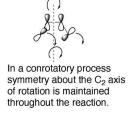# Question #72514, Chemistry / Organic Chemistry

Explain the electrocyclic and sigmatropic reaction in detail.
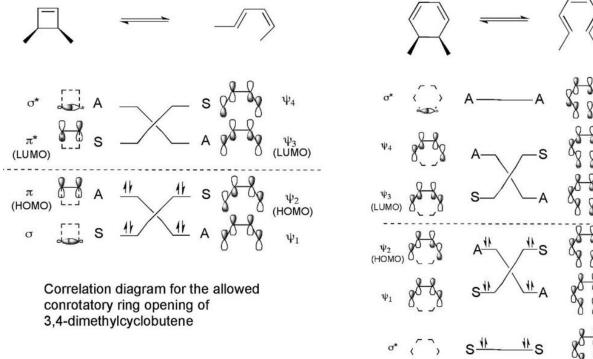
Answer:

In organic chemistry, an **electrocyclic reaction** is a type of pericyclic rearrangement where the net result is one pi bond being converted into one sigma bond or vice versa. The Diels-Alder reaction is a common example. The especially interesting thing about this reaction is its stereochemistry. When performing an electrocyclic reaction, it is often desirable to predict the cis/trans geometry of the reaction's product. The first step in this process is to determine whether a reaction proceeds through conrotation or disrotation. Reactions can be either photochemical or thermal and their mexanisms are different.

Mechanism of thermal reactions:

In a conrotatory process symmetry about the C_2 axis of rotation is maintained throughout the reaction.

In a disrotatory process symmetry about the σ_v reflection plane is maintained throughout the reaction.

Correlation diagrams, which connect the molecular orbitals of the reactant to those of the product having the same symmetry, can then be constructed for the two processes.

Correlation diagram for the allowed conrotatory ring opening of 3,4-dimethylcyclobutene

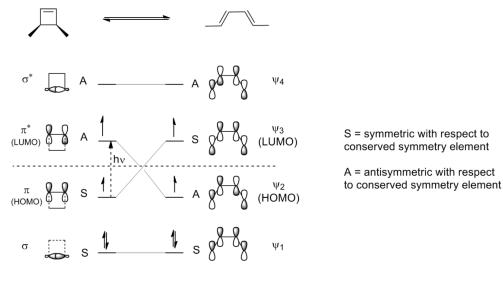Correlation diagram for the allowed disrotatory ring opening of 5,6-dimethylcyclohexa-1,3-diene

S = symmetric to symmetry element
A = antisymmetric to symmetry element
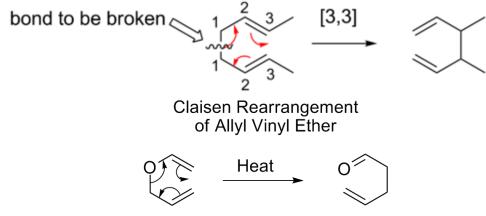
Mechanism of photochemical reactions:

If the ring opening of 3,4-dimethylcyclobutene were carried out under photochemical conditions the resulting electrocyclization would be occur via a disrotatory mode instead of a conrotatory mode as can be seen by the correlation diagram for the allowed excited state ring opening reaction.

σ^*	A ——————— A	ψ_4
π^* (LUMO)	A	S ψ_3 (LUMO)
	hv	
π (HOMO)	S	A ψ_2 (HOMO)
σ	S	S ψ_1

S = symmetric with respect to conserved symmetry element

A = antisymmetric with respect to conserved symmetry element

correlation diagram for the excited state disrotatory
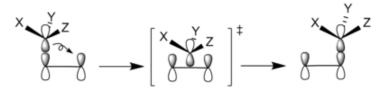ring-opening *cis*-3,4-dimethylcyclobutene

A sigmatropic reaction in organic chemistry is a pericyclic reaction wherein the net result is one σ-bond is changed to another σ-bond in an uncatalyzed intramolecular process. The most well-known of the sigmatropic rearrangements are the [3,3] Cope rearrangement, Claisen rearrangement, Carroll rearrangement

[3,3] sigmatropic shifts are well studied sigmatropic rearrangements. The Woodward–Hoffman rules predict that these six electron reactions would proceed suprafacially, via a Huckel topology transition state.. A convenient means of determining the order of a given sigmatropic rearrangement is to number the atoms of the bond being broken as atom 1, and then count the atoms in each direction from the broken bond to the atoms that form the new σ-bond in the product, numbering consecutively. The numbers that correspond to the atoms forming the new bond are then separated by a comma and placed within brackets to create the sigmatropic reaction order descriptor

Claisen Rearrangement
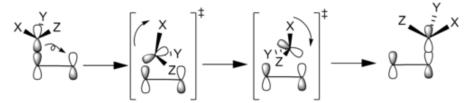of Allyl Vinyl Ether

In principle, all sigmatropic shifts can occur with either a retention or inversion of the geometry of the migrating group, depending upon whether the original bonding lobe of the migrating atom or its other lobe is used to form the new bond

Sigmatropic Shift with Retention of Stereochemistry

Sigmatropic Shift with Inversion of Stereochemistry

In cases of stereochemical retention, the migrating group translates without rotation into the bonding position, while in the case of stereochemical inversion the migrating group both rotates and translates to reach its bonded conformation. However, another stereochemical transition effect equally capable of producing inversion or retention products is whether the migrating group remains on the original face of the π system after rebonding or instead transfers to the opposite face of the π system. If the migrating group remains on the same face of the π system, the shift is known as suprafacial, while if the migrating group transfers to the opposite face is called an antarafacial shift, which are impossible for transformations that occur within small- or medium-sized rings.