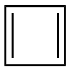
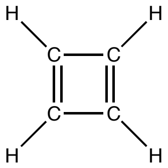
Chem 263 Notes Sept. 15, 2009

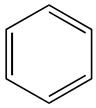
Conjugated Systems continued

Eg. Cyclobutadiene

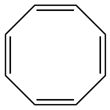




Usually, sp^2 carbons have a bond angle of 120°, but in this molecule bond angle is about 90°.

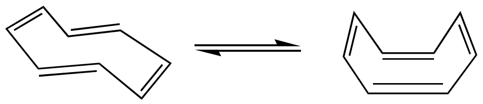


According to naming rules this is 1,3,5-cyclohexatriene but this molecule is almost always referred to by its common name, **benzene**
This is an aromatic compound (information regarding aromatic compounds will be in a later lecture) – especially stable and reacts differently

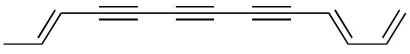


cyclooctatetraene

This molecule is not conjugated due to its conformation, more information will be provided in another lecture on aromaticity and aromatic compounds



Note that you could start numbering this molecule at any carbon, but if one of the hydrogens were replaced with another group (eg. a methyl group) than that would become position 1



(3*E*,11*E*)-trideca-1,3,11-trien-5,7,9-triyne

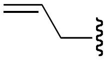
The above compound is part of a plant defense mechanism (anti-nematode) from canola to kill predatory worms.

All double bonds and triple bonds in the above compound are conjugated.

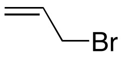
It is a derivative of a tridecane (13 carbons). Know the names of the first 20 alkanes. Begin numbering at the end of the longest chain with maximum number of multiple bonds so as to give the first multiply bonded carbon the lowest number. There is no stereochemistry in the triple bonds because they are linear (180°). Stereochemistry is only potentially possible in the double bonds.

Nomenclature of Allyl and Vinyl Groups (the squiggly line represents attachment to any group)

Allyl Group

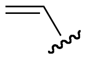


Example

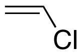


allyl bromide

Vinyl Group

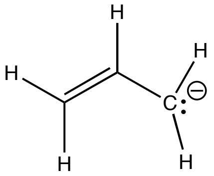


Example



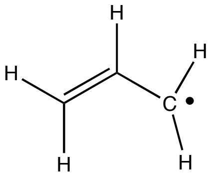
vinyl chloride

Allyl intermediates include:



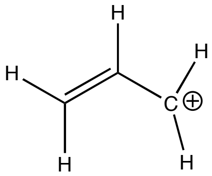
Allyl anion

Has 8 e^- at C
C is negative



Allyl radical

Has 7 e^- at C
C is neutral but reactive



Allyl cation

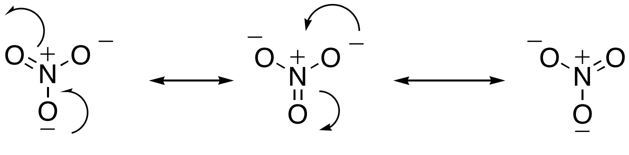
Has 6 e^- at C
C is positive

All are conjugated intermediates, the excess or deficient electrons at the carbon atom are conjugated to the double bond.
All are stabilized through resonance structures.

Resonance Forms

Resonance forms (resonance structures) are different pictures of the same molecule obtained by moving electrons without changing the position of the atoms.

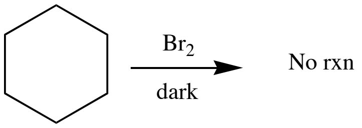
Shown below are the resonance forms of sodium nitrate ($NaNO_3$). The anion on oxygen is a conjugated anion. Resonance forms are connected by a double headed arrow.

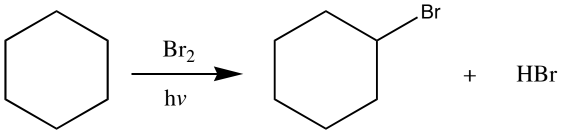


Review of Reactions

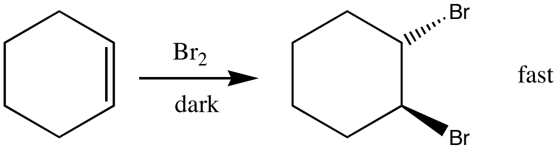
(note reaction will frequently be abbreviated as rxn in this course)

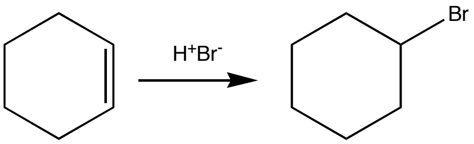
Substitution:



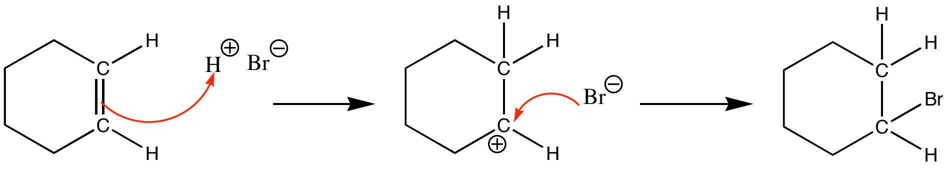


Addition:



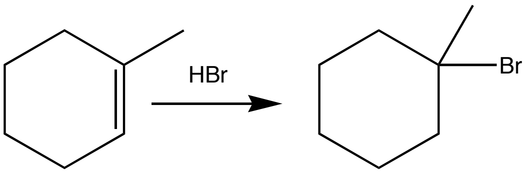


Mechanism:

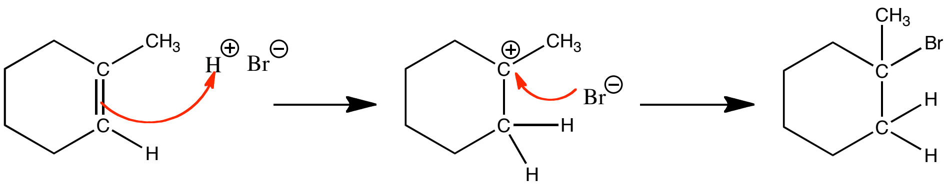


Carbocation intermediate

An example of a reaction following the Markovnikov Rule:

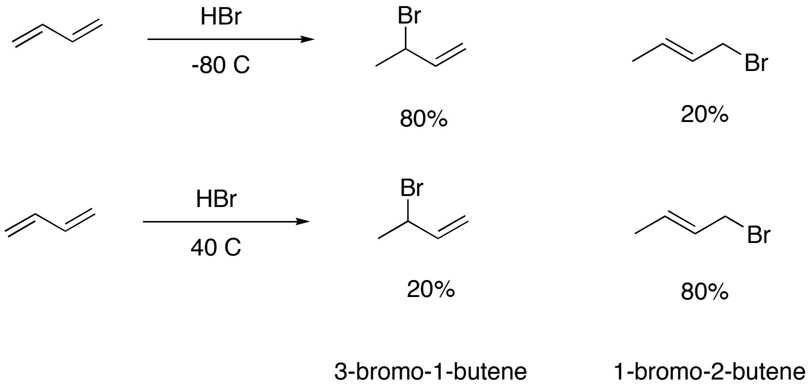


1-methylcyclohexene



the 3° carbocation is the most stable,
it has more groups stabilizing
the postive charge

Addition Rxn Conjugated System

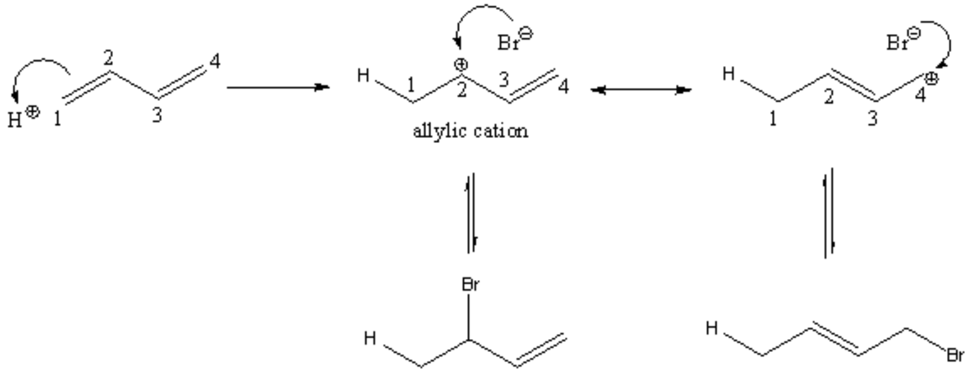


These are structural isomers.

The product 3-bromobutene is a **1,2-additon** product, whereas 1-bromo-2-butene is the product of an **1,4-addition** reaction. The numbers (**1,2-** or **1,4-**) indicate the position where the H and Br added to the 1,3-butadiene. 3-Bromobutene had hydrogen and bromine atom added to C**1** and C**2** of 1,3-butadiene (hence **1,2**-addition), whereas in 1-bromo-2-butene, the hydrogen and bromine atoms are added to C**1** and C**4** of 1,3-butadiene (therefore it is an **1,4**-addition).

Why does the temperature affect the ratio obtained?

To understand, look at mechanism of the reaction:

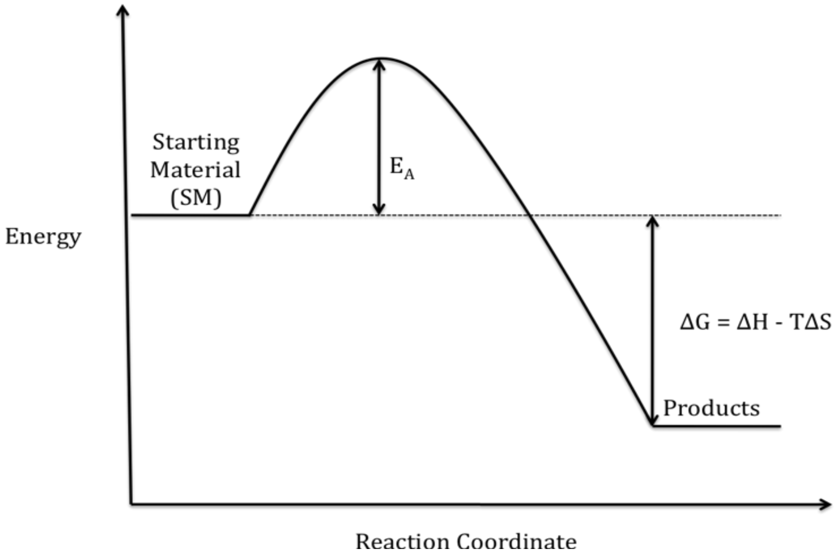


From the 2 resonance forms (connected by the double-sided arrow) of the allylic cation shown in the above figure, we see that the positive charge is shared between the two carbons (C2 and C4) with each carrying a portion of the positive charge.
Note: the allylic cation has two electrons delocalized across the three carbons. It was drawn to have two resonance forms, but it is a ***single entity***, therefore we cannot differentiate and speak of one form being a primary carbocation (therefore less stable) and the other being a secondary carbocation (therefore more stable).

***Answer to the above question*:**

- 3-bromo-1-butene has a higher yield at the lower temperature because it is kinetically more favoured. It formed faster than 1-bromo-2-butene. **Kinetic Control**
- 3-bromo-1-butene has lower yield than 1-bromo-2-butene at higher temperature due to **thermodynamic control**. The addition of bromine to the allylic cation is reversible at high temperature. 3-Bromo-1-butene can be converted back to the allylic cation and then form 1-bromo-2-butene, which is the thermodynamically more favoured product.

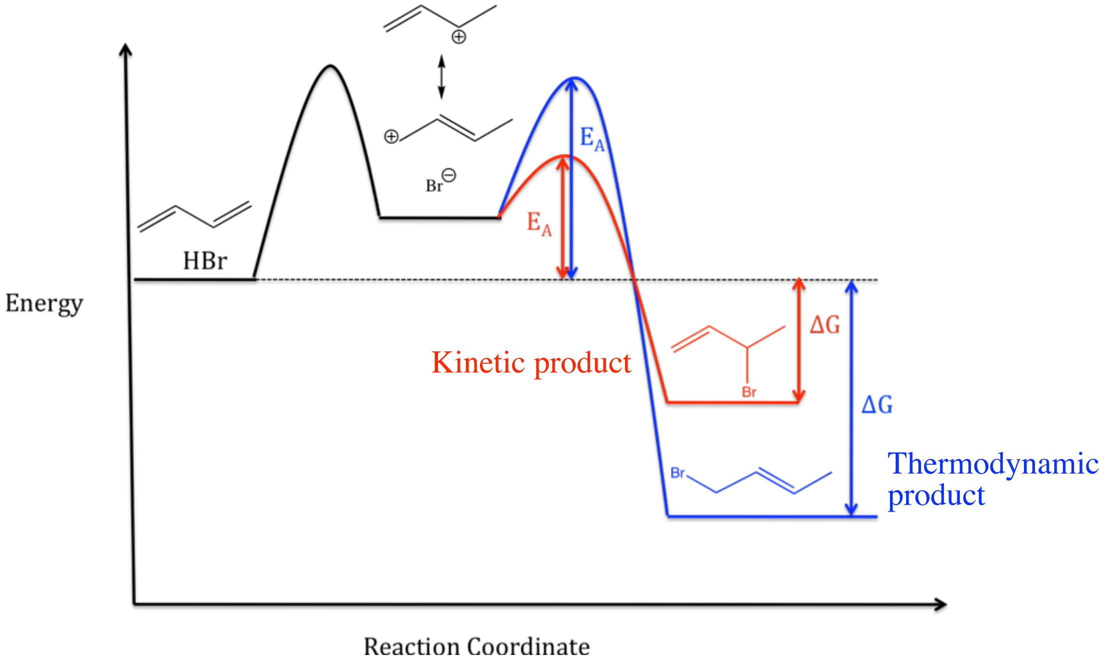
To understand thermodynamic and kinetic control let's begin by looking at the energy diagram of a reaction.



ΔG = free energy of the reaction – this determines ratio of starting material and product
ΔH = enthalpy of the reaction
T = temperature in (degrees) Kelvin
ΔS = entropy
E_A = activation energy (the amount of energy needed for reaction to proceed). This is a factor that determines the rate of a reaction. When E_A is small, the reaction is fast and when it is large the reaction is slow.

For an exothermic reaction, there is release of heat and ΔG is always negative (depicted in the energy diagram, the starting material would be higher on the energy diagram than the product).

Now let's look at the energy diagram of our butadiene and HBr addition reaction



One thing to point out in the energy diagram is that the activation energy barrier to form the 1,2-product 3-bromo-1-butene is much *smaller* than the 1,4-product 1-bromo-2-butene (so that it can be formed easier and **faster**. We call this **kinetically** favoured). However, the energy of 1-bromo-2-butene is lower than 3-bromobutene, so that it is more **stable** than 3-bromo-1-butene (we call it the **thermodynamically** favoured product). (Why is 1-bromo-2-butene more stable? This could be explained as follows: the bromine atom is bulky. It likes to stay away from the rest of the molecule to avoid steric clashes.)

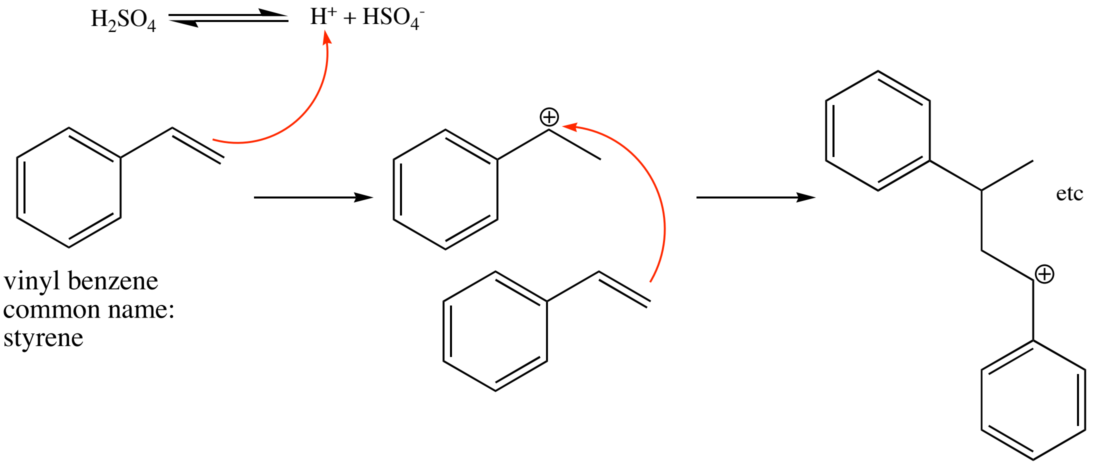
At low temperature, the lower activation energy pathway (coloured red in diagram) dominates and the reaction proceeds to form 3-bromo-1-butene. There is not enough energy for most molecules to overcome the E_A barrier to form 1-bromo-2-butene. At high temperature, there is a large amount of energy available to overcome the E_A barrier forming 1-bromo-2-butene (coloured in blue). Since the bromine addition to the allylic cation is reversible, 3-bromo-1-butene can be reversed back to the allylic cation which then reform 1-bromo-2-butene. This is why the yield of 1-bromo-3-butene is high at a high temperature.

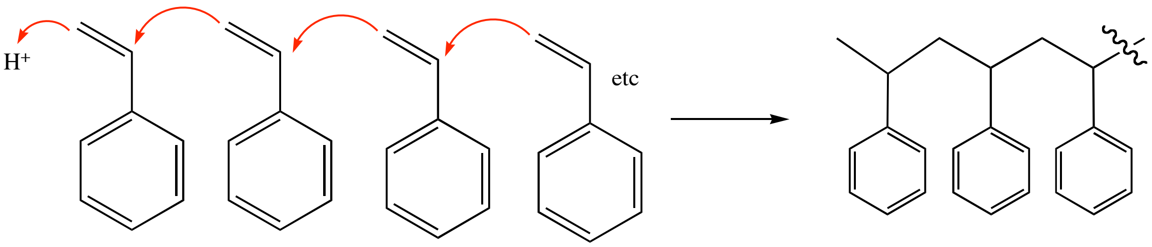
Practical application of addition reactions of conjugated systems

Example: Polystyrene Synthesis

Styrene (shown below) is a hydrocarbon molecule (contains only C and H atoms) that has a double bond conjugated with a benzene ring. A benzene ring is aromatic, and especially stable and it is less reactive than the alkene in the chain. We will see why in the next section.

When styrene is allowed to react with an acid (e.g. sulfuric acid), the protonation occurs to give the conjugated carbocation. In this case, the carbocation formed is called a benzylic cation (the carbon directly attached to a benzene ring is called benzylic center). The benzylic cation can react with the starting compound styrene and form another benzylic cation. If this reaction continues, it leads to eventual formation of polystyrene shown below (i.e. Styrofoam).





If you add heat, the reaction can be reversed to give styrene, which explains the hydrocarbon flavor in your HOT coffee.