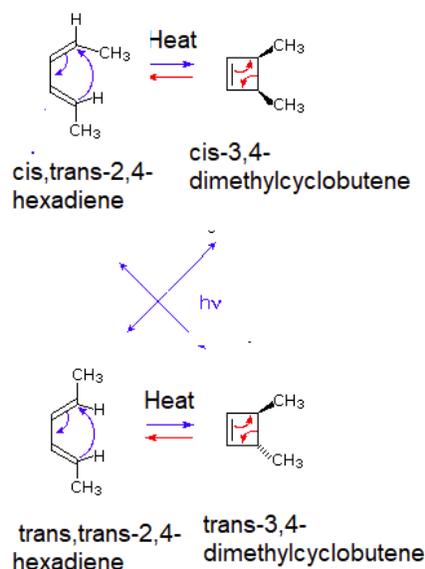
6 pi Electrocyclic Reaction

4 pi Electrocyclic Reaction

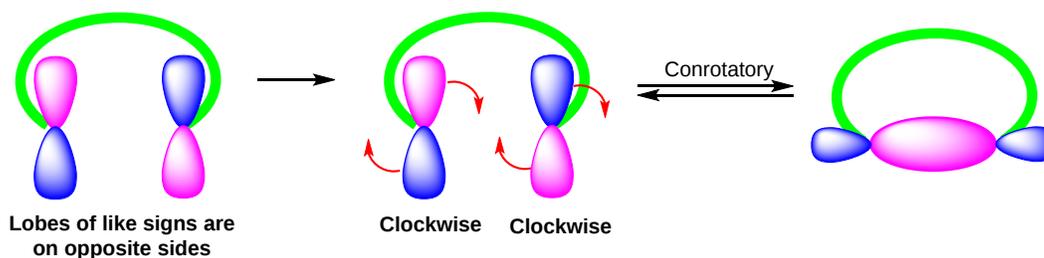
A striking feature of electrocyclic reactions that proceed by concerted mechanisms is their high degree of stereospecificity. For example, *2-trans, 4-cis, 6-trans-2,4,6-octatriene* undergoes ring closure to *cis-5,6-dimethyl-1,3-cyclohexadiene* under thermal conditions i.e. when heated. Similarly the isomeric *2-trans, 4-cis, 6-cis-2,4,6-octatriene* produces *trans-5,6-dimethyl-1,3-cyclohexadiene*, as noted below. However these results are completely reversed if the reaction is run under photochemical conditions (Irradiation with ultraviolet light). For example if *2-trans, 4-cis, 6-cis-2,4,6-octatriene* is irradiated with UV light *cis-5,6-dimethyl-1,3-cyclohexadiene* would be produced.



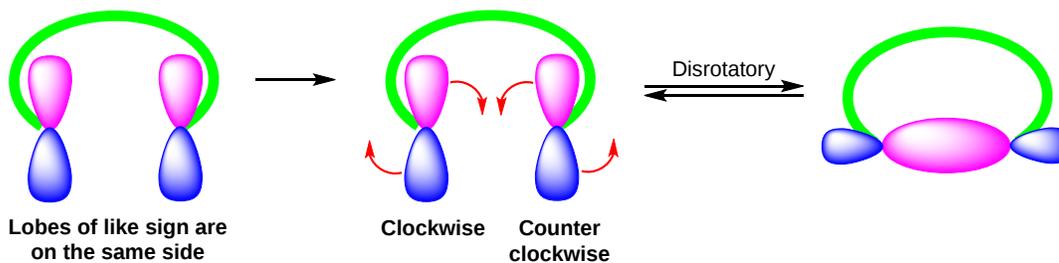
Similar results are seen with the 4 pi electrocyclic reaction of *cis,trans-2,4-hexadiene* being heated to exclusively form *cis-3,4-dimethylcyclobutene* and being irradiated with UV light to exclusively form *trans-3,4-dimethylcyclobutene*. Likewise, *trans,trans-2,4-hexadiene* forms *trans-3,4-dimethylcyclobutene* when heated and *cis-3,4-dimethylcyclobutene* when being irradiated with UV light.



The stereospecificity of electrocyclic reaction can be explained by considering the terminal lobes of the molecular orbital for the conjugated π -electron system. For electrocyclic reactions to occur, molecular orbital lobes with the same sign from the HOMO of the molecule must rotate to form/break the key ring sigma bond. If the orbital lobes involved both rotate in the same direction (both counterclockwise or both clockwise), the process is called conrotatory. This typically occurs when orbital lobes of the same sign are on opposite sides of the molecule.



If the orbitals involved rotate in opposite directions (one clockwise and one counterclockwise), the process is called disrotatory. These differences in rotation are critically important when stereocenters are formed or broken. This typically occurs when orbital lobes of the same sign are on the same side of the molecule.



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