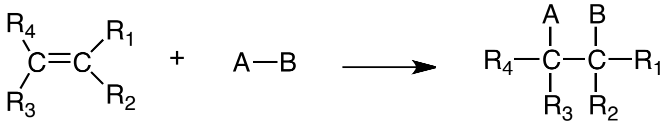
# Chapter 8
# Addition Reactions to Alkenes

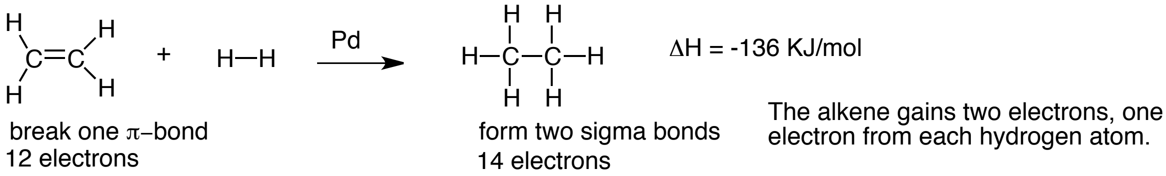
In this chapter will we study the addition reactions of alkenes. We will see that the π–electrons of the double bond are loosely held and that their maximum electron density is above and below the plane of the sigma framework of the alkene. These π–electrons are therefore quite reactive as nucleophiles and we will see that we can add a variety of electrophiles to the double bond.



Alkenes are unsaturated hydrocarbons, whereas alkanes are saturated hydrocarbons with all of the valences filled with hydrogens. Unsaturated hydrocarbons such as alkenes have valence sites available for the addition of more hydrogens.

## Hydrogenation of Alkenes

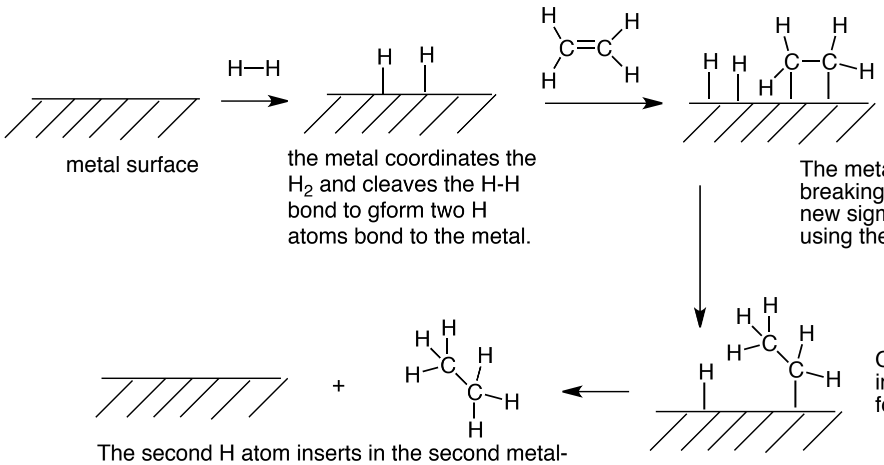
Catalytic hydrogenation of alkenes is a very important reaction. Hydrogen atoms are added to an unsaturated alkene (or an alkyne) to form a saturated alkane. A catalyst is need. It can be palladium, platinum, nickel or rhodium.



The reaction is very favorable in terms of energy. It is highly exothermic since we break a relatively weak π–bond and form two stronger C-H sigma bonds.

This reaction is a reduction reaction. The alkene is reduced to the alkane as it gains two electrons and two hydrogen atoms, one electron from each hydrogen.

The reaction is very slow without the use of a metal catalyst. The role of the catalyst is to provide a surface for the reaction to proceed. The metal helps to cleave the H-H bond to make two hydrogen atoms and then to deliver the hydrogen atoms to the alkene that is also held or coordinated to the metal surface there its empty d orbitals. This is shown schematically below.



the metal coordinates the $H_2$ and cleaves the H-H bond to gform two H atoms bond to the metal.

The metal coordinates the alkene, breaking the π-bond to form two new sigma bonds to the metal using the two π–electrons.

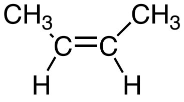
One of the H atoms inserts into the metal-carbon bond to form a new sigma C-H bond.

The second H atom inserts in the second metal-carbon bond to give the fully saturated and fully reduced alkane. the metal is unchanged.

We can use the heat of hydrogenation as a good measure of alkene stability. The lower the heat of hydrogenation, the more stable the alkene.

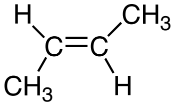
$CH_3CH_2CH{=}CH_2 + H_2 \xrightarrow{Pd} CH_3CH_2CH_2CH_3$ ΔH = -126 KJ/mol

mono-substituted



*cis*-disubstituted

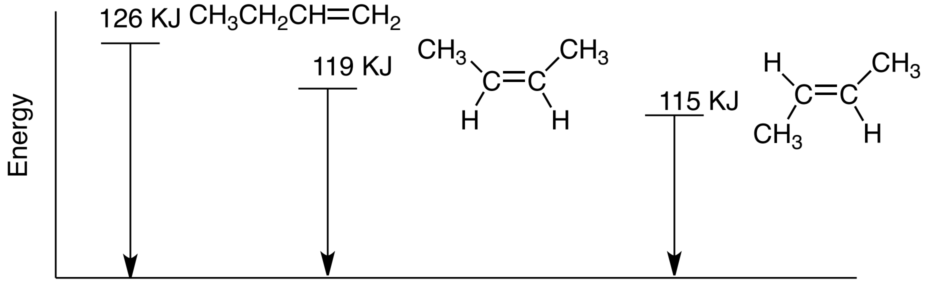
$+ H_2 \xrightarrow{Pd} CH_3CH_2CH_2CH_3$ ΔH = -119 KJ/mol



*trans*-disubstituted

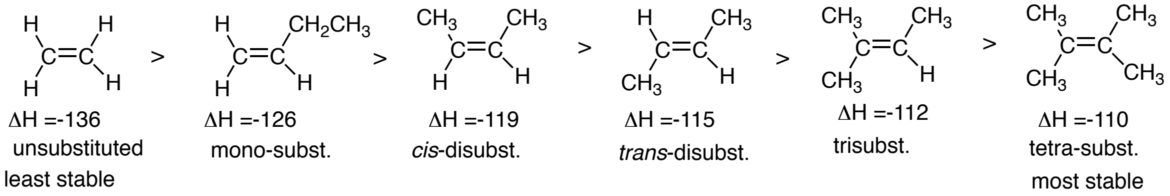
$+ H_2 \xrightarrow{Pd} CH_3CH_2CH_2CH_3$ ΔH = -115 KJ/mol

We can see that the most stable alkene is the *trans*-disubstituted alkene, because it has the lowest heat of hydrogenation and therefore must be the lowest in energy. The *cis*-disubstituted alkene is slightly higher in energy due to increased steric interaction between the methyl groups on the same side of the ring. The mono-substituted alkene is the least stable since it has the highest heat of hydrogenation. We can display this graphically:



Recall Zaitsev's rule: the more substituted with electron donating alkyl groups, the more stable the alkene. We can now put this on a quantitative basis by comparing the heats of hydrogenation.

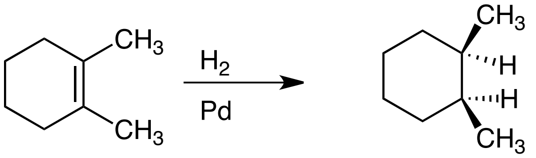
Heat of Hydrogenation (KJ/mol)



## Stereochemistry

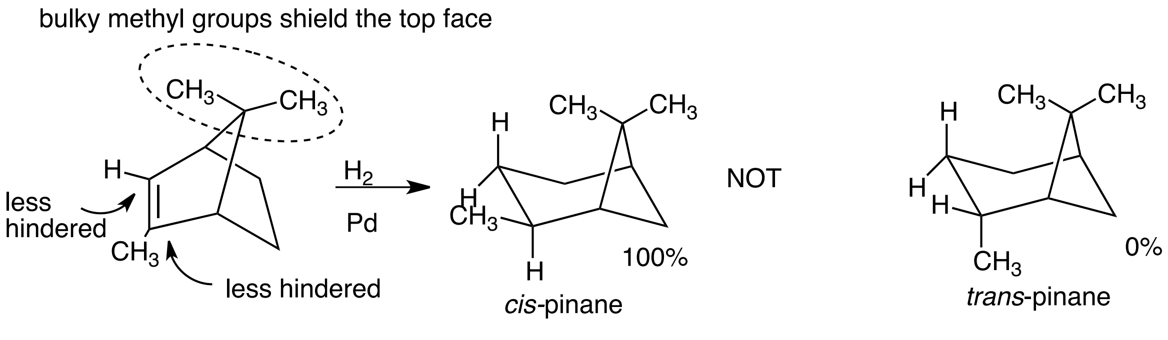
We see that both hydrogens are attached to the same face of the alkene due to coordination by the metal catalyst surface. We call this *syn* addition. The reaction is completely stereoselective. Two products are possible but only the *syn* addition product is formed.

When we have a cyclic alkene, we can see this *syn* addition product clearly. For example, with 1,2-dimethylcyclohexene, we get only the *cis*-1,2-dimethylcyclhexane product.



*cis* product only

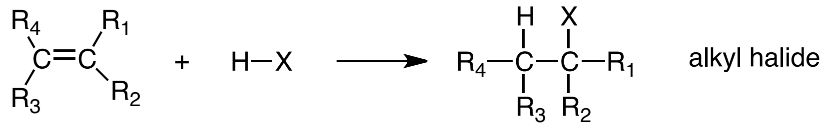
With α–pinene, we get only the *cis*-product and we see that the hydrogen atoms add only from the bottom, less hindered face away from the two methyl groups in the bridge.



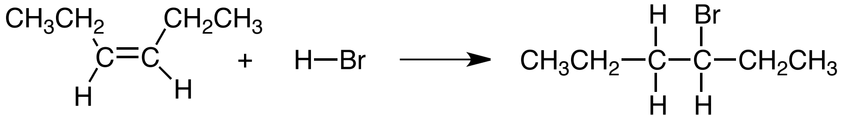
## Addition of Hydrogen Halides, HX

We can add hydrogen halides, H-X to alkenes to give alkyl halides.

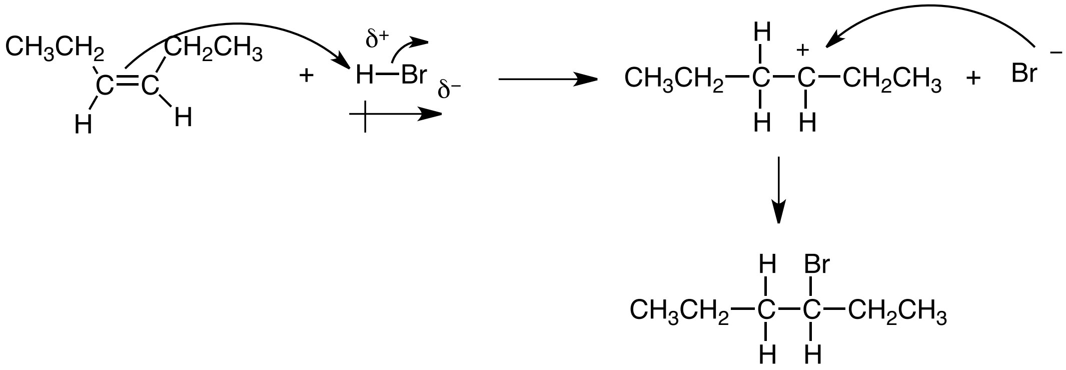
General reaction



Ex:



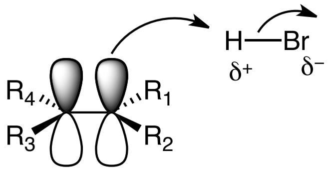
The mechanism involves nucleophilic attack by the π–electrons of the double bond on the partial positive charge of the hydrogen attached to the bromine. This hydrogen is the electrophile. A carbocation intermediate is formed and $Br^-$ is produced. The second step involves nucleophilic attack of the bromine anion on the carbocation to form the alkyl halide.



The rate of the reaction with different alkyl halides parallels the acid strength of the alkyl halide.

| H—I | > | H—Br | > | H—Cl | >> | H—F |
|---|---|---|---|---|---|---|
| most acidic<br>fastest | | | | | | least acidic<br>slowest |

The π–electrons of the alkene are exposed above and below the plane of the sigma framework and reactive toward positively charged electrophiles.

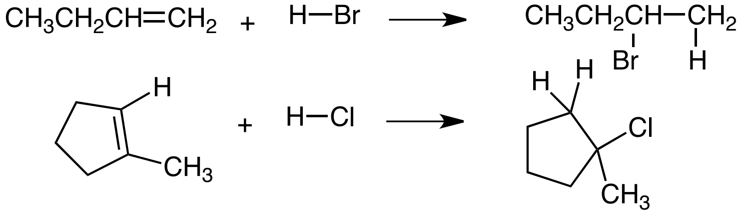


**Regioselectivity**

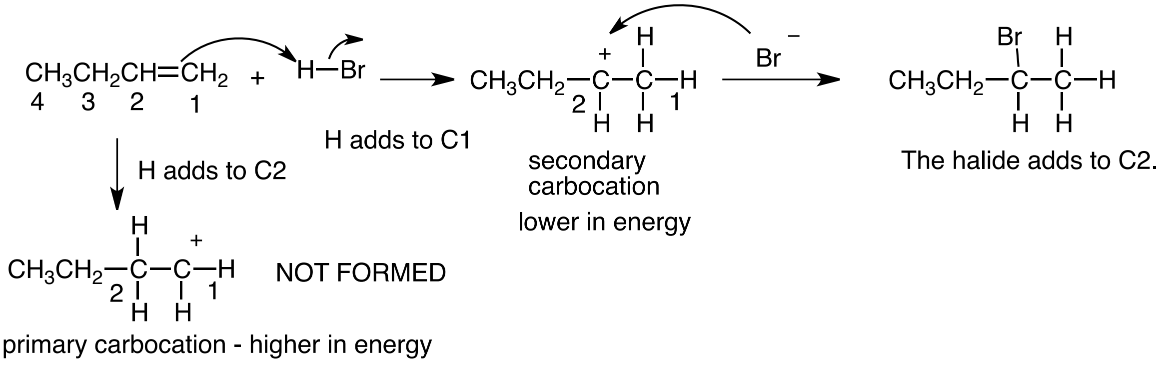
In an unsymmetrical alkene, there is a choice as to where the hydrogen will add and where carbocation will form and subsequently where the nucleophilic halogen will attack. This is called the regioselectivity of the reaction.

The regioselectivity of addition to alkenes is given by Markovnikov's rule after the famous Russian chemist who formulated it in 1870. There are several ways to state this rule.

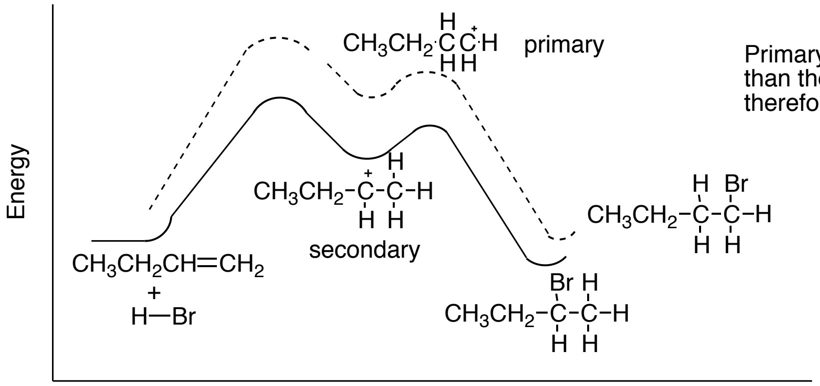
The original formulation states that when an unsymmetrical alkene reacts with an hydrogen halide, the hydrogen adds to the carbon that already has more hydrogens and the halogen adds to the carbon with the least hydrogens.



A more modern and more general formulation of the rule is to simply state that the hydrogen or **<u>electrophile adds to the alkene so as to form the more stable carbocation</u>**. The halogen (nucleophile) then adds to this carbocation. The result is that the halogen becomes attached to the more substituted carbon.



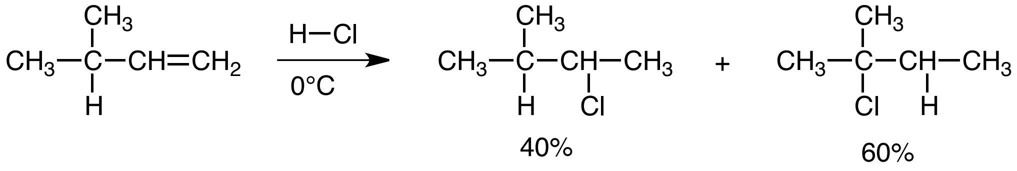
According to Hammond's postulate there is a late transition state since the first step of the reaction is endothermic. Therefore there is lots of (+) charge in the transition states. Since alkyl groups are electron-donating groups, the transition state that has the (+) charge developing at the carbon with the more alkyl substituents will be lower in energy.



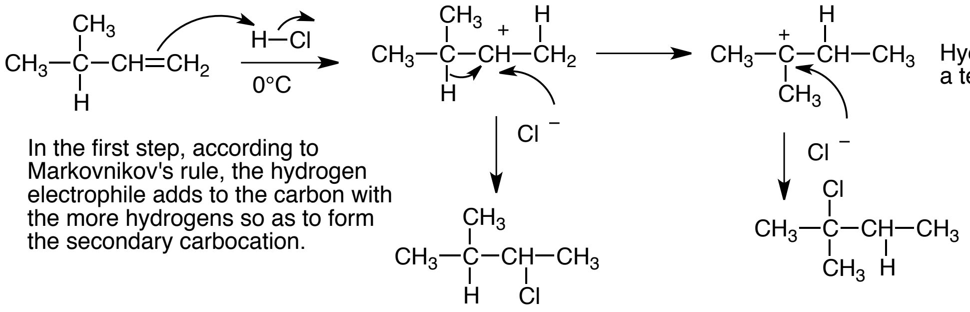
Primary carbocation is higher in energy than the secondary carbocation; therefore it forms more slowly.

## Rearrangements

As a general rule, whenever there is a carbocation intermediate, we will see rearrangements and we do see them in the addition of hydrogen halides to alkenes. The fact that rearranged products are observed, confirms the existence of the carbocation intermediates.



The reaction proceeds by means of a hydride shift to form the more stable, tertiary carbocation.



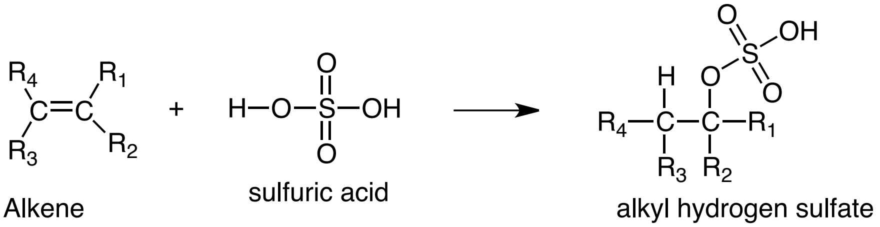
In the first step, according to Markovnikov's rule, the hydrogen electrophile adds to the carbon with the more hydrogens so as to form the secondary carbocation.

Hydride shift to give a tertiary carbocation.

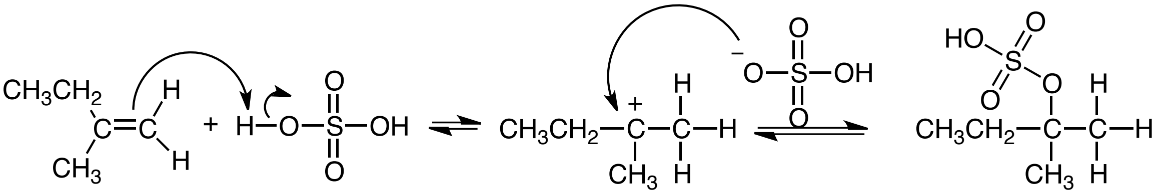
Note that a methyl shift would simply form another secondary carbocation so this shift does not occur. The rearrangement occurs because a higher energy intermediate is transformed into a lower energy one.

## Addition of Sulfuric Acid to Alkenes

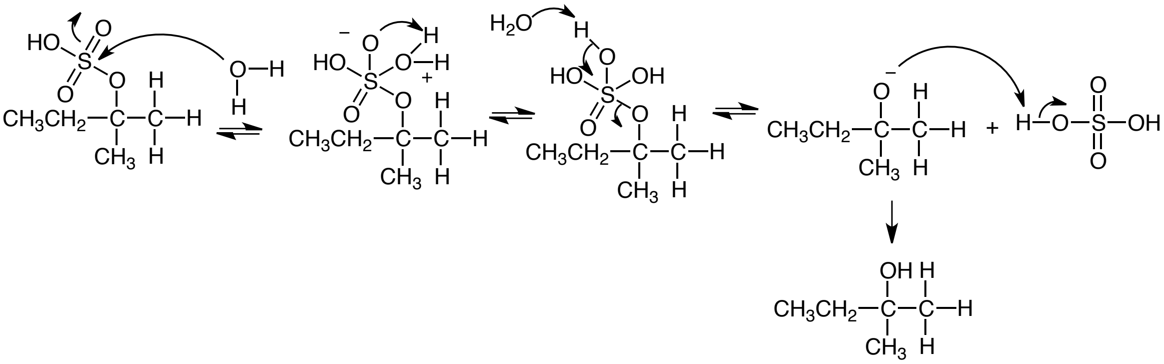
Sulfuric acid will add to alkenes in accordance with Markovnikov's rule with the initial hydrogen adding to the less substituted carbon (i.e. the carbon with the more hydrogens).



For example:



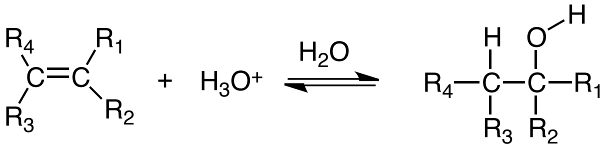
The alkyl hydrogen sulfates can be converted into alcohols by heating them with water. This is an example of a hydrolysis reaction (i.e. cleavage of a bond by reaction with water).



Overall, these two steps represent a hydration of the alkene. This reaction is synthetically useful only for mono- and di-substituted alkenes. Tri- and tetra-substituted alkenes undergo polymerization reactions, as will be discussed later in this chapter.

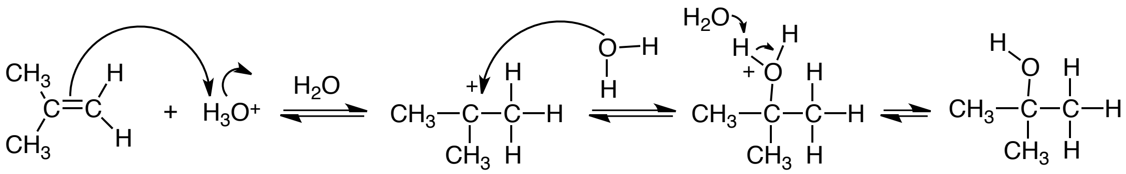
## Acid Catalyzed Hydration of Alkenes

Water can also be added to alkenes using aqueous acid. This reaction is the exact reverse of the dehydration reaction and proceeds in accordance with Markovnikov's rule.



According to Le Chatelier's principle, we drive the reaction in favor of hydration by using an excess of water with acid catalysis. We drive the reaction in favor of dehydration by using anhydrous conditions with sulfuric acid and removal of the water as it is formed.

For example:



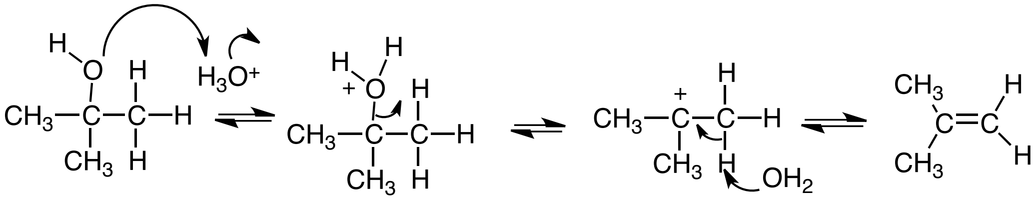
The proton adds to the less substituted carbon so as to form the more substituted and stable carbocation.

The carbocation undergoes nucleophilic attack by water. The extra proton is then transferred to another molecule of solvent water, acting as a base, so as to form the more substituted alcohol.

The first step of the reaction – the formation of the carbocation – is the slow step. We can see this clearly by comparing the relative rates of hydration of differentially substituted alkenes. Alkenes which lead to tertiary carbocations in the first step react $10^{11}$ times more rapidly than alkenes that lead to primary carbocations.

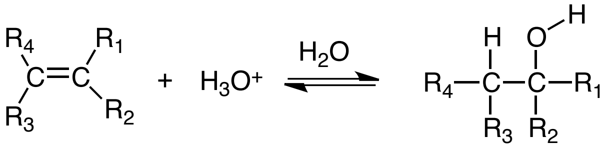
| | realtive rate | carbocation intermeidate | |
|---|---|---|---|
| $CH_2{=}CH_2$ | 1 | $CH_3-\overset{+}{C}H_2$ | primary |
| $CH_3-CH{=}CH_2$ | $1.6 \times 10^6$ | $CH_3-\underset{CH_3}{\underset{\vert}{\overset{+}{C}H}}$ | secondary |
| $CH_3-\underset{CH_3}{\underset{\vert}{C}}{=}CH_2$ | $2.5 \times 10^{11}$ | $CH_3-\underset{CH_3}{\underset{\vert}{\overset{+}{C}}}-CH_3$ | tertiary |

As we noted, acid catalyzed hydration is the exact reverse of acid catalyzed dehydration.



**Thermodynamics of Addition-Elimination Equilibria**

For the hydration-dehydration reaction:



Le Chatelier's principle states that a system at equilibrium adjust so as to minimize any stress applied to it. In the hydration/dehydration reaction, the stress is the water. If there is a large excess of water, the reaction will favor hydration, so as to use up the water. If there is little or no water present, then the reaction will favor dehydration, so as to lower the concentration of alkene.

Again:

To favor hydration – use large excess of water with a catalytic amount of acid.

To favor dehydration, use low concentration of acid and remove water and/or the alkene as it forms.

At constant temperature and pressure, the spontaneous direction for a reaction is the one in which the free energy will decrease. This is given by:

$\Delta G = G_{products} - G_{reactants}$ spontaneous when $\Delta G < 0$

A reaction in which $\Delta G$ decreases is said to be exergonic.
A reaction in which $\Delta G$ increases ($\Delta G > 1$) is said to be endergonic.

When $\Delta H$ decreases ($\Delta H$ is negative) the react is exothermic. When $\Delta H$ increases ($\Delta H$ is positive), the reaction is endothermic.

For:

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta G = \Delta G^\circ + \frac{RT \ln [C]^c [D]^d}{[A]^a [B]^b}$$

$R = 8.314$ J/mol.K
$T$ = temperature in K

At equilibrium, $\Delta G = 0$

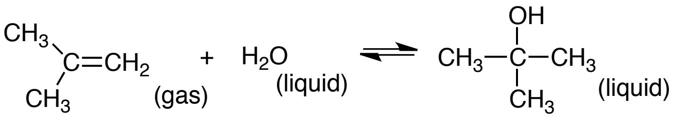
And

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Therefore, $\Delta G° = -RT \ln K$ ($\Delta G°$ = standard state values for the energy)

And, $\Delta G° = \Delta H° - T\Delta S°$

For the reaction the following reaction in the gas phase:



$\Delta G° = -5.4$ KJ Exergonic (spontaneous)

$\Delta H° = -52.7$ KJ Exergonic (spontaneous)

$\Delta S° = -0.16$ KJ/K Decreases (unfavorable)

We see that the sign of $\Delta G°$ is negative. This is an exergonic reaction and the equilibrium constant is greater than one (favorable).

Using the relationship $\Delta G° = \Delta H° - T\Delta S°$ we can calculate the equilibrium constant, K, to be 9 for this reaction.

The $\Delta H$ term is dominated by the bond strength. A negative $\Delta H$ almost always means that bonding is stronger in the products than in the reactants. Stronger bonding reduces the free energy of the products and contributes to a more negative $\Delta G$.

The entropy term, $\Delta S°$, is a measure of the increase or decrease in the disorder of the system. A more ordered system has less entropy and is less probable than a more disordered one.

For a chemical reaction, the main factor is the number of moles of material on each side of the balanced equation and their physical states. A liquid phase has more entropy (less order) than the solid phase and a gas phase has more entropy than a liquid phase.

Entropy increases when more molecules are formed from fewer ones. An example of a reaction in which there is an increase in entropy is an elimination reaction in which one molecule becomes two or three molecules ($+\Delta S°$). In addition reactions, there is a decrease in entropy ($-\Delta S°$), since two molecules become one.

In the above addition reaction, the hydration of the alkene, the entropy decreases, thereby increasing $\Delta G°$, because two separate molecules, water and the 2-methylpropene, come together to make one molecule, 2-methyl-2-propanol. The product is more ordered than the starting materials.

In typical addition reactions of alkenes, the competition between addition versus elimination is strongly temperature dependent.

Addition is favored at low temperature. Elimination is favored at higher temperatures.

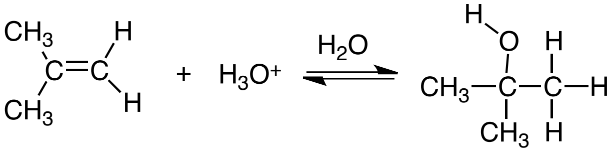
For:

$$CH_2{=}CH_2 \text{ (gas)} \quad + \quad H_2 \text{ (gas)} \rightleftharpoons CH_3{-}CH_3 \text{ (gas)} \qquad \Delta H° < 0$$

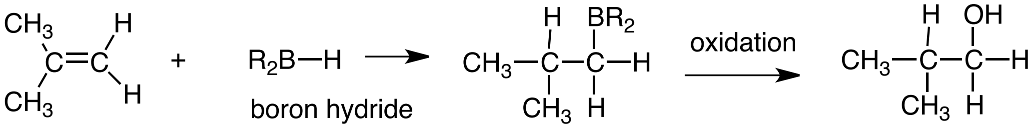
ΔH° is sufficiently negative that the equilibrium lies to the right at relatively low temperatures. But at temperatures > 750°C, the TΔS° term dominates because the entropy term is negative ((decrease in disorder) and so –(-TΔS°) becomes positive and dominates at high temperatures. The equilibrium for this reaction shifts to the left for temperatures above 750° C.

## Hydroboration-Oxidation of Alkenes

Boron hydride addition to alkenes followed by oxidation will give alcohols in which the –OH group is attached to the less substituted carbon, the opposite regiochemistry to that observed with the simple acid catalyzed hydration of alkenes.



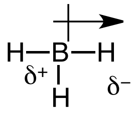
OH group is attached to the more substituted carbon.



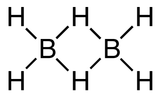
OH group is attached to the less substituted carbon.

This very useful and important reaction was developed by H. C. Brown of Purdue University who won the Nobel Prize in 1977 for this work.

The reaction proceeds by means of a one-step, concerted addition of the boron hydride to the alkene. Hydrogen is more electronegative than boron, so the electrophile in this reaction is boron. Note also that boron only has six electrons, so it is a very powerful electrophile. In fact, the molecule shown below, borane ($BH_3$) does not really exist as a monomer. The boron can partially stabilize itself by forming a dimer, called diborane, $B_2H_6$. Very often alkyl groups are substituted for two of the hydrogens on the borane to form an organoborane. This stabilizes the molecule and makes it more bulky. This is represented as $R_2BH$. The larger the R groups the more selective the organoborane



Boron is less electronegative than hydrogen, so the dipole moment puts a partial minus charge on hydrogen and a partial positive charge on boron.



diborane, $B_2H_6$

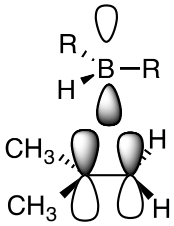
As we have seen, according the Markovnikov's rule, the electrophile adds to the less substituted carbon so as to allow the positive charge to be supported at the more substituted and therefore more electron rich carbon. In the present case, the addition of the electrophile (the boron) and the nucleophile (the hydride) are concerted, so that there is no real carbocation but there is some build-up of positive charge in the transition state. There is a four-center transition state. The electrophilic boron adds to the less substituted carbon. There are two reasons for this.

(1) The positive charge that does build up in the transition state is best supported by the carbon that has the more alkyl substituents in accordance with Markovnikov's rule.

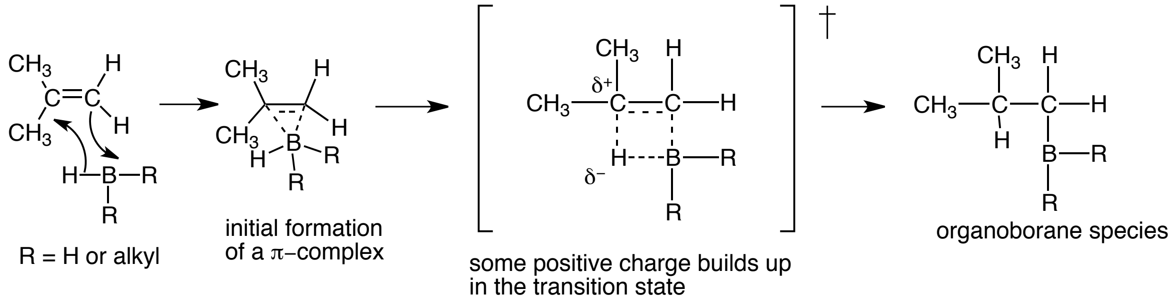
(2) Another reason that the boron adds to the less substituted carbon is due to steric hindrance. The organoboron hydride is generally fairly bulky and there is less steric hindrance for addition to the less substituted carbon. In fact, the larger the R substituents on the organoboron hydride, the greater the selectivity for addition of the organoborane to the less substituted carbon.

Because this is a concerted, *syn* addition both the boron and the hydrogen are delivered from the same side of the alkene to give a *cis* product.

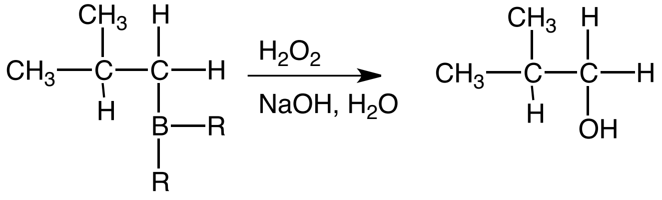
The empty p orbital of the boron initially overlaps with the π–orbital of the alkene to form a π–complex.



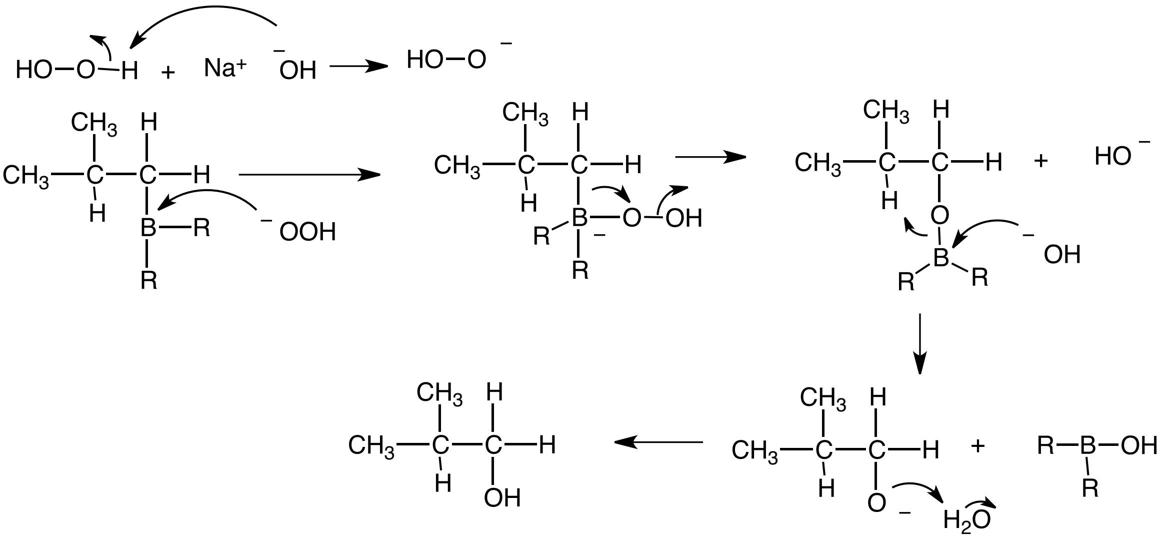
The boron hydride with empty p orbital interacts with the filled π–orbtal of the alkene to form a π–complex.



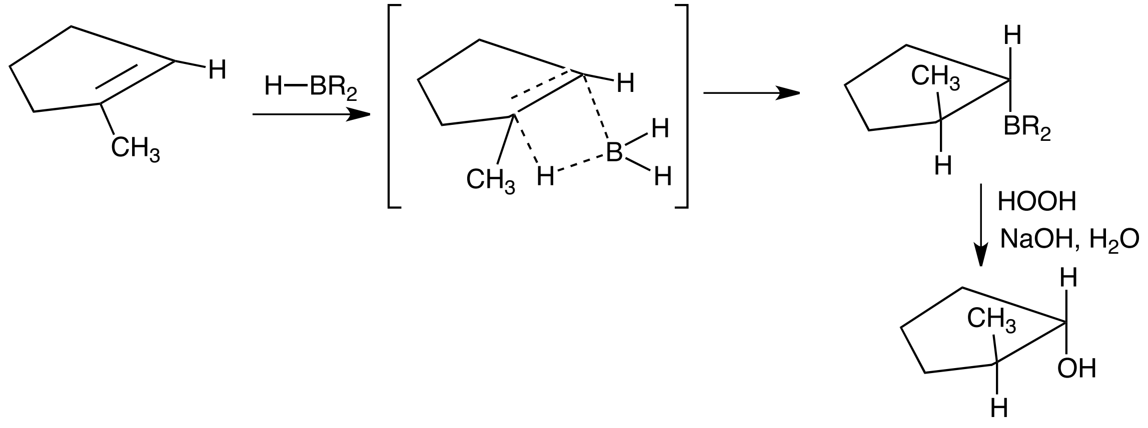
An organoborane species is formed as the product of the first reaction. This is a stable molecule and can be isolated. Generally, however, it is not isolated but treated directly *in situ* with an oxidizing agent such a hydrogen peroxide in aqueous sodium hydroxide. The boron is replaced stereospecifically to give the *cis* alcohol.



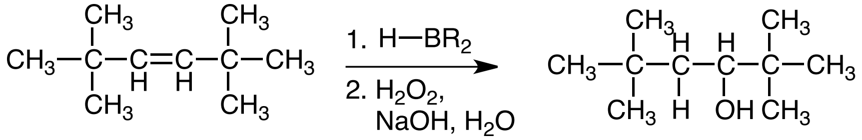
The mechanism involves nucleophilic attack on the boron by the deprotonated peroxide anion. Then the carbon attached to the boron migrates from the boron to the first oxygen of the peroxide, cleaving the very weak O-O bond to form the new C-O bond. Cleavage of this species by the hydroxides and protonation of the oxyanion by water completes the mechanism.



We can see that it is a *syn* addition by looking at a cyclic example.



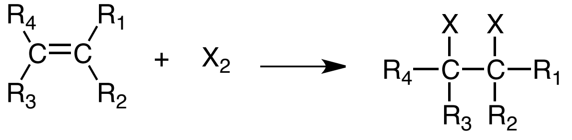
We do not see rearrangements since there is no carbocation intermediate in this concerted addition.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{H}{C}=\underset{H}{C}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[2.\ H_2O_2,\ NaOH,\ H_2O]{1.\ H-BR_2} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

## Addition of Halogens

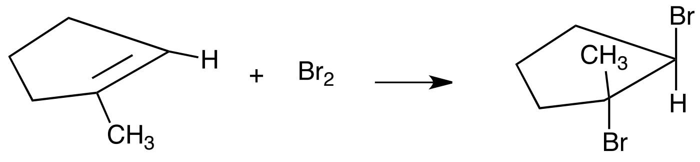
Halogens will add to alkenes to form vicinal (neighboring) dihalides. The first halide adds as the electrophile to form a halonium ion, a bridged species in which the halide is partially bonded to both carbons of the alkene. The second halide then attacks this halonium ion from the backside to give the *trans* product. Generally the reactions occur with no rearrangements being observed.



$$R_4R_3C=CR_1R_2 + X_2 \longrightarrow R_4-\overset{X}{\underset{R_3}{C}}-\overset{X}{\underset{R_2}{C}}-R_1$$

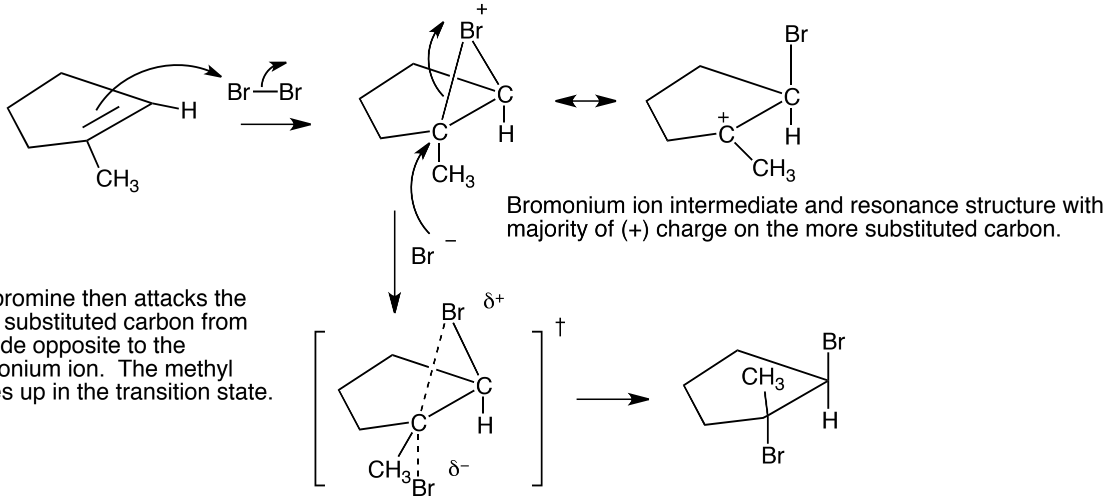
vicinal dihalide, X = Br, Cl

For example:



*trans*-1,2-dibromo-1-methylcyclopentane

The mechanism occurs by means of nucleophilic attack the π–electrons of the alkene on the Br-Br bond. Though there is initially no dipole in the Br-Br bond, a dipole moment is created as the π–electrons of the alkene approach. The two electrons in the Br-Br bond are pushed toward one of the Br's as the π–electrons approach the other one. The bromonium ion is created. One lone pair from the large, electron-rich bromine atom helps to stabilize the adjacent carbocation by overlap with the p orbital. This stabilizes the carbocation enough that no rearrangements are observed. It is not a real carbocation, though there is some partial positive charge, which builds up at the more substituted carbon.

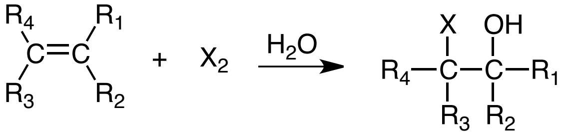


Bromonium ion intermediate and resonance structure with majority of (+) charge on the more substituted carbon.

The bromine then attacks the more substituted carbon from the side opposite to the bromonium ion. The methyl moves up in the transition state.

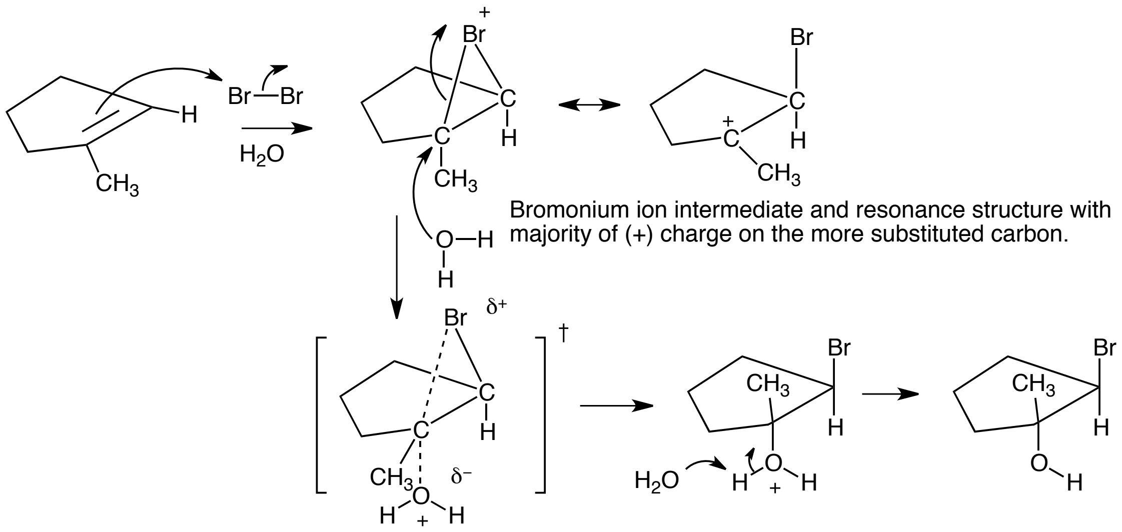
## Halohydrin Formation

When an excess of water is used along with the halogen, a halohydrin is formed. A halohydrin is a 1,2-hydroxy halide.



halohydrin, X = Br, Cl

First step in the mechanism is identical to that in the addition of halogen. We see a halonium ion (either the bromonium ion or chlorinium ion). Then water, as the nucleophile, attacks the more substituted carbon from the backside.



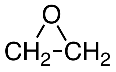
Bromonium ion intermediate and resonance structure with majority of (+) charge on the more substituted carbon.

Water, present in much higher concentration than the $Br^-$, acts as the nucleophile. It attacks the more substituted carbon from the side opposite to the bromonium ion. The methyl moves up in the transition state and we form the *trans*-1,2-bromo-alcohol.

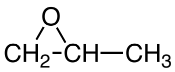
## Epoxidation of Alkenes

Epoxides are three-membered ring ethers.

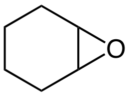
Nomenclature: In the IUPAC system, name the epoxides as "epoxy" derivatives of alkanes, list the "expoxy" substituent in alphabetical order with the other substituents and specify the position of the epoxide by two numbers.



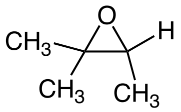
ethylene oxide
(epoxy ethane)



propylene oxide
(1,2-epoxypropene)

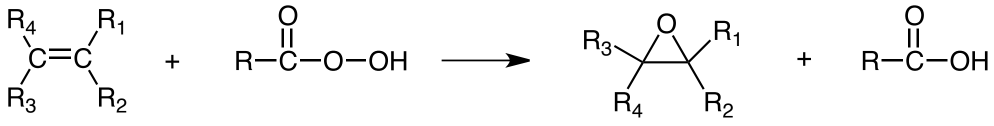


1,2-epoxycyclohexane

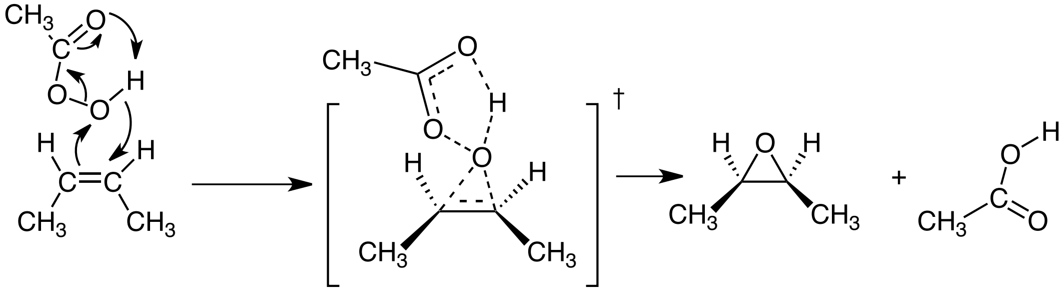


2,3-epoxy-2-methylbutane

Epoxides can be made easily from alkenes in a one-step using a peroxy carboxylic acid.



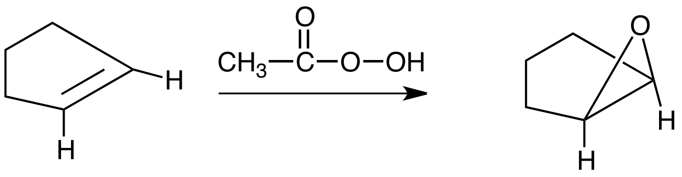
A common peroxy acid is peroxy acetic acid. The reaction proceeds as a one-step concerted *syn* addition.



Electron donating groups on the double bond increase the rate of the reaction.

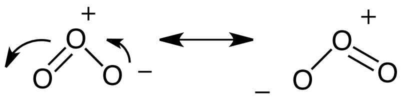
| | relative rate |
|---|---|
| $CH_2{=}CH_2$ | 1 |
| $CH_3{-}CH{=}CH_2$ | 22 |
| $(CH_3)_2C{=}CH_2$ | 484 |
| $(CH_3)_2C{=}CH{-}CH_3$ | 6526 |

And:



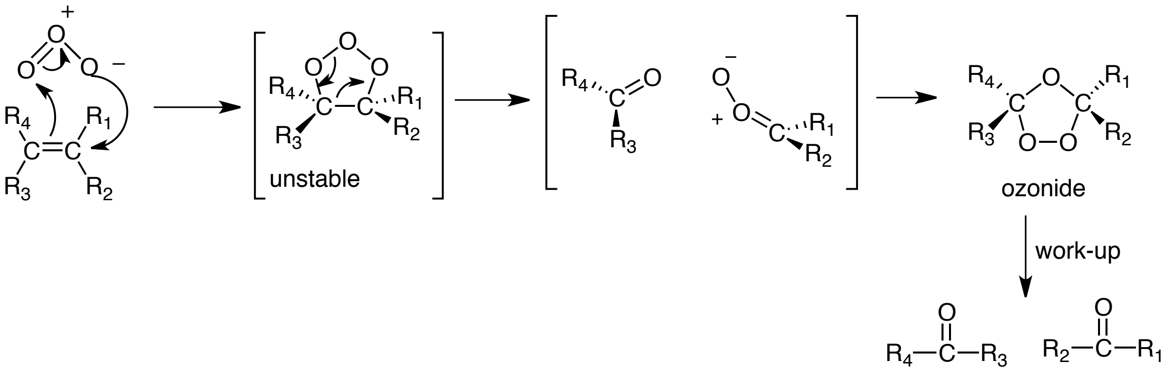
## Ozonolysis of Alkenes

Alkenes can be cleaved to generate two carbonyl groups in place of the C=C bond using the highly reactive reagent, ozone. Ozone is generated i*n situ* from molecular oxygen using a high intensity electric current.



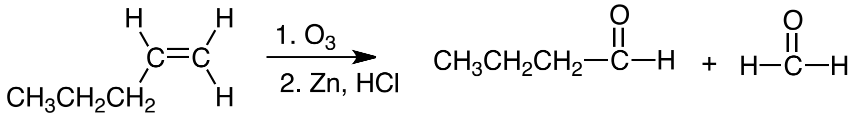
neutral zwitterion

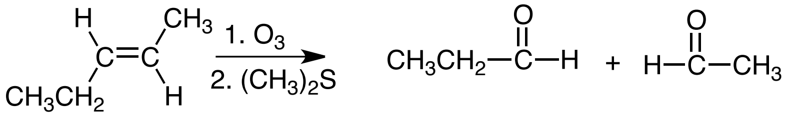
Ozone adds to alkene in a concerted, one step reaction. The initial intermediate then decomposes to form the semi-stable (explosive!) ozonide. This is then cleaved under reductive conditions to give aldehydes, ketones depending on the substituents on the alkene or carboxylic acids when cleaved under oxidative conditions.

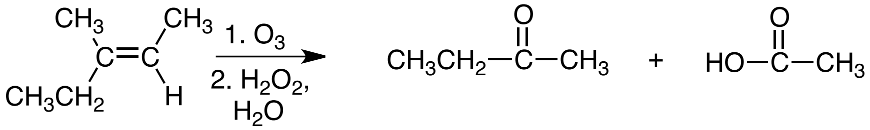


We can form a variety of products depending on (1) the substituents on the alkene and (2) the work up conditions. Work up using reductive conditions [Zn, HCl or $(CH_3)_2S$] will give aldehydes (if there is a hydrogen substituent on the alkene or ketones. Work-up using oxidative conditions ($H_2O_2$, $H_2O$) will give carboxylic acids instead of aldehydes if there is at least one hydrogen on the alkene or ketones if there are no hydrogens on the alkenic carbon.

For example:







## Retrosynthetic Analysis and Alkene Intermediates