

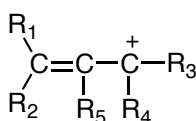
Chapter 11

Conjugation in Alkadienes and Allylic Systems

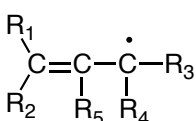
Conjugated Systems

Conjugated systems are those in which a π -bond is connected or “conjugated” (from the Latin *conjugare* which means to link or yoke together) to another system that contains either a p-orbital or another π -bond. Conjugated systems have a special stability and a special reactivity.

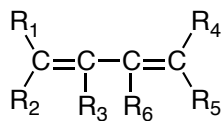
Examples are shown below.



conjugated carbocation



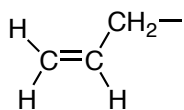
conjugated radical



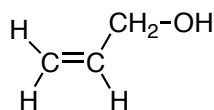
conjugated double bonds (diene)

We will look first at systems in which π -bonds are connected to p-orbitals, the conjugated carbocation and the conjugated radical.

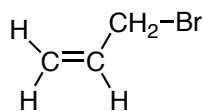
We have some new terminology to describe these systems. There is the allyl group and allyl bromide or allyl alcohol.



allyl group

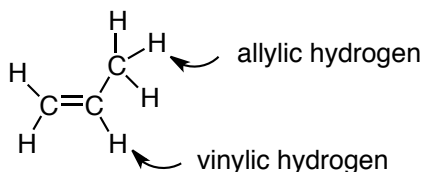


allyl alcohol

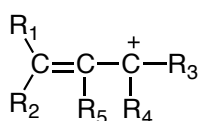


allyl bromide

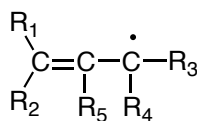
And we have vinylic hydrogens, attached directly to the double bond, and allylic hydrogens on carbons next to the double bonds.



We use the same terminology to describe the conjugated carbocation (allylic carbocation) and the conjugated radical (allylic radical).

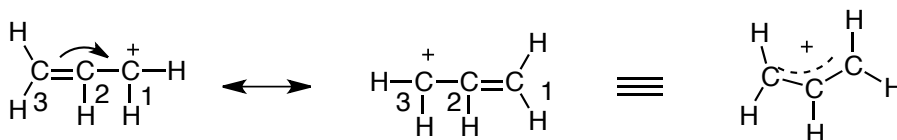


allylic carbocation



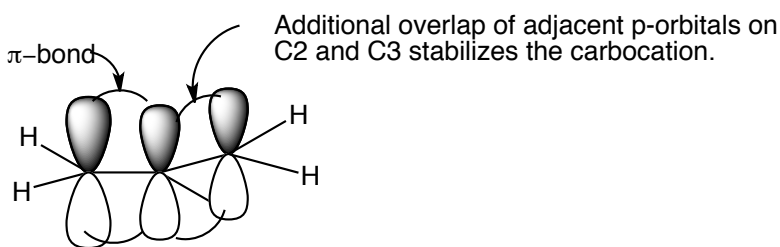
allylic radical

We will look at the allylic carbocation first. It is particularly stable since it is stabilized by resonance donation of the adjacent π -bond. The $C=C$ bond donates electrons to the carbocation. Note that the carbocation must be on the carbon next to the π -bond.

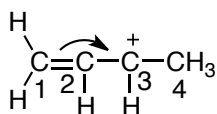
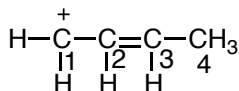


The (+) charge is spread out equally over carbon 1 and carbon 3. There is no (+) charge on the central carbon; the (+) charge is delocalized to the ends of the system so that, as we will see, nucleophiles will attack both carbon 1 and carbon 3 but not carbon 2. This spreading out of the charge helps to lower the energy of the allylic carbocation.

A drawing in which the orbitals involved are shown helps in visualizing why the energy of the system is lowered. There is an additional partial π -bond between carbon 2 and carbon 3. Looking at the orbital picture, we can formulate another definition of a conjugated system: it is one in which there is continuous overlap of p-orbitals. In this case, the overlap extends over three carbons.



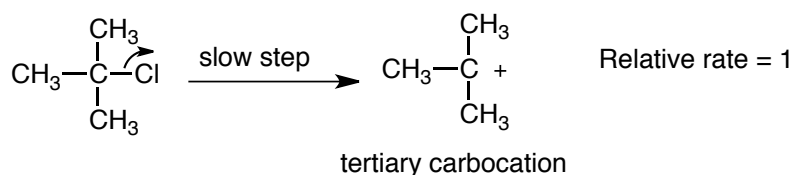
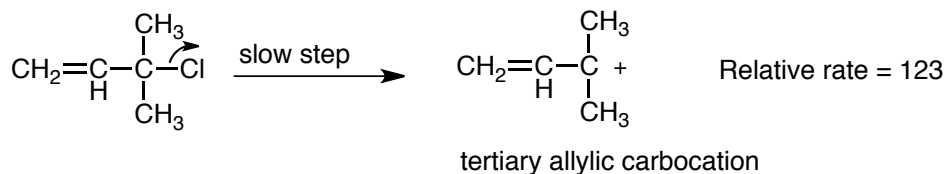
In the system above, the (+) charge is distributed evenly over the two terminal carbons but in the following system the charge is not evenly distributed. More charge will reside on the more substituted carbocation.

secondary allylic carbocation
more stable

primary allylic carbocation

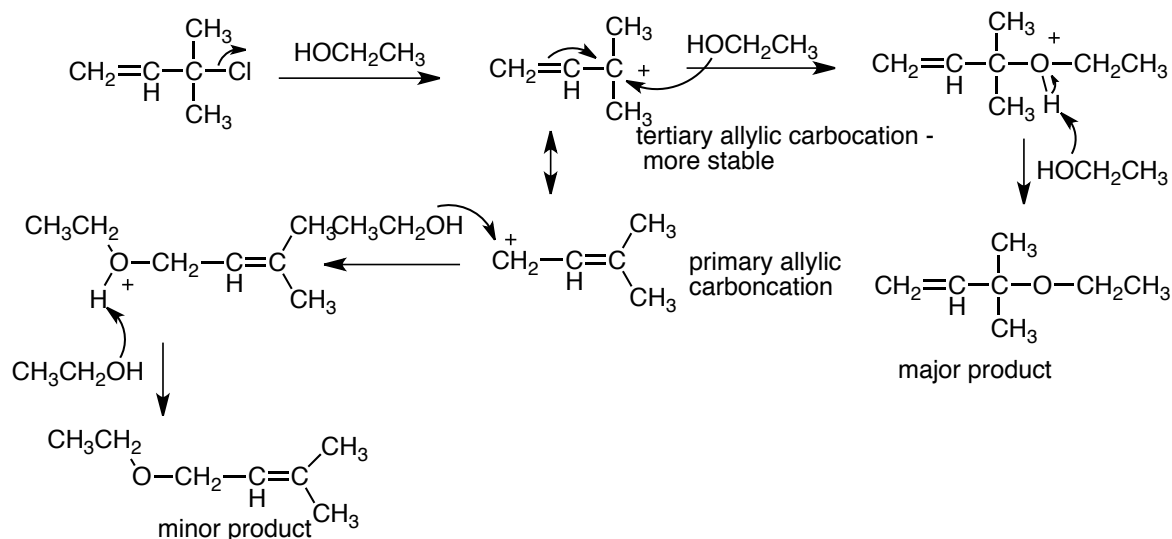
S_N1 Reactions of Allylic Halides

Allylic halides are very reactive in S_N1 reactions. They are much more reactive than tertiary alkyl halides. For example look at the following solvolysis reactions. The tertiary allylic chloride reacts 123 times faster than the tertiary chloride.



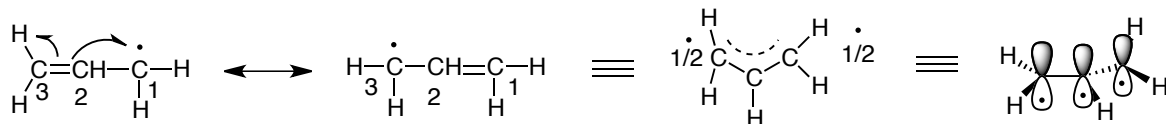
The tertiary allylic carbocation forms faster than the tertiary carbocation because it is lower in energy and therefore has a lower energy transition state and a lower activation energy. Recall that it is the size of this activation energy that determines the rate of the reaction.

The tertiary allylic carbocation is resonance stabilized, with the (+) charge distributed over two carbons. Therefore we see two products formed.



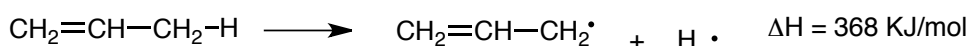
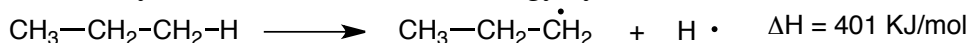
Allylic Free Radicals

Allylic free radicals are also stabilized by resonance. The free electron is delocalized on C1 and C3 at the ends of the allylic system so that there is a $\frac{1}{2}$ of an electron on each terminal carbon.



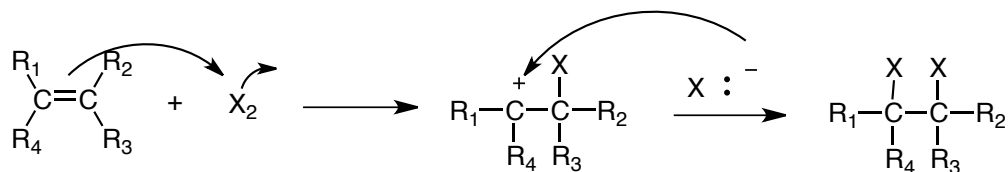
Looking at an orbital picture, it can be seen that there is continuous overlap of the p-orbitals.

We can see the extra stability of the allylic radical reflected in the bond dissociation energy of the allylic C-H bond in propene. When it is compared to a C-H bond in propane we find that the allylic C-H bond is lower in energy by 42 KJ/mol.



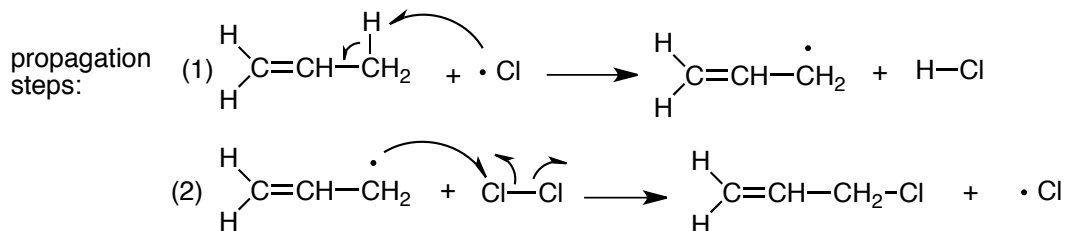
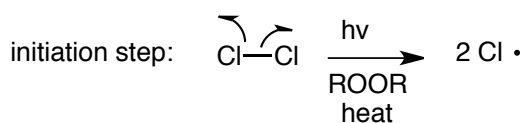
It is easier to break an allylic C-H than a normal sp^3 carbon C-H bond. Therefore, using radical halogenation conditions, we can selectively functionalize the allylic position of a molecule.

Alkenes typically react with halides at lower temperature by addition to the double bond.

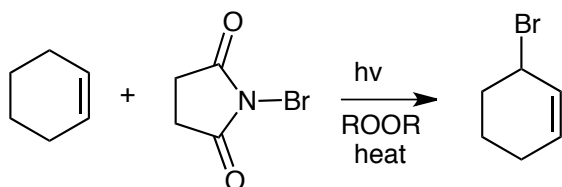
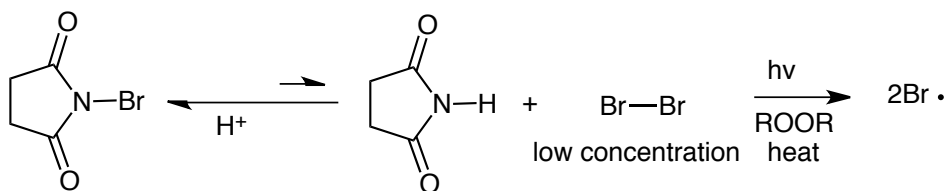


But at lower temperatures and in conditions where radicals are formed and where there is a low concentration of the halogen, substitution at the allylic position is the predominant reaction. The mechanism proceeds through initial cleavage of the X-X bond. This can be accomplished by ultraviolet light ($h\nu$), or a radical initiator such as a peroxide or simply by heating. Often in the lab, all three are used. Radical formation is followed by selective abstraction of an allylic hydrogen to give a resonance stabilized allylic radical. The allylic radical then reacts with a halogen, X_2 , to form the allylic halogen and generate a new radical.

The fact that the second propagation step generates a new radical means that this is a radical chain reaction.

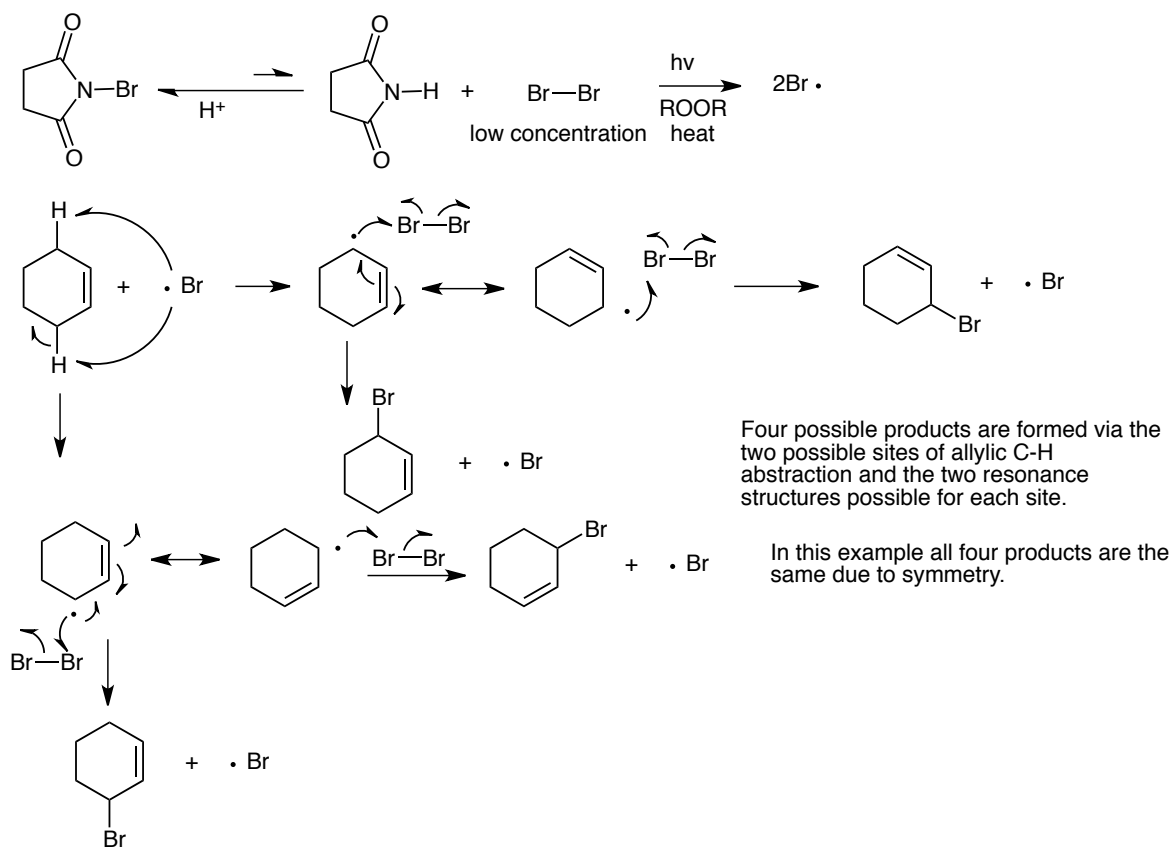


A very good reagent for allylic bromination is *n*-bromosuccinimide or NBS. Acid catalysis generates a very small concentration of molecular bromine, Br_2 , which is then cleaved in the radical forming conditions (heat, $h\nu$, ROOR).

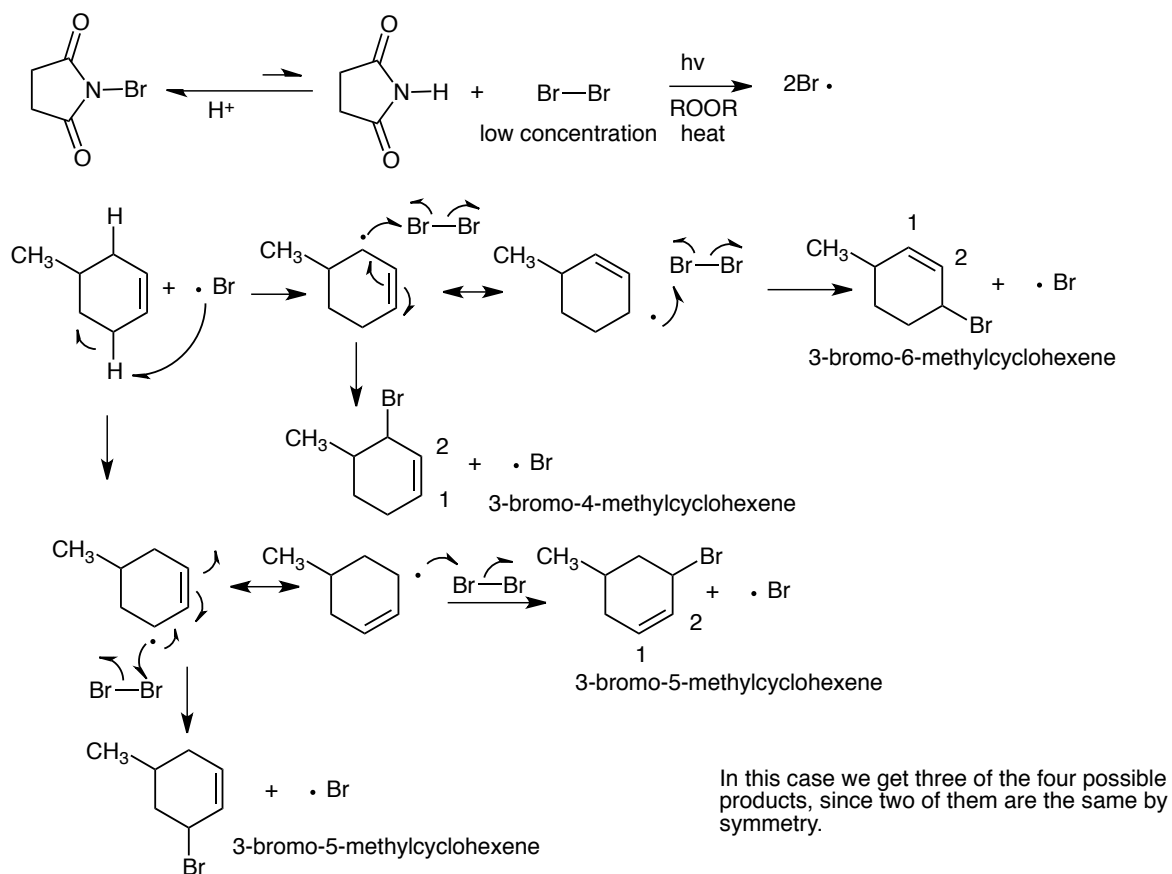


It is important to maintain a very low concentration of the Br_2 ; otherwise it can add directly to the double bond to give the 1,2-dibromide compound rather than the allylic bromination.

Note also that four possible products may be formed due to the two sites of allylic C-H abstraction, each of which has two resonance structures. In the example of cyclohexene only one product is formed due to symmetry.



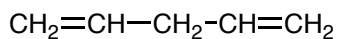
In the above example all of the four possible products turn out to be the same molecule due to symmetry but we can easily break the symmetry by looking at the radical bromination of 4-methylcyclohexene. In this case we get three of the four possible isomers, since two of the products are the same by symmetry.



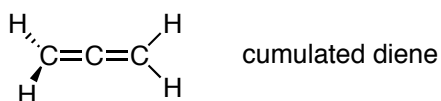
Dienes

There are three possible relationships between two alkenes (dienes) in a single molecule:

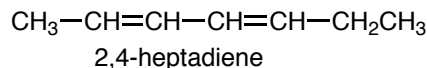
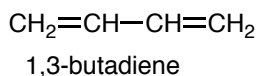
(1) The alkenes may be isolated. Isolated dienes have at least one $-\text{CH}_2-$ group between the two alkenes. They are non-conjugated.



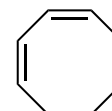
(2) The alkenes can be cumulated. The two double bonds are attached to the same carbon.



(3) The alkenes may be conjugated. The two carbon-carbon double bond units are connected by a single bond. The double bonds are in a 1,3-relationship.



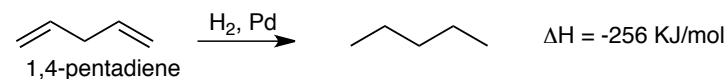
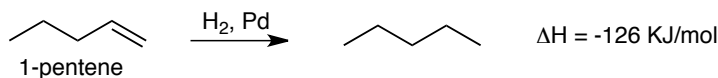
1,3-cyclohexadiene



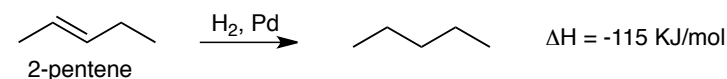
1,3-cyclooctadiene

Just like in the allylic carbocation and the allylic radical we see a special stability by having the two double bonds next to each other. They are conjugated and there is extra overlap of the continuous p-orbitals.

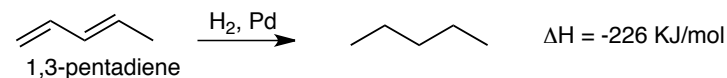
To measure this extra stability, look at the heats of hydrogenation of the following molecules.



This is exactly twice as much as for a single bond since the two double bonds are isolated and not conjugated.

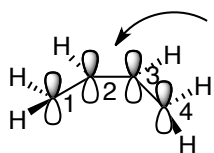


Energy given off is slightly less than for 1-pentene since the internal double bond is stabilized by two electron donating alkyl substituents.



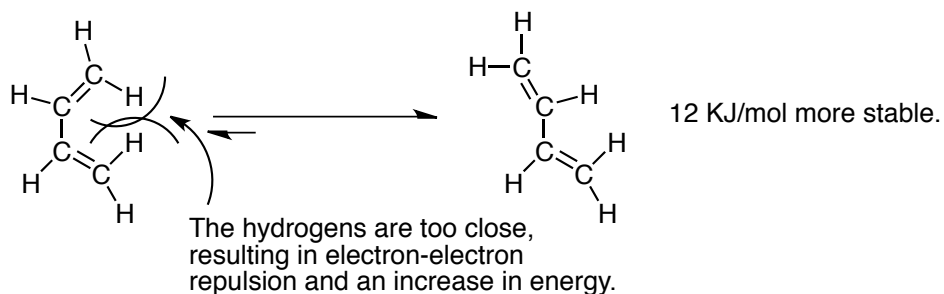
For 1,3-pentadiene, we expect a ΔH of $-126 + (-)115 = -241 \text{ KJ/mol}$ but the experimental value is -226 KJ/mol . This tells us that the conjugated diene is stabilized by 15 KJ/mol .

We see that 1,4-pentadiene, with two isolated double bonds, has a heat of hydrogenation that is exactly twice that of a single double bond but that the heat of hydrogenation for 1,3-pentadiene is 15 KJ/mol less than we would expect. This indicates that the conjugated system is more stable than the isolated system. This is very similar to the allyl cation and allyl radical and is due to the extra overlap in the continuous system of p-orbitals. There are 4 sp^2 carbons in a row, all connected together and each with a p-orbital. We see that between C2 and C3 of this system there is a partial bond, an extra bond that helps to stabilize the system.

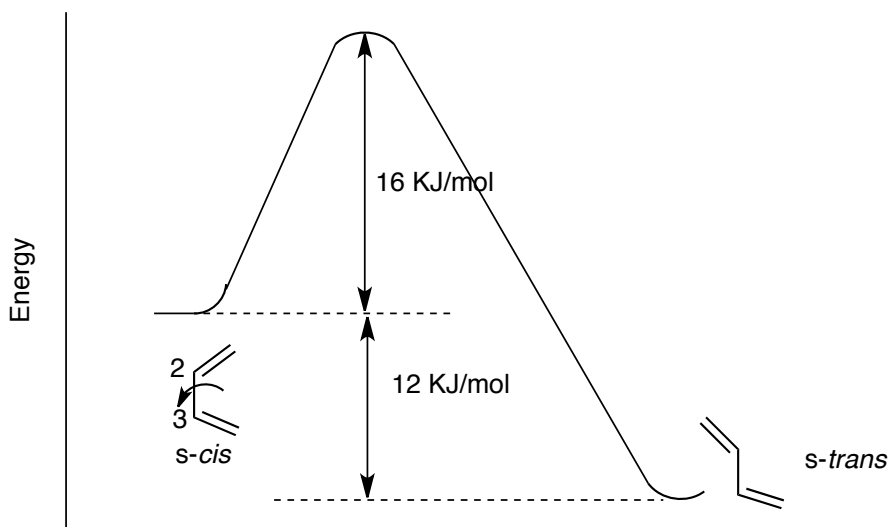


Extra overlap of p-orbitals between C2 and C3 that helps to stabilize the system. In a conjugated system of dienes there is continuous overlap of the p-orbitals in the contiguous arrangement of the sp^2 carbons.

The overlap is best when the 4 sp^2 carbons of the conjugated system are in the same plane. There are two conformations possible, the *s-cis* and *s-trans*. The *s-trans* conformation is more stable by 12 KJ/mol due to steric hindrance in the *s-cis* conformation.

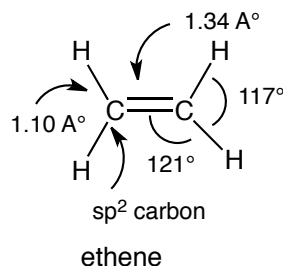
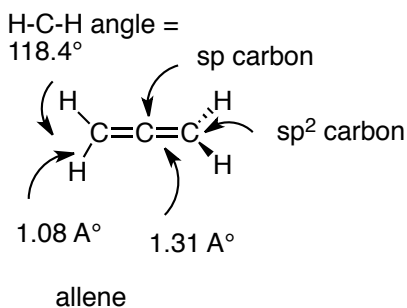


These two conformations interconvert by rotation around the C2-C3 bond. But this rotation breaks the extra overlap between C2 and C3 so there is an energy barrier to this rotation. The barrier to rotation is 16 KJ/mol.



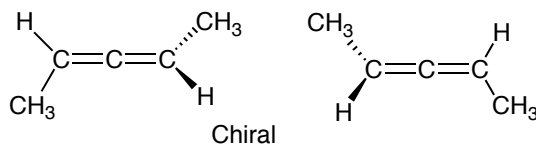
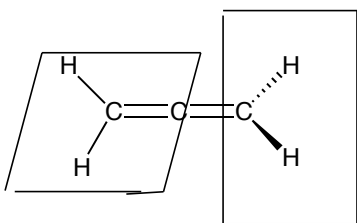
Allenes

Allenes have two double bonds to a central carbon. This carbon is sp -hybridized and the two terminal carbons are sp^2 -hybridized.



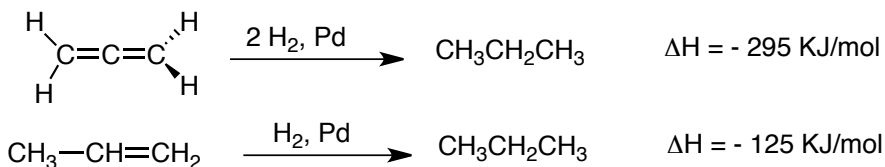
We see that compared to an alkene like ethene, the bond between an sp-carbon and an sp²-carbon is slightly shorter and so is the sp² C-H bond.

A major feature of the allene geometry is the non-planarity of the allene. The double bonds are non-conjugated and lie in different planes. This twists the substituents on the terminal carbons so that these also lie in different planes. This means that 1,3-disubstituted allenes are chiral molecules.



2,3-pentadiene These two molecules are enantiomers.

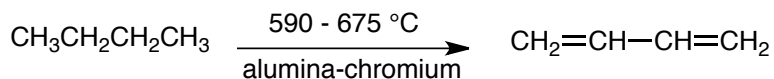
Looking at the heat of hydrogenation, we see that allenes are less stable than isolated double bonds. The heat of hydrogenation is more than twice that of isolated, terminal double bonds, indicating that allenes are destabilized by having cumulated double bonds.



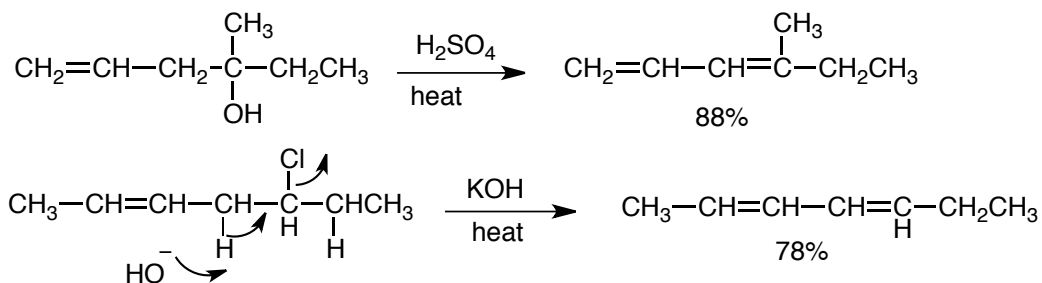
Here we see that $\Delta\text{H} >$ twice the heat of hydrogenation of a single, isolated double bond, so allenes are less stable than isolated double bonds.

Preparation of Dienes

Dienes are prepared on an industrial scale by dehydrogenation of alkanes using special catalysts such as chromium on alumina at very high temperatures. At high temperatures, the entropy term (which is temperature dependent) dominates the reaction.

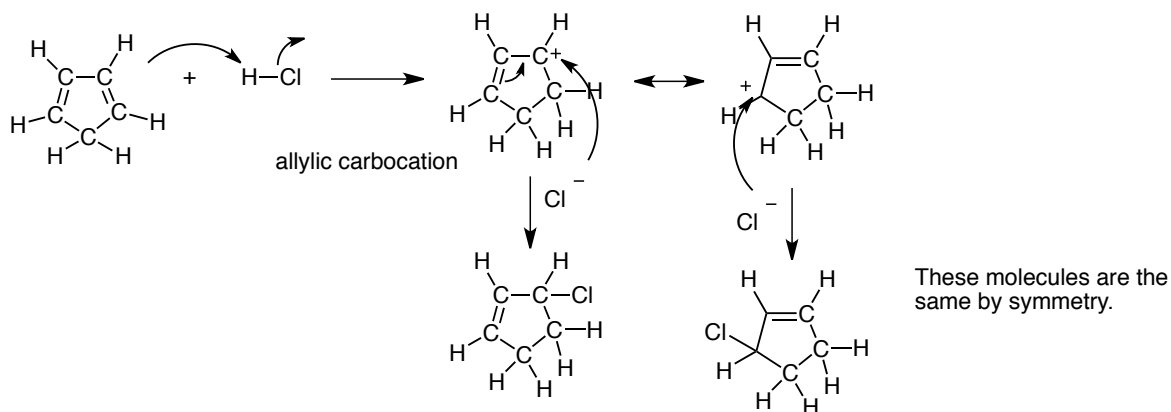


On a laboratory scale, dienes are most conveniently prepared by elimination reactions of unsaturated alcohols and unsaturated halides. The second double bond forms so as to go into conjugation with the first double bond.

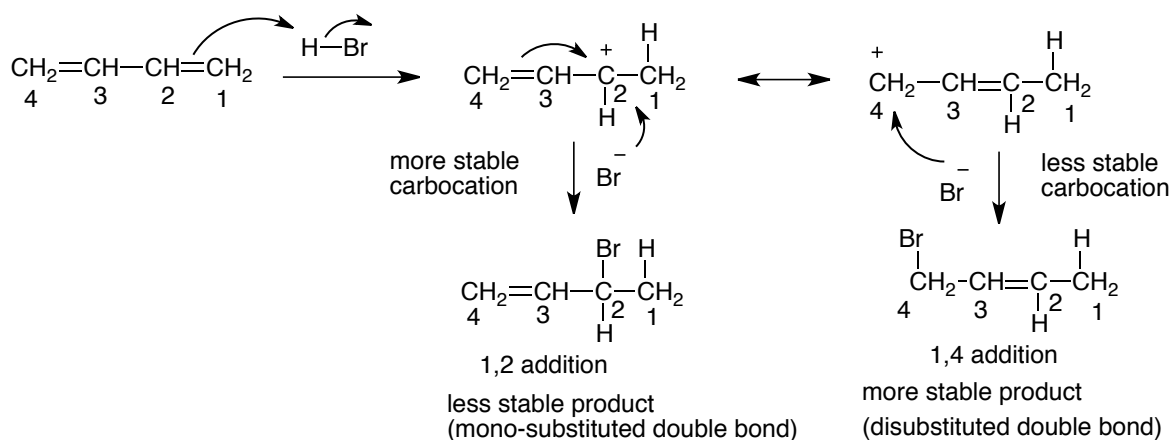


Addition of Hydrogen Halides to Conjugated Systems

In accordance with Markovnikov's rule, the hydrogen of the HX reagent will add to a diene system so as to form the more stable carbocation; this is the allylic carbocation.

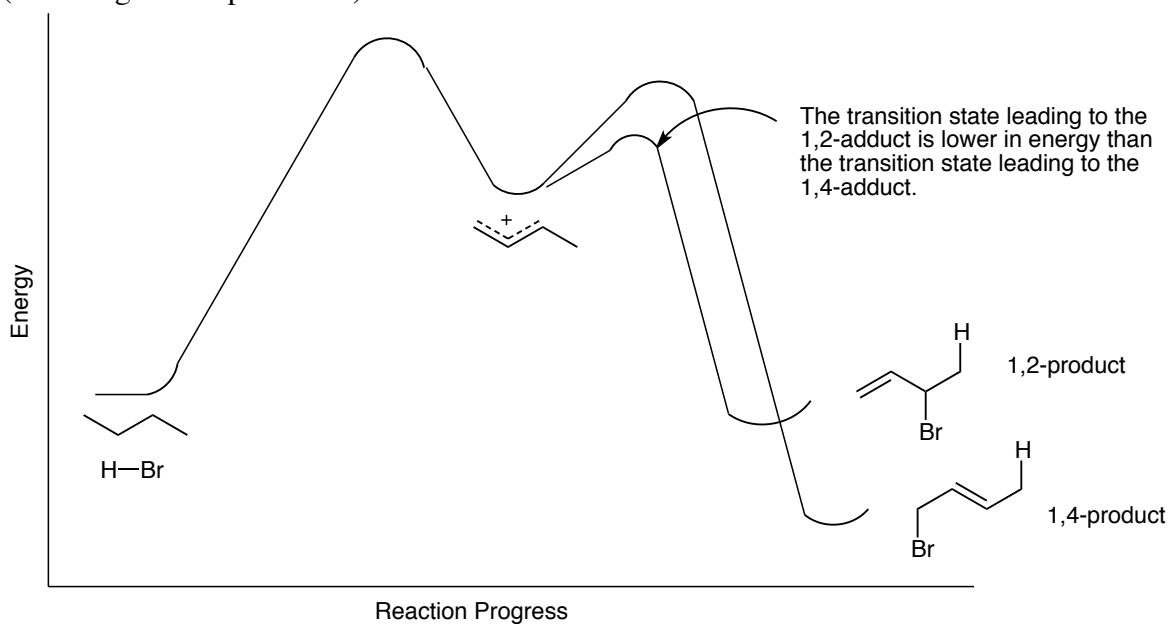


With 1,3-butadiene we see two products. One product is the result of 1,2-addition and the other is the result of 1,4-addition.



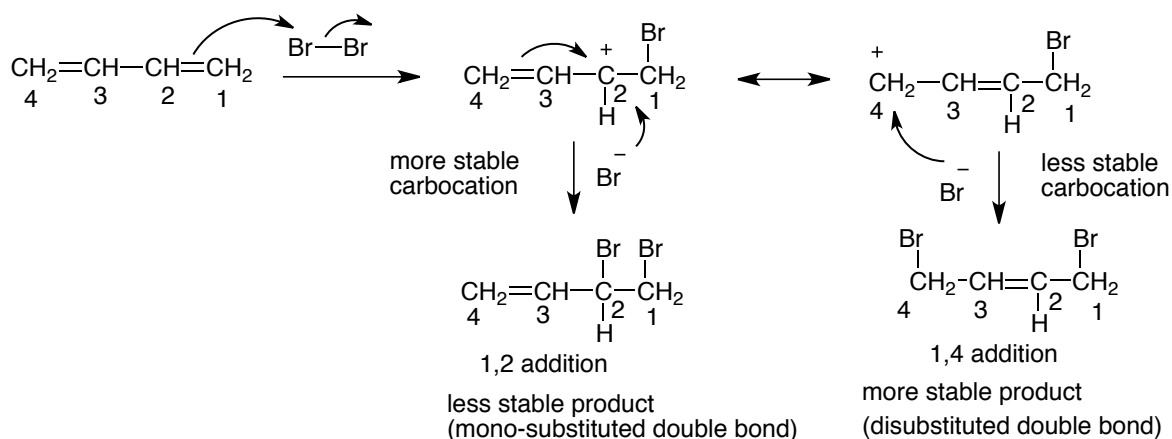
The ratio of the products formed is dependent on the temperature. At very low temperatures (-80°C), the 1,2-adduct is favored. This is the kinetic product and it is formed faster because the carbocation intermediate that leads to the 1,2-adduct is a secondary allylic carbocation. This is more stable – lower in energy - than the primary allylic carbocation that leads to the 1,4-addition product.

But note also, that the 1,2-adduct is less stable than the 1,4-adduct. This is because the 1,4-adduct is a disubstituted double bond, which is more stable than the mono-substituted 1,2-adduct. At higher temperatures, the 1,4-adduct is favored. It is the thermodynamic product and it is the major product under conditions in which the reaction is reversible (i.e. at higher temperatures.)



Addition of Halogens

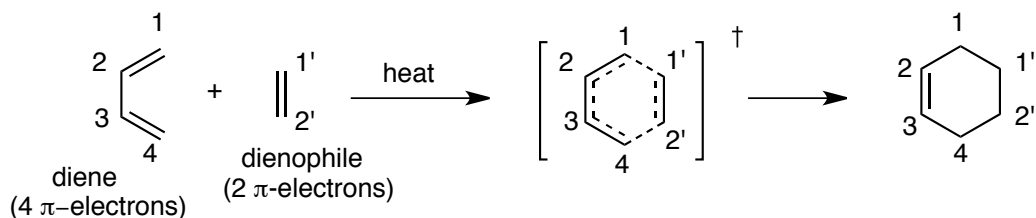
We also see 1,2- versus 1,4-addition in the reaction of halogens, X_2 , with alkenes.



Diels-Alder Reaction

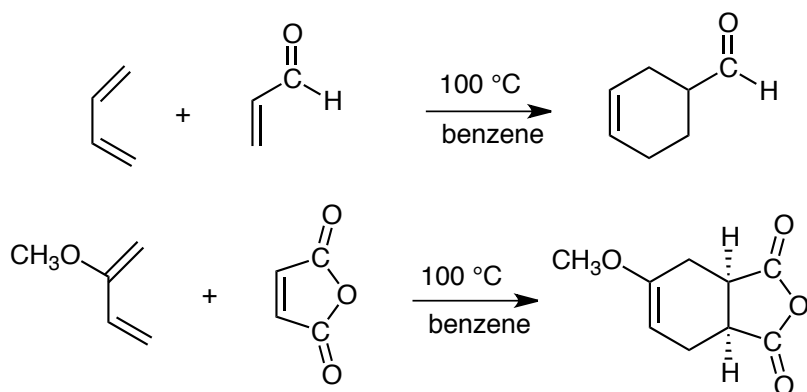
The Diels-Alder reaction is often called the single most useful and most important reaction in all of organic chemistry. It was developed by Otto Diels and Kurt Alder at the University of Kiel. They were awarded the Nobel Prize for their work in 1950.

In the Diels-Alder reaction, a 1,3-diene reacts with an alkene (called the dienophile) to give a new six-membered ring compound that contains a double bond. There are a total of six π -electrons involved, 4 π -electrons from the diene (two in each of the two double bonds) and two π -electrons from the dienophile. So these reactions are often called 4+2 cyclizations.

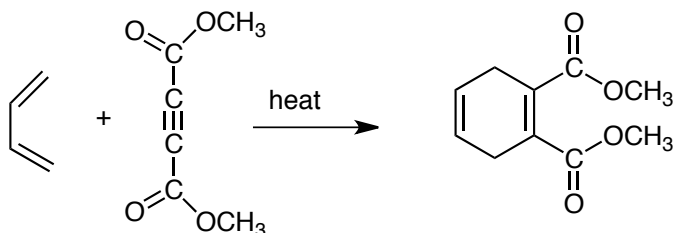


These reactions have a high energy barrier since we are breaking three π -bonds in the transition state but the reactions are overall thermodynamically favorable since we are also forming two new sigma bonds, which are stronger than the broken π -bonds.

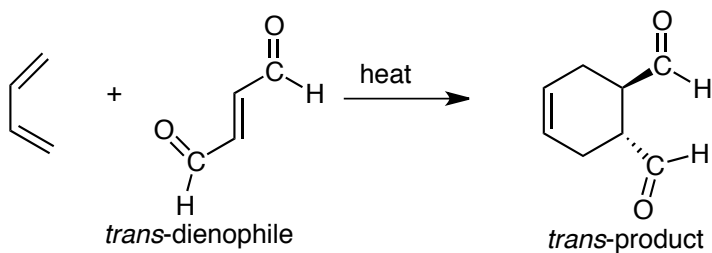
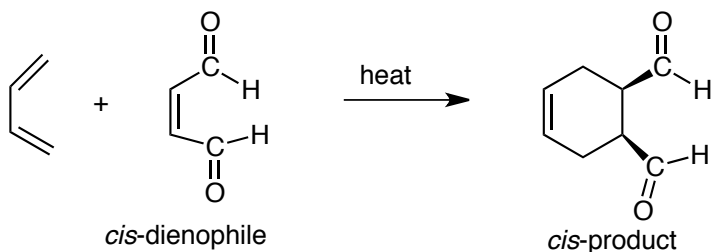
The reaction is accelerated by electron withdrawing groups on the dienophile and by electron donating groups on the diene.



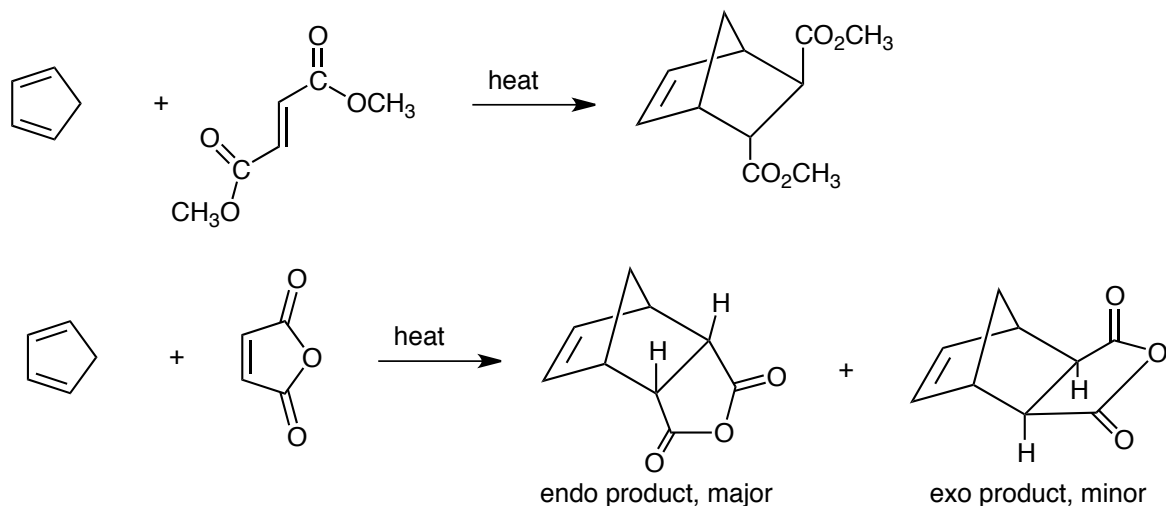
Triple bonds can also serve as dienophiles but they are less reactive than double bonds and require electron withdrawing groups.



Diels-Alder reactions are stereospecific. *Cis*-dienophiles give *cis*-products and *trans*-dienophiles give *trans*-products.



Cyclic dienes can give bridged bicyclic or tricyclic products.



π-Molecular Orbitals of Ethylene and 1,3-Butadiene

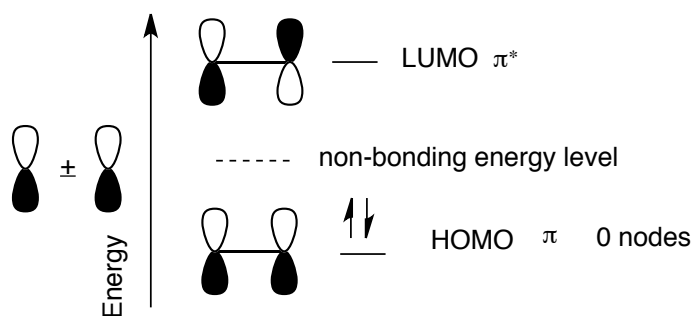
To get a better understanding of the Diels-Alder reaction we need to examine the π-molecular orbitals that are involved.

The orbitals that contain the π-electrons that are involved in the reaction are called the frontier molecular orbitals. The highest energy occupied molecular orbital is called the HOMO and the lowest energy unoccupied molecular orbital is called the LUMO.

When electrons are transferred from a molecule, it is the HOMO electrons that are involved. The HOMO electrons are the ones that actually react. They are the highest energy electrons and are therefore the most weakly held.

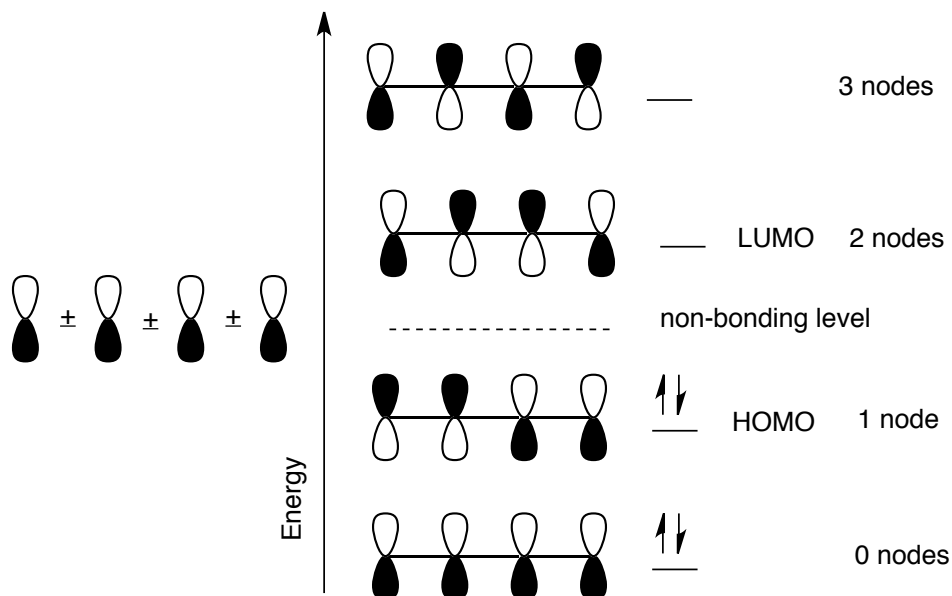
When electrons are transferred to a molecule, they go into the lowest energy unoccupied orbital (the LUMO).

For ethylene, we can construct the molecular orbitals from the atomic orbitals. These atomic orbitals are the two p-orbitals. They overlap to form a bonding π-orbital and an anti-bonding π-orbital. We usually label the anti-bonding molecular orbital with an asterisk (or star).

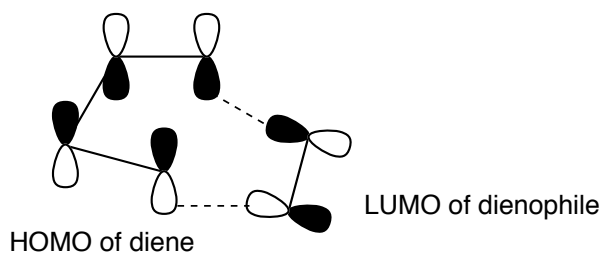


Both the bonding π and anti-bonding π^* orbitals of ethylene are anti-symmetric with respect to the plane of the molecule (the wave functions change sign as they pass through this plane). The bonding π orbital has no nodes other than this plane.

For 1,3-butadiene:

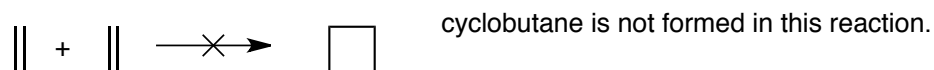


In the Diels-Alder reaction electrons flow from the HOMO of the diene into the LUMO of the dienophile.



In order for the orbitals to overlap in a bonding fashion the signs of the waves must be the same. This leads to constructive overlap (the wave functions reinforce each other). If the signs are not the same, the wave functions will cancel.

So we can see from this analysis that the Diels-Alder reaction is very favorable. Another reaction that looks like it might be favorable turns out to be unfavorable according to our orbital analysis.



We know that when we form a bond, we need a filled orbital as the nucleophile (HOMO) to interact with an empty orbital as the electrophile (LUMO). We see in ethene that the signs of the HOMO and LUMO orbitals do not add in a constructive fashion.

