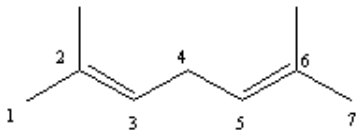


Conjugated Molecules

- Conjugated molecules have *alternating* single and multiple (i.e. double or triple) bonds.

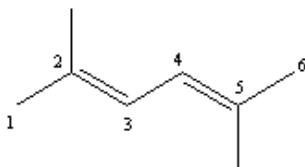
Example 1:



Nomenclature: **2,6-dimethylhepta-2,5-diene**

This molecule is **not conjugated** because it does not have alternating single and multiple bonds (the arrangement of the bonds starting from C2 is double, single, single and double). Between the two double bonds, there is a saturated center (C4) and two intersecting single bonds.

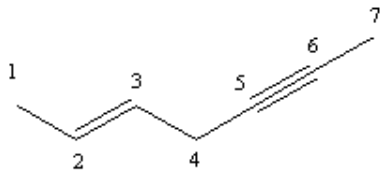
Example 2:



Nomenclature: **2,5-dimethylhexa-2,4-diene**

This molecule is **conjugated** because the arrangement of the bonds starting at C2 is double, single, and double. They are alternated.

Example 3:

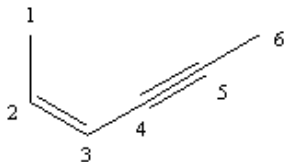


Nomenclature: **(2E)-hept-2-en-5-yne**

note: (2E) is a stereochemical identifier. The letter “E” indicates the arrangement of the double bond (where E usually refers to *trans* and Z refers to *cis*). The number “2” indicates the position of the double bond.

This molecule is **not conjugated** because the single and multiple bonds are not alternated.

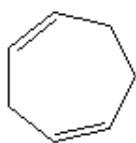
Example 4:



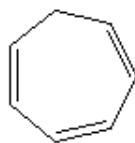
Nomenclature: **(2Z)-hex-2-en-4-yne**

This molecule is **conjugated** because there is an alternation of multiple and single bonds (double, single, and triple starting from C2).

More examples:



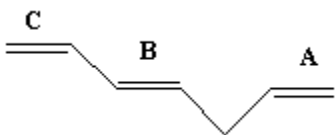
Not Conjugated



Conjugated

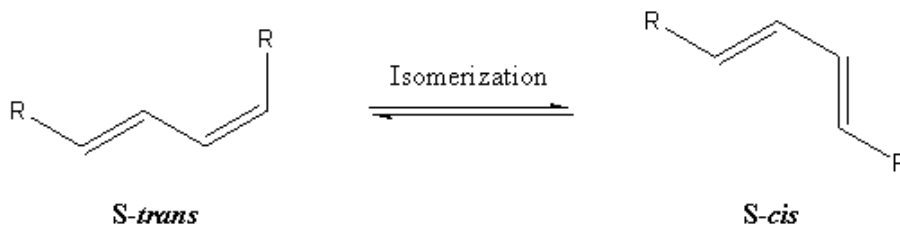
note: the term conjugation refers to parts of the molecule. If you can find one conjugated system within the molecule, that molecule is said to be conjugated.

Example:



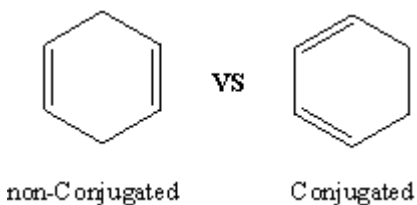
In this molecule, the double bond A is not conjugated. However, since double bond B is conjugated with double bond C, the molecule is said to be conjugated.

Special Nomenclature:



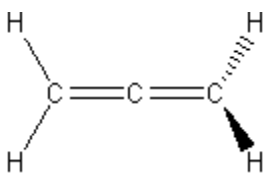
The Letter "S" stands for "single" and indicates that we are talking about the conjugated double bonds. The term *cis/trans* refers to the stereochemistry of the double bonds around the single bond.

Characteristics of conjugation

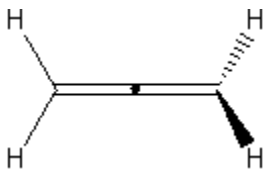


The conjugated system is thermodynamically more stable than non-conjugated system, hence it is at lower energy.

Cumulated double bonds



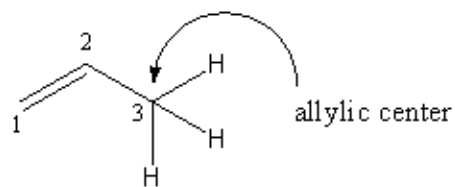
This molecule is known as **allene** (containing two double bonds which share a carbon atom). It can also be written as:



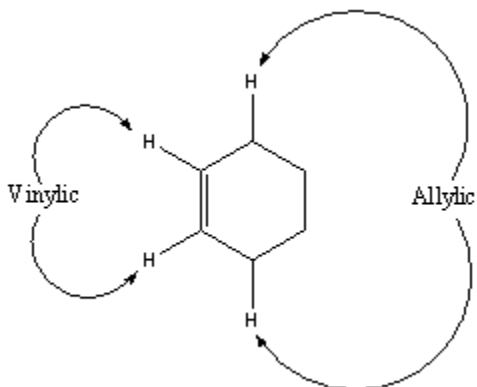
The carbon at the center is abbreviated as a single dot.

Introduction to allylic system

The term **allyl** refers to the group $\text{H}_2\text{C}=\text{CH}-\text{CH}_2$. The carbon next to the double bond is the allylic center.

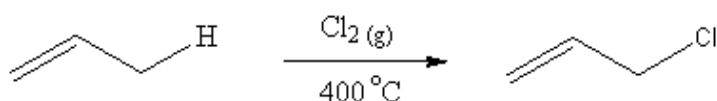


The hydrogens attached to the allylic center (C3) are called *allylic* hydrogens.



The hydrogen **directly** attached to the double bond carbon is **vinyllic**, whereas the hydrogen attached to the carbon adjacent to the double bond is **allylic**.

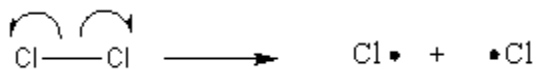
The allyl radical



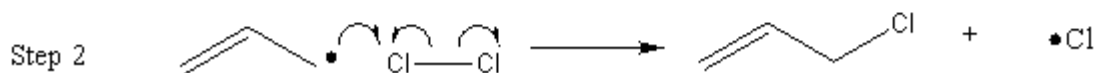
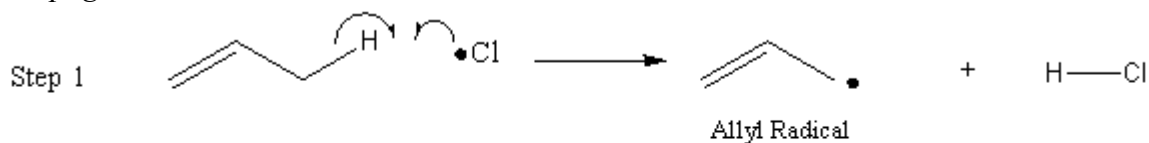
Note the condition of reaction is in gas phase.

Mechanism of the radical reaction

Initiation:

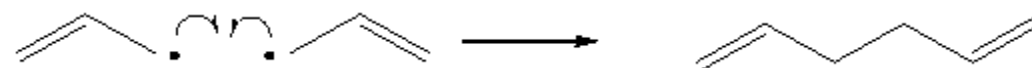


Propagation:



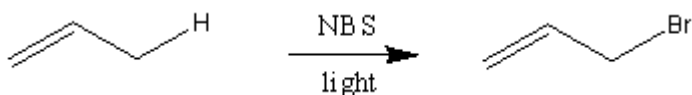
The chlorine radical formed here can also be used in step 1 of propagation, hence propagate the reaction.

Termination:



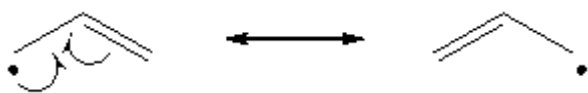
The termination step may produce side product.

In solution, the radical reaction is carried out using N-bromosuccinimide (NBS), which is a source of bromine radical.



The radical reaction is carried out only at the allylic position. Why?

The allylic radical is **resonance stabilized** and will be formed more easily than others:



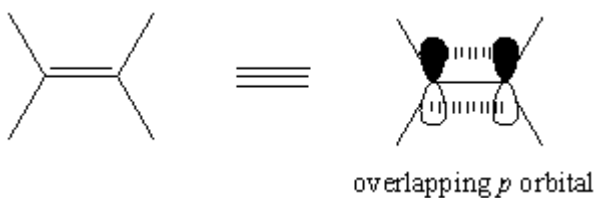
The combination of the two resonance form is represented as:



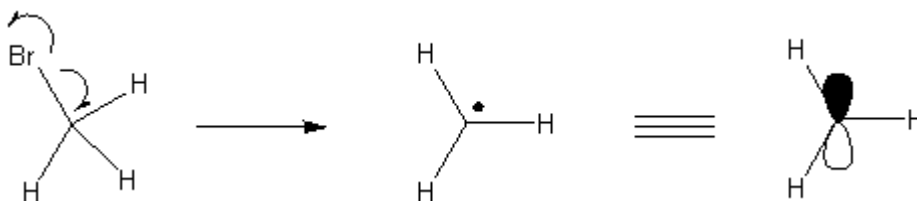
The dashed partial bonds represent the bonds that are double in one resonance form and single in the other. The carbon at each end carries $\frac{1}{2}$ of the radical electron density.

Orbital description

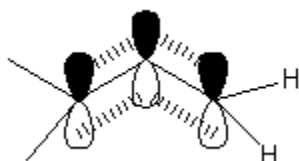
Double bond: a double bond is held together by a σ bond made up of overlapping sp^2 orbitals and a π bond made from $2p$ orbitals overlapping side by side.



Methyl radical: a methyl radical is sp^2 hybridized and has one electron occupying the p orbital.

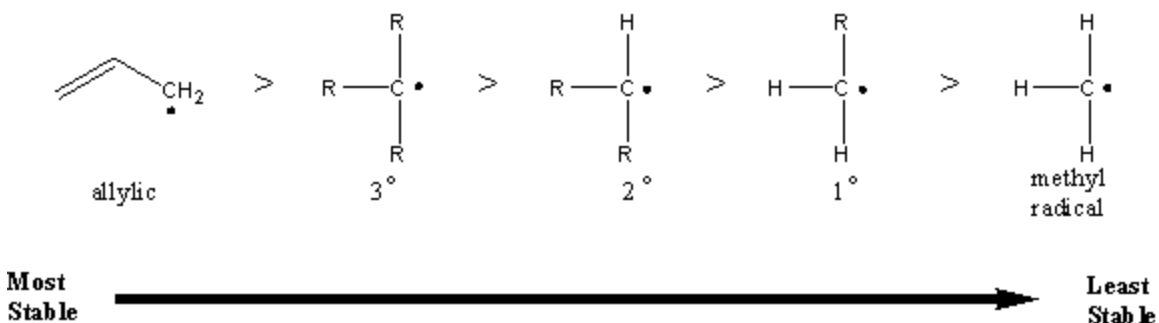


When the two different pieces (a double bond and a methyl radical) are brought together, we see the molecular orbital of an allylic radical. The three electrons in the system are shared (delocalized) between the three carbon atoms.



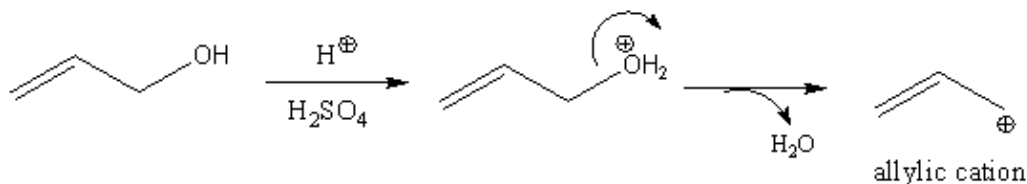
All three carbons are sp^2 hybridized with overlapping $2p$ orbitals.

Stability of radicals:

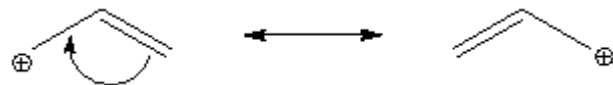


The allylic radical is stabilized through resonance, whereas other radicals shown depend on electron donating ability of the R group (inductive effect or hyperconjugation).

The allyl cation



The allylic cation is stabilized through resonance, similar to allylic radical.



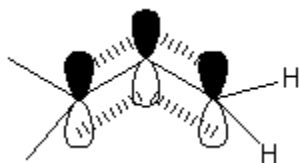
The combination of the two resonance form is shown below:



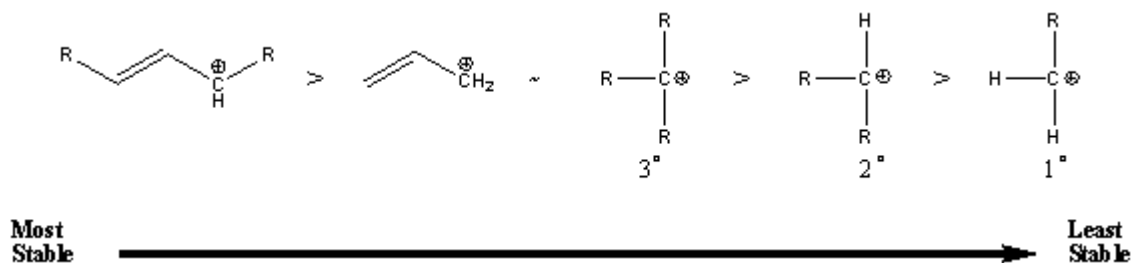
The positive charge is shared equally between the two end carbons.

Orbital description

As with allylic radical, the allylic cation has all three carbons sp^2 hybridized with overlapping $2p$ orbitals. However, there are only 2 electrons delocalized through 3 carbon atoms.

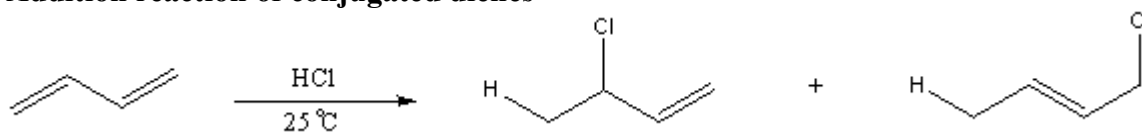


Stability of cations:

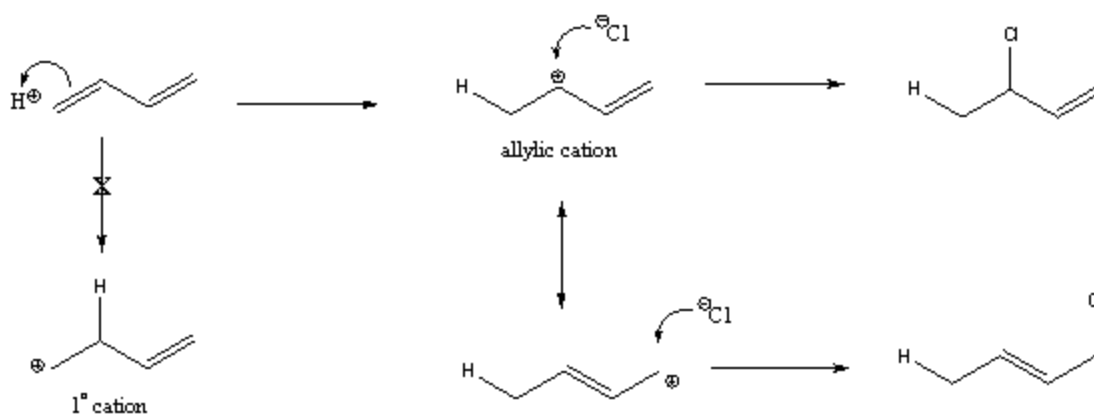


The allylic cation with alkyl groups attached is more stable than allylic cation with only H attached. This again, depends on electron donating ability of R groups.

Addition reaction of conjugated dienes



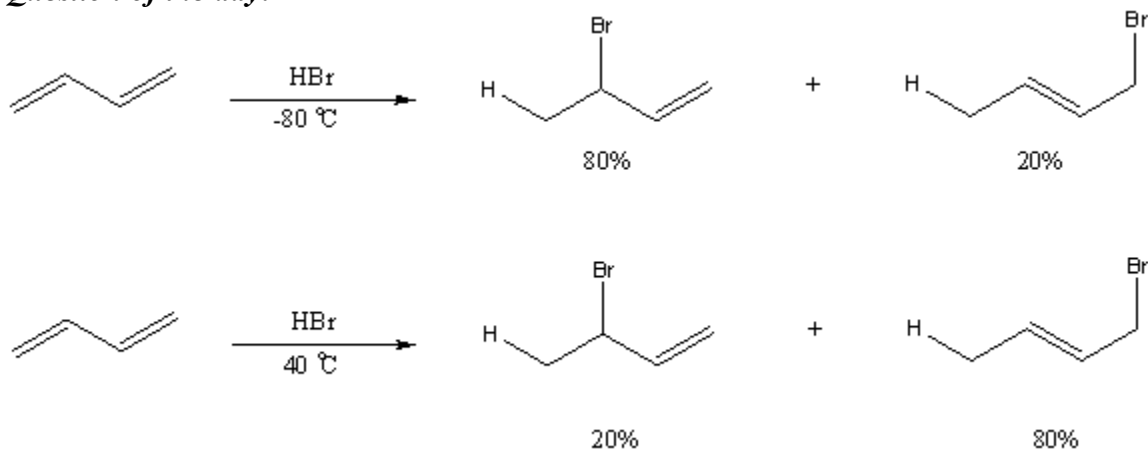
Mechanism:



The first step is the protonation of the double bond. There is a choice of an allylic cation which is resonance stabilized, and the un-stabilized primary cation. The allylic cation is formed since it is lower in energy.

The resonance description of the allyl cation shows the source of the two products.

Question of the day:



Why does change in temperature give different yield of the product?