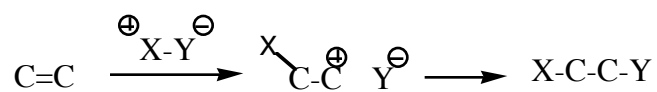
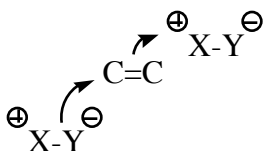


ADDITION

Many reagents add to the alkene bond. The reactions are called electrophilic additions and thus a carbocation is formed on a carbon atom. The reaction is regioselective as controlled by the formation of the more stable carbocation. The reactions follow somewhat complex kinetic expressions showing that a simple mechanism is not being followed. For example, below possibly two molecules of the reagent are reacting with the substrate in the rate determining step.

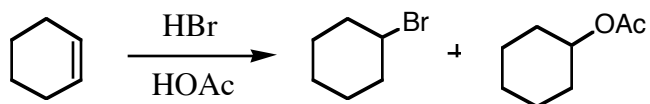
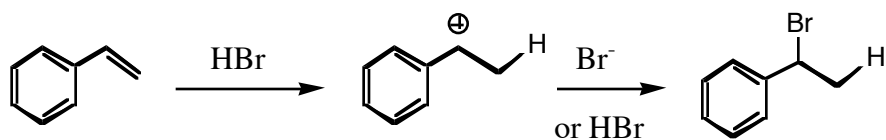


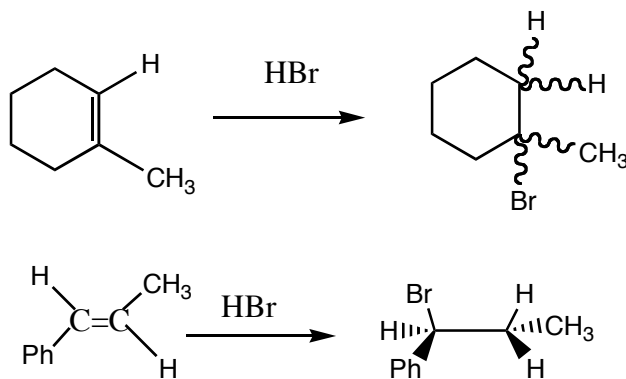
$$\text{rate} = k [\text{alkene}][\text{XY}] + k[\text{alkene}][\text{XY}][\text{Y}^-] + k[\text{alkene}][\text{XY}]^2$$



Additions of HCl, HBr

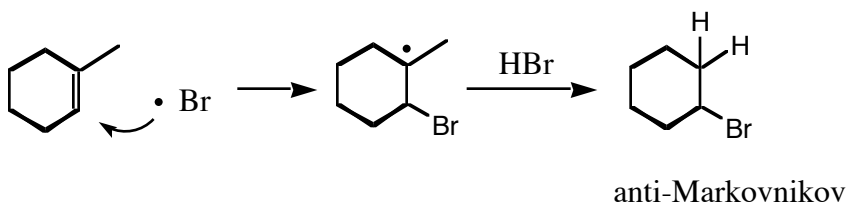
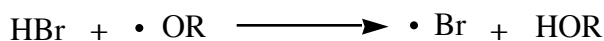
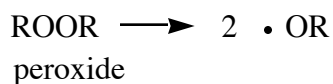
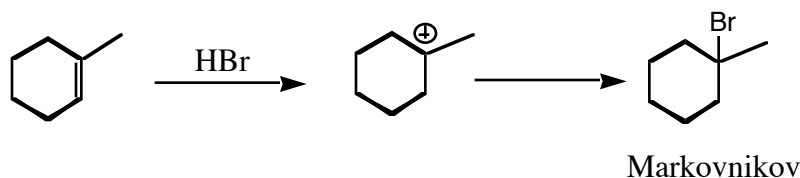
The ionic addition of HX produces the more stable carbocation which then reacts with the bromide ion. The result is that the bromide is attached to the more substituted part of the alkene. This stereoselective reaction is called Markovnikov addition.





The addition of HBr in the presence of a radical initiator such as a peroxide follows a regioselective results which is opposite to the ionic addition. The two reactions are referred to as Markovnikov and anti-Markovnikov additions but result because of the operation of two entirely different mechanisms.

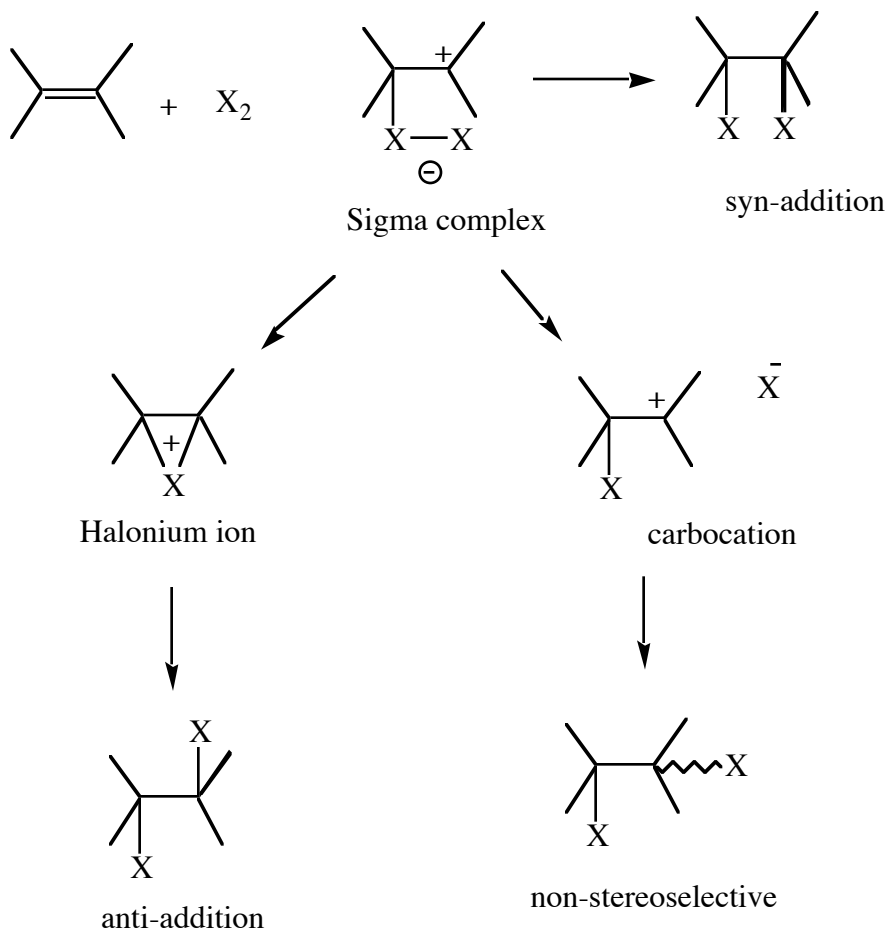
The ionic mechanism (Markovnikov) produces the more stable carbocation which reacts with bromide. The radical mechanism (anti-Markovnikov) adds the Br radical first to give the more stable radical which reacts with HBr to abstract a hydrogen atom.



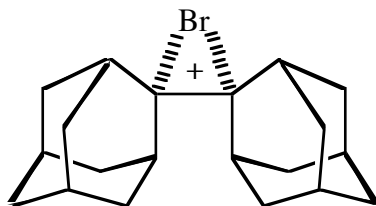
Additions of Halogens and pseudohalogens.

Halogenation of organic compounds occurs readily with halogens (X_2), mixed halogens ($X-Y$) and pseudohalogens (X -function). The reaction kinetics contain higher

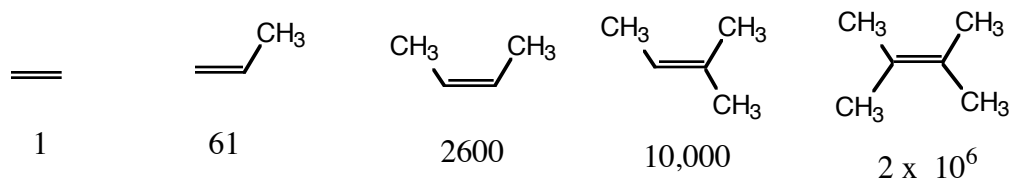
level terms just as addition of HX and thus may have more than one molecule of halogen in the rate controlling step. The possible stereochemical result of halogenation is shown in the mechanism below. Most electrophilic halogenations occur through the path involving a halonium ion to give anti addition, but syn addition is also observed as well as non stereoselective addition.



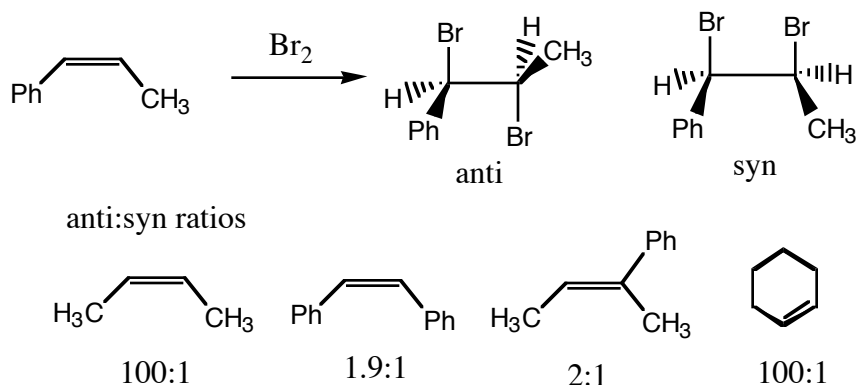
In the bromination of an adamantyl alkene a stable bromonium ion has been isolated.



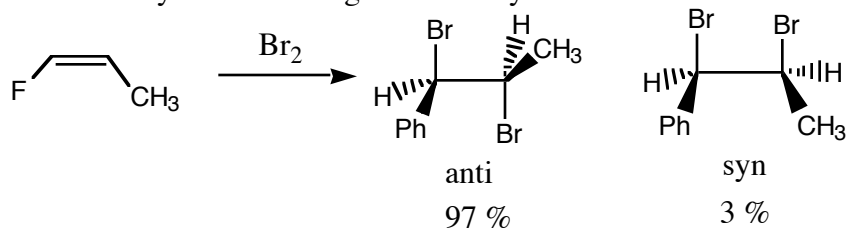
The reactivity of alkyl substituted alkenes is shown below. The order reflects the nucleophilicity of the alkene for the electrophilic halogen.



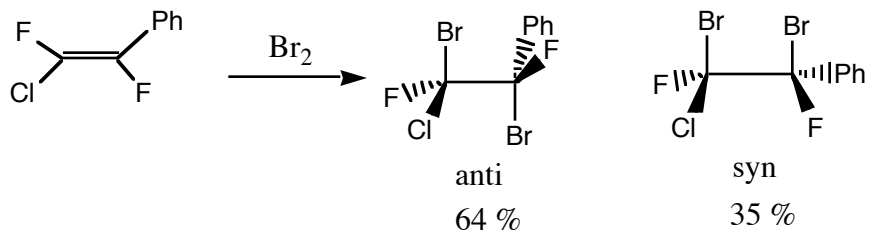
The amount of syn addition increases with phenyl substituted alkenes. This is a result of the increased stability of the intermediate benzylic cations..



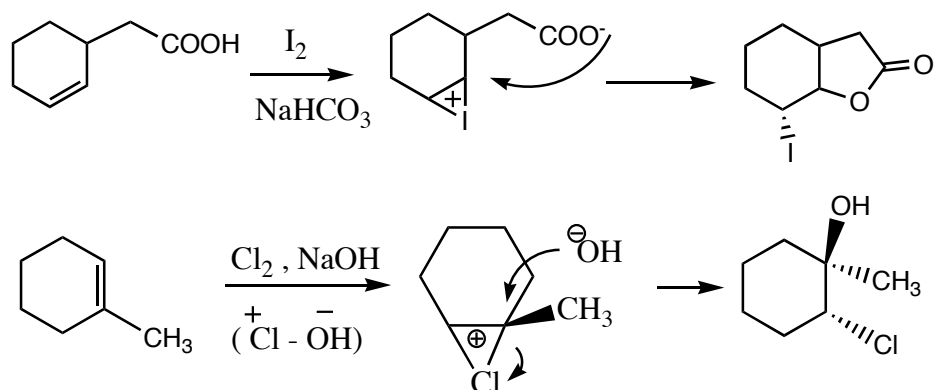
Fluorinated aliphatic alkenes also show a preference for anti addition as shown below, but fluorinated styrenes show high levels of syn addition.



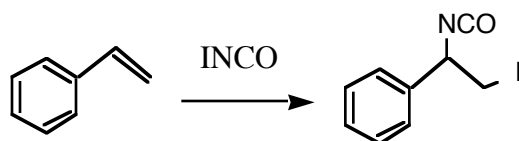
Fluorinated styrenes, as well as other halogenated styrenes, give an increased amount of syn addition. Sometimes the syn addition product is the major product. In these cases, less halonium ion is formed because the fluorine atom and the phenyl ring stabilize the cation.



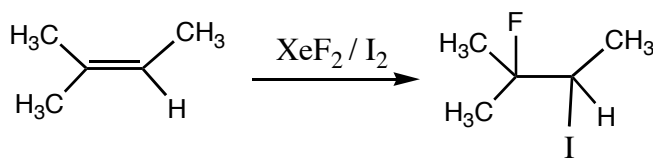
A few representative examples of halogen addition are shown below.



Pseudo halogens are composed of compounds such as I-NCO and I-N₃. These reagents add with the halogen positive followed by the negative functional part. The function allows for further organic transformations.

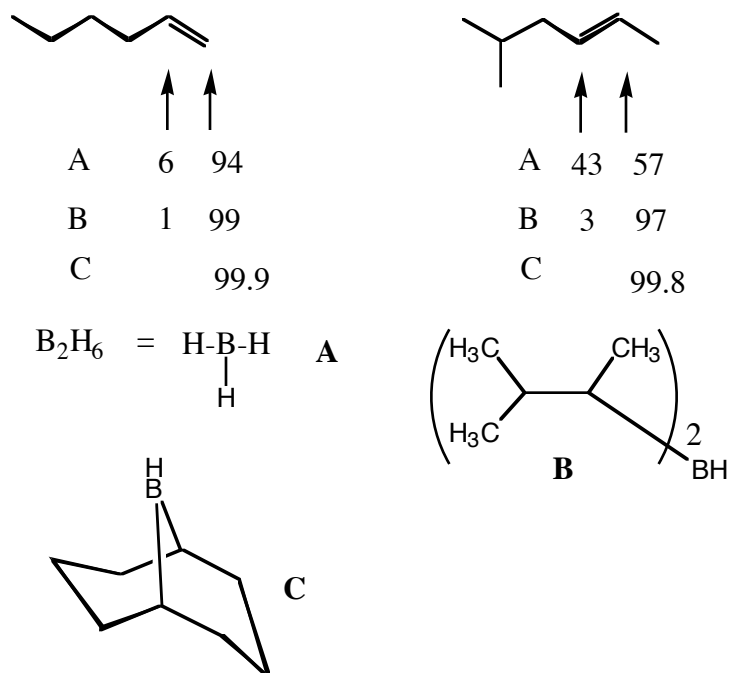


Mixed halogens can be added to alkenes. While addition of F₂ is usually a hazardous proposition, the use of BrF or IF proceed smoothly. IF can be produced in situ from the reaction of xenon difluoride and iodine. In the example shown the F anion adds at the site of the more stable cation.



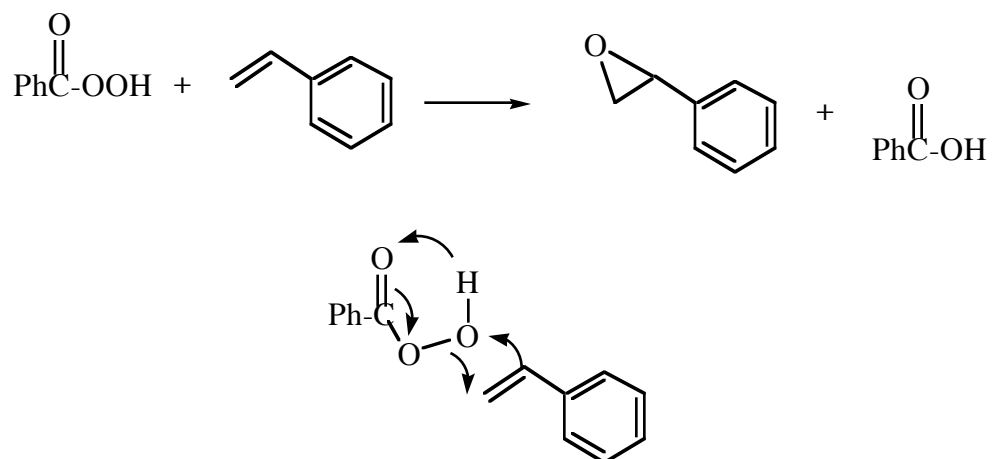
Addition of Boranes (Hydroboration)

Alkenes react with BH₃ (a commercial reagent is a complex with Me₂S) followed by oxidation with peroxide and base to give alcohols. The reaction is very selective and subject to steric effects. It is not an ionic addition, but is nearly a four-center addition with the boron atom going to the less substituted carbon atom.

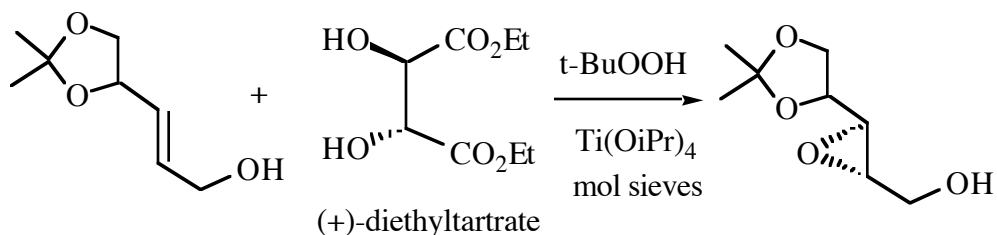


Epoxidation and Hydroxylation

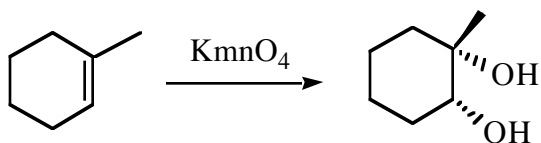
Alkenes undergo addition of peroxy reagents to produce alkenes as shown below. The reaction occurs through a concerted addition of an oxygen atom to the alkene.



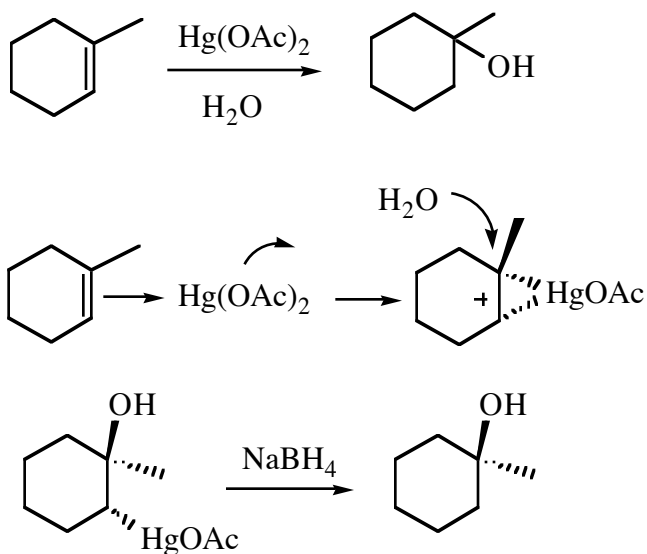
A procedure known as Sharpless epoxidation allows the preparation of chiral epoxides by using chiral oxidation agents.



Alkenes also add hydroxyl groups to produce glycols on reaction with cold potassium permanganate.

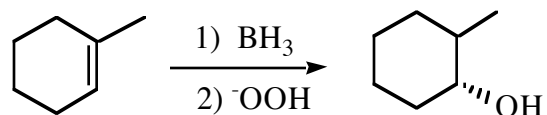


A single hydroxyl function is added in a process called oxy-mercuration-demercuration. In this reaction, mercuric acetate reacts with the alkene to produce an intermediate three membered ring similar to that seen in halogenation, called a mercurinium ion. Nucleophilic solvent present such as water, alcohol, or acetate can open the ring to give an oxygenated mercury compound. Reaction of the intermediate with sodium borohydride reduced the C-Hg bond to a C-H bond.

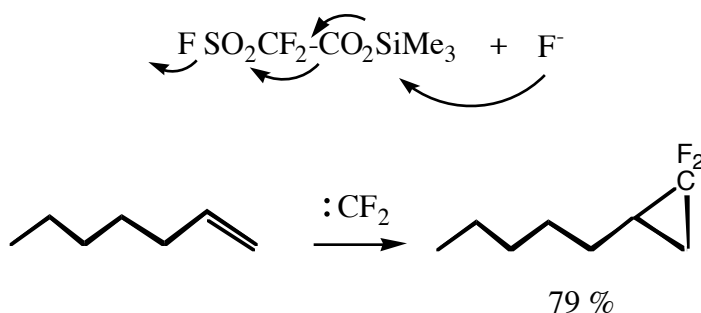


The nucleophilic solvent, water in this case, attacks the carbocation at the more stable tertiary position. After reduction the tertiary alcohol is formed. This is the same regioselectivity observed in acid-catalyzed hydration but the mercuration reaction proceeds much cleaner except for the presence of mercury compounds.

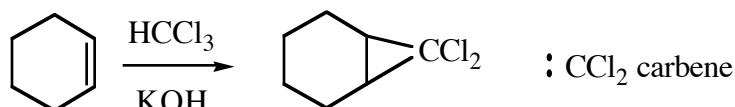
Hydroboration-oxidation gives the the reverse selectivity shown below. Thus for synthetic purposes the processes compliment each other.



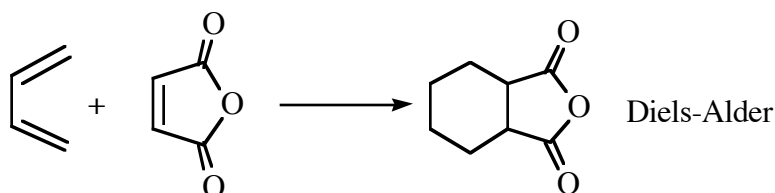
Alkenes also undergo addition of carbon units. The addition of divalent carbon, carbenes or carbenoids, produce three membered rings. A very useful method for making difluorocyclopropanes comes from treatment of the trimethylsilyl ester below with catalytic fluoride. Several products occur including the difluorocarbene which reacts immediately with any alkene present.



Dichlorocarbene can be easily generated and captured by an alkene as shown.



The addition of dienes in the Diels-Alder reaction provides six membered rings.



Carbene addition and the Diels-Alder reaction are covered in more detail in the chapter on orbital symmetry.

Addition of Fluorine to Unsaturated compounds

From Hudlicky book

Purrington

Some reagents ArIF_2 , CsOso_4F XeF_2 HF , Cf_3of

Feiring

Addition of HF to alkenes and to acetylenes, Halogen Fluoride addition, OF reagents FCLO_3 , Sf , NOF ,