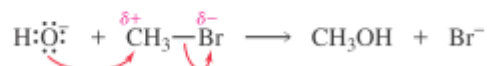


Pericyclic Reactions

Reactions of organic compounds can be divided into three classes: **polar reactions**, **radical reactions**, and **pericyclic reactions**. A polar reaction is one in which a nucleophile reacts with an electrophile. Both electrons in the new bond come from the nucleophile.

a polar reaction



A radical reaction is one in which a new bond is formed using one electron from each of the reactants.

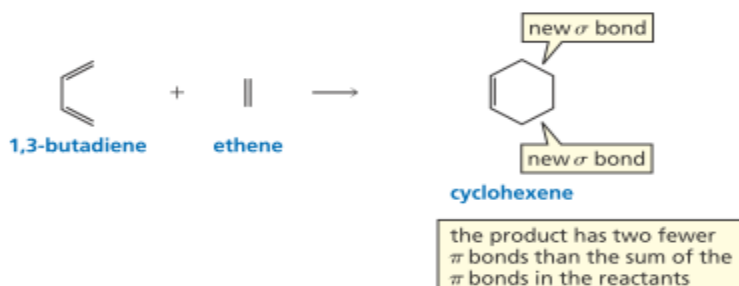
a radical reaction



A pericyclic reaction occurs as a result of reorganizing the electrons in the reactant(s). Three most common types of pericyclic reactions are **cycloaddition reactions**, **electrocyclic reactions**, and **sigmatropic rearrangements**.

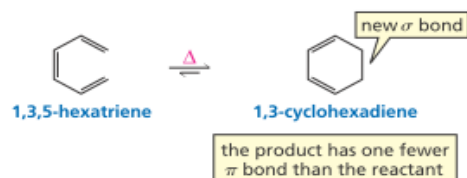
In a **cycloaddition reaction**, two different π -bond containing molecules react to form a cyclic compound. Each of the reactants loses a π -bond, and the resulting cyclic product has two new σ -bonds. The Diels–Alder reaction is a familiar example of a cycloaddition reaction.

a cycloaddition reaction

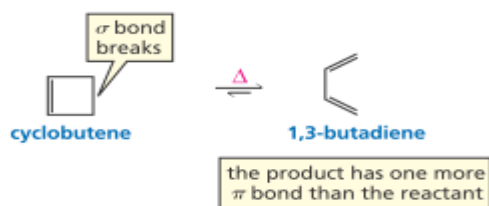


An **electrocyclic reaction** is an intramolecular reaction in which a new σ -bond is formed between the ends of a conjugated π -system. The product is a cyclic compound that has one more ring and one fewer π -bond than the reactant.

an electrocyclic reaction



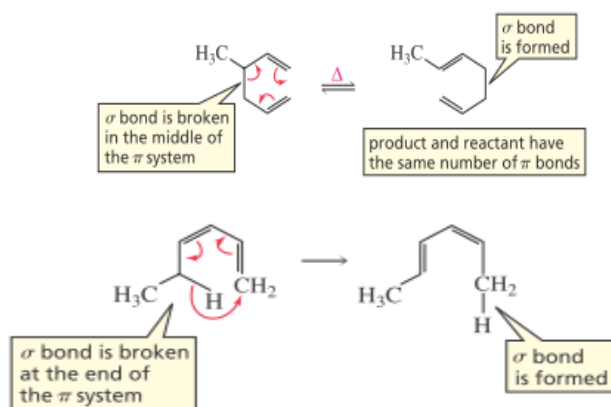
Electrocyclic reactions are reversible. In the reverse direction, an electrocyclic reaction is one in which a σ -bond in a cyclic reactant breaks, forming a conjugated π -system that has one more π -bond than the cyclic reactant.



In a **sigmatropic rearrangement**, a σ -bond is broken in the reactant, a new σ -bond is formed in the product, and the π -bonds rearrange. The number of π -bonds does not change.

The σ -bond that is broken can be in the middle of the π -system or at the end of the π -system. The π -system consists of the double-bonded carbons and the carbons immediately adjacent to them.

sigmatropic rearrangements



Notice that **electrocyclic reactions** and **sigmatropic rearrangements** occur within a single π -system they are intramolecular reactions. In contrast, cycloaddition reactions involve the interaction of two different π -systems, they are usually intermolecular reactions. The three kinds of pericyclic reactions share the following common features:

- They are all concerted reactions. This means that all the electron reorganization takes place in a single step. Therefore, there is one transition state and no intermediate.
- Because the reactions are concerted, they are highly stereoselective.
- The reactions are generally not affected by catalysts.

The configuration of the product formed in a pericyclic reaction depends on:

- the configuration of the reactant
- the number of conjugated double bonds or pairs of electrons in the reacting system
- whether the reaction is a thermal reaction or a photochemical reaction

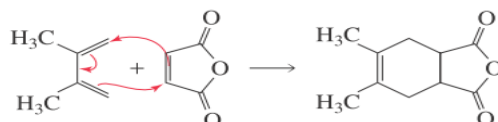
Table below for a comparison of the number of bonds broken and formed in each of the three major types of pericyclic reactions:

	CHANGE IN THE NUMBER OF σ BONDS	CHANGE IN THE NUMBER OF π BONDS
Cycloaddition	+2	-2
Electrocyclic	+1	-1
Sigmatropic	0	0

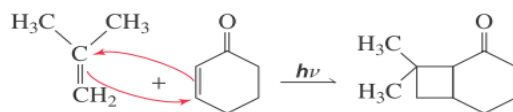
Cycloaddition Reactions

In a cycloaddition reaction, two different π -bond containing molecules react to form a cyclic molecule by rearranging the π -electrons and forming two new σ bonds. Cycloaddition reactions are classified according to the number of π electrons that interact in the reaction.

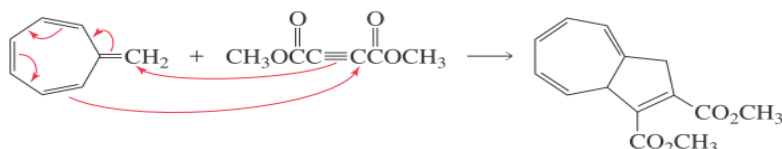
[4 + 2] cycloaddition (a Diels–Alder reaction)



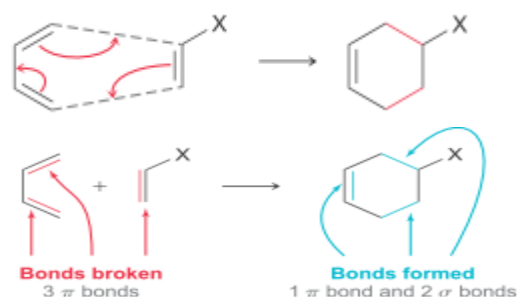
[2 + 2] cycloaddition



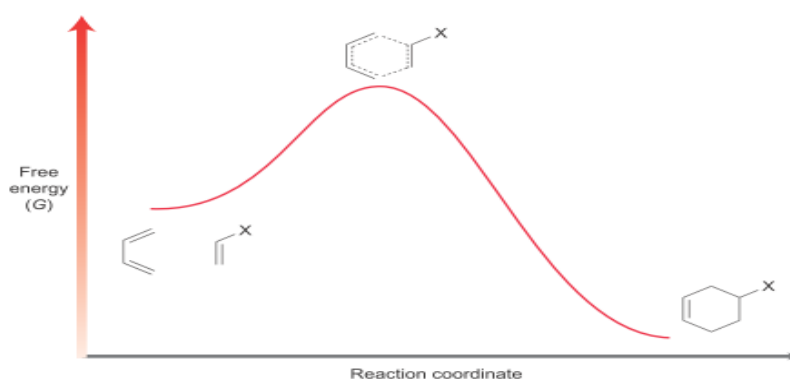
[8 + 2] cycloaddition



The Diels–Alder reaction is one of the best known examples of a cycloaddition reaction. The Diels–Alder reaction is a [4+2] cycloaddition reaction because one reactant has four interacting π -electrons (diene) and the other reactant has two interacting π -electrons (dienophile). Only the π -electrons participating in electron rearrangement are counted.

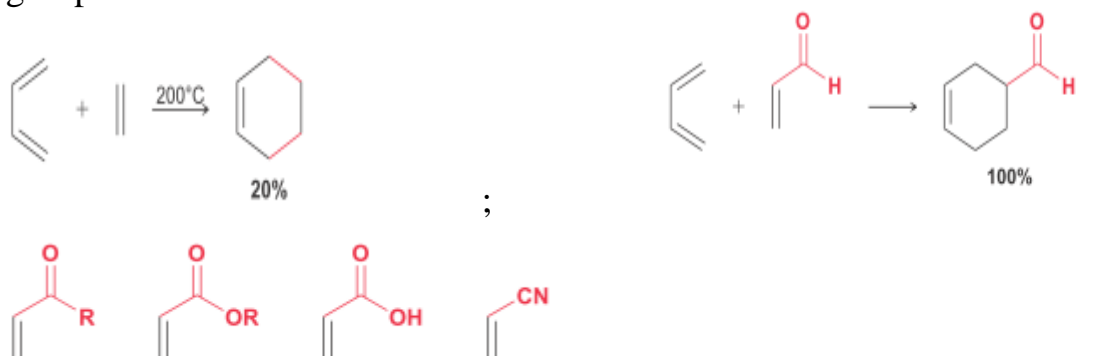


The arrows can generally be drawn in either a clockwise or a counterclockwise fashion. Since the reaction takes place in just one step, the energy diagram has just one peak, where the top of the peak represents the transition state (Figure below). The transition state is a six-membered ring in which three bonds are breaking and three bonds are forming simultaneously.



The Dienophile

The starting materials for a Diels-Alder reaction are a diene and a compound that reacts with the diene, called the dienophile. When the dienophile does not contain any substituents, the reaction exhibits a large activation energy and proceeds slowly. If the temperature is raised to overcome the energy barrier, the starting materials are favored over the products, and the resulting yield is low: A Diels-Alder reaction will proceed more rapidly and with a much higher yield when the dienophile has an electron-withdrawing substituent such as a carbonyl group:



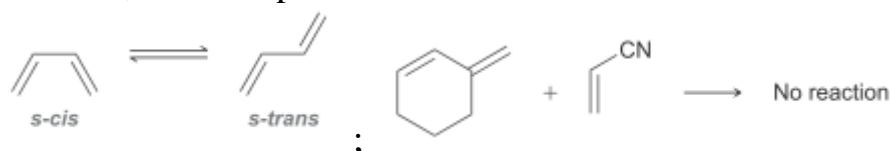
When the dienophile is a 1,2-disubstituted alkene, the reaction proceeds with stereospecificity.

Specifically, a cis alkene produces a cis disubstituted ring, and a trans alkene produces a trans disubstituted ring.



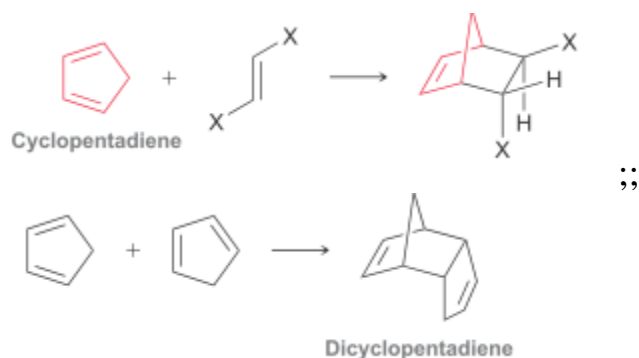
The Diene

Recall that 1,3-butadiene exists as an equilibrium between the *s-cis* conformation and the *s-trans* conformation. The Diels-Alder reaction only occurs when the diene is in an *s-cis* conformation. When the compound is in an *s-trans* conformation, the ends of the diene are too far apart to react with the dienophile. Some dienes are incapable of adopting an *s-cis* conformation, and are therefore unreactive toward a Diels-Alder reaction; for example:

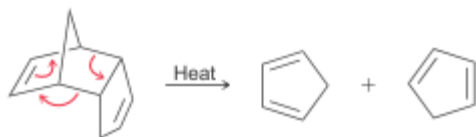


Other dienes, such as cyclopentadiene, are permanently locked in an *s-cis* conformation. Such

dienes react extremely rapidly in Diels-Alder reactions. In fact, cyclopentadiene is so reactive toward Diels-Alder reactions that it even reacts with itself to form a dimer called dicyclopentadiene.

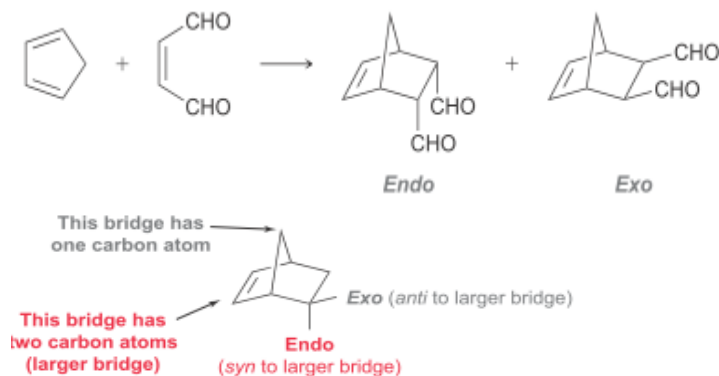


When cyclopentadiene is allowed to stand at room temperature, it is completely converted into the dimer in just a few hours. For this reason, cyclopentadiene cannot be stored at room temperature for long periods of time. When cyclopentadiene is to be used as a starting material in a Diels-Alder reaction, it must first be formed from dicyclopentadiene via a retro Diels-Alder reaction and then used immediately or stored at very low temperature.



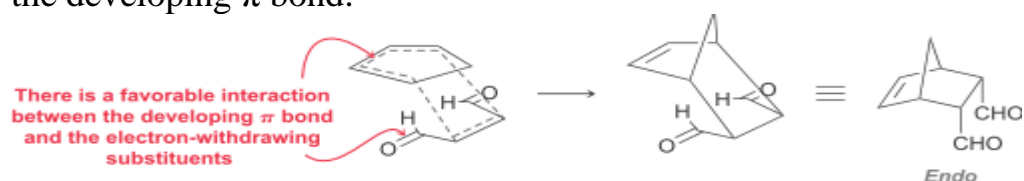
Endo Preference

When cyclopentadiene is used as the starting diene, a bridged bicyclic compound is obtained as the product. In such a case, we might expect to obtain the following two products.

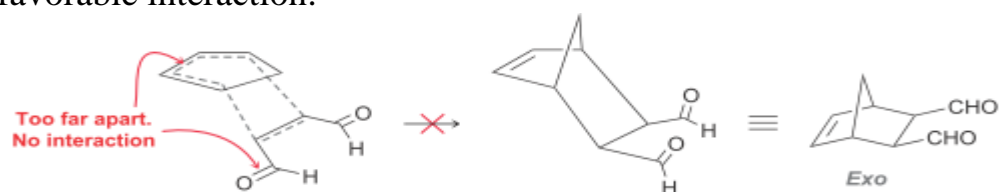


In one cycloadduct, the electron-withdrawing substituents occupy endo positions, and in the other cycloadduct, the substituents occupy exo positions. The endo positions are syn to the larger bridge, and the exo positions are anti to the larger bridge.

In general, the endo cycloadduct is highly favored over the exo cycloadduct. In many cases, the endo product is the exclusive product. The explanation for this preference is based on an analysis of the transition states leading to the endo and exo products. During formation of the endo product, a favorable interaction exists between the electron-withdrawing substituents and the developing π bond.



The transition state leading to the exo product does not exhibit this favorable interaction:



The transition state leading to formation of the endo product is lower in energy than the transition state leading to formation of the exo product (Figure below). As a result, the endo product is formed more rapidly.