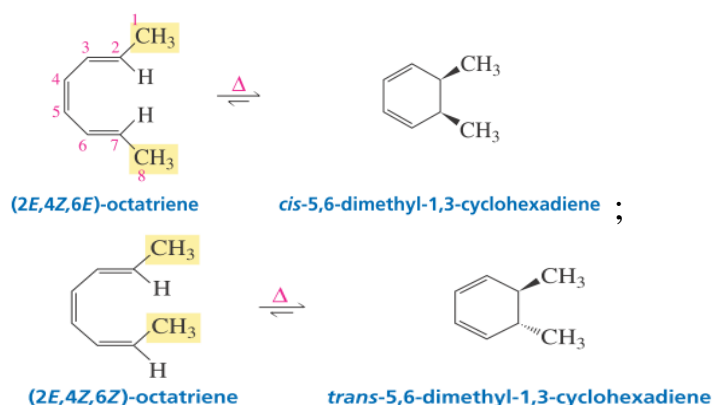


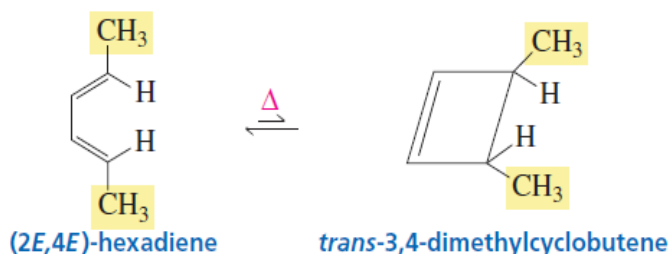
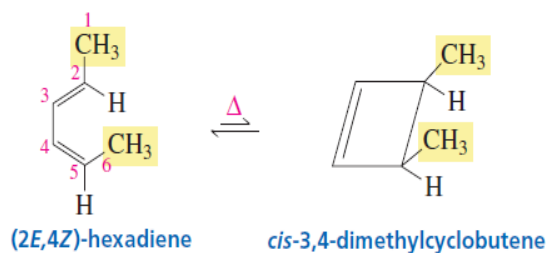
Electrocyclic Reactions

An electrocyclic reaction is an intramolecular reaction in which the rearrangement of electrons leads to a cyclic product that has one fewer π -bond than the reactant. An electrocyclic reaction is completely stereoselective—it preferentially forms one stereoisomer. For example, when (2E,4Z,6E)-octatriene undergoes an electrocyclic reaction under thermal conditions, only the cis product is formed; when (2E,4Z,6Z)-octatriene undergoes an electrocyclic reaction under thermal conditions, only the trans product is formed. Recall that E means the high-priority groups are on opposite sides of the double bond, and Z means the high-priority groups are on the same side of the double bond.

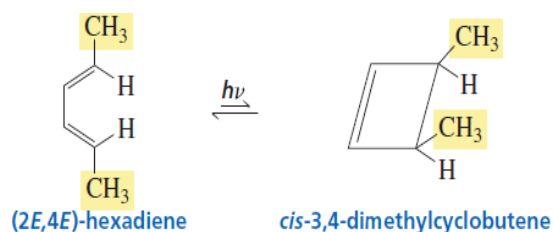
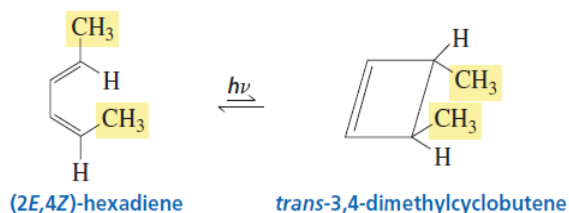


However, when the reactions are carried out under photochemical conditions, the products have opposite configurations: The compound that forms the cis isomer under thermal conditions forms the trans isomer under photochemical conditions, and the compound that forms the trans isomer under thermal conditions forms the cis isomer under photochemical conditions.

Under thermal conditions, (2E,4Z)-hexadiene cyclizes to cis-3,4-dimethylcyclobutene, and (2E,4E)-hexadiene cyclizes to trans-3,4-dimethylcyclobutene.



As we saw with the octatrienes, the configuration of the product changes if the reactions are carried out under photochemical conditions: The *trans* isomer is obtained from (2*E*,4*Z*)-hexadiene instead of the *cis* isomer; the *cis* isomer is obtained from (2*E*,4*E*)-hexadiene instead of the *trans* isomer.



Electrocyclic reactions are reversible. The cyclic compound is favored for electrocyclic reactions that form six-membered rings, whereas the open-chain compound is favored for electrocyclic reactions that form four-membered rings because of the angle strain and torsional strain associated with four-membered rings.

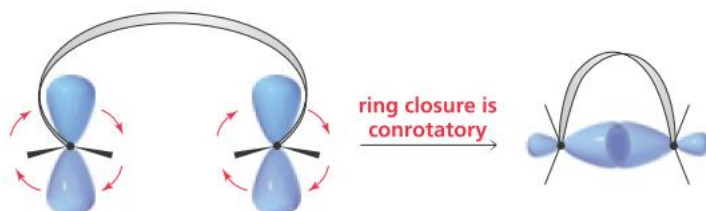
A photochemical reaction is one that takes place when a reactant absorbs light. A thermal reaction takes place without the absorption of light. Despite its name, a thermal reaction does not necessarily require more heat than what is available at room temperature. Some thermal reactions do require additional heat in order to take place at a reasonable rate, but others readily occur at, or even below, room temperature.

If a molecule absorbs light of an appropriate wavelength, the light will promote an electron from its ground-state HOMO to its LUMO. The

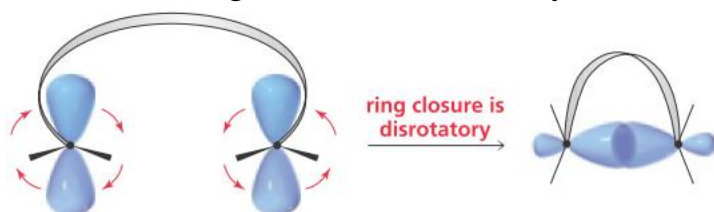
molecule is then in an excited state. In a thermal reaction the reactant is in its ground state; in a photochemical reaction the reactant is in an excited state.

Some molecular orbitals are symmetric and some are asymmetric (also called dissymmetric), and they are easy to distinguish. If the p orbitals at the ends of the molecular orbital are in-phase, the molecular orbital is symmetric. If the two end p orbitals are out-of phase, the molecular orbital is asymmetric.

The product of an electrocyclic reaction results from the formation of a new σ -bond. For this bond to form, the p orbitals at the ends of the conjugated system must rotate so they overlap head-to-head (and rehybridize to sp^3). Rotation can occur in two ways. If both orbitals rotate in the same direction (both clockwise or both counterclockwise), ring closure is conrotatory.

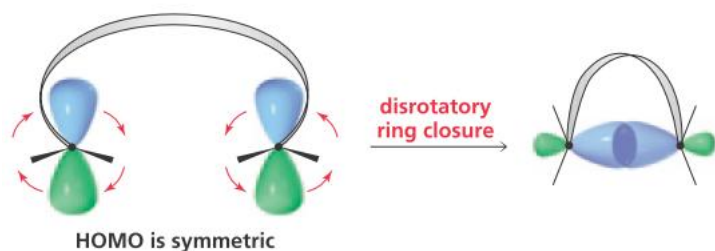


If the orbitals rotate in opposite directions (one clockwise, the other counterclockwise), ring closure is disrotatory.



The mode of ring closure depends on the symmetry of the HOMO of the compound undergoing ring closure. Only the symmetry of the HOMO is important in determining the course of the reaction because this is where the highest energy electrons are. These are the most loosely held electrons and therefore the ones most easily moved during a reaction.

To form the new σ bond, the orbitals must rotate so that in-phase p orbitals overlap, because in-phase overlap is a bonding interaction. Out-of-phase overlap would be an antibonding interaction. If the HOMO is symmetric (the end orbitals are identical), rotation will have to be disrotatory to achieve in-phase overlap. In other words, disrotatory ring closure is symmetry-allowed, whereas conrotatory ring closure is symmetry-forbidden.



If the HOMO is asymmetric, rotation has to be conrotatory in order to achieve in-phase overlap. In other words, conrotatory ring closure is symmetry-allowed, whereas disrotatory ring closure is symmetry-forbidden.

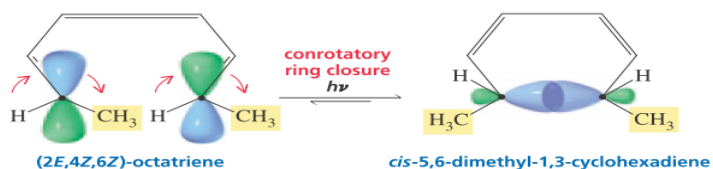
The ground-state HOMO of a compound with three conjugated π bonds, such as (2E,4Z,6E)-octatriene, is symmetric. This means that ring closure under thermal conditions is disrotatory. In disrotatory ring closure of (2E,4Z,6E)-octatriene, the methyl groups are both pushed up (or down), which results in formation of the cis product.



In disrotatory ring closure of (2E,4Z,6Z)-octatriene, one methyl group is pushed up and the other is pushed down, which results in formation of the trans product.



If the reaction takes place under photochemical conditions, we must consider the excited-state HOMO rather than the ground-state HOMO. The excited-state HOMO of a compound with three π bonds is asymmetric. Therefore, under photochemical conditions, (2E,4Z,6Z)-octatriene undergoes conrotatory ring closure, so both methyl groups are pushed down (or up) and the cis product is formed.

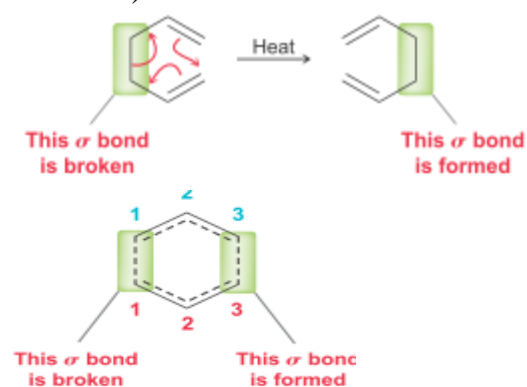


We have just seen why the configuration of the product formed under photochemical conditions is the opposite of the configuration of the product formed under thermal conditions: The ground-state HOMO is symmetric—so disrotatory ring closure occurs, whereas the excited-

state HOMO is asymmetric—so conrotatory ring closure occurs. Thus, the stereochemical outcome of an electrocyclic reaction depends on the symmetry of the HOMO of the compound undergoing ring closure.

Sigmatropic Rearrangements

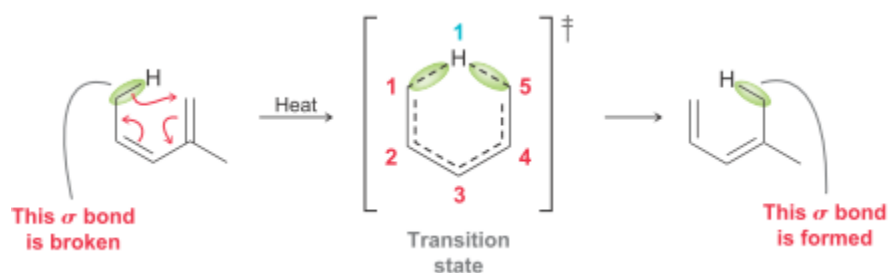
A sigmatropic rearrangement is a pericyclic reaction in which one σ bond is formed at the expense of another. In the process, the π bonds change their location. The term sigmatropic comes from the Greek word, tropos, which means “change.” A sigmatropic rearrangement is therefore a reaction in which a σ bond has undergone a change (in its location).



There are many different types of sigmatropic rearrangements. The previous example is called a [3,3] sigmatropic rearrangement. The two numbers in the brackets indicate the number of atoms separating the bond that is forming and the bond that is breaking in the transition state (Figure above).

Notice that the transition state is cyclic, which is a characteristic feature of all pericyclic reactions. In the transition state, the bond that is breaking and the bond that is forming are separated by two different pathways, each of which is comprised of three atoms (one path is labeled in red and the other in blue). Therefore, it is called a [3,3] sigmatropic rearrangement.

The following is an example of a [1,5] sigmatropic rearrangement, also sometimes referred to as a [1,5] hydrogen shift. In the transition state, the bond that is breaking and the bond that is forming are separated by two different pathways: one is comprised of five atoms (labeled in red), and the other is comprised of only one atom (labeled in blue).



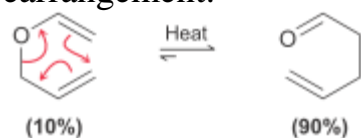
The Cope Rearrangement

A [3,3] sigmatropic rearrangement is called a Cope rearrangement when all six atoms of the cyclic transition state are carbon atoms. The equilibrium for a Cope rearrangement generally favors formation of the more substituted alkene. In the example below, both π bonds of the reactant are monosubstituted, but in the product, one of the π bonds is disubstituted. For this reason, the equilibrium for the reaction favors the product.

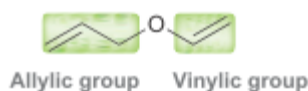


The Claisen Rearrangement

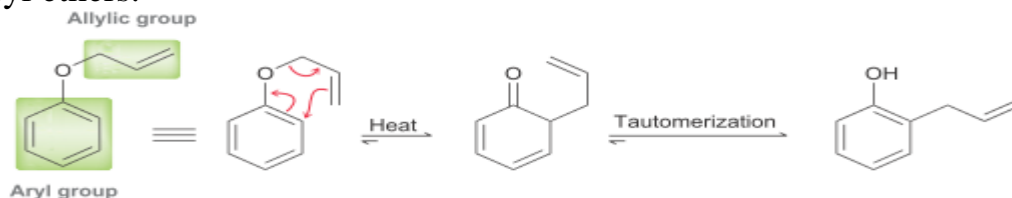
The oxygen analogue of a Cope rearrangement is called a Claisen rearrangement.



The Claisen rearrangement is a [3,3] sigmatropic rearrangement and is commonly observed for allylic vinylic ethers.



The equilibrium greatly favors the product because of formation of a C=O bond, which is thermodynamically more stable (lower in energy) than a C=C bond. The Claisen rearrangement is also observed for allylic aryl ethers.



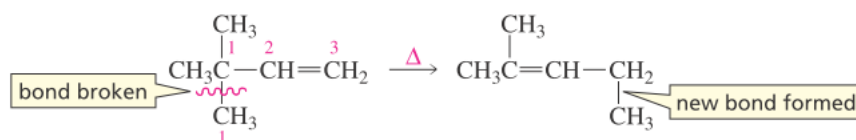
Aryl groups possess an aromatic ring (a six-membered ring drawn with alternating double and single bonds), which is particularly stable. In the case of allylic aryl ethers, the Claisen rearrangement initially destroys the aromatic ring but is rapidly followed by a spontaneous tautomerization process that

regenerates the aromatic ring. In this tautomerization process, the conversion of a ketone into an enol is a testament to the stability of the aromatic ring system.

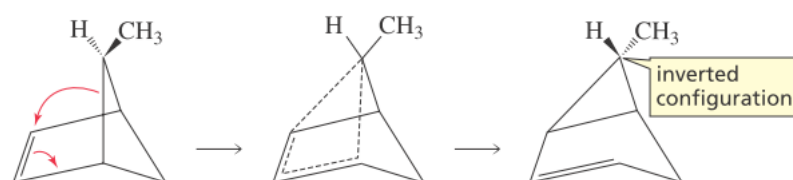
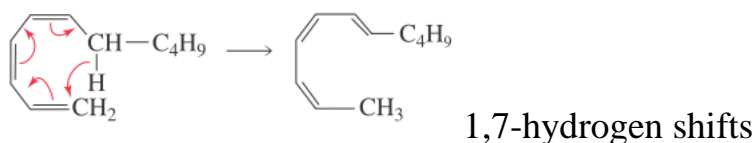
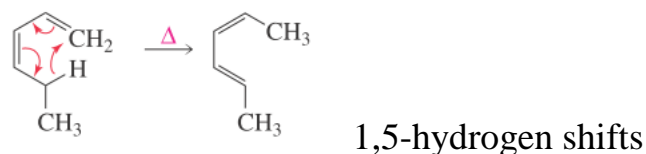
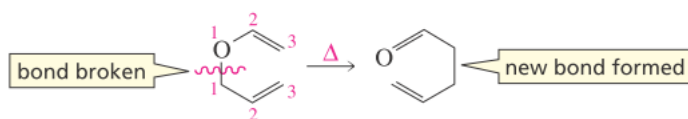
A [1,3] sigmatropic rearrangement involves a π bond and a pair of σ electrons, or we can say that it involves two pairs of electrons. A [1,5] sigmatropic rearrangement involves two π bonds and a pair of σ electrons (three pairs of electrons), and a [1,7] sigmatropic rearrangement involves four pairs of electrons. The symmetry rules for sigmatropic rearrangements are nearly the same as those for cycloaddition reactions the only difference is that we count the number of pairs of electrons rather than the number of π bonds? Recall that the ground-state HOMO of a compound with an even number of conjugated double bonds is asymmetric, whereas the ground-state HOMO of a compound with an odd number of conjugated double bonds is symmetric.

Examples :

a [1,3] sigmatropic rearrangement



a [3,3] sigmatropic rearrangement



carbon

Migration of