The Diels-Alder Reaction: A concerted cycloaddition process

The Diels-Alder reaction involves two components, an alkene and a 1,3-diene, and it produces a cyclohexene structure. The alkene is usually substituted by one or more electron-withdrawing groups, while the diene may be substituted with electron donors. In the absence of these groups, the reaction rates are much slower. The alkene is referred to as the **dienophile**, meaning “the component that is attracted to dienes”. Highly activated dienes and dienophiles may react simply by mixing, but it is usually necessary to heat the mixture somewhat. A solvent may be used, or the diene and dienophile may be mixed together and heated directly.

![Diels-Alder Reaction](https://example.com/diels_aelder.png)

Experiments have suggested that there are no intermediates along the reaction coordinate. In other words, the **Diels-Alder reaction is concerted**. All bond formation occurs in one smooth process involving all six of the pi electrons from the diene and dienophile. If you think about what this means, you should be able to see that the diene must add across only one face of the dienophile because it is impossible for the two ends of the diene to simultaneously approach an alkene from opposite faces. Likewise, the dienophile must add to one face of the diene.

![Diels-Alder Reaction](https://example.com/diels_aelder_concerted.png)

Notice as well that the double bond in the product will always end up between the carbons that were the middle pair in the starting diene. In the scheme above, these are carbons “d” and “e”.

It should also be evident that the diene must adopt the so-called **s-cis conformation** in order to react with a dienophile in this way, despite the fact that this conformation is more sterically strained than the preferred s-trans conformer. Dienes that cannot adopt this conformation cannot undergo the Diels-Alder reaction.

![Diels-Alder Reaction](https://example.com/diels_aelder_conformations.png)

It is also possible to use an **alkyne** as the dienophile in a Diels-Alder reaction. In this situation, the product will be a **cyclohexadiene**, since only one pi bond of the alkyne will be involved in the cycloaddition.
The Diels-Alder reaction may be either kinetically- or thermodynamically-controlled. Generally we can assume that a Diels-Alder reaction is under kinetic control if the temperature is not greater than about 100 °C and the reaction time is less than about 12-18 hours. Reactions performed at higher temperatures and/or allowed to proceed for long periods of time have the opportunity to equilibrate and are said to occur under thermodynamic conditions.

The product of a kinetically-controlled reaction can be predicted from an understanding of the preferred transition state. Although it may seem counter-intuitive, both experimental observations and the results of advanced theoretical calculations agree with the idea that the dienophile prefers to approach the diene with its electron-withdrawing substituent(s) under the diene structure (what is called “endo” approach) rather than in the less sterically crowded “exo” orientation. The kinetic product of a Diels-Alder reaction results from endo approach. If the reaction were to be conducted under thermodynamic conditions, the major product would be the one that is more stable, usually the exo isomer.

The stereochemistry of the product can be deduced from the structures of the starting materials, by considering what the transition structure would look like. Consider the following example, the reaction of E,Z-2,4-hexadiene with maleic anhydride:

Notice that the product is initially formed in something like a boat conformation. You can see that the groups that were on the “inside” of the diene in the s-cis geometry end up in the “flagpole” positions in the boat. The groups that were on the “outside” end up in the “bowsprit” positions.

As we know, the boat is not the most stable conformation and it rapidly will flip into something more reasonable, but this is how it emerges from the reaction.

This is also a good time to remark that in the example above, the diene and the dienophile are both achiral compounds, while the product is chiral. Because the starting materials are not chiral, a chiral product must be formed as an equal mixture of the two possible enantiomers (a...
racemate). Note that the stereochemistry of the transition state shown was chosen arbitrarily – the mirror image transition state would have the diene and dienophile interacting on the opposite faces and would give the enantiomer of the product shown.

The endo transition state for the Diels-Alder reaction of \(E,E\)-2,4-hexadiene and acrylonitrile is shown at right. This structure was determined using a modestly sophisticated quantum mechanical calculation on a regular PC.

Notice the cyano group of the dienophile at the bottom of the image, oriented to the back and lying under the diene. You can also see that atoms that will become tetrahedral in the product have only slightly departed from their initial trigonal planar geometries and the bond lengths are still very close to their initial values. The distances shown between the carbons that will become bonded are significantly longer than the expected length they will have when C-C single bonds are fully formed (ca. 1.54 Å). This is a fairly “early” transition state in the terminology of the Hammond Postulate – that is, it is reactant-like. Bond formation and breaking are not very far advanced yet.