# 1.5: THE DIELS-ALDER CYCLOADDITION REACTION

## OBJECTIVES

After completing this section, you should be able to

1. write an equation to represent a typical Diels-Alder reaction.
2. draw the structure of the product formed when a given conjugated diene reacts with a given dienophile in a Diels-Alder reaction.
3. identify the diene and dienophile that must be used to prepare a given compound by a Diels-Alder reaction.
4. explain the general mechanism of the Diels-Alder reaction, without necessarily being able to describe it in detail.

## KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- Diels-Alder cycloaddition
- pericyclic reaction
- Diene
- Dienophile

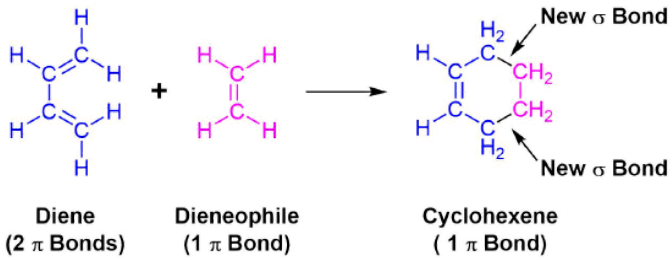
## STUDY NOTES

The Diels-Alder reaction is an example of an organic chemical reaction which does not proceed by either a polar or a free radical pathway, but rather a pericyclic reaction.

Although we do not expect you to be able to provide a detailed account of the mechanism of this reaction, you should learn enough about the Diels-Alder reaction to fulfillthe objectives stated above. You will find it useful to contrast the mechanism of the Diels-Alder reaction with the polar and radical mechanisms studied earlier.

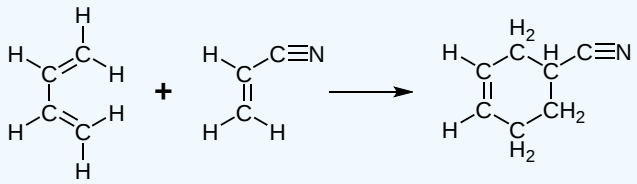
The unique character of conjugated dienes manifests itself dramatically in the **Diels-Alder Cycloaddition Reaction**. The Diels-Alder reaction is an important and widely used synthetic method for making six-membered rings. In the Diels-Alder reaction, a conjugated diene, simply referred to as the **diene**, reacts with a double or triple bond co-reactant called the **dienophile**, because it combines with (has an affinity for) the diene. During the reaction, two pi-bonds are converted to two sigma-bonds. The Diels-Alder cycloaddition is classified as a pericyclic process. Pericyclic reactions involve the redistribution of bonding electrons in a single step mechanism and will be discussed in greater detail in **Chapter 15**. In particular, the Diels-alder reaction is called a [4+2] process because the diene has four pi-electrons that shift position in the reaction and the dienophile has two.

### GENERAL REACTION




An example of the Diels-Alder reaction is the cycloaddition of 1,3-butadiene to cyanoethene (acrylonitrile) to form 4-cyanocyclohexene.

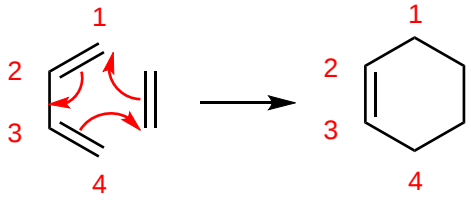
## EXAMPLE 1.5.1



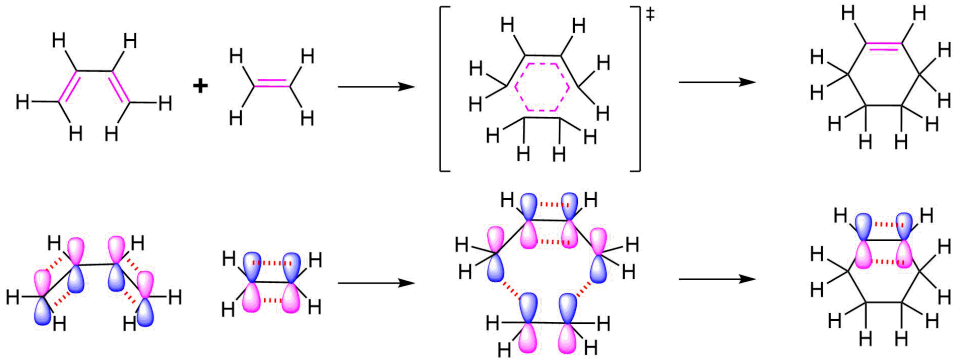
**1,3-Butadiene** **Cyanoethene** **4-Cyanocyclohexene**

## MECHANISM

All of the electron rearrangements of the Diels-Alder reaction take place once in a single mechanistic step. During this step carbons 1 and 4 of the diene and both alkene carbons of the dienophile, rehybridize from $sp^2$ to $sp^3$ and electrons rearrange to create two new sigma bonds in the cyclic product. Carbons 2 and 3 of the diene remain $sp^2$ hybridized and form a new pi bond in the product.

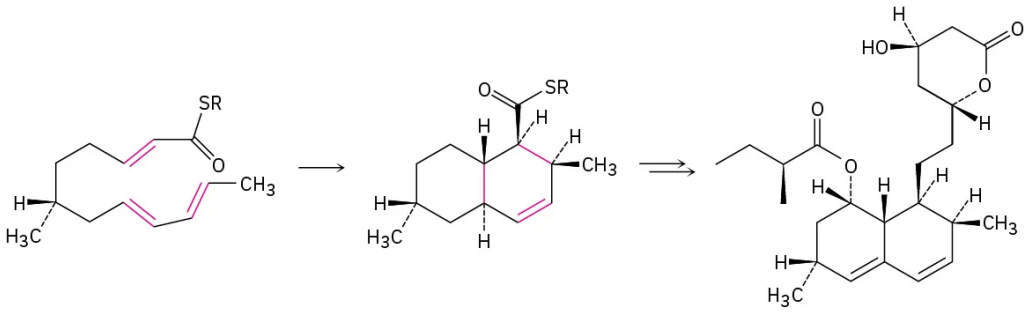



The mechanism occurs through a cyclic transition state in which there is head-on overlap of two p orbitals on carbons 1 and 4 of the diene with the two p orbitals from the alkene of the dienophile to form two new sigma bonds in the cyclohexene product. The remaining two p orbitals from the diene overlap to form the new pi bond.



## BIOLOGICAL DIELS–ALDER REACTIONS

Biological Diels–Alder reactions are also known but are uncommon. One example occurs in the biosynthesis of the cholesterol-lowering drug lovastatin (trade name Mevacor) isolated from the bacterium *Aspergillus terreus*. The key step is the *intramolecular* Diels–Alder reaction of a triene, in which the diene and dienophile components are within the same molecule.



**Lovastatin**

Lovastatin is in a class of medications called **HMG CoA reductase inhibitors (statins)**. It works by slowing the production of cholesterol in the body to decrease the amount of cholesterol that may build up on the walls of the arteries and block blood flow to the heart, brain, and other parts of the body.