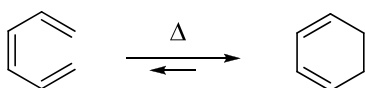


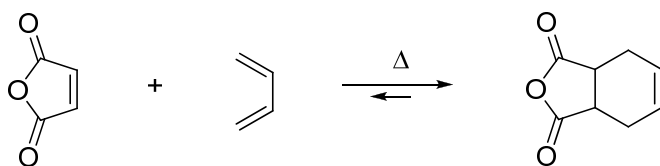
Chapter 29 Information

There are three types of organic reactions.

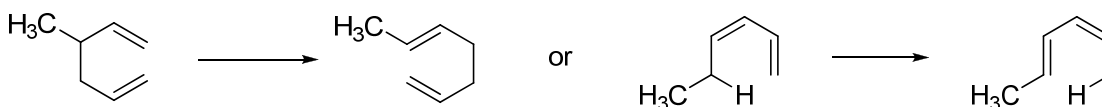
1. Polar reactions. These are of the S_N1/S_N2 /EAS/etc. type; a nucleophile reacts with an electrophile, and both electrons in the new bond come from the nucleophile.
2. Radical reactions. A new bond is formed using one electron from each of the reactants.
3. Pericyclic reactions. The electrons in one or more reactants are reorganized in a cyclic manner. There are three major types.
 - a. *Electrocyclic*. An intramolecular reaction in which a new sigma bond is formed between the ends of a conjugated pi system. The product is cyclic, with one more ring and one less pi bond than the starting material. These reactions are reversible.



- b. *Cycloaddition*. Two different molecules, each containing at least one pi bond, react to form a cyclic compound. Each loses a pi bond, and two new sigma bonds are formed. The Diels-Alder reaction is a classic cycloaddition.



- c. *Sigmatropic rearrangement*. A sigma bond is broken, a new sigma bond is formed, and the pi bonds rearrange.



Features of pericyclic reactions include:

- They are concerted reactions. Therefore there is one transition state and no intermediate.
- They are highly stereoselective (because they are concerted).
- They are generally not affected by catalysts or by changes in the solvent.

The configuration of the product is determined by:

- The configuration of the starting material(s).
- The number of pi electrons (whether conjugated pi bonds or lone pairs) in the reacting system.
- Whether the reaction is done under thermal or photochemical conditions.
 - Photochemical: when the reactant absorbs light (usually indicated with $h\nu$).
 - Thermal: when the reactant does not absorb light (doesn't always mean heat is explicitly added).

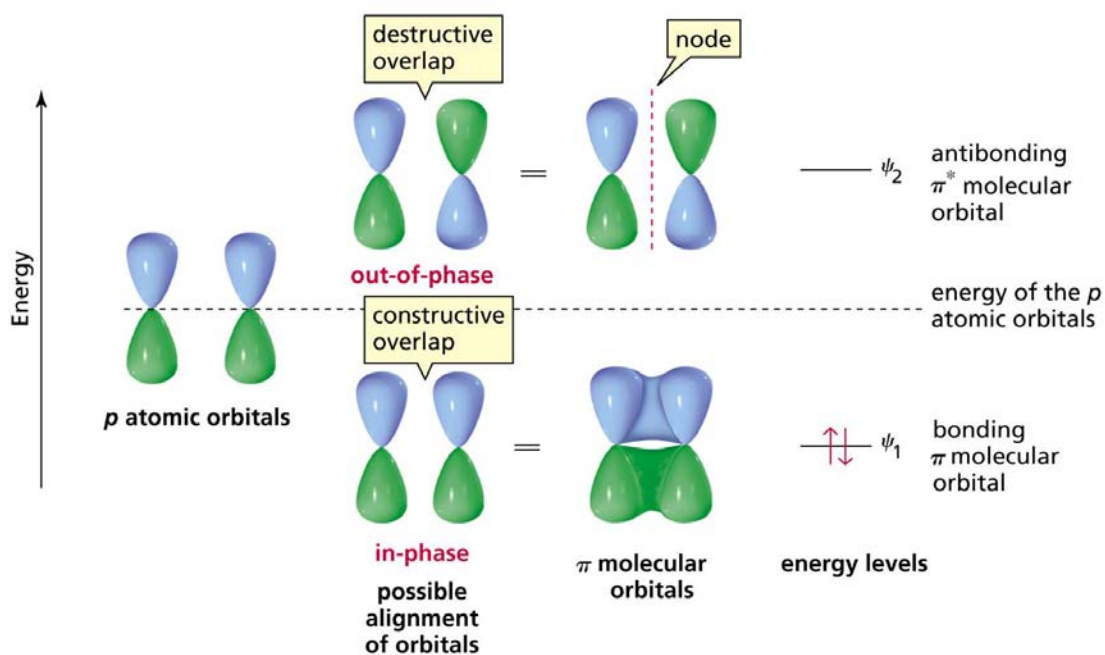
It took a long time before chemists figured out pericyclic reactions. Some work only photochemically; some work only thermally; some work under both sets of conditions. Why is that? The answer came in 1965 – R.B. Woodward and Roald Hoffmann (both at Harvard at the time) came up with the “conservation of orbital symmetry” theory. This theory is based on the “frontier molecular orbital” theory proposed by Fukui in 1954, and states that “*in-phase orbitals overlap during the course of a pericyclic reaction*”. To understand this, we need to review some basic molecular orbital theory.

Review sections 1.6 and 7.8 in the textbook.

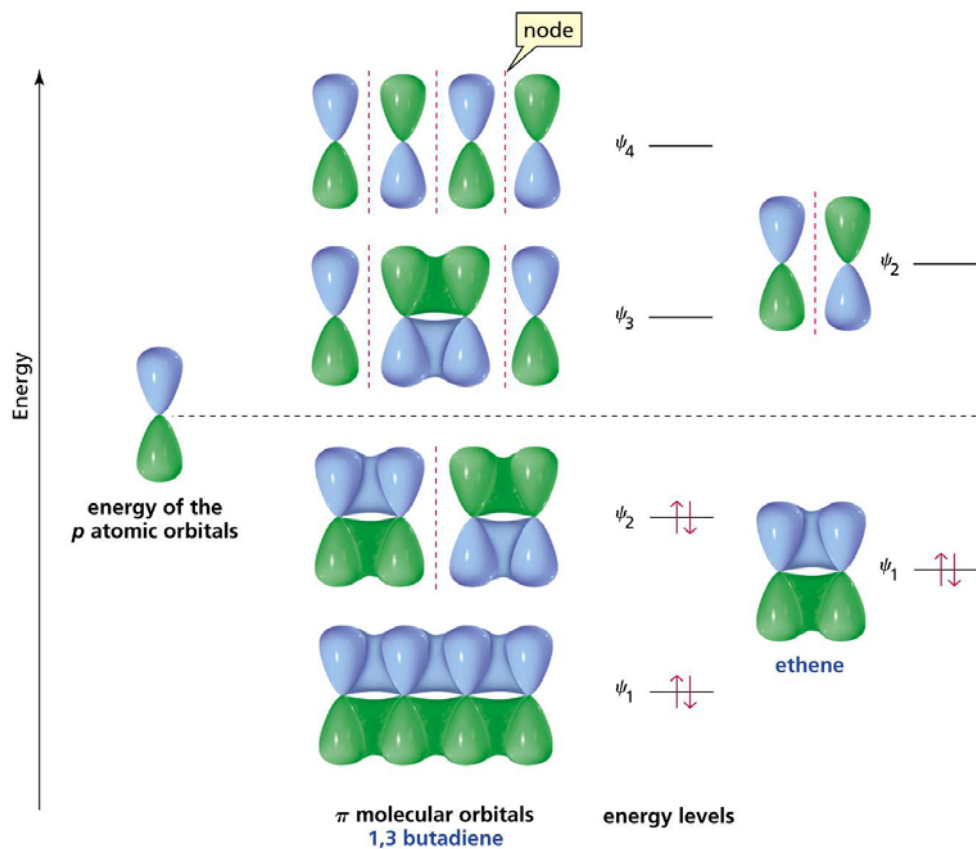
- Focusing on the pi system, we know that the two lobes of a p-orbital have opposite phases. If the lobes of two orbitals overlap in-phase, a bond is formed. If they overlap out of phase, a node is formed.
- Molecular orbitals fill according to Hund's Rule, the Pauli Exclusion Principle, and the aufbau principle.
- Because the p-orbitals (and the pi system) is perpendicular to the sigma framework, we can treat the pi system independently of the sigma framework.
- We describe molecular orbitals as linear combinations of atomic orbitals (LCAO). For every atomic orbital that is put in, a molecular orbital results.

Draw example MO schemes (see next pages) and identify bonding, antibonding, HOMO, LUMO, nodes, symmetric, asymmetric.

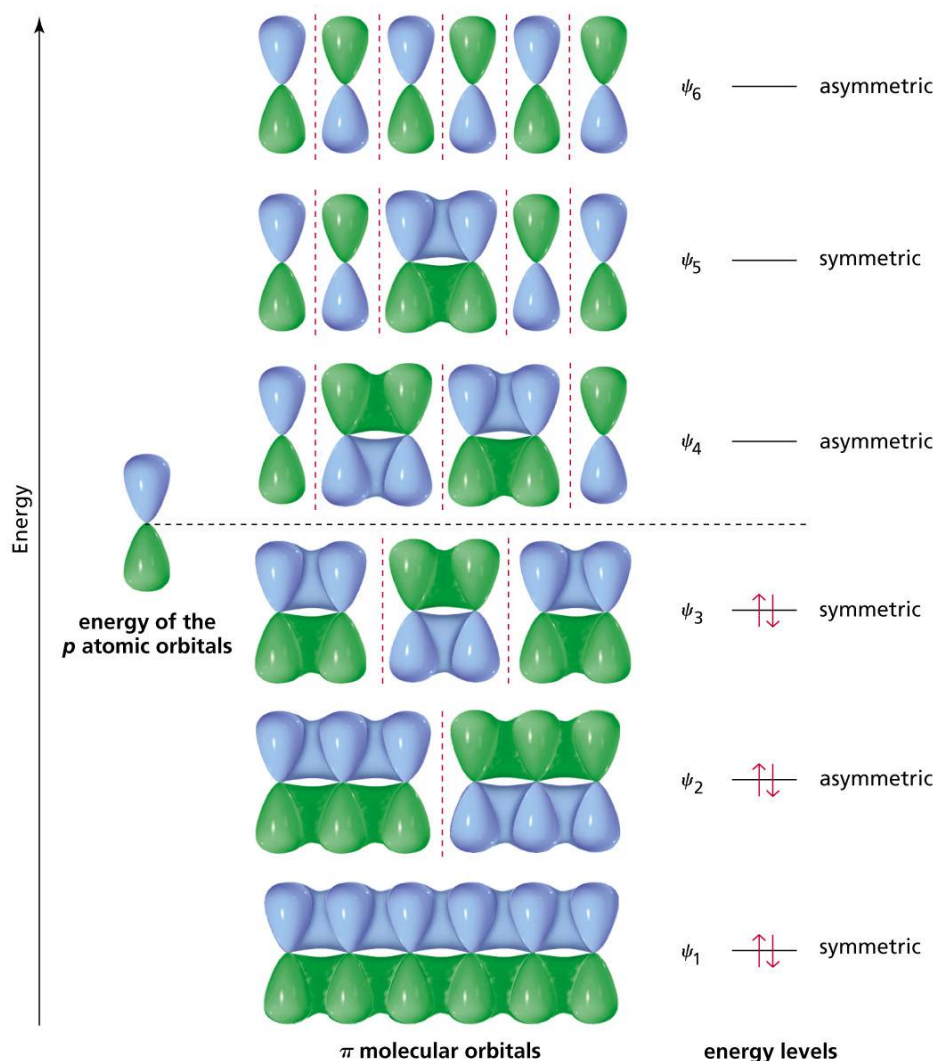
Draw the MO scheme for ethylene.



Draw the MO scheme for 1,3-butadiene.



Draw the MO scheme for 1,3,5-hexatriene.



The normal electronic configuration is the ground state. If a molecule absorbs light of the appropriate wavelength, an electron will be promoted from the HOMO to the LUMO (these are called the “Frontier Orbitals”), resulting in an excited state (with a new HOMO and a new LUMO).

In a thermal reaction, the molecule is in the ground state. In a photochemical reaction, the molecule is in the excited state.

This is important, because by knowing the difference between the thermal and photochemical reactive molecular orbital, you can determine the way in which the orbitals forming the new sigma bond(s) must overlap in order to form a bond (constructive overlap).

Conrotatory – both orbitals are rotating in the same direction.

Disrotatory – the orbitals are rotating in opposite directions.

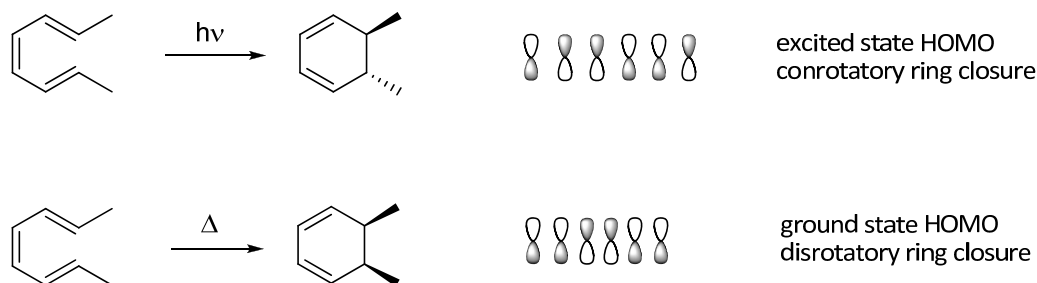
The mode of ring closure depends on the symmetry of the HOMO of the compound undergoing ring closure, because that is where the highest-energy electrons are located, and these are the electrons that react.

Now let's look at the three types of pericyclic reactions from an MO perspective.

1. Electrocyclic reactions.

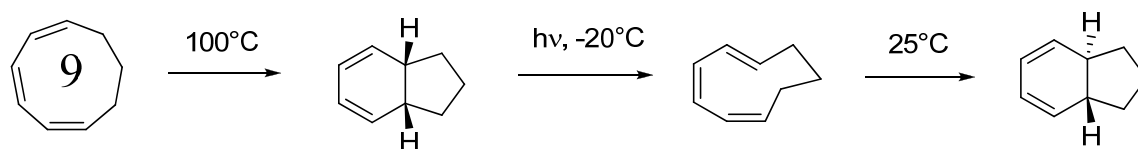
- Symmetric HOMO \rightarrow disrotatory ring closure is symmetry-allowed (in-phase orbitals will overlap); Conrotatory is symmetry-forbidden (out-of-phase orbitals would overlap).
- Asymmetric HOMO \rightarrow conrotatory ring closure is symmetry-allowed; Disrotatory is symmetry-forbidden.

Consider 1,3,5-hexatriene, under both photochemical and thermal conditions.



Notice that the photochemical reaction goes via the excited state, and that particular HOMO is asymmetric. The thermal reaction goes via the ground state HOMO, and that one is symmetric.

Look at what the different modes of ring closure do to the stereochemistry of the product. Also note that, because of the "principle of microscopic reversibility" these same rules hold for the ring-opening reverse reactions.

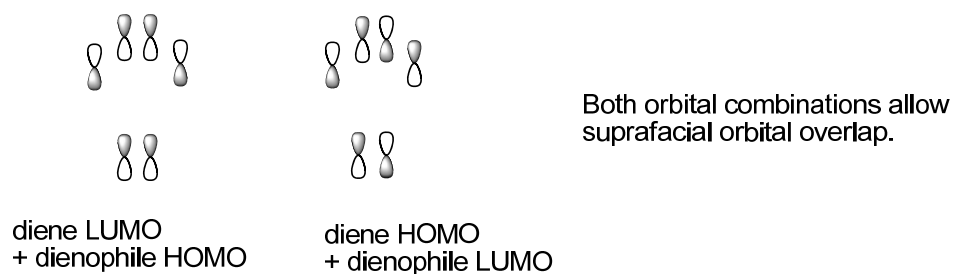


The first step is thermal; therefore undergoes a disrotatory ring closure resulting in a *cis* ring fusion. The photochemical ring opening is conrotatory, and changes the stereochemistry of one of the double bonds. Therefore, when the thermal ring closure is done again, the disrotatory ring closure gives a *trans* ring fusion in the final product.

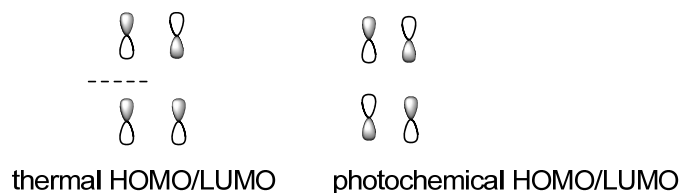
2. Cycloaddition reactions. These are classified as to the number of π electrons that interact to give the product. For example, a Diels-Alder reaction is an example of a [4+2] cycloaddition.

- The orbitals of one reactant must overlap with the orbitals of the other reactant. Therefore we must know the symmetry of the frontier molecular orbitals for both reactants.
- Two modes of overlap.
 - Suprafacial – both new sigma bonds form on the same side of the π system. Cycloadditions that form small rings (4, 5, 6) must be suprafacial due to geometric constraints.
 - Antarafacial – the two new sigma bonds form on opposite sides of the π system.

- c. Use the LUMO of one pi system and the HOMO of the other pi system. Look at a [4+2]:



Now look at a [2+2]: it works under photochemical conditions, but not under thermal.



3. Sigmatropic rearrangements. These all involve a migration of some sort. The migrating group can slide from one orbital to another in either a suprafacial or an antarafacial fashion (similar to cycloadditions). Sigmatropic rearrangements have cyclic transition states; since many are 6 e⁻ or less, they are required to be suprafacial because of the geometric constraints of small rings.