



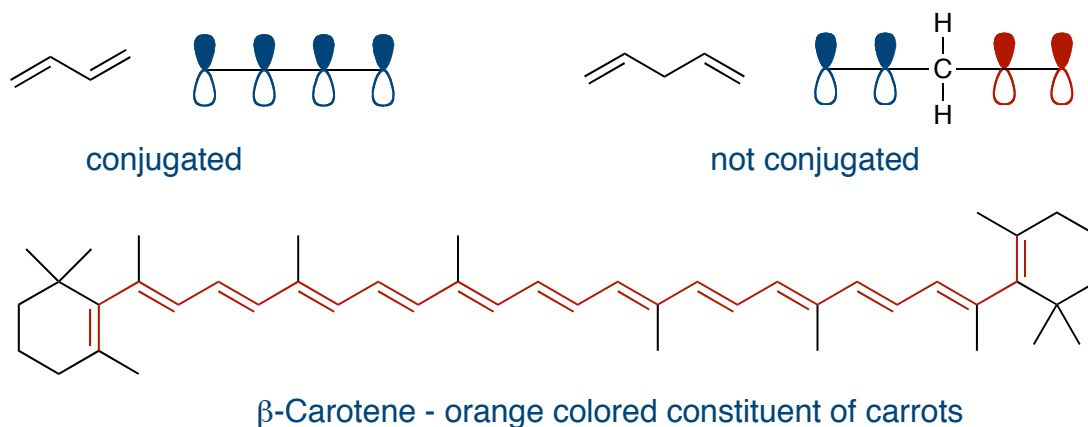
Chem 342 • Organic Chemistry II

Lecture Summary 05 - 26 Jan 2009

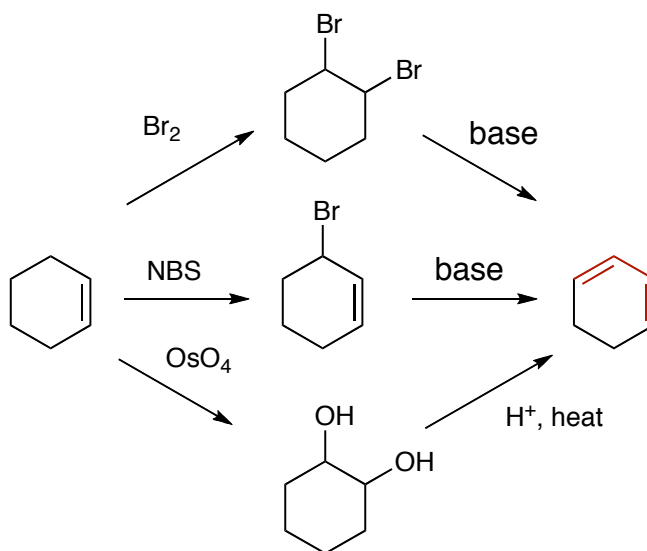
Chapter 14 - Conjugated Dienes and Ultraviolet Spectroscopy

Conjugated Polyenes

Double bonds are conjugated when their pi-bond systems are contiguous. That is, all the p-orbitals are next to each other.

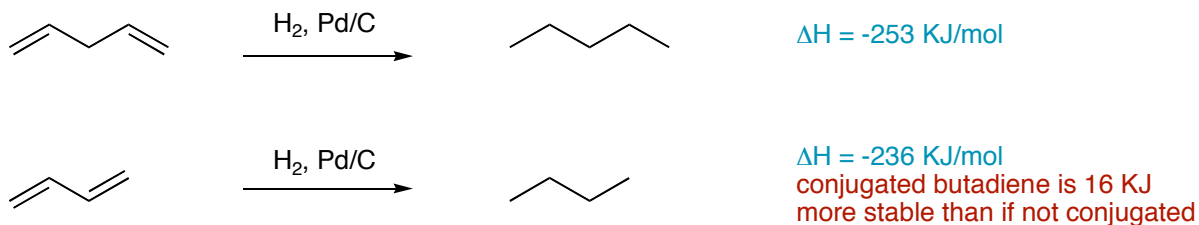


The most general method to make dienes is by the elimination of allylic halides or dihalides. One can also dehydrate alcohols to generate two double bonds.



Stability

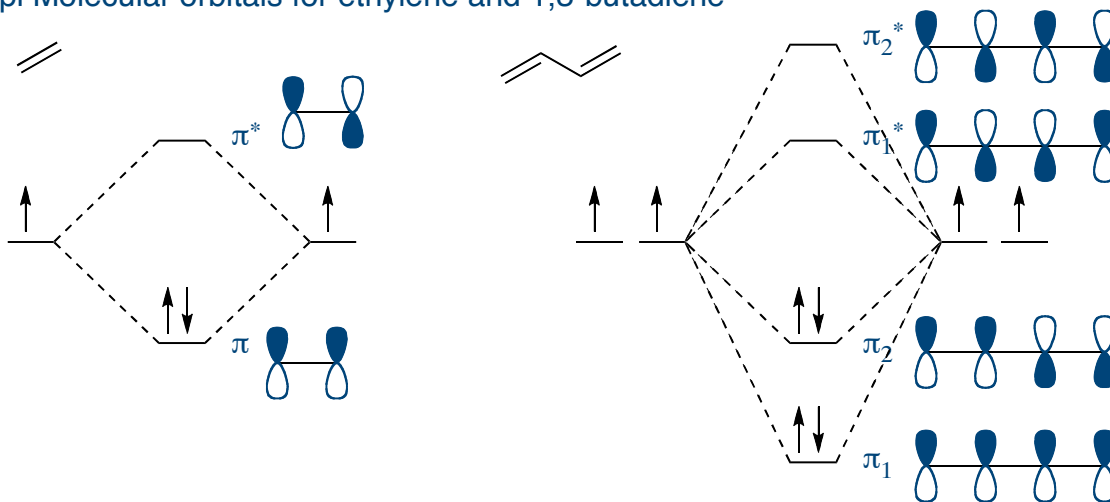
Conjugation provides more stability than would be predicted by just the energetics of the pi-bond. The overlap of orbitals from one alkene to the other lowers the energy. Any kind of delocalization of electrons (eg. you can draw resonance forms) afford greater stability. Diene stability can be measured by look at the heat of hydrogenation.



Molecular Orbitals

Conjugated pi-systems can be described using molecular orbital theory. It shows that the pi bonds of a conjugated system has a lot of overlap in the lowest filled orbitals. For example, in butadiene, the lowest energy molecular orbital has the same sign on each carbon above and below the sp^2 plane. Thus, we can think of a conjugated diene as a single pi-system with all four electrons spread out among the four carbons.

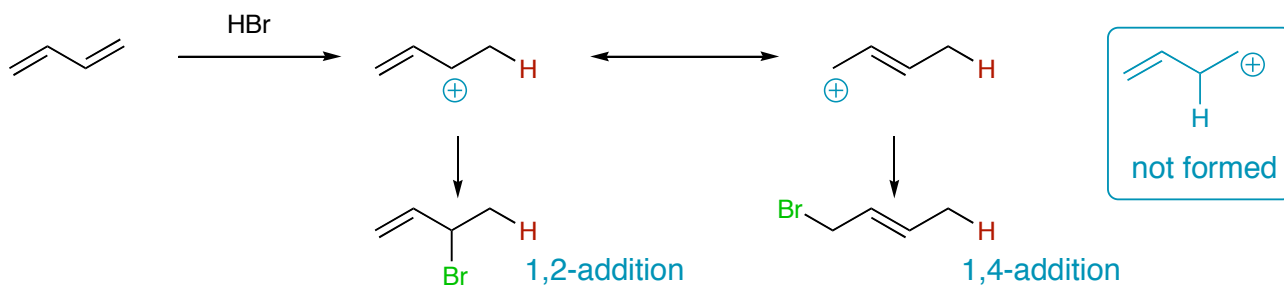
pi Molecular orbitals for ethylene and 1,3-butadiene



Note that in the lowest orbital all four carbons share the same sign above and below demonstrating that the electrons are shared equally throughout the structure.

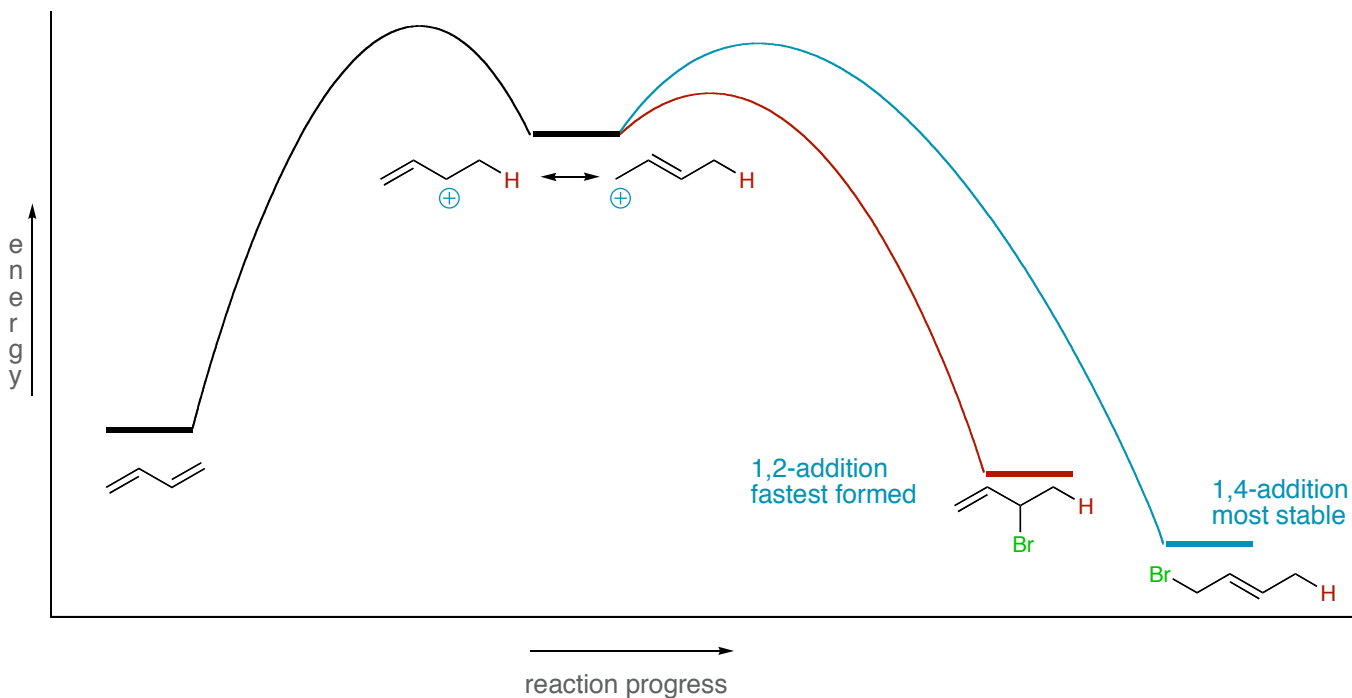
Reactions of Dienes

Conjugated dienes react with electrophiles to form the product of the most stable carbocation intermediate. Since the carbocation is allylic, the nucleophile can add to two different carbons to afford the 1,2-product or the 1,4-product. Usually a mixture is obtained.



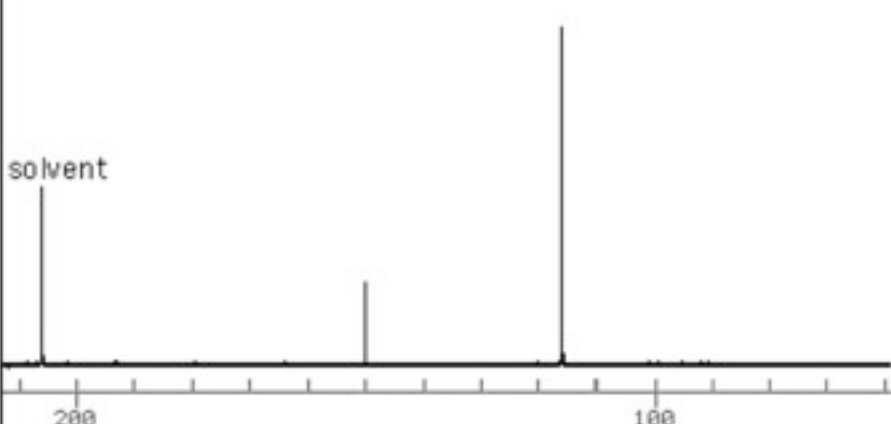
Kinetic Control	0 °C	71%	29%
Thermodynamic Control	40 °C	15%	85%

Product ratios can be controlled by the kinetics (which one forms faster, non-reversible, low temp) or the thermodynamics (which one is more stable, reversible, higher temp).

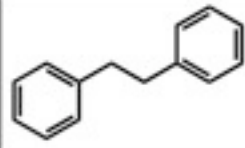
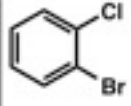
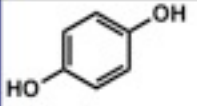


Daily Quiz

Q: Which molecule corresponds to the following C-13 NMR data?



The NMR spectrum shows three distinct peaks. The first peak is labeled 'solvent' and is located at approximately 200 ppm. The second peak is at approximately 155 ppm. The third peak is at approximately 125 ppm. The x-axis is labeled with 200 and 100 ppm.

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