## Addition Reactions

The π bond of a double bond is weak, so it is easily broken. This allows alkenes to undergo addition reactions. Because an alkene is a nucleophile, the first species it reacts with is an electrophile.

When an alkene undergoes an electrophilic addition reaction with HBr, the first step is a relatively slow addition of a proton (an electrophile) to the alkene (a nucleophile). A **carbocation intermediate** (an electrophile) is formed, which then reacts rapidly with a bromide ion (a nucleophile) to form an alkyl halide. Notice that each step involves the reaction of an electrophile with a nucleophile. *The overall reaction is the addition of an electrophile to one of the* sp*2 carbons of the alkene and the addition of a nucleophile to the other* sp^2 *carbon.*
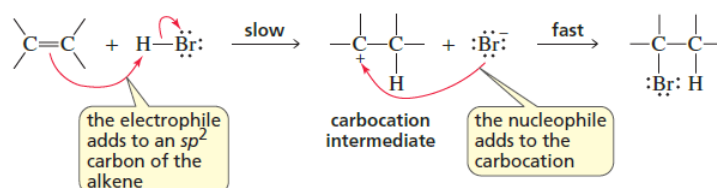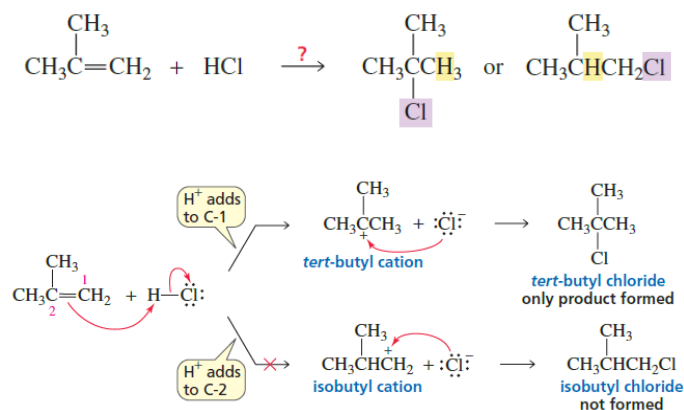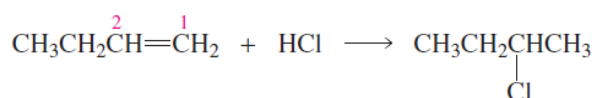

Examples:
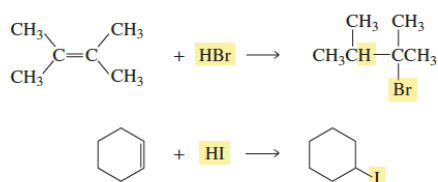
The alkenes in the above reactions have the same substituents on both sp^2 carbons, it is easy to predict the product of the reaction: the electrophile (H$^+$) adds to either one of the sp^2 carbons, and the nucleophile adds to the other sp^2 carbon. It does not matter which sp^2 carbon the electrophile adds to because the same product is obtained in either case.

But what happens if the alkene does not have the same substituents on both sp^2 carbons?
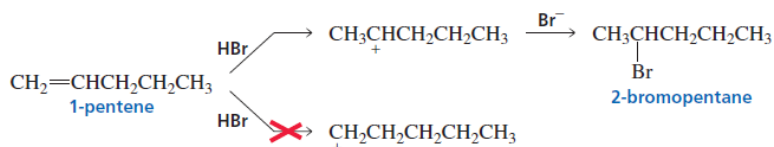

Markovnikov's rule

Markovnikov rule describes the regiochemistry where 'The electrophile (H$^+$) adds preferentially to the sp^2 carbon bonded to the most hydrogens'

In the above example, electrophile (in this case, H⁺) adds preferentially to C-1 because it is the sp^2 carbon bonded to the most hydrogens. Or we can say that H⁺ adds to C-1 to form a secondary carbocation, which is more stable than the primary carbocation that would be formed if H⁺ added to C-2.

When H⁺ adds to 1-pentene, a secondary and a primary carbocation could be formed. The primary carbocation is unstable, hence not formed. Thus, 2-bromopentane is the only product of the reaction which is formed via secondary carbocation.

Anti-Markovnikov rule

Anti-Markovnikov rule describes the **regiochemistry** where 'The electrophile (H⁺) adds preferentially to the sp² carbon bonded to the least hydrogens'
Examples of Anti-Markovnikov includes Hydroboration-Oxidation and Radical Addition of HBr.

Anti-Markovnikov radical addition of haloalkane can only happen to HBr and there must be presence of Hydrogen Peroxide (H_2O_2). Hydrogen Peroxide is essential for this process, as it is the chemical which starts off the chain reaction in the initiation step.

Initiation Steps
Hydrogen Peroxide is an unstable molecule, if we heat it or irradiate with sunlight, two free radicals of OH will be formed. These OH radicals will go on and attack HBr, which will take the Hydrogen and create a Bromine radical. Hydrogen radical do not form as they tend to be extremely unstable with only one electron, thus bromine radical which is more stable will be readily formed.
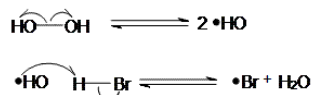
Propagation Steps
The Bromine Radical will go on and attack the **LESS SUBSTITUTED** carbon of the alkene. More substituted carbon is more stable due to induction and hyperconjugation. After a carbon radical is formed, it will go on and attack the hydrogen of a HBr.
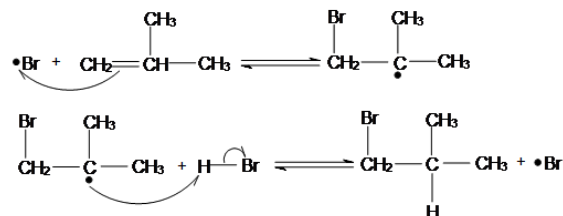
Another example for anti-Markovnikov addition is hydroboration-oxidation,

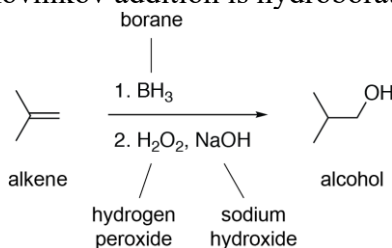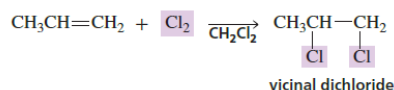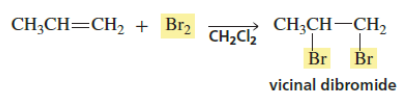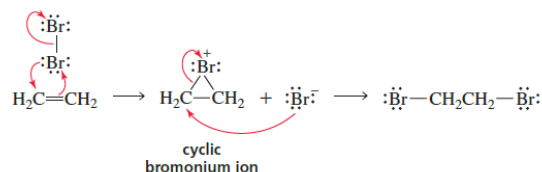**The Addition of a Halogen to An Alkene**

The halogens Br_2 and Cl_2 add to alkenes. The product of the reaction is a vicinal dihalide.

Mechanism for the addition of bromine to an alkene

■ As the π electrons of the alkene approach a molecule of Br_2, one of the bromines accepts those electrons and releases the shared electrons to the other bromine, which leaves as a bromide ion. Because bromine's electron cloud is close enough to the other sp^2 carbon to form a bond, a cyclic bromonium ion intermediate is formed rather than a carbocation intermediate.
■ The cyclic bromonium ion intermediate is unstable because of the strain in the three membered ring and the positively charged bromine, which withdraws electrons strongly from the ring carbons. Therefore, the cyclic bromonium ion reacts rapidly with a nucleophile (Br⁻).

Note: The addition of Br_2 is anti because the two bromine atoms add to opposite sides of the double bond.
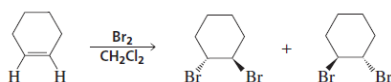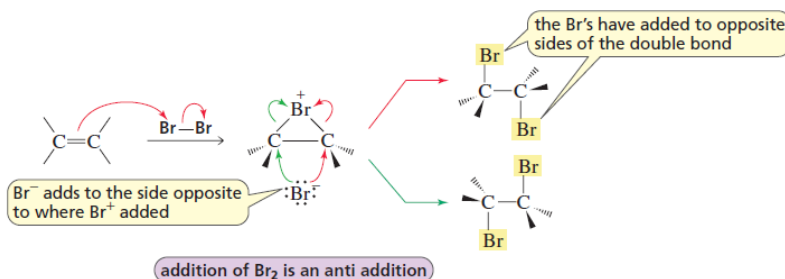
Addition of a Hydrogen Halide to an Alkyne

The product of the electrophilic addition reaction of an alkyne with HCl is an alkene. Therefore, a second addition reaction can occur if excess hydrogen halide is present. The second addition—like other alkene addition reactions—is regioselective: the H+ adds to the less substituted sp^2 carbon.

The product of the second addition reaction is a geminal dihalide, a molecule with two halogens on the same carbon. "Geminal" comes from geminus, which is Latin for "twin."

The addition of a hydrogen halide to an alkyne can be stopped after the addition of one equivalent of hydrogen halide because an alkyne is more reactive than the halo-substituted alkene that is the reactant for the second addition reaction.

Mechanism for electrophilic addition of a hydrogen halide to an alkyne

- The alkyne (a nucleophile) reacts with an electrophile to form a π-complex.
- Chloride ion adds to the π-complex, forming a halo-substituted alkene.

Addition of a Halogen to an Alkyne

The halogens Cl_2 and Br_2 also add to alkynes. In the presence of excess halogen, a second addition reaction occurs. The mechanism of the reaction is exactly the same as the mechanism for the addition of Cl_2 or Br_2 to an alkene.

Addition of water

Alkene reacts with water to give alcohol.

Alkynes also undergo the acid-catalyzed addition of water. As expected, the electrophile (H+) adds to the less substituted sp carbon.

The initial product of the reaction is an enol. An enol has a carbon–carbon double bond with an OH group bonded to one of the sp^2 carbons. (The suffix "ene" signifies the double bond, and "ol" signifies the OH group.) The enol immediately rearranges to a ketone. A ketone and its corresponding enol are called keto–enol tautomers. (**Tautomers** are constitutional isomers that are in rapid equilibrium.)

electrophile
adds here

$$CH_3CH_2CH=CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2CH-CH_2$$

alkene

$$\underset{\text{OH}}{|} \quad \underset{\text{H}}{|}$$

alcohol

electrophile
adds here

$$CH_3CH_2C\equiv CH + H_2O \xrightarrow{H_2SO_4} CH_3CH_2C=CH_2 \rightleftharpoons CH_3CH_2C-CH_3$$

alkyne   enol   ketone

Examples:

$$CH_3CH_2C\equiv CCH_2CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$$

symmetrical
internal alkyne

$$CH_3C\equiv CCH_2CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 + CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$$

unsymmetrical
internal alkyne