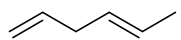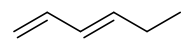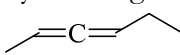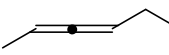# Loudon Chapter 15 Review: Dienes and Aromaticity
Jacquie Richardson, CU Boulder – Last updated 1/16/2018

This chapter looks at the behavior of carbon-carbon double bonds when several of them are in the same molecule. There are several possible ways they can be grouped:


Isolated or ordinary diene - same stability as two normal alkenes

Conjugated diene - more stability than two normal alkenes

Cumulated diene - less stability than two normal alkenes
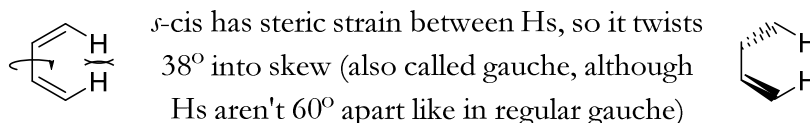
Conjugated dienes
Conjugated dienes are more stable than would be expected for two isolated alkenes. The reason for this is due to the MO (molecular orbitals) are set up. Even though we'd expect the π orbitals of the double bonds to be localized to each pair of double-bonded carbons, there's actually overlap between the two alkenes. (The exact reason for this is explained in section 15.1 of Loudon, but we won't go into this level of detail.)

1,3-Butadiene

Overlap between p orbitals
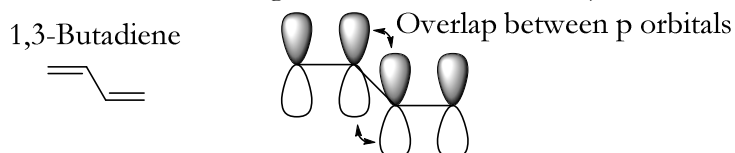
Since there is so much stabilization provided by overlap of these orbitals, conjugated dienes strongly prefer to be in conformations where the *p* orbitals are all coplanar. This means that, in terms of orbital overlap, the single bond prefers to be either in an *s*-cis or *s*-trans conformation. These are named after cis and trans double bonds, even though unlike an actual double bond, the single bond is more-or-less free to rotate.

 s-cis   *s*-trans
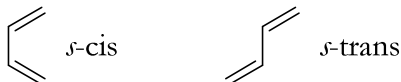
However, the *s*-cis form has a problem: there is steric strain between the protons on the inside edge of the molecule. This forces it to rotate about 38° into a skewed form.

s-cis has steric strain between Hs, so it twists 38° into skew (also called gauche, although Hs aren't 60° apart like in regular gauche)

Cumulated dienes
Cumulated dienes have an *sp*-hybridized carbon in the middle. The two perpendicular *p* orbitals on this carbon form π orbitals to the outer two carbons. The molecule below, allene, is the simplest possible cumulated diene.
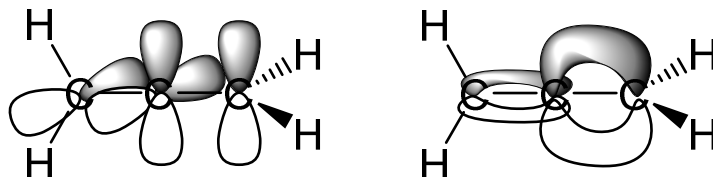

2 p orbitals on central C ⟶ 2 perpendicular π orbitals

Since these orbitals are perpendicular, they do not overlap, so cumulated dienes do not benefit from any added stability. Because of their lower stability, we won't see much of cumulated alkenes - most of this chapter deals with conjugated alkenes.

An interesting side effect of these perpendicular orbitals is that these molecules can be chiral without having any asymmetric carbons. We saw some examples of these molecules in Ch. 6.


Nonsuperimposable mirror images
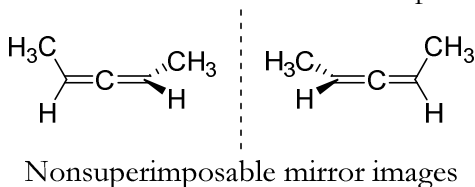
The Diels-Alder reaction
This is probably the most important part of this chapter – it will come up in syntheses in the future. The general idea is that we bring together a four-carbon piece and a two-carbon piece to make a six-membered ring. The four-carbon piece has two double bonds and is called the diene; the two-carbon piece has either a double or a triple bond and is called the dienophile. The electrons all move around the ring at the same time. This is one example of a cycloaddition – a reaction that forms a new ring. This is also an example of a pericyclic reaction – a concerted reaction with a cyclic flow of electrons. The product is sometimes called an adduct, since it results from addition of two molecules.

Diene   Dienophile   Diene   Dienophile
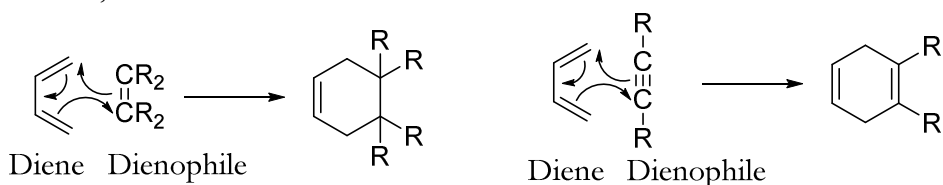
The R groups on the diene can be an H or any sort of R group, though it works best with an electron-donating group (EDG). However, each dienophile must have at least one electron-withdrawing group (EWG) for this reaction to work well (although if not, it can still be forced to react by higher temperatures and pressures).

The dienophile must have at least one of these:
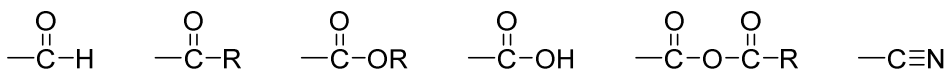
Numbering is extremely useful in keeping track of what happens during this reaction. You can also draw in a faint dotted line to indicate where the bonds are about to form, so that you can track connections more easily. Here, you're making a bond from C2 to C3, and from C6 to C1. Meanwhile, C7 and C8 don't participate in the reaction at all – they just fold out of the way and allow the reaction to happen. That's why they end up as a bridge across the newly-formed six-membered ring.
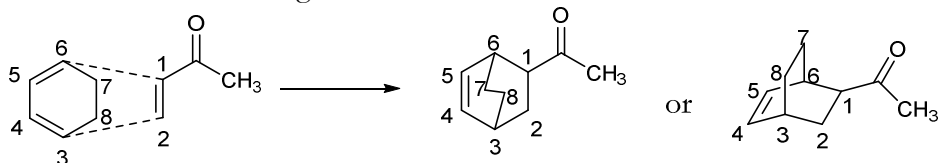

Here, the new bonds are C1-C6 and C2-C7. Meanwhile C5 folds out of the way, and C8, C9 and C10 don't participate at all. Even though this molecule doesn't have any electron-withdrawing groups, the reaction still goes under reasonable conditions in this particular case.
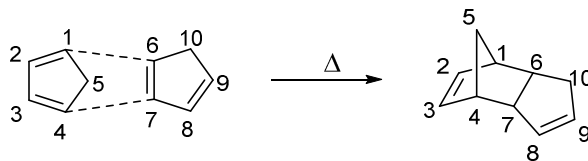
Another requirement for this to happen is that the diene has to be *s*-cis, or close to it. If a molecule is prevented from forming this shape, Diels-Alder can't happen. If it's locked so that it's always *s*-cis, the reaction will be easier than on a normal linear molecule.
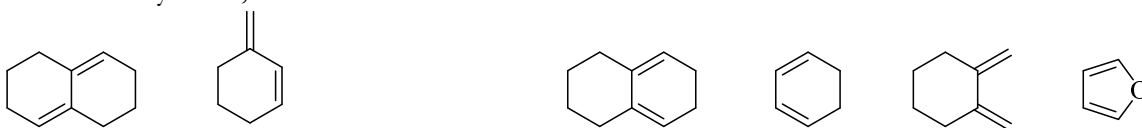
Can't do Diels-Alder   Great at Diels-Alder

The general rule is that the more time the molecule spends *s*-cis, the easier this reaction will be. Sometimes the diene will appear to be freely rotating but is hindered by some bulky R groups. We can label the four groups coming off the ends of the diene as R_o or R_i, depending on whether they're on the outside or inside. The rule is that the bigger the R_i groups are, the less time the molecule will spend in this shape, and the harder it will be to do Diels-Alder.
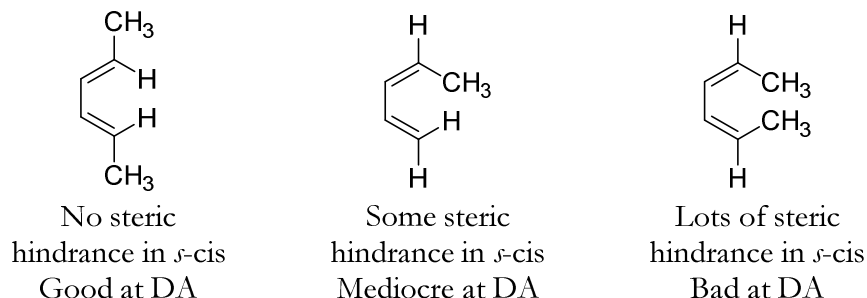
No steric	Some steric	Lots of steric
hindrance in *s*-cis	hindrance in *s*-cis	hindrance in *s*-cis
Good at DA	Mediocre at DA	Bad at DA

The stereochemistry for this reaction is determined by the fact that it's concerted, so each molecule adds only to a single face of the other. Groups that are *trans* in the dienophile are *trans* in the product, and groups that are *cis* in the dienophile are *cis* in the product.
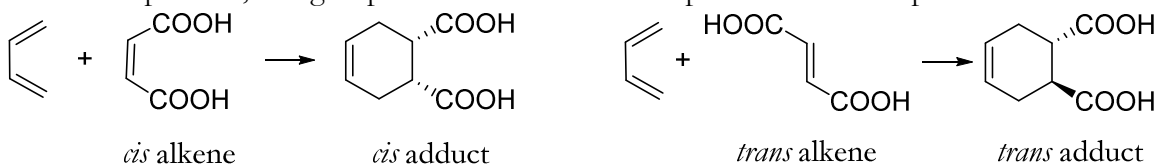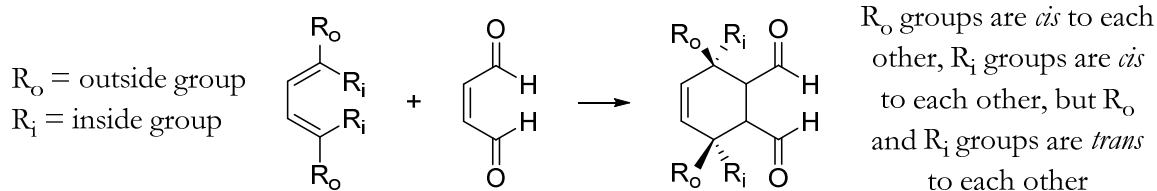
cis alkene   *cis* adduct   *trans* alkene   *trans* adduct

If the two end carbons of the diene both end up becoming stereocenters, then we can track a similar relationship: groups that are both outside the diene end up *cis* to each other.
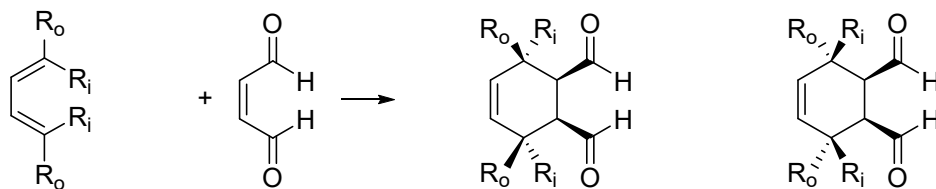
R_o = outside group
R_i = inside group

R_o groups are *cis* to each other, R_i groups are *cis* to each other, but R_o and R_i groups are *trans* to each other

But what if there are stereocenters in what used to be both the dienophile and the diene? Then there are two possible outcomes: *endo* and *exo*.

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R_o = outside group
R_i = inside group

Dienophile groups on same face as R_o: *endo*

Dienophile groups on opposite face to R_o: *exo*

The *endo* product is usually favored, although the *exo* can be favored at higher temperatures.

1,2 vs. 1,4 addition

A lot of the different chemistry that dienes do is caused by resonance. The position one away from a double bond is called the allylic position. Any time a molecule has a charge or a radical at the allylic position, it can move around by resonance. This makes it more stable than a non-allylic charge/radical.
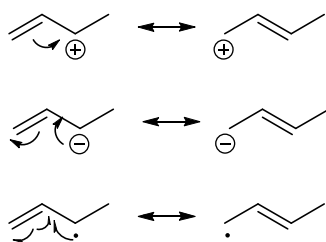
Because of this, conjugated alkenes can behave differently from regular alkenes. Under conditions that would add HBr to regular alkenes, we get some product that looks as if the molecule is acting like a normal alkene and adding an H and a Br to carbons 1 and 2. But some product forms where the new atoms are added four carbons apart from one another, to carbons 1 and 4.

1,2-product   1,4-product
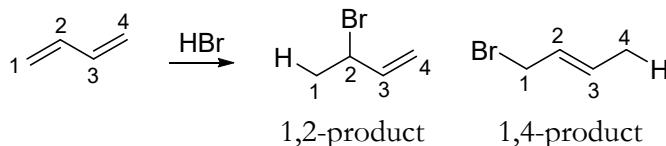
This makes sense once you factor in resonance to the normal HBr addition mechanism. Either one of the resonance forms can be attacked by the bromine.
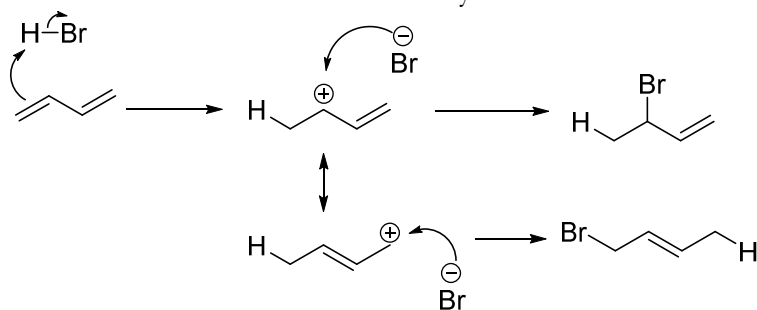
Based on what we know of alkene stability, the 1,4-product is the most stable because it has the most groups attached to the alkene. But the 1,2-product is usually faster to form, because the bromine is closer to carbon 2 at first. This means that the 1,2-product is favored under low-energy conditions and is the kinetic product. The 1,4-product is favored under high-energy conditions that allow it to equilibrate back and forth before it settles into one state, so

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it's the thermodynamic product. You can skew the amounts of products towards the kinetic side by using lower temperatures and towards the thermodynamic side by using higher temperatures.

Loudon also gives a brief review of resonance structures during this chapter (see Ch. 3 notes for earlier coverage). We covered how to create different resonance structures by arrow-pushing, but now we can look at how to evaluate relative stability and determine which resonance forms contribute more to the averaged-out molecular structure.

1. Identical structures are equally important contributors.

   These forms are equally important

2. Structures with complete octets on each atom are more important than structures without.

   Right form is more important

3. If everything has a full octet, negative charges are more stable on more electronegative atoms and positive charges are more stable on less electronegative atoms.

   Right form is more important

4. The orbital geometry has to be realistic for a given resonance form – if one form is breaking rules for geometry (like Bredt's rule, VSEPR bond angles, etc.) then it's not a resonance contributor.

   Right form cannot exist because it breaks Bredt's rule
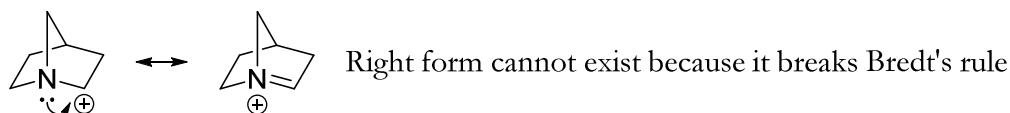
Aromaticity

Even though we've done a lot of reactions on alkenes, none of them work on benzene. That's because aromatic rings have totally different behaviors from normal alkenes. They are much more stable than they would be if the alkenes had no interactions at all. In fact, the alkenes don't even exist as distinguishable double bonds – they average out around the ring, so that every bond is halfway between single and double.
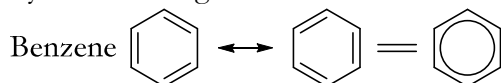
Benzene

Benzene is not the only molecule that fits this description – lots of others have the same behavior. There are four conditions that a molecule must meet:

1. It has to be cyclic
2. It has to be planar
3. All of the atoms around the ring have to have some involvement in the pi system, either through pi bonds, lone pairs (maybe due to a negative charge), empty orbitals (maybe due to a positive charge), or radicals. In other words, all the atoms have to have at least one unhybridized p-orbital, so they have to be sp- or sp^2-hybridized.
4. If it has $4n+2$ pi electrons, it's aromatic (more stable). If it has $4n$ electrons, it's antiaromatic (less stable). It doesn't matter what n is as long as it's an integer. This is called the Huckel $4n+2$ Rule.

Not all carbons have involvement in π system = nonaromatic
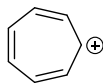
All carbons have involvement in π system, and there are 6 π electrons altogether = aromatic
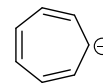
All carbons have involvement in π system, and there are 8 π electrons altogether = antiaromatic (if it's planar)

Aromatic means that the molecule is more stable than it would otherwise be, due to this effect. **Antiaromatic** means that it's less stable. **Nonaromatic** means that it has no change in either direction, because one or more of these rules aren't being met. The reasons for the changes in stability have to do with orbital levels – it turns out that aromatic molecules always have all bonding orbitals filled, while antiaromatic molecules have two half-filled orbitals. (These can be described by Frost circles, which are a way to calculate relative MO energy levels.)

In the case of larger rings (larger than about 6 atoms), if the rules work out to them being antiaromatic, they'll usually bend out of plane to avoid it. COT is the best-known example of this. It behaves just like a regular alkene, with no unusual behavior due to antiaromaticity.
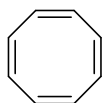
Cyclooctatetraene (COT) would be antiaromatic, but it twists up to avoid the penalty of lowered stability. This makes it nonaromatic instead.

Sometimes you have the option of whether to include a lone pair towards the total pi electrons or not. This is often the case for heterocycles, rings with atoms other than carbon. You can do this by setting the hybridization of the atom with the lone pair: if it's hybridized the lone pair is not involved in the π system, but if it's unhybridized then it is involved. Note that you can only count one lone pair per atom, at most. Sometimes the lone pairs are excluded anyway due to geometry, especially if the atom already has a double bond. The molecule will choose the best outcome, based on stability.
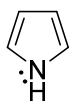
If you count the lone pair: 6 π e⁻ so it's aromatic

If you don't count the lone pair: not every atom has an involvement in the π system, so it's nonaromatic.

Best outcome: count the lone pair (LP is p)
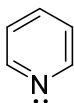
If you count the lone pair: 8 π e⁻, so it's antiaromatic

If you don't count the lone pair: 6 π e⁻, so it's aromatic

Best outcome: don't count the lone pair (LP is sp^2)

If you don't count either lone pair: not every atom has an involvement in the π system, so it's nonaromatic.

If you count one lone pair: 6 π e⁻, so it's aromatic

Best outcome: count one lone pair (one LP is p and the other is sp^2)

There are also ways to explain the participation or nonparticipation of a lone pair based on geometric requirements. For instance, pyridine (the middle molecule above) couldn't have its lone pairs participating anyway, since the hybridization of the nitrogen forces the lone pair to point out away from the ring. In general, a participating lone pair will be p-hybridized (which allows that atom to be part of the pi-system) and a non-participating lone pair will be whatever hybridization is left over on that atom.

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Ch. 15 Synthesis Practice
Here's a synthesis practice problem, using these new reactions.
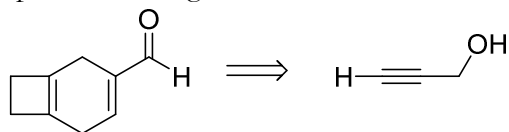
We're making a six-membered ring, so Diels-Alder is the obvious choice. Let's start placing the disconnects so we know where to cut. Note that we're leaving the EWG (the carbonyl) on the side that has only two ring carbons, because the dienophile must have an EWG.
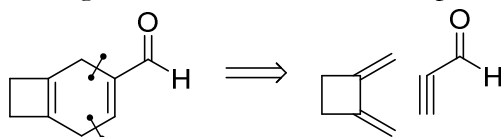
One of these sides looks similar to the precursor, just the C-O bond is changed.
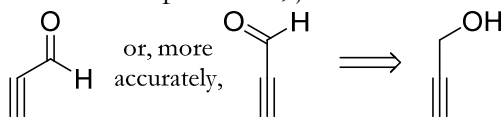
Now we can put it together with the reagents.