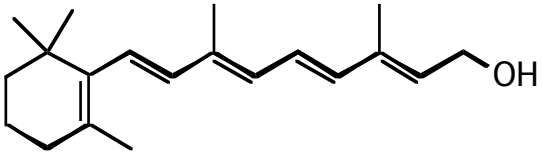
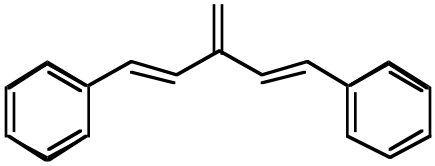
Conjugation.

Conjugation relies on the partial overlap of p-orbitals on adjacent double or triple bonds. One of the simplest conjugated molecules is 1,3-butadiene.

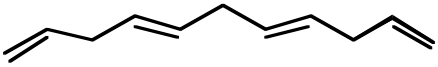
Conjugation comes in three "flavors," the simplest of which is the normal straight-through (linear) conjugation seen in many biomolecules (such as Vitamin A).



However, it is possible for two systems to be in "cross-conjugation" with each other, as in the example below (the two benzene rings are cross-conjugated, NOT conjugated!):



Conjugation is broken completely by the introduction of saturated (sp^3) carbon:



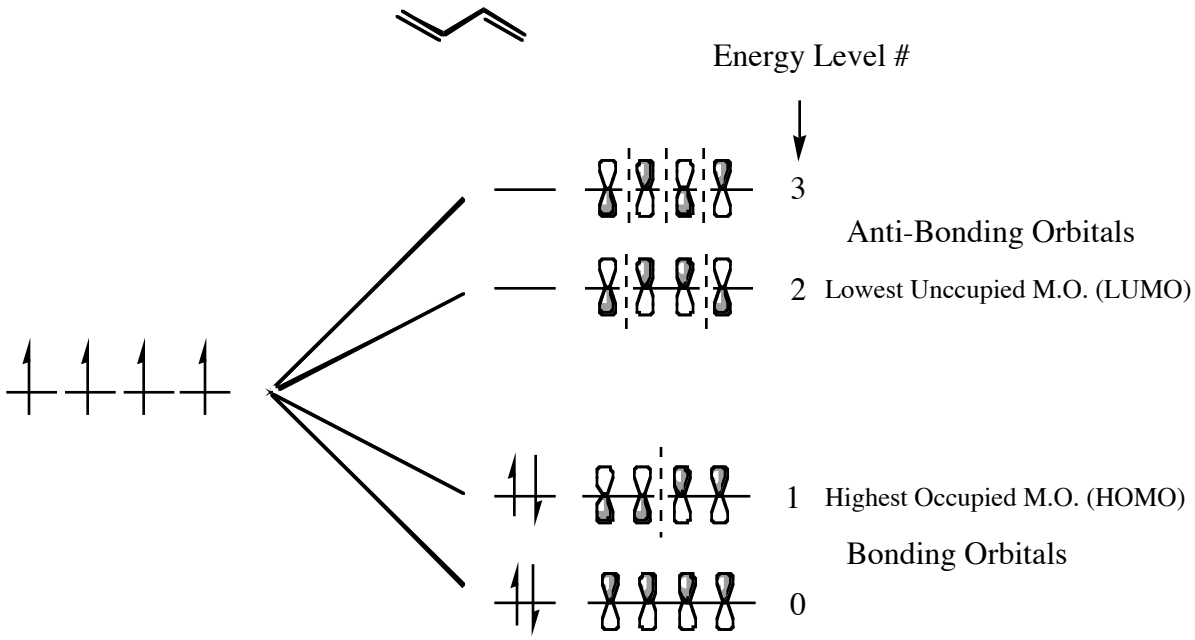
There are a lot of double bonds, but there is NO conjugation in this molecule.

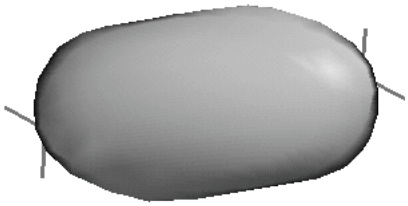
For linearly conjugated systems, it is quite straightforward to look at the molecular orbital picture of the various energy levels in the molecule. Here are a list of guidelines for the preparation of such a picture:

1) For every p-orbital, there is a π-molecular orbital.
2) Each molecular orbital (M.O.) has its own, unique energy associated with it.
3) For molecules with an even number of π-bonds, half of the M.O.'s are higher in energy than the starting p-orbitals, and half are lower in energy.
   For molecules with an odd number (n) of carbons in the conjugated framework (i.e. allyl radical), (n-1)/2 M.O.'s are higher in energy, (n-1)/2 are lower in energy, and there is ONE nonbonding M.O., with the same energy as the p-orbitals.
4) The lowest energy M.O. has 0 nodes. The highest energy M.O. has n-1 nodes, where n is the total number of M.O.'s.
5) The number of nodes increases by one for each higher energy level.
   a) M.O.'s with an odd number of nodes always have a node in the middle.
   b) M.O.'s with an even number of nodes NEVER have a node in the middle.
6) Each M.O. will hold *2* electrons.

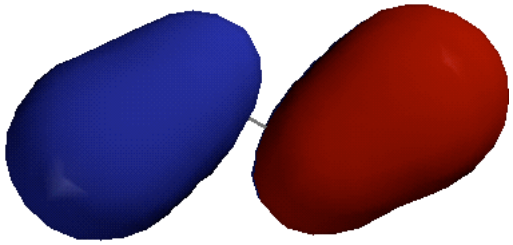
The MO diagram for butadiene is shown below. Things you should note:
1) the progression of nodes (from 0 to 1 to 2 to 3)

2) A filled set of bonding orbitals.
3) An EMPTY set of anti-bonding orbitals.
4) Electrons with PAIRED SPINS!
Below the MO diagram, I have put calculated Electron Density Plots for each M.O.

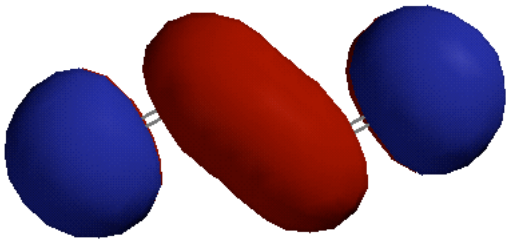




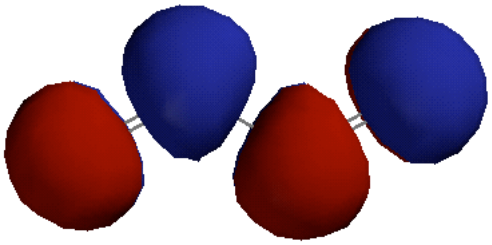
Level 0 (lowest energy)



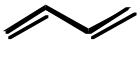
Level 1 (HOMO)



Level 2 (LUMO)

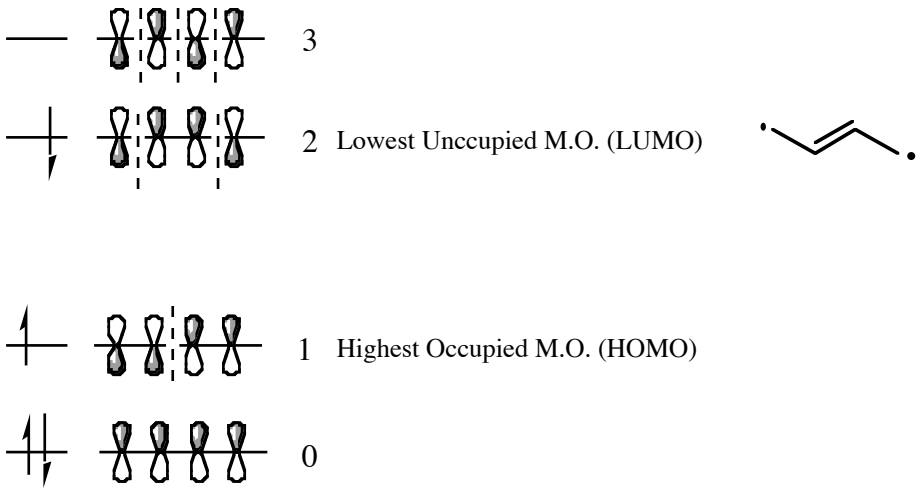


Level 3 (Highest Energy)

These plots show that the lowest energy level has electron density spread over the entire conjugated backbone. The HOMO looks more like two double bonds, and is the best representation of the way we write the structure, namely:  . The LUMO has its

double-bond character in the center of the molecule, while the Highest anti-bonding orbital shows NO interaction between any of the p-orbitals.

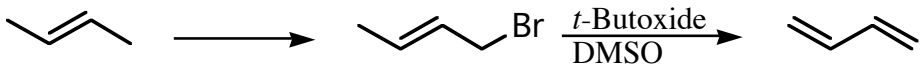
What if we put the molecule into its first excited state? The orbital diagram then looks like the diagram below. The actual structure of the molecule is best represented by the electron density shown in the LUMO diagram (above), yielding the diradical structure shown on the right. You should be able to derive structures such as this from the orbital pictures of the HOMO and LUMO of any M.O. diagram.



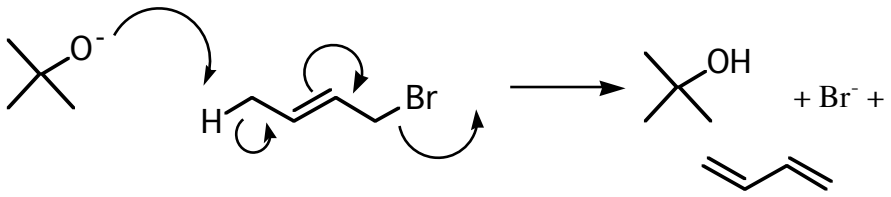
Preparation of Conjugated Systems:

There are a number of methods for the preparation of conjugated systems. One possibility is by allylic bromination, followed by either normal (2) or conjugate (1) elimination:

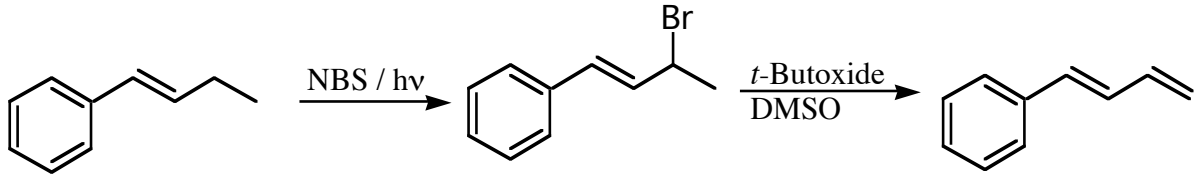
1



Conjugate Elimination:

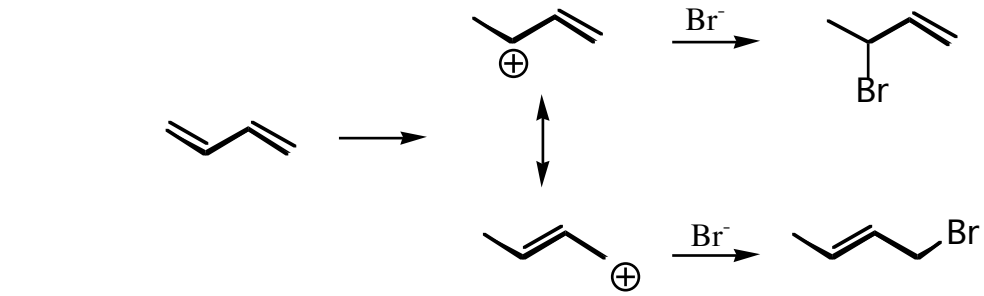


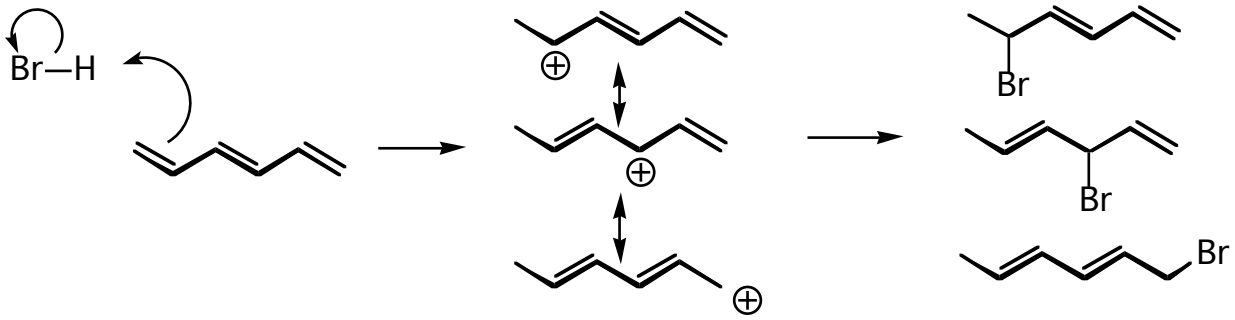
2



Reactions of Conjugated Systems:

As your text states, conjugated systems do not give simple products on addition of HX or X_2. Simply put, the charge generated from the initial electrophilic addition to one of the double bonds is delocalized over the entire conjugated system, leading to multiple products:



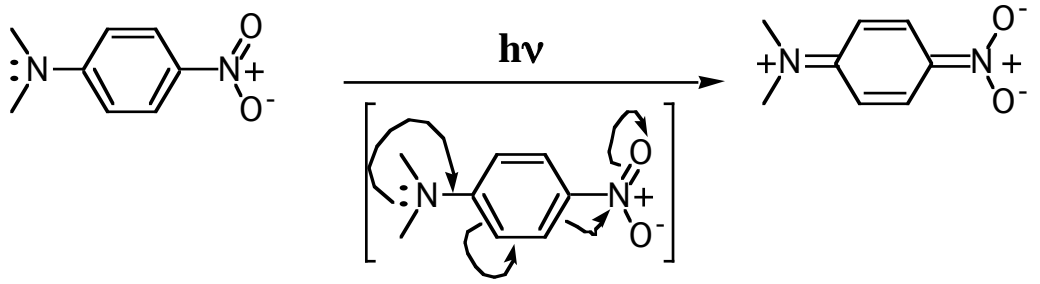


The ratio of products varies with the reaction temperature, and depends both on which material is formed faster, and which product is most stable (See Ch. 14.6).

UV-Vis Spectroscopy.

UV-Vis spectroscopy is based on exciting the electronic levels in *conjugated* molecules. What occurs is simply a promotion of one electron from the molecule's HOMO into its LUMO. The molecule generally takes on the electronic character of the LUMO in this instance, generally having a diradical character. The greater the degree of conjugation in the molecule (i.e. the more levels in the M.O. picture), the easier it will be to excite an electron into the LUMO. At sufficiently low energy level differences, the energy required to promote an electron to the LUMO can be provided by visible light, yielding a colored compound. Another way to say this is that if a compund is colored, an easy route must exist for the promotion of an electron.

Along with increasing the degree of conjugation, there are other ways to facilitate the excitation of an electron. One method is to facilitate what is called intramolecular charge transfer. This is usually accomplished by the preparation of a "push-pull" system, as shown below:

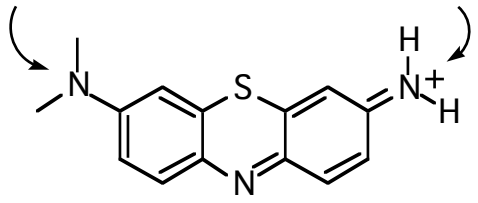


The ease with which this charge-transfer reaction takes place depends on the strength of the "push" component (in this case, the dimethylamine group) and the strength of the "pull" component (the nitro group). Thus by varying the push and pull moieties, and by changing the length of the conjugated bridge separating them, we can control the color of the molecule! Some examples of colored compounds are shown below – be sure you understand why they have different colors!

Azure A

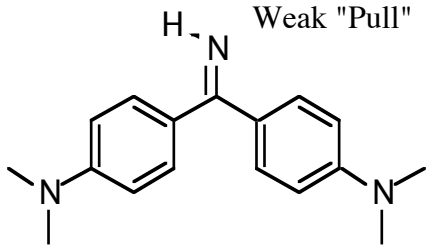
Strong "Push" end

Strong "Pull"



Auramine O

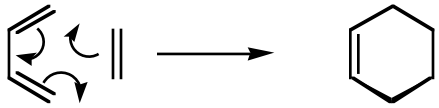
Weak "Pull"



Strong "Push"

The Diels Alder Reaction

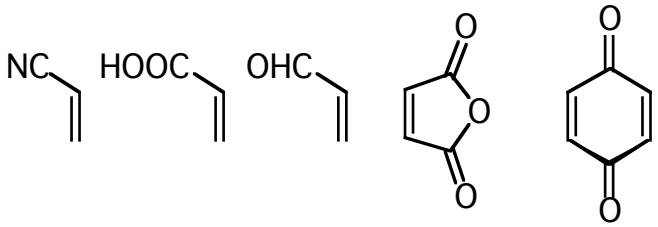
One of the most spectacular reactions in organic chemistry. In linking two carbon molecules together, it forms *two* single bonds and *one* double bond, all in one step. At its simplest:



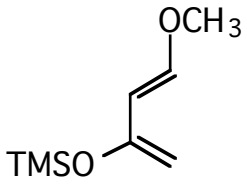
A diene reacts with an alkene (called a dienophile) in a concerted reaction to give a cyclohexene. No intermediates of an ionic or radical nature have been detected for this reaction. It goes in one step.

There are some qualifications, however. The reaction depicted above requires extreme temperatures and pressures in order to go. For a Diels-Alder reaction to work at room temperature, a number of criterial must be met:

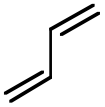
1) An electron-poor dienophile is required. Some examples:



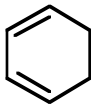
2) An electron-rich diene is helpful:



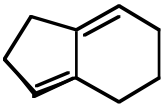
3) The diene MUST be in an S-cis configuration:



Good
(can rotate to S-cis)

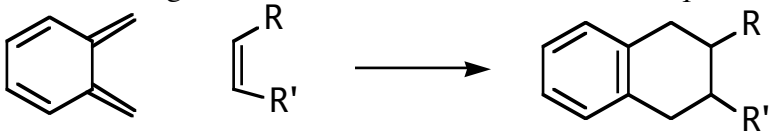


Excellent
(Locked into S-cis)



Bad
(Locked S-trans. Booo)

Note also that in some cases the Diels-Alder reaction is reversible(!), i.e. a cyclohexadiene can revert back to a diene and a dienophile. Occasionally, the retro Diels-Alder is more favorable than the forward reaction. In these cases, there are some special tricks that can be used to force the reaction along. One such case is the use of an *ortho-quinodimethane*:

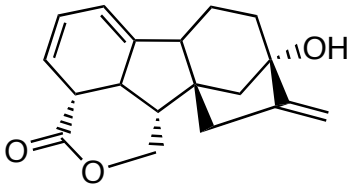


o-quinodimethane

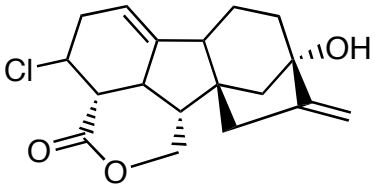
The quinodimethane regains aromatic characted after the Diels-Alder reaction, which acts as a great impetus to drive the reaction.

Your text has an excellent description of the endo-preference of the Diels Alder reaction. However, I would like to make the point here that configuration is retained after the Diels Alder reaction. If your dienophile is *cis*, the product MUST be *syn*., and if the dienophile is *trans*, the product will be *anti*.

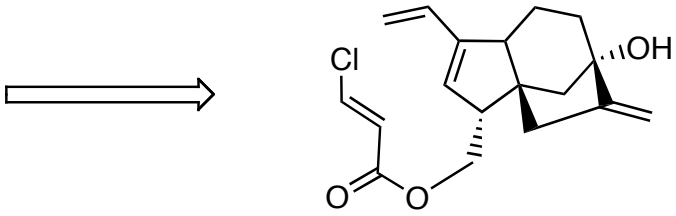
I will close this chapter with a brief look at a couple of fragments (involving Diels-Alder Chemistry) of E.J. Corey's synthesis of Gibberellic Acid



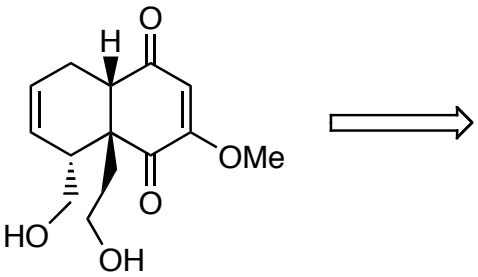
Remember, a diene can be formed from elimination of an allyl halide (Cl or Br)



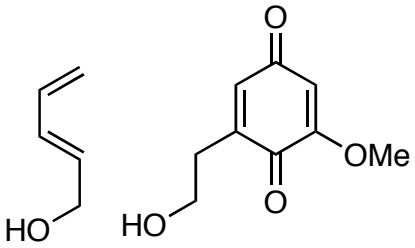
AHA! Here we see a cyclohexene ring! These can be easily formed by a Diels Alder reaction!



An excellent example of a TETHERED Diels-Alder system - these reactions work QUITE well!



A Precursor to the stuff shown above - contains a cyclohexene!!!! -> Diels Alder!!!!



A Diels-Alder reaction forms the bicyclic system!