

## 10.1: Introduction

Pericyclic reactions differ from the ones we have looked at so far because they are not easily understood in Lewis acid- Lewis base terms. There is not always a clear nucleophile and electrophile in these reactions. In fact, they may appear to involve completely non-polar reactants.

The classic example of a pericyclic reaction is a Cope rearrangement. In a Cope rearrangement, a molecule reorganizes itself, trading in some sigma bonds for pi bonds, so that by the end of the reaction the atoms are connected in a slightly different way. At first, it doesn't seem like much has happened in this reaction, but if you look closely, you can see how specific bonds have changed places.

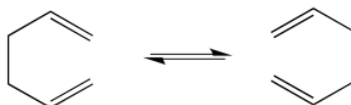


Figure 10.1.1: A very simple Cope rearrangement in 1,5-hexadiene.

Highlighting specific bonds with colour is helpful here. Keeping track of electrons with arrows usually helps, too.

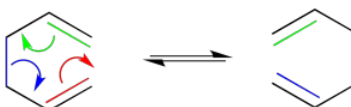


Figure 10.1.2: The Cope rearrangement highlighted with colour.

Cycloadditions are very closely related to pericyclic reactions. The most common example of a cycloaddition reaction is a Diels Alder reaction. A Diels Alder reaction takes place between two alkenes. Below, you can see a Diels Alder reaction between ethene and 1,3-butadiene.



Figure 10.1.3: Diels Alder reaction between ethene and 1,3-butadiene.

Once again, keeping track of electrons can help us to establish what is going on here.



Figure 10.1.4: Diels Alder reaction with electron movement highlighted.

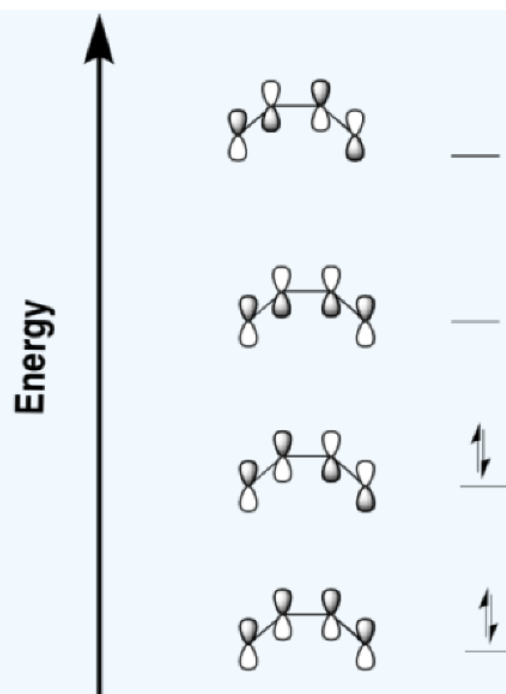
Normally, we think of both of these compounds as nucleophiles. It isn't easy to see why one would react with the other. It isn't easy to see how electrons would be attracted from one molecule to the other.

Instead, pericyclic reactions rely on weak attractions between (or within) molecules that can lead to electronic interactions that result in new bond formation. Normally, pericyclic reactions are studied using molecular orbital calculations to map out these electronic interactions. That analysis makes use of group theory, the mathematics of symmetry. However, they are also explained qualitatively using simplified molecular orbital pictures; that's the approach we'll take here.

### ? Exercise 10.1.1

Pericyclic reactions depend on molecular orbital interactions. Draw the  $\pi$ -bonding molecular orbitals for butadiene, ranked in energy. In other words, draw a Hückel molecular orbital diagram for butadiene.

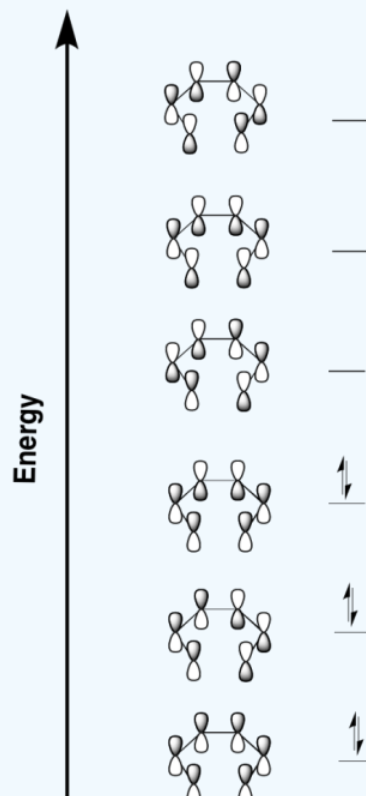
**Answer**



### ? Exercise 10.1.2

Draw a Hückel molecular orbital diagram for hexatriene.

**Answer**



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