# Alkenes

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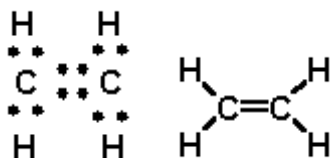## Structure

### Ethylene

Ethylene, or ethene, is one of the most valuable products obtained from petroleum refining. Ethylene is the starting material for polyethylene which is found in a variety of commercial products including milk bottles and plastic bags. Ethylene is also a natural product which is released when fruits ripen. It is ethylene that is released from ripening and rotting fruits that causes one bad apple to spoil the barrel.

Ethylene is the simplest member of the alkene family which consists of hydrocarbons containing one or more carbon-carbon double bonds. The Lewis dot representation for ethylene shows the double bond resulting from sharing of two pairs of electrons between the two carbon atoms. This assignment of electrons satisfies the octet rule giving carbon and hydrogen stable electronic structures.



**Lewis Dot and Line Bond Structures of Ethene**

In the molecular orbital representation of ethylene, the three directed bonding groups are assigned to

three sp$^2$ orbitals derived by combining the one 2s and two 2p orbitals. The sp$^2$ orbitals are 120$^o$ apart. The one remaining p orbital is perpendicular to the plane of the sp$^2$ orbitals.
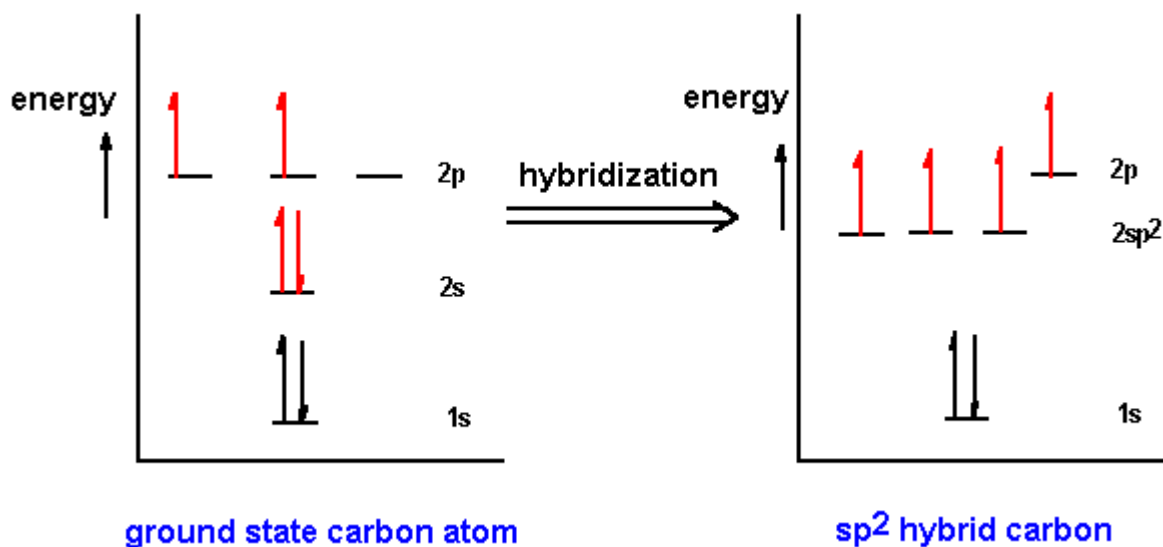
**Hybridization of carbon to form sp$^2$ orbitals**

**sp$^2$ molecular orbitals**
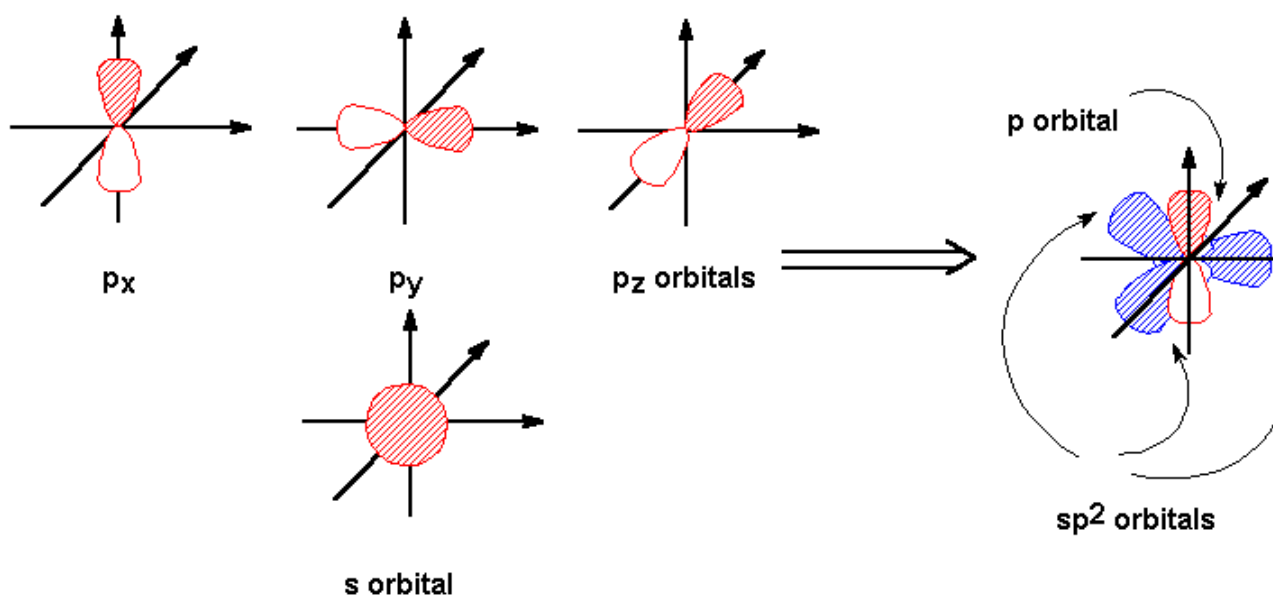
Two sp$^2$ hybridized carbon atoms overlap to form a carbon-carbon double bond. One bond, formed by overlap of two sp$^2$ orbitals has electron density linearly distributed between the two carbon nuclei and is called a sigma bond. The other bond results from overlap of the two p orbitals with electron density above and below the line connecting the two nuclei and is designated as a pi bond.

sp² hybrid carbon atoms

hydrogen atoms

π bond

σ bond

ethylene
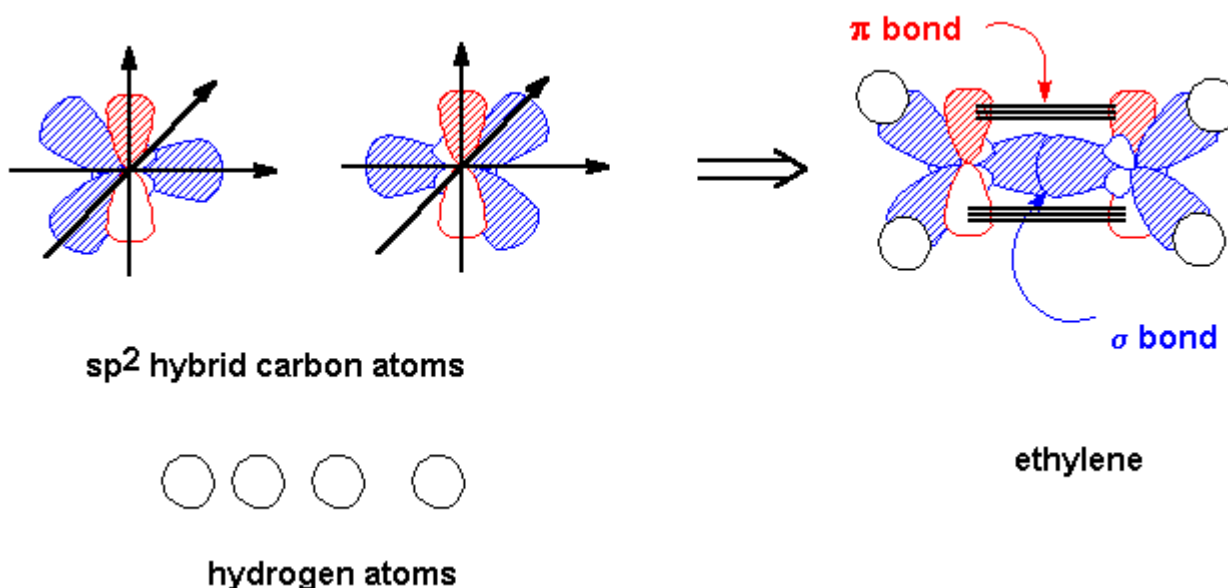
An important feature of a carbon-carbon double bond is that free rotation like we observed for ethane is no longer possible.
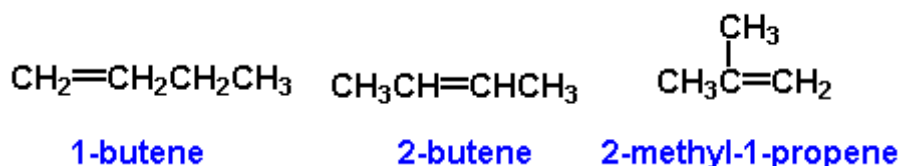
**Propene**

Propene, commonly known as propylene, is the second member of the alkene family. The alkenes have the general formula $C_nH_{2n}$. Propylene is usually produced during petroleum refining or as a coproduct of ethylene production. Polypropylene is an important commercial product made from propene and is found in carpets, ropes, yarns, and fishing gear. Propene is named by changing the -ane ending of the parent alkane with -ene. The line bond and condensed structures of propene and the molecular model are shown below.

or

$CH_3CH=CH_2$
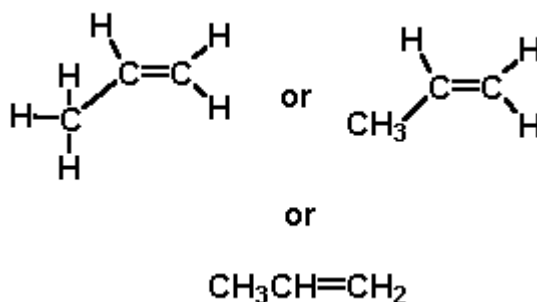
Line bond and condensed representations of propene.

## Butene

Butene ($C_4H_8$) can exist as three constitutional isomers. Two isomers, 1-butene and 2-butene, differ only in the position of the double bond. The third butene isomer has a different carbon skeleton and is named as a propene derivative following the IUPC rules.

$$CH_2{=}CH_2CH_2CH_3 \qquad CH_3CH{=}CHCH_3 \qquad \overset{CH_3}{\underset{}{CH_3C{=}CH_2}}$$

**1-butene**              **2-butene**         **2-methyl-1-propene**

With 2-butene we encounter a new structural feature. Since the double bond is not free to rotate, two forms of 2-butene are possible depending on the relative position of the methyl groups. These two forms are geometric isomers. The isomer in which the two methyl groups are on opposite sides of the double bond is called *trans*-2-butene. The other isomer with the methyl groups on the same side of the double bond is *cis*-2-butene.

**trans-2-butene      cis-2-butene**
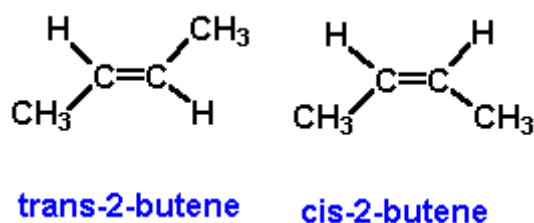
What can we say about the relative stability of the four isomers of butene? We have seen that *heats of combustion* provide a measure of stability. The higher the heat released when a mole of a substance is burned, the less stable it is. Even though the combustion of the three butene isomers can be represented by the same general equation, the heats of combustion are different as shown in the table.

$$C_4H_8 + 6\ O_2 \longrightarrow 4\ CO_2 + 4\ H_2O$$

If we compare the straight chain alkenes, we observe a general trend.

- The isomer with the most substituted double bond is the most stable.
- Trans alkenes are more stable than cis alkenes.

The trans- isomer is more stable than the cis isomer because the two methyl groups are farther apart and electron repulsion is lower. Compare the Chime models for cis- and trans-2-butene. These models display the atoms in a ball-and-stick representation with a dot surface of the *van der Waals radii* showing the steric interaction of the two methyl groups. The influence of nonbonded interactions on the stability of organic molecules is an important consequence of the three-dimensional structure of molecules.

# Chemical Reactions of Alkenes

**Reaction Map**

A concept map showing some of the important reactions of alkenes reveals the two basic types of reactions of alkenes - addition and oxidation.
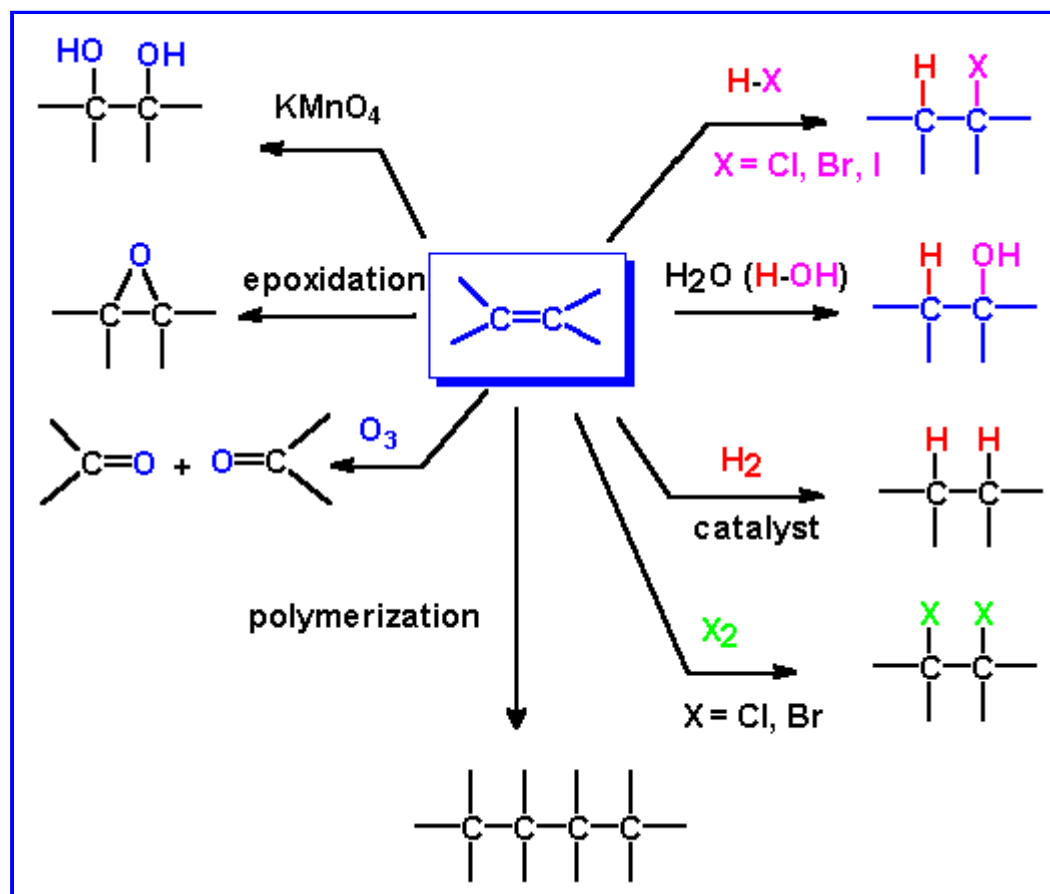


## Addition Reactions:

Alkenes undergo addition reactions with a variety of reagents of the general type A-B. This reaction can often be reversed in an elimination reaction to produce an alkene.
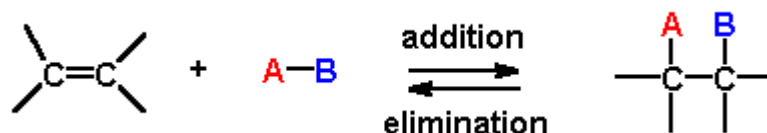


## Addition of Hydrogen Halides

Alkenes react readily with the hydrogen halides HCl, HBr, and HI. Hydrogen fluoride is not reactive with alkenes.

Addition of HCl to ethylene provides a good example of an addition reaction and a simple system to begin our study of the mechanism of this reaction.

ethylene                              chloroethane
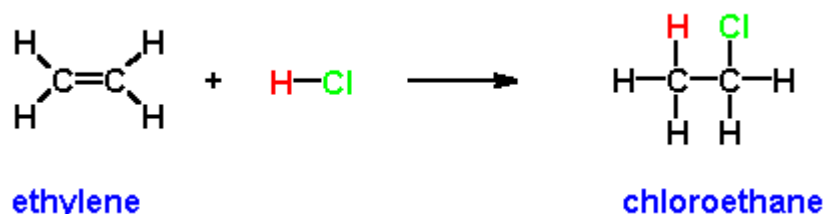
A mechanism is a stepwise description of a reaction. The ability to understand one reaction in detail provides a great deal of predictive power for many related reactions.

Using our previous models for bonding, ethylene has a region of high electron density due to the $\pi$ bonding and HCl is polarized due to the high electronegativity of chlorine. When ethylene collides with H-Cl, the $\pi$ electrons from ethylene can bond to the electron deficient hydrogen atom to form a C-H bond.  At the same time the electrons in the H-Cl bond are transferred to the electronegative chlorine atom. The products of this collision are a positive charged carbon ion (a carbocation) and a chloride anion. This carbocation is designated as primary ($1^o$) because the positive charge resides on a primary carbon atom. Carbocations are frequently encountered in organic reactions.
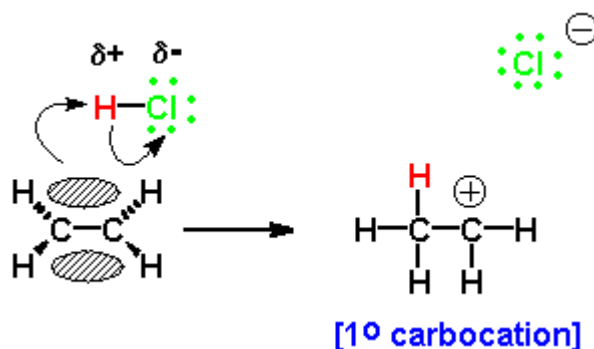


[1° carbocation]

Since the positively charged carbocation lacks a stable octet of electrons, we predict that it should be unstable. This is the case and the carbocation reacts readily to gain an additional pair of electrons. One way it can do this is to react with the chloride ion to form the stable chloroethane.
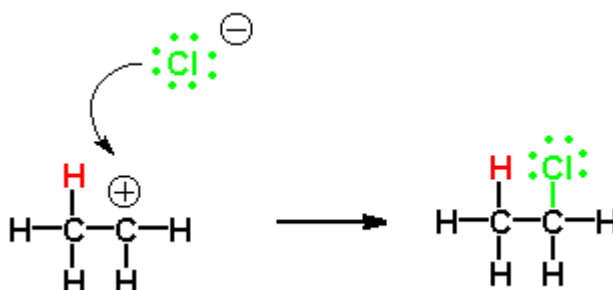


We can describe this reaction in several ways. A curved arrow indicates the direction of movement of a pair of electrons. Electrons are donated from ethylene to hydrogen, and the chloride ion donates electrons to the carbocation. We can describe the reagent that donates electrons, ethylene and the chloride ion, as a Lewis base or as a nucleophile. The reagent that accepts a pair of electrons is the Lewis acid or the electrophile.

Our proposed mechanism for this reaction proceeds by two steps:

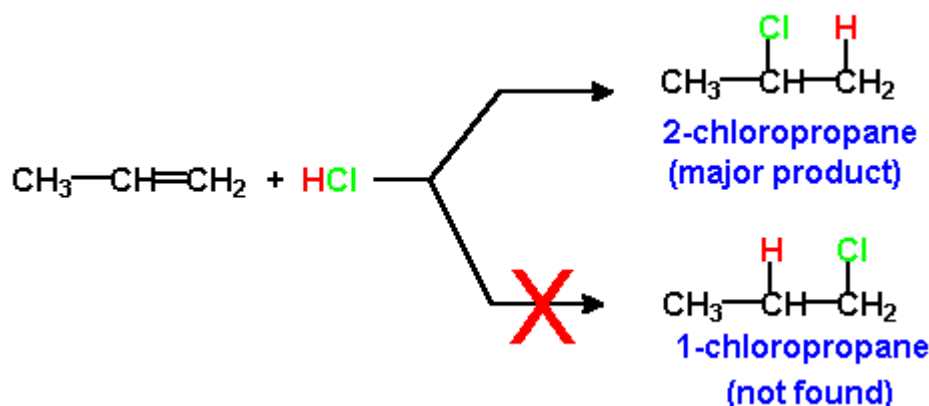- addition of a hydrogen ion to an alkene to form a carbocation

- reaction of the carbocation with a nucleophile

The carbocation is unstable but has a finite, although brief, lifetime. Such species that form between reactants and products are called intermediates. Intermediates cannot usually be isolated under normal conditions but their existence can be demonstrated by a variety of means. Our mechanism can be represented on an energy level diagram.
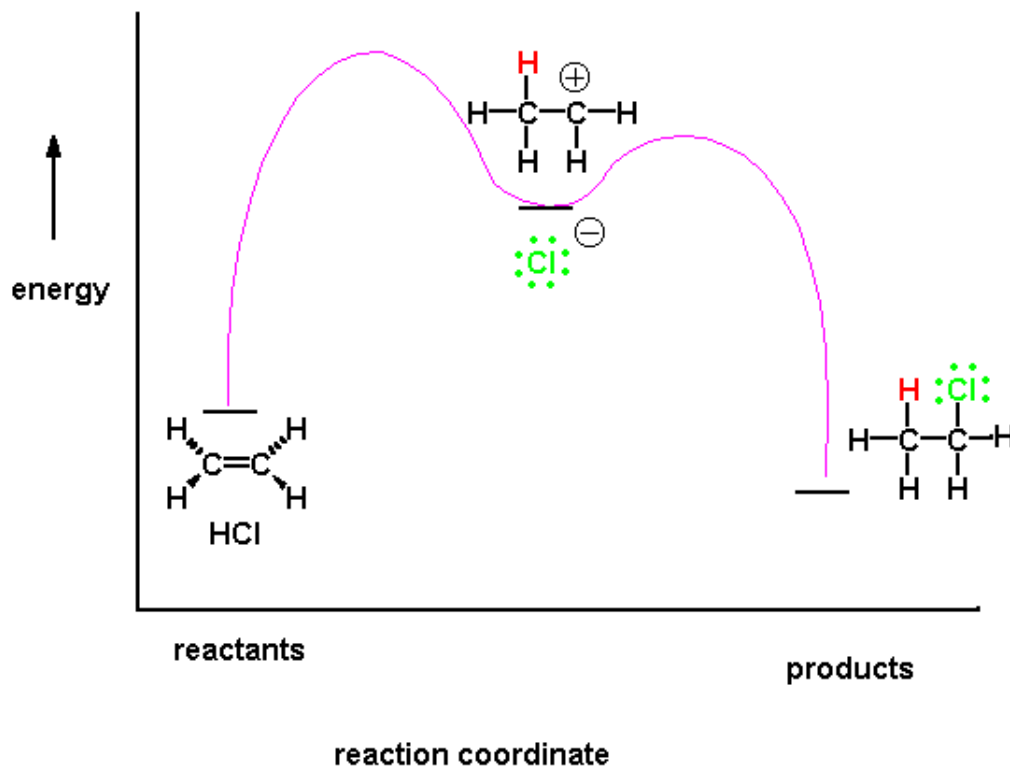


## Addition of HCl to Propene - Markovnikov Addition

When HCl is added to propene two possible products may be formed, but only one isomer, 2-chloropropane, is produced. The other possible isomer, 1-chloropropane is not formed. This type of reaction in which a reagent adds preferentially in one direction is described as regioselective.



Based on a series of experimental results, the Russian chemist Vladimir Markovnikov, formulated a general rule to predict the direction of addition of a hydrogen halide (HX) to an alkene. Markovnikov's rule states that when HX undergoes addition to alkenes, the hydrogen attaches to the

carbon of the double bond which has the greater number of hydrogen atoms attached. In the case of propene, C-1 has 2 hydrogens attached while C-2 has only one, therefore, the hydrogen of HCl attaches to C-1 and the chlorine to C-2.

Markovnikov's rule is predictive but for any explanation of these results we need to consider the mechanism of the reaction. As in the case of ethene, the first step of the mechanism is the addition of $H^+$ to the alkene to form a carbocation. Attachment of the proton to C1 gives a secondary ($2^o$) carbocation which would react with chloride ion to give 2-chloropropane, the product of the reaction. Attachment of the proton at C2 would give a primary ($1^o$) carbocation which would give 1-chloropropane which is not observed in the reaction. This indicates that the $2^o$ carbocation is formed in preference to the $1^o$ carbocation. In chemical reactions the preferred intermediate is lower in energy (more stable). Thus, $2^o$ carbocations are more stable than $1^o$ carbocations.
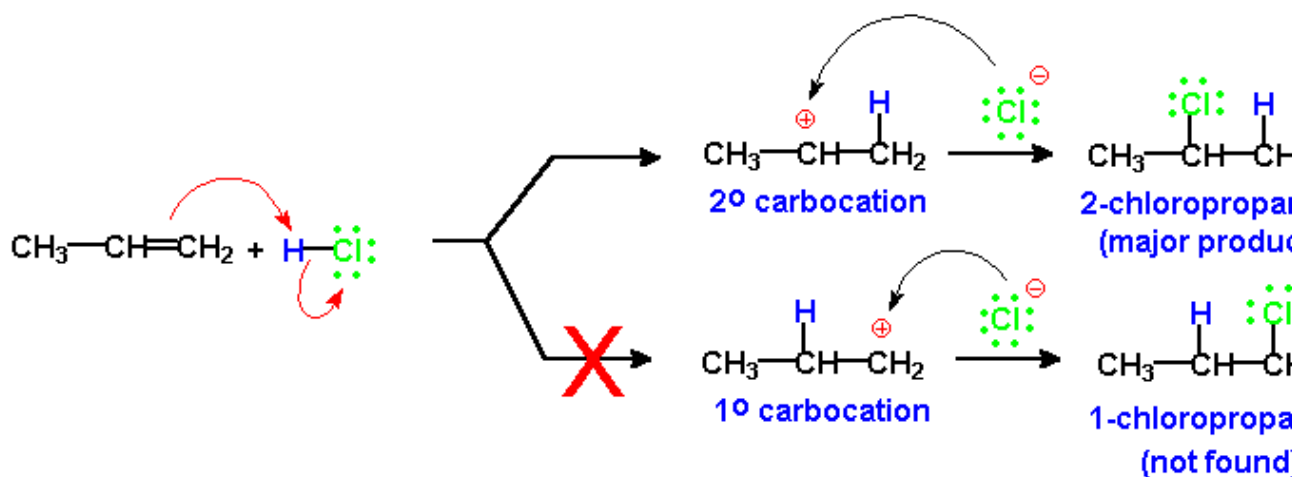
An alternative description of these reactions using an energy level diagram shows the relative stability of the carbocation intermediates. The lower energy pathway is both the preferred and the faster reaction.
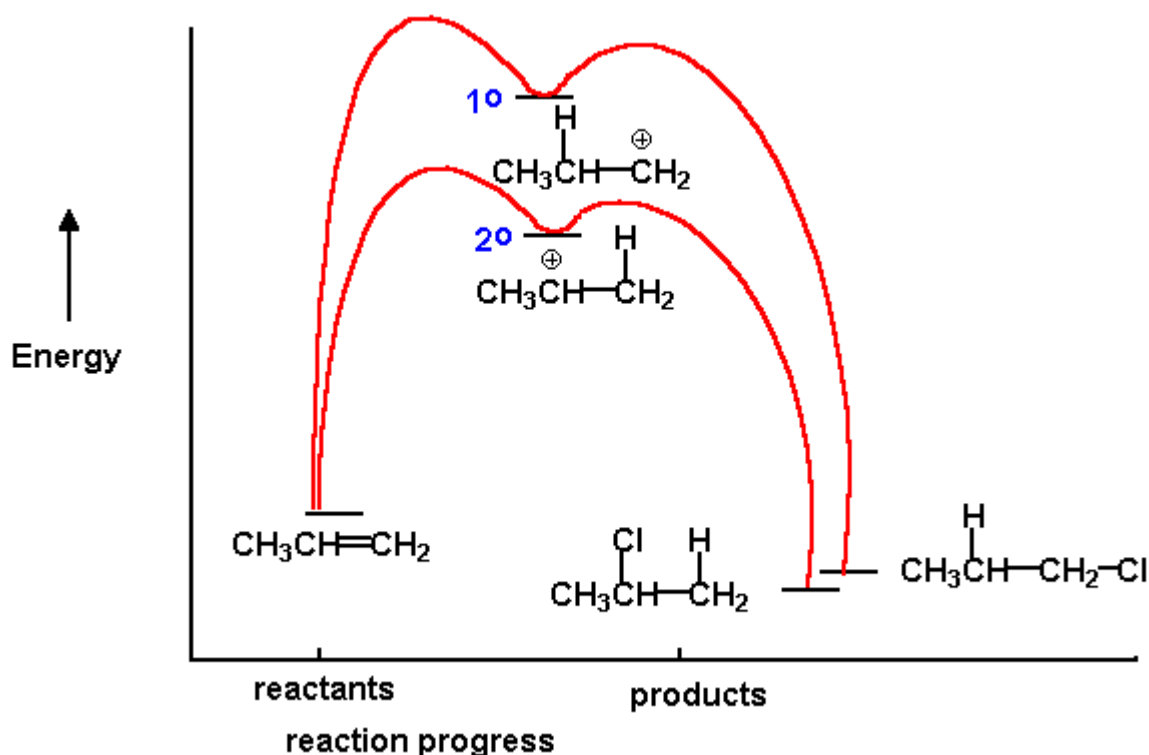
The addition of HCl to 2-methylpropene shows a similar regioselectivity. Although two possible directions of addition are possible, only one product is formed, 2-chloro-2-methylpropane, in accordance with Markovnikov's rule.
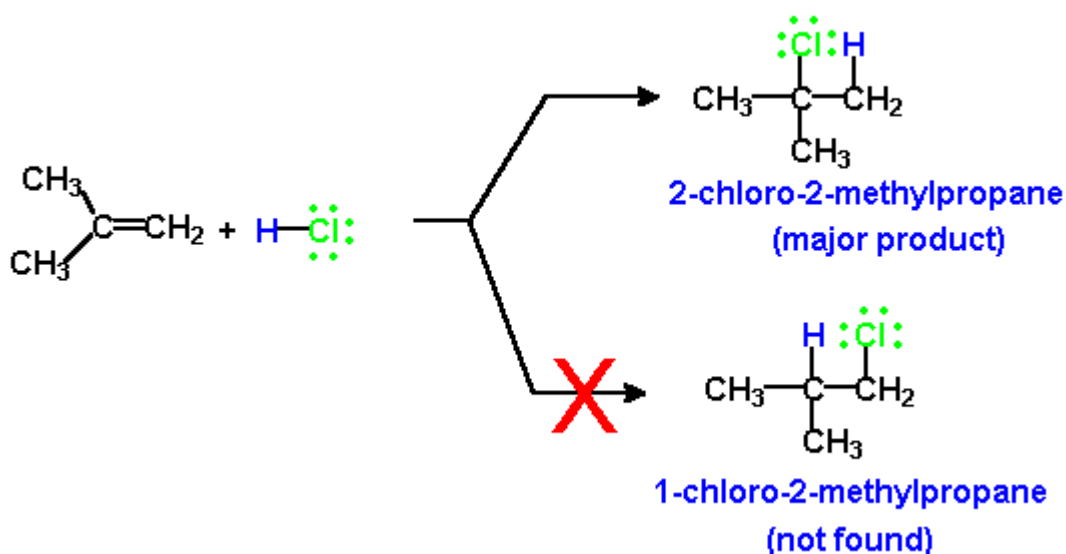
Consideration of the mechanism reveals that the observed product is formed by a $3^o$ carbocation intermediate, not the alternative $2^o$ carbocation. Thus, $3^o$ carbocations are more stable than $2^o$ carbocations.
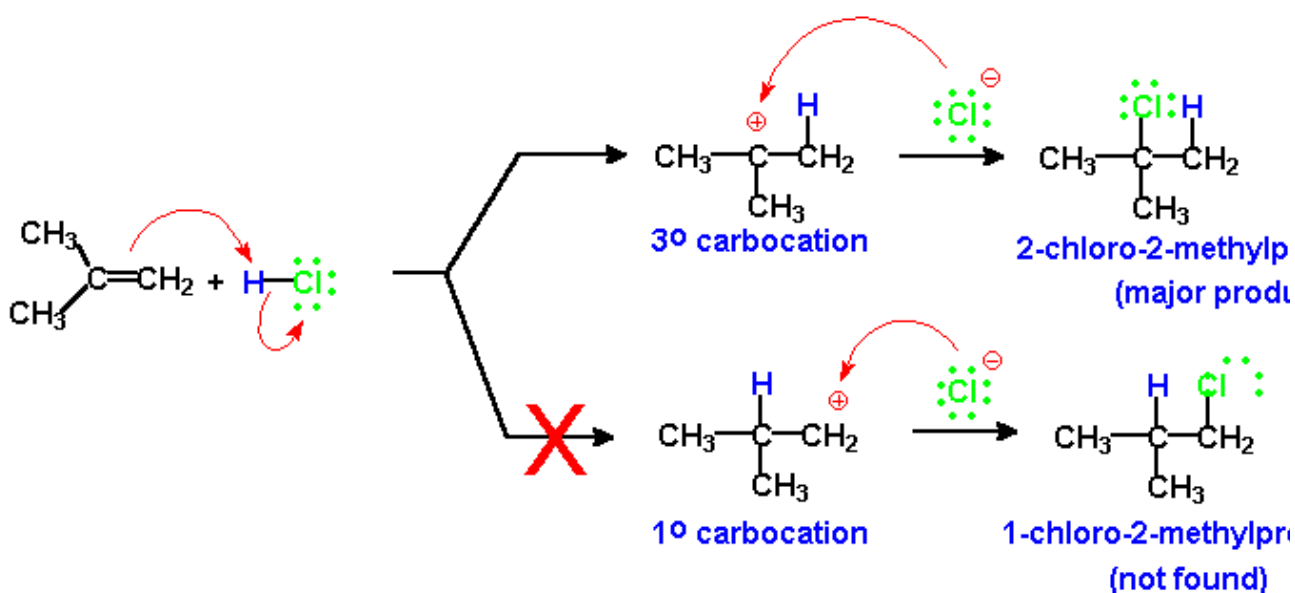
## Carbocation Stability

The stability of carbocations depends on their structure. Tertiary carbocations are the most stable and form faster than secondary carbocations, which are more stable and form faster than primary carbocations. This general order is important because carbocations are very common intermediates and will be encountered frequently in our exploration of organic chemistry.
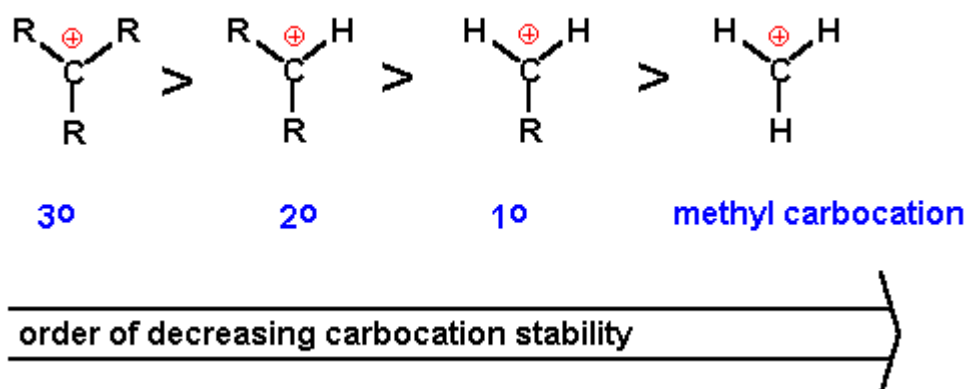
## Structure of Carbocations

Carbocations have three pairs of electrons about the central carbon atom which makes it trigonal, $sp^2$ hybridized. The three bonds are planar and an empty p orbital is perpendicular to the plane. Alkyl groups attached to the carbocation stabilize the positive charge by donating electron density to the positively charged carbon.
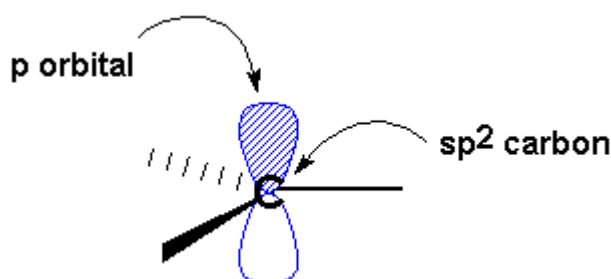
## Addition and Elimination of $H_2O$: Hydration and Dehydration of Alkenes

Alkenes react with water to form alcohols only in the presence of an acid catalyst. This reaction is reversible and, by controlling the conditions of the reaction, alkenes can be converted to alcohols or alcohols may be dehydrated to give alkenes.
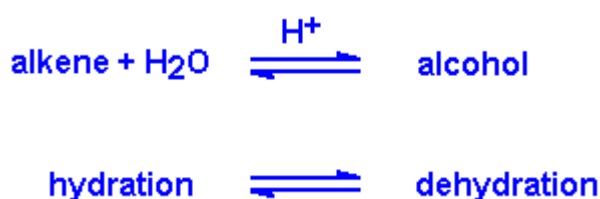
By application of LeChatelier's principle to control equilibrium, hydration of an alkene is usually favored by using excess water in the reaction. Dehydration is favored by conditions that remove water or the alkene.

The simplest example is the hydration of ethene to give ethanol. One industrial process for the commercial production of ethanol uses this reaction. The ethene coming from the catalytic cracking of petroleum. Fermentation of carbohydrates from corn and other renewable resources is the competitive commercial process.
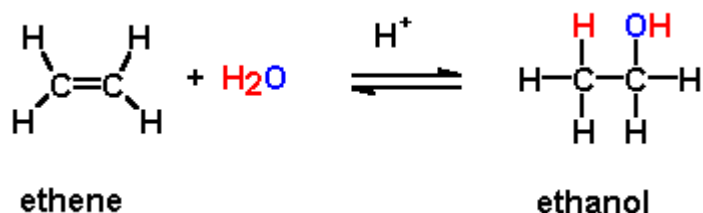


## Mechanism:

The mechanism for this reaction involves the following steps:
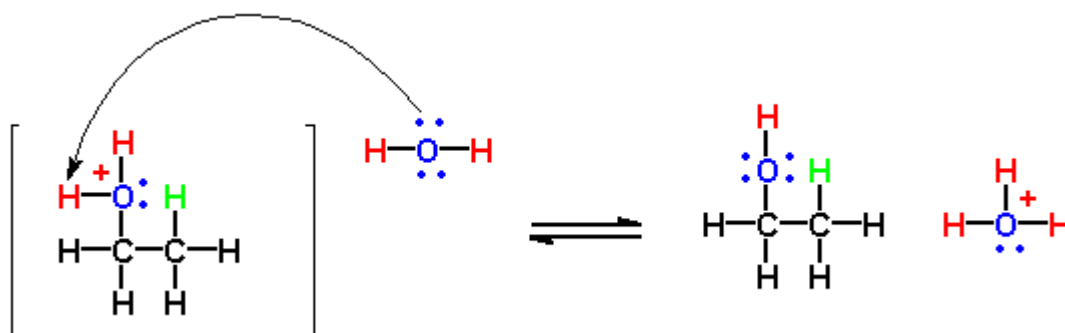
- Protonation of the alkene to form an intermediate carbocation.
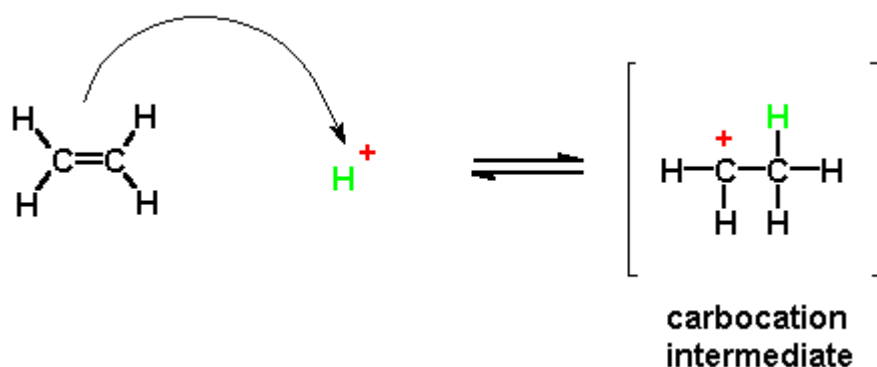


- Nucleophilic addition of water to the carbocation.
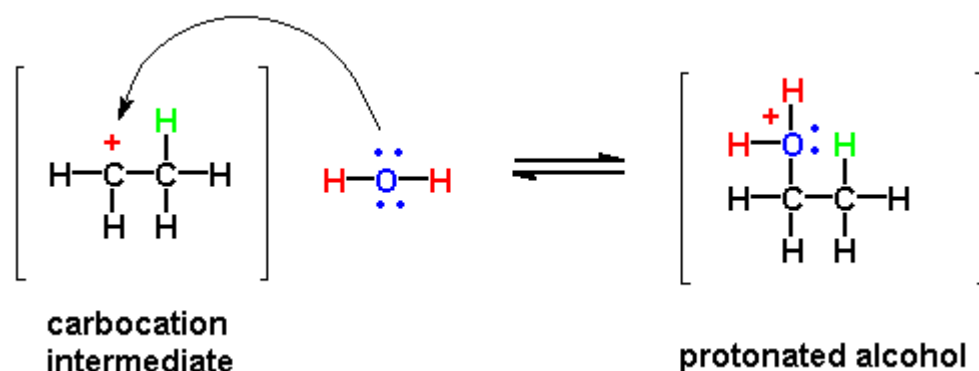
- Deprotonation of the hydronium ion to regenerate the proton catalyst.

This mechanism is strictly true only in dilute aqueous solutions. This reaction is usually carried out in fairly concentrated solutions of sulfuric acid. Under these conditions, water and sulfuric acid compete for nucleophilic addition to the intermediate carbocation. Addition of sulfuric acid produces an alkyl hydrogen sulfate. Upon heating in boiling water this intermediate is converted into an alcohol and the sulfuric acid is regenerated.

## Orientation:

Since this reaction proceeds through a carbocation intermediate, the alcohol derived from the more stable carbocation is formed predominately. The direction of addition follows Markovnikov's rule. For example, hydration of 2-methylpropene gives 2-methyl-2-propanol not 2-methyl-1-propanol.
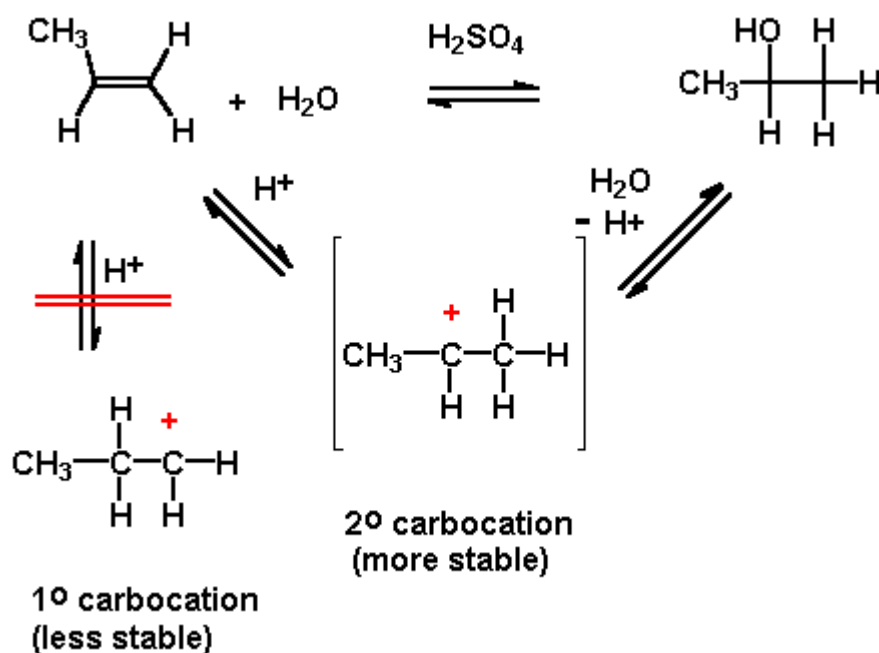
## Relative Rate:

The rate of reaction is determined by the slowest step in the mechanism - the formation of the carbocation. Alkenes that can produce a $3^o$ carbocation react more rapidly than those producing $2^o$ or $1^o$ carbocations.

## Addition of Hydrogen (Hydrogenation)

Hydrogen gas ($H_2$) adds to alkenes to produce alkanes only in the presence of a catalyst. This process is called catalytic hydrogenation.



Catalysts can be either homogeneous (soluble in the reaction solvent) or heterogeneous (insoluble in the solvent). Usually hydrogenation uses heterogeneous catalysts which are transition metals - platinum, rhodium, ruthenium or nickel.

Catalytic hydrogenation results in the *cis*-addition of hydrogen to the double bond. Hydrogenation of 1,2-dimethylcyclohexene gives predominately cis-1,2-dimethylcyclohexane.
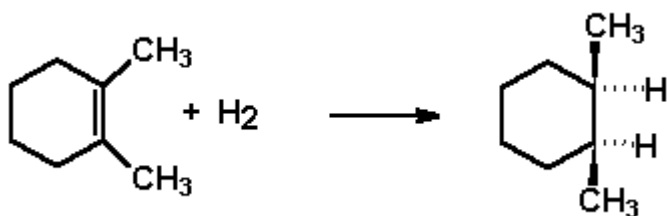


Hydrogen is also usually added to the least hindered side of the alkene.
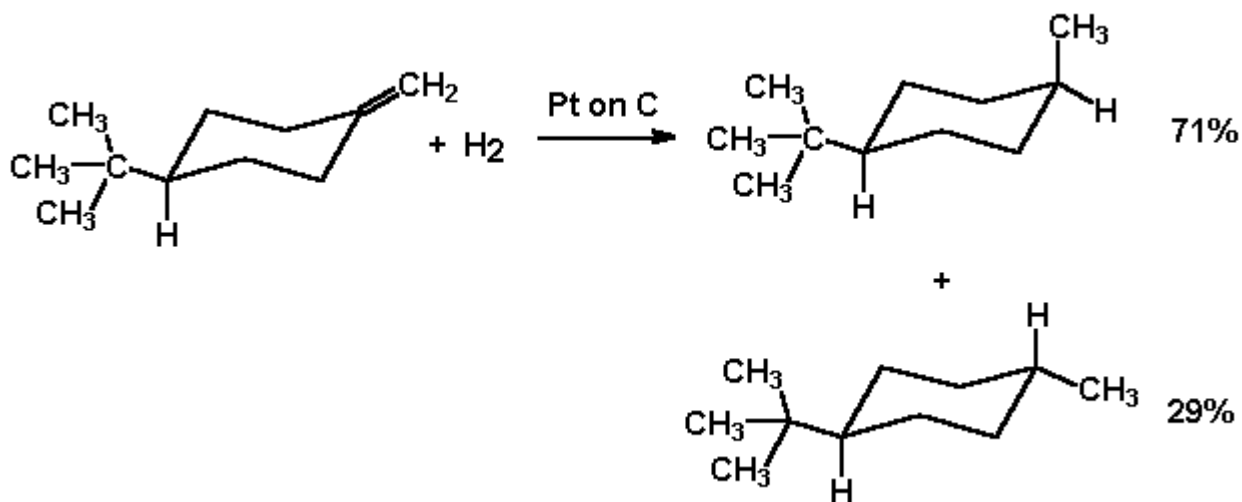


Examination of the molecular model shows the t-butyl groups and the 1,4-diaxial hydrogens hinder the top face of the molecule.

**Mechanism:**

The observations that catalytic hydrogenation usually give *cis*-addition and that the addition occurs from the least hindered side of the molecule, led chemists to propose the following mechanism for the reaction. Click here to view an <u>animation</u> of this reaction.
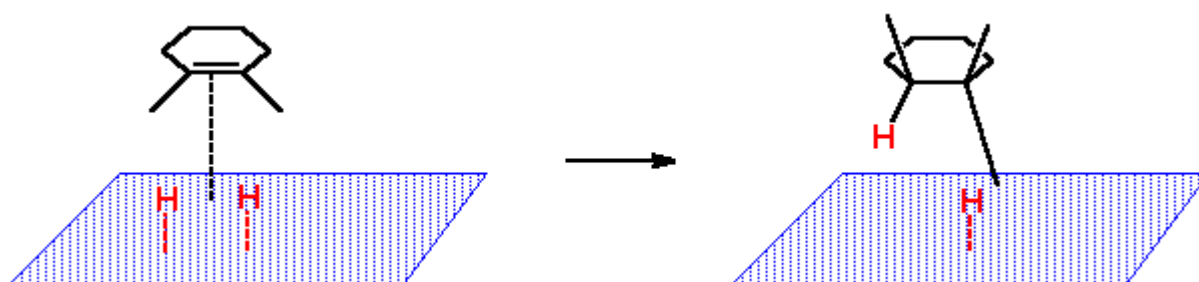
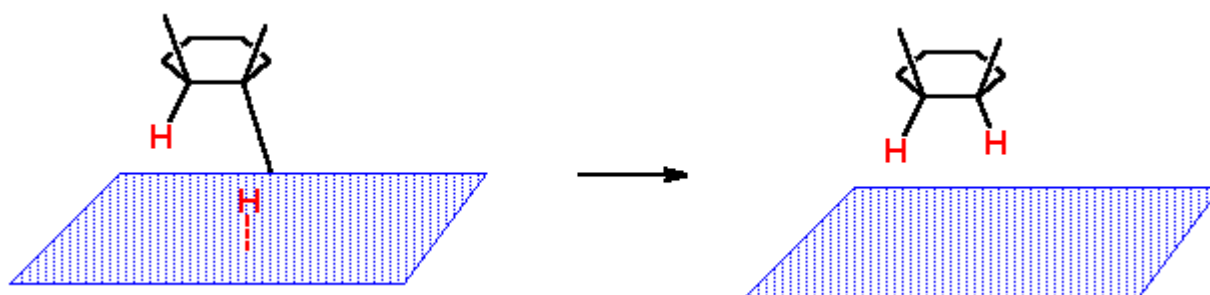Step 1: Adsorption of hydrogen on the catalyst to weaken the H-H bond.
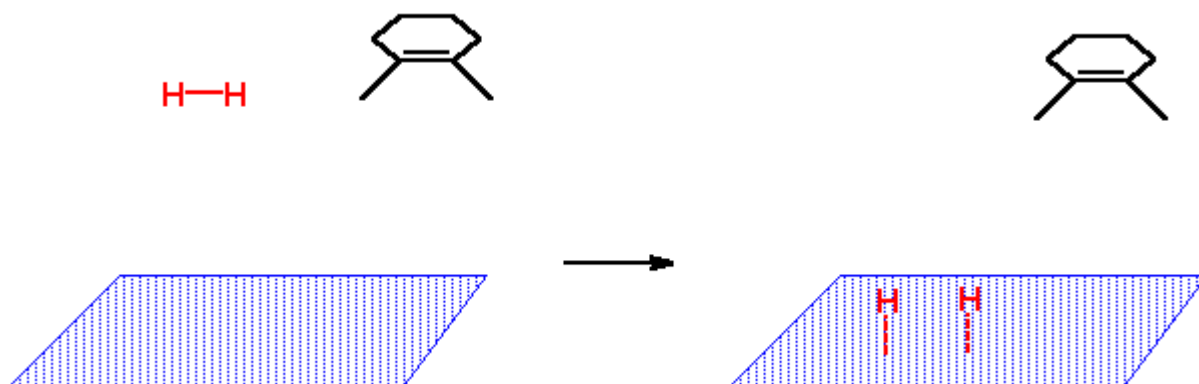
Step 2: -bonding of alkene to catalyst
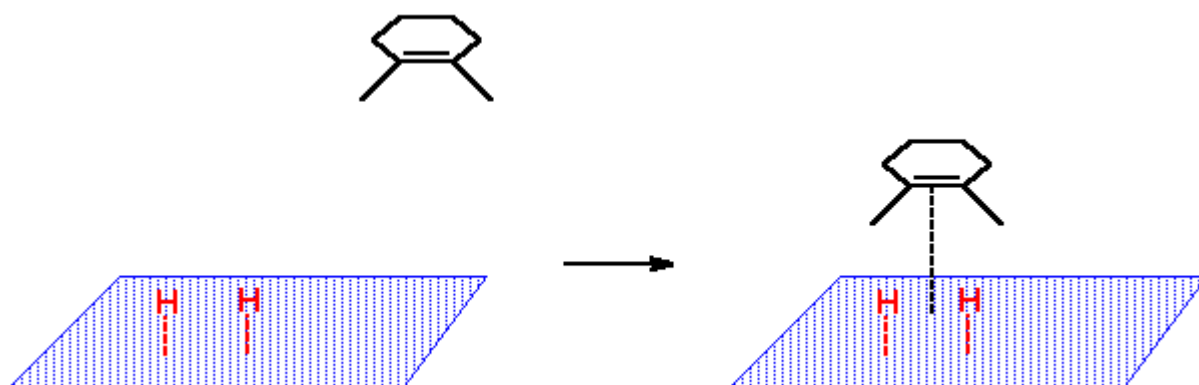
Step 3: Transfer of a hydrogen atom to alkene

Step 4: Transfer of a second hydrogen atom to alkene

## Heats of Hydrogenation:

Hydrogenation of alkenes is an exothermic process, and the heat of hydrogenation may be used to measure to relative stability of alkenes like we saw earlier for heats of combustion. For example, the heats of hydrogenation of the four isomers of butene are given in the table.
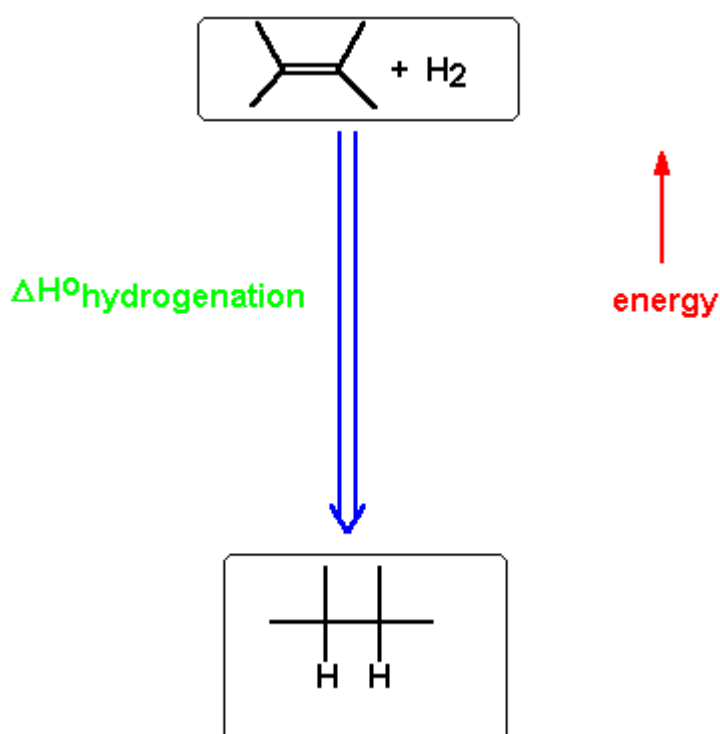


## Ozonolysis of Alkenes

Ozone ($O_3$) is a pungent gas and is one of the allotropic forms of oxygen. Ozone is formed when diatomic oxygen combines with an oxygen atom. The oxygen atom is produced by decomposition of an oxygen molecule by energy from light or an electrical current.
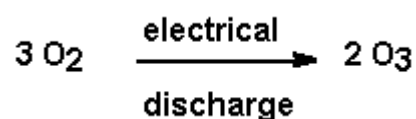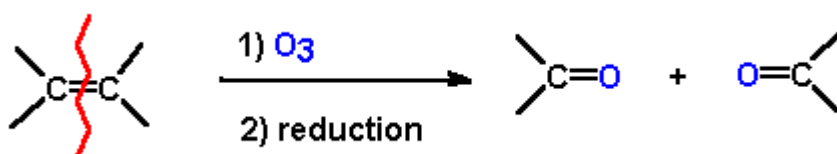
The three oxygen atoms are arranged in a bent shape.

Electronically, resonance structures for ozone reveal that the central oxygen atom is positively charged and the two terminal oxygens have equal negative charges.
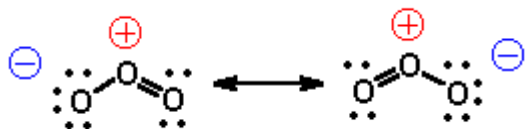


Ozone cleaves carbon-carbon double bonds to give two carbonyl compounds.



The intermediate in this process is a 5 membered ring called an ozonide. Ozonides are unstable, explosive compounds and are usually reduced to the carbonyl compounds with zinc in acetic acid, triphenylphosphine, or dimethylsulfide.
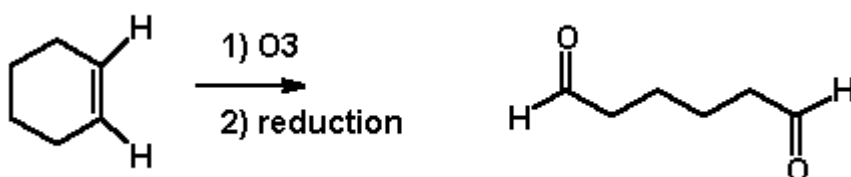


ozonide
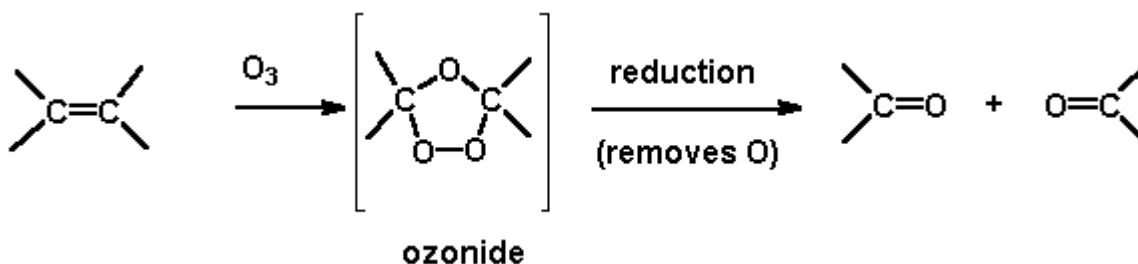
Under these reductive conditions, the products of the reaction are aldehydes or ketones
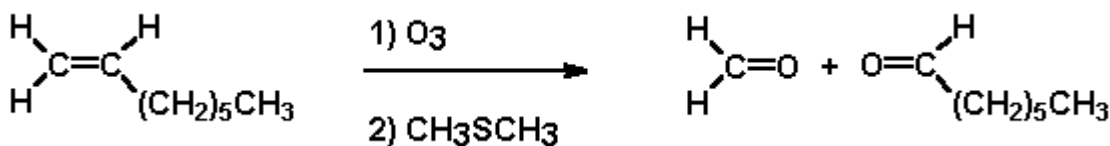


Under nonreductive conditions aldehydes are not isolated but are oxidized to carboxylic acids.

Ozonolysis is used as a synthetic route to carbonyl compounds. For example, reductive ozonolysis of cyclohexene produces 1,6-hexanedial.

Ozonolysis is also used to locate the position of double bonds in unknown molecules. Muscalure is the pheromone released by female house flies to attract males. Chemists at the U.S. Department of Agriculture's Agricultural Research Service isolated the pheromone by washing the cuticle of the females with hexane or ether to remove the waxy layer containing the pheromone. Chromatographic separation gave a 23-carbon alkene with high activity. Microozonolysis of 10μg of the pheromone gave nonanal and tetradecanal.
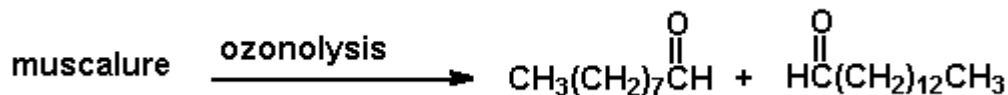


The pheromone had to be 9-tricosene. Synthesis of both the Z- and E-isomers was performed, and the natural pheromone was shown to be Z-tricosene by comparison with the synthetic material.



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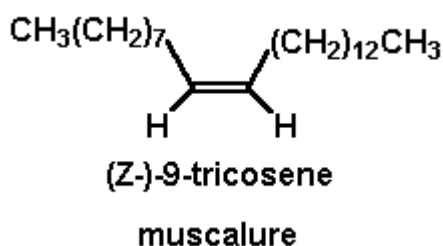
# Conjugated Systems

Conjugation is an important concept in organic chemistry. A conjugated system contains alternate double and single bonds. The simplest conjugated system is 1,3-butadiene.
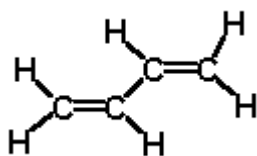


Exercise:

Identify each ofthe following compounds as conjugated or nonconjugated.  Click on a structure for the answer.



Molecular Orbital Description

The molecular orbital description of 1,3-butadiene shows that the p-orbitals of the four sp2 carbon

atoms are adjacent and overlap with each other. This overlap allows the 4 pi electrons to be delocalized over all four carbon atoms. Delocalization of electrons stabilizes a molecule. The delocalization of electrons is revealed by measurement of the bonds lengths for 1,3-butadiene which show that the double bonds are longer than isolated double bonds and the C-C single bond is shorter than normal.
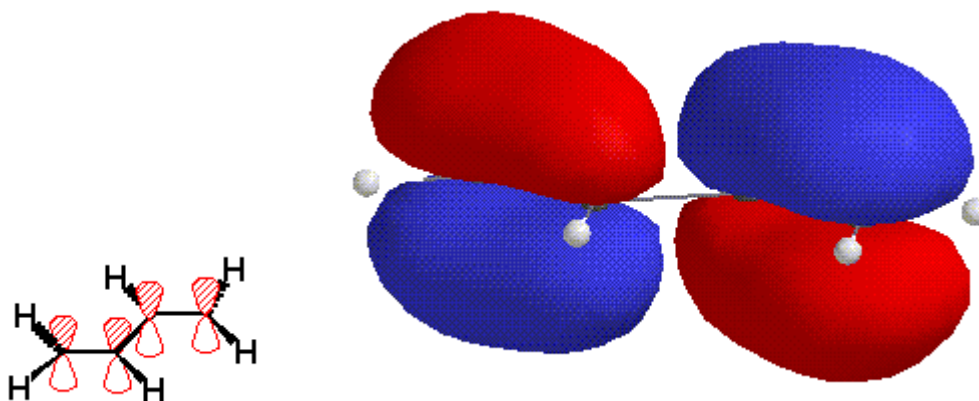


Molecular representation of the pi orbitals of 1,3-butadiene.
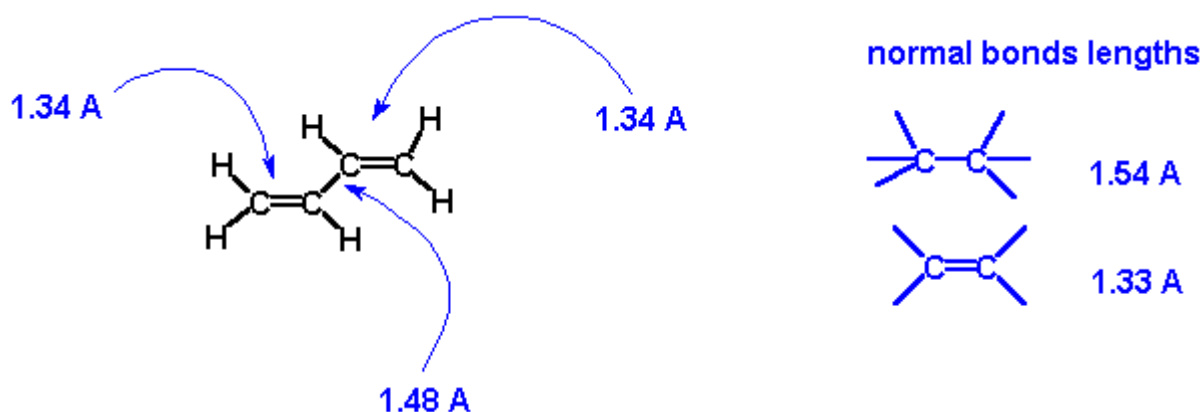


## 1,4-Addition

Electrophilic addition of HBr to 1,3-butadiene gives a mixture of two products. The major product is the one expected for addition of HBr across a C-C double bond (1,2-addition). The minor product results from addition of H to the first carbon of the conjugated system and the Br to the fourth carbon (1,4-addition). These processes are called 1,2- and 1,4-addition regardless of the numbers given to the double bonds in naming the compounds.



1,2-addition                    1,4-addit
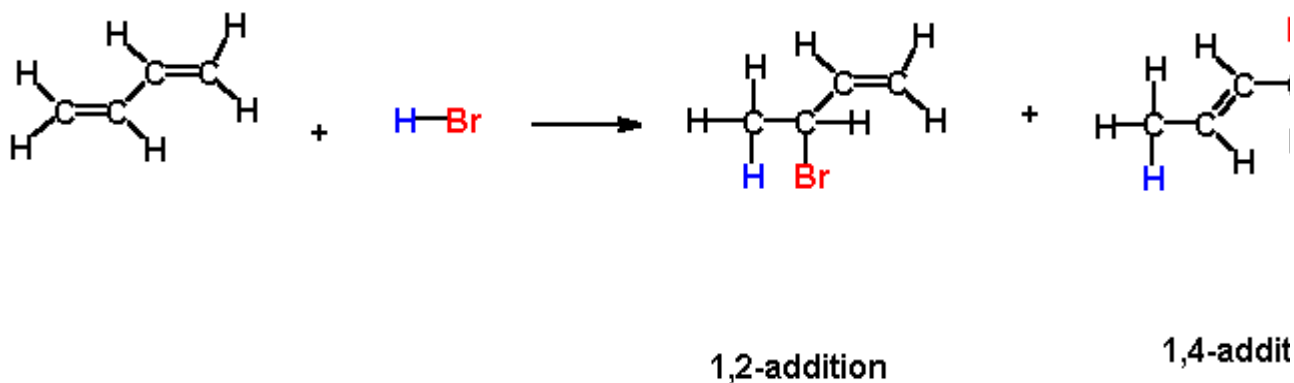
A look at the mechanism of the reaction explains the formation of the two products. The initial step of the reaction is Markovnikov addition of a proton to a C-C double bond. The intermediate, called an allylic carbocation, is resonance stabilized. The two resonance contributors reveal that the positive charge is shared by both C-2 and C-4. The bromide ion then adds to either carbon atom. The exact distribution of products depends on the temperature of the reaction. Allylic carbocations are relatively stable and are almost as stable as tertiary carbocations.
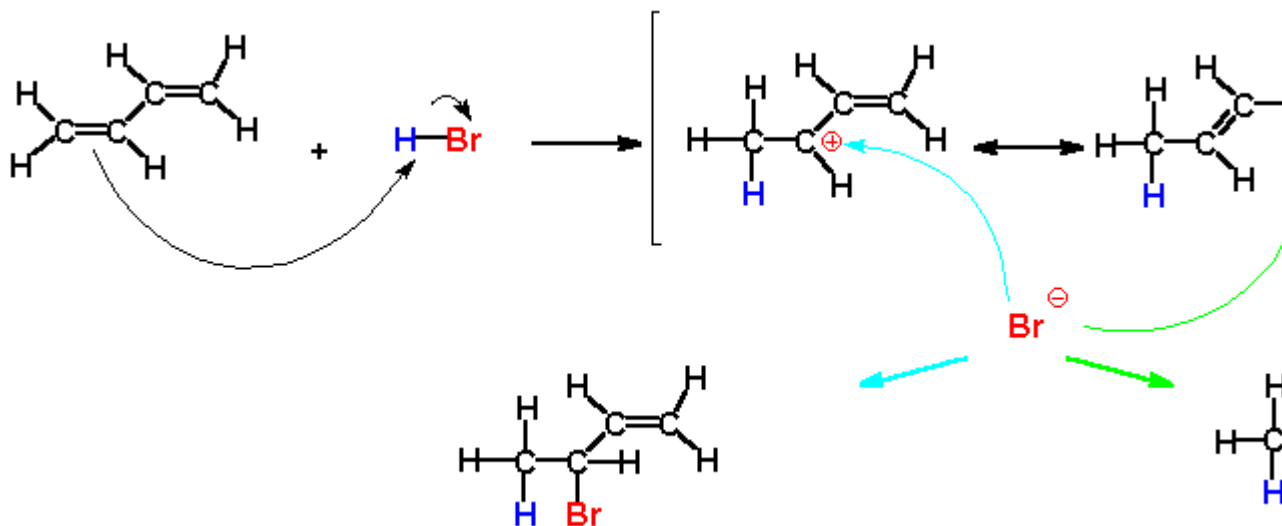
A molecular orbital model show the electron density of the carbocation. The blue areas show the location of the positive charge. Note that it is localized on C1 and C3.
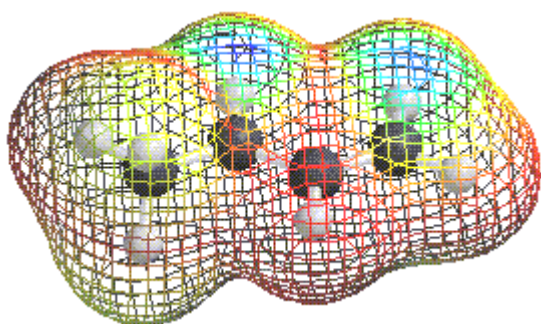
# Organic Nomenclature

These rules were developed by the International Union of Pure and Applied Chemistry (IUPAC). A complete list of the IUPAC rules is available at the ACD Labs site.

IUPAC names are written in the form:

functional
group

substituents

prefix-parent-suffix

number of carbon atoms
in parent chain
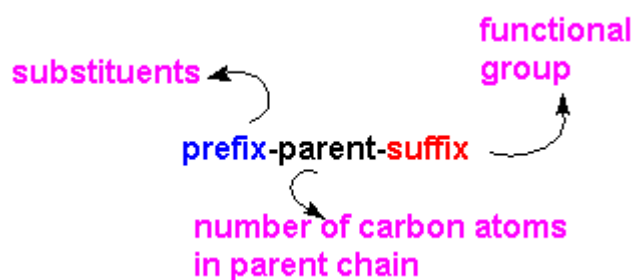
## IUPAC Rules for Alkenes

### I. Identify the parent hydrocarbon

Find the longest continuous chain of carbon atoms containing the double bond. The name of the straight-chain alkane with that number of carbon atoms is the parent name. Designate the double bond by changing the family name (suffix) from -ane to -ene.

### II. Number the parent chain

Number the parent chain starting from the end nearer the double bond.

If the double bond is the same distance from both ends, begin with the end nearer the first branch point.

### III. Assign each substituent a name and a number

Use the same rules as for branched-chain alkanes above.

### IV. Form a single word name for the alkene

Combine the numbers and names of all substituents with the parent name to form one word. Use hyphens to separate numbers from names. Use commas to separate numbers.

- If two or more substituents are attached to the parent chain, write them in alphabetical order. If two or more substituents are identical, use prefixes di-, tri-, tetra-, penta-, etc. Each substituent must have a number, even if the numbers must be repeated. Do not use prefixes for alphabetizing.

- Indicate the position of the double bond by giving the number of the first carbon of the double bond before the -ene ending. If more than one double bond is present use the suffixes -diene, triene, etc.

# Stereoisomers of Alkenes

Alkenes can have stereoisomers due to restricted rotation about double bonds.   These stereoisomers can be disignated as *cis/ trans* isomers or by the E/Z convention.

# *cis* and *trans* Isomers

*Cis* isomers have atoms or groups of atoms on the same side of the reference plane containing the doubly bonded atoms. for trans isomers, the atoms or groups are on opposite sides of the double bond.  These designators are written in italics and placed in front of the IUPAC name of the alkene.



cis-2-butene          trans-2-butene
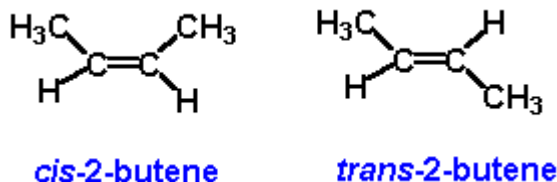
If there are several double bonds in the molecule, designate the stereochemistry of each double bond.

The *cis/trans* designation applies only for two groups (other than hydrogen) attached to a double bond.   For alkenes with more than two groups, the E/Z designation must be used.

# *E* and *Z* Convention

Atoms or groups attached to a double bonded atom are assigned a priority and are compared to the atoms attached to the other doubly bonded atom.  If high priority groups are on the same side of the reference plane perpendicular to the double bond the designation is *Z* (from the German zussamen - together).  If high priority groups are on opposite sides of the reference plane the designation is *E* (from the German entgegan - opposite). The *E* or *Z* descriptor precedes the IUPAC name of the alkene and is written as an italicized capital letter and placed in parentheses followed by a hyphen.



**Rules for establishing high and low priority.**

1.   For each atom directly attached to the double bond atom, assign priorities in order of decreasing atomic number. The atom with the higher atomic number has the higher priority.

2.   When two atoms attached to the doubly bonded atom are the same, continue comparing the next atoms attached until there is a difference.  This comparison is often easier if you convert the isomer to a line-bond drawing.

2.   If the groups attached to doubly bonded atoms are themselves multiple bonds, consider each pi bond as being a single bond with the terminal atom attached.
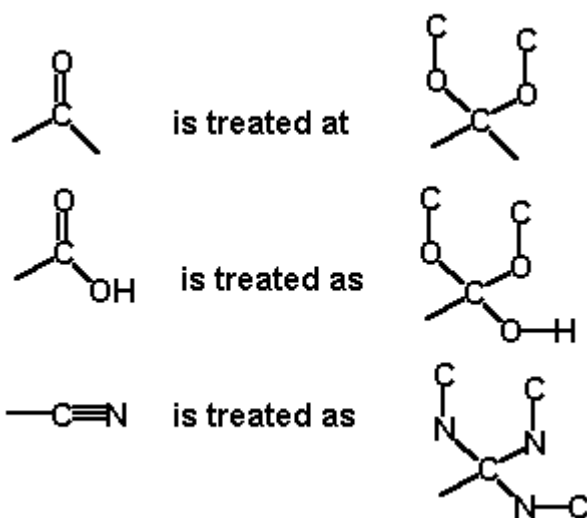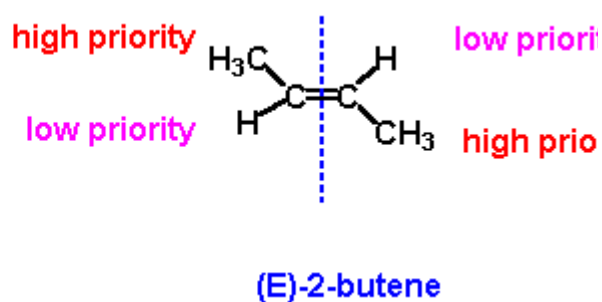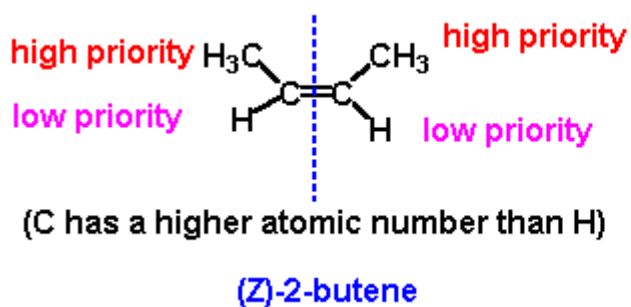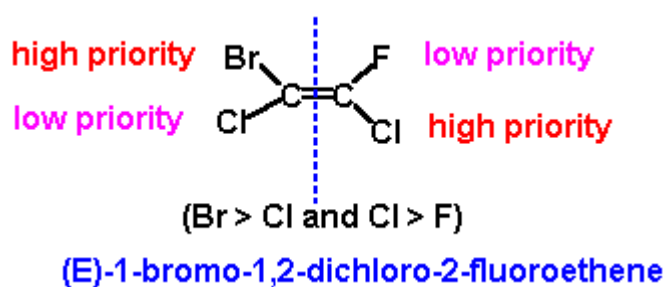
2. _____

**Exercise 3**

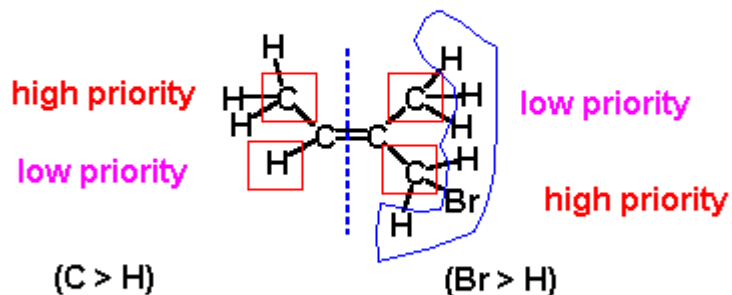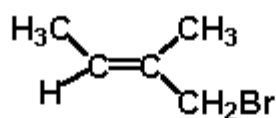Name the following compound using the IUPAC system.
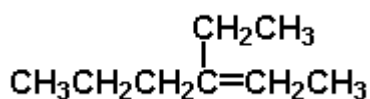


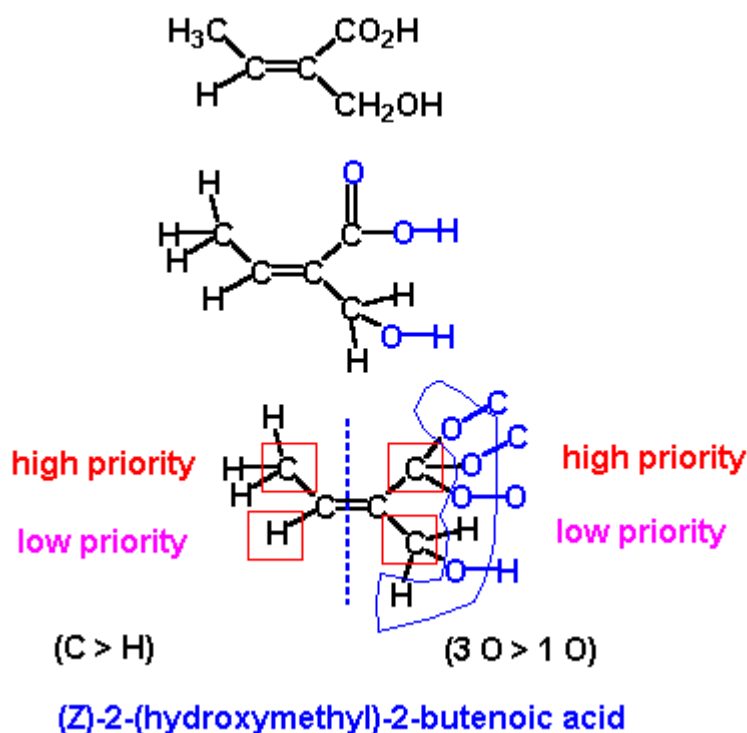For the isomers of 2-butene, C has a higher priority than H due to its higher atomic number.



For 1-bromo-1,2-dichloro-2-fluoroethene, the Cl has a lower priority than Br but higher priority than F.

high priority   Br          F   low priority

low priority    Cl          Cl  high priority

(Br > Cl and Cl > F)

(E)-1-bromo-1,2-dichloro-2-fluoroethene

For 1-bromo-2-methyl-2-butene, two carbon atoms are attached to the same doubly bonded atom. The next atoms are compared and a difference is fond (Br > H).
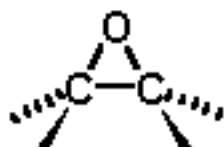
$H_3C$        $CH_3$

H             $CH_2Br$

high priority                        low priority

low priority                         high priority

(C > H)              (Br > H)

(E)-1-bromo-2-methyl-2-butene

high priority

low priority

(C > H)                              (3 O > 1 O)

(Z)-2-(hydroxymethyl)-2-butenoic acid

# Epoxidation

Epoxides are cyclic ethers in which the oxygen atom is part of a strained three-membered ring called an oxirane.



As predicted from the strain energy of small rings, epoxides are usually very reactive species and provide a rich variety of chemical reactivity.

Epoxide may be prepared from alkenes by several routes:

- direct oxidation of the double bond

    Organic peracids (peroxyacids) convert alkenes to epoxides. Peracids are carboxylic acids with an extra oxygen atom inserted between the carbonyl group and the OH group. A very common reagent is m-chloroperbenzoic acid which is available commercially. Many other peracids are unstable and must be prepared as needed.
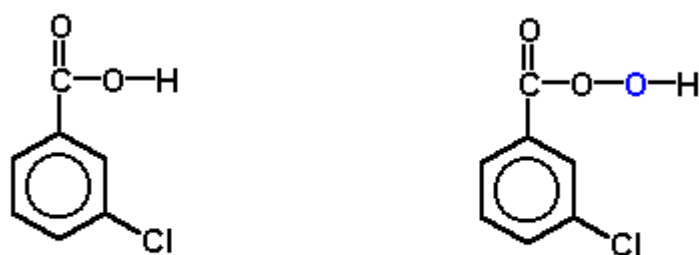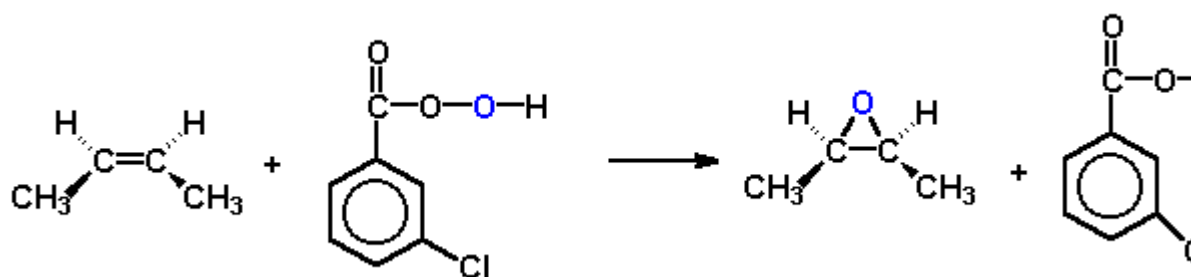
**m-chlorobenzoic acid       m-chloroperbenzoic acid**

The peracid transfers an oxygen atom to the alkene in a single step so the stereochemistry of the double bond is retained. Thus, *trans*-2-butene gives *trans*-1,2-dimethyloxirane.
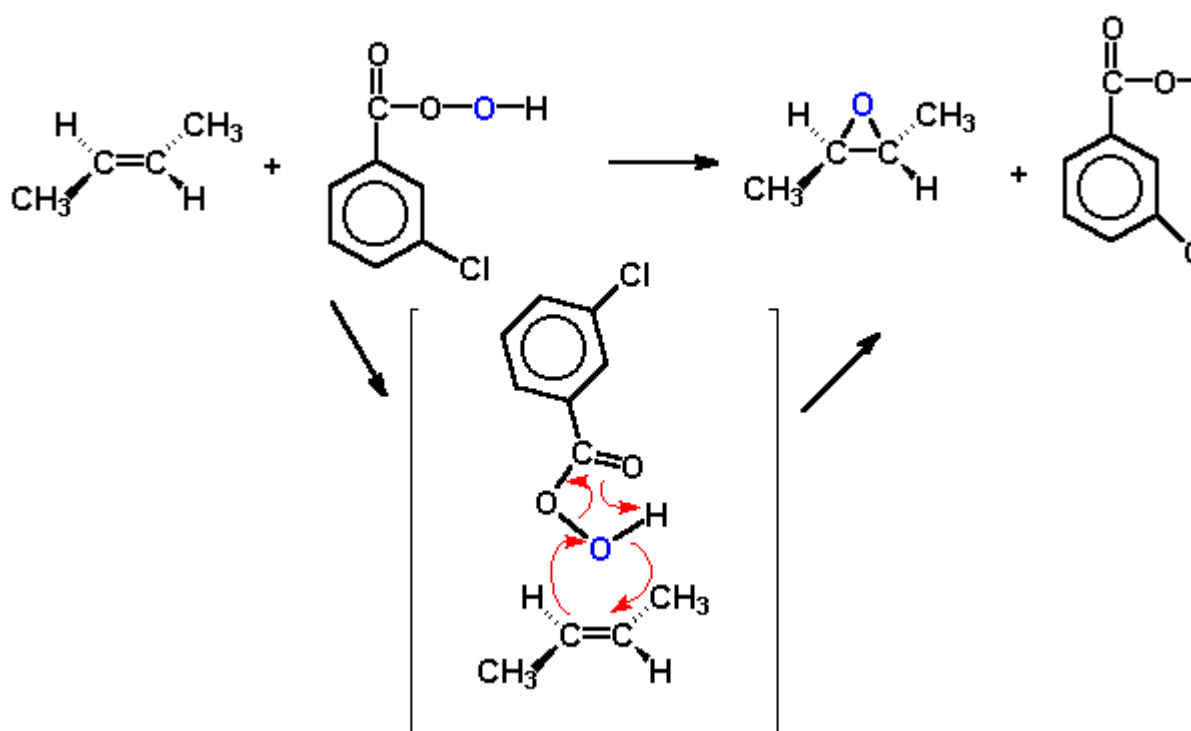
Correspondingly, peracid epoxidation of *cis*-2-butene gives *cis*-1,2-dimethyloxirane.

The mechanism of peracid epoxidation involves nucleophilic attack of the pi-electrons from the double bond. As predicted, the rate of epoxidation increases with increasing alkyl substitution. For example, 1,2-dimethyl-1,4-cyclohexadiene reacts at the tetrasubstituted instead of the disubstituted double bond.
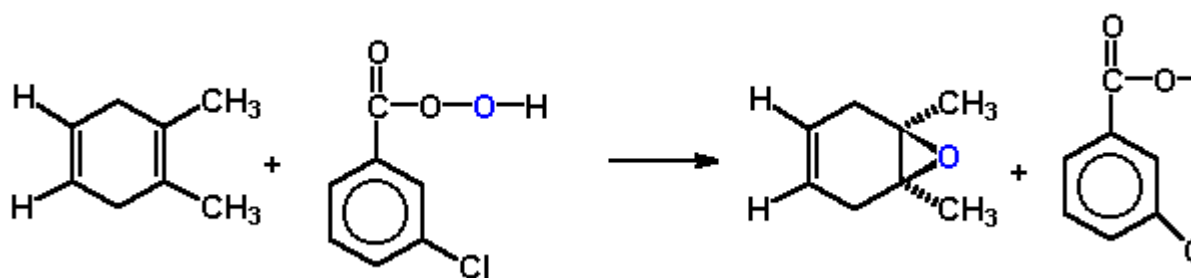
With cyclic olefins the epoxide oxygen is usually added from the least hindered side of the double bond. For example, epoxidation of norbornene gives 96% of the exo diol.

96%                                                    4%
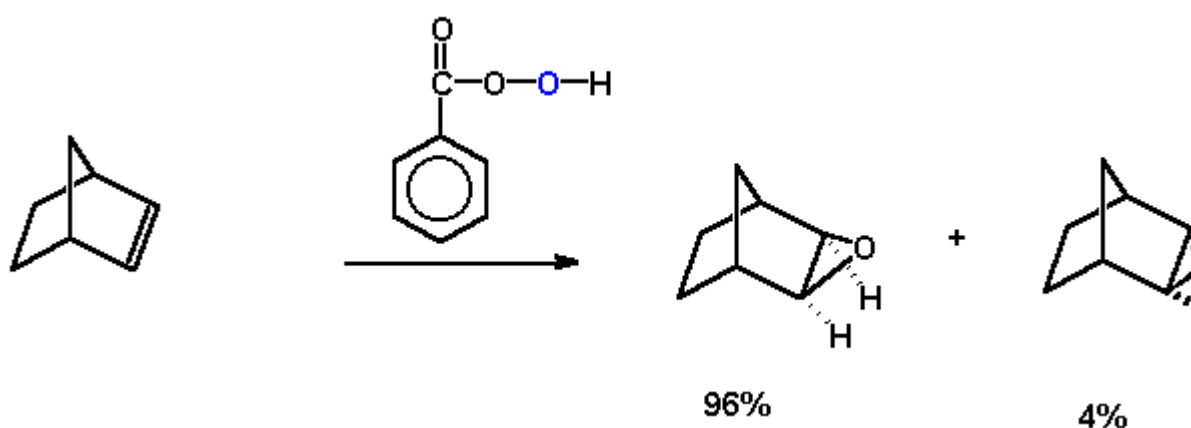
- nucleophilic displacement of halohydrins

Halohydrins are prepared by the addition of aqueous hypochlorous acid (HOCl) or hypobromous acid (HOBr) to alkenes. Conveniently this is done by using aqueous solutions of the halogen. This electrophilic addition proceeds by formation of the intermediate halonium ion as we have seen in the case of direct addition of halogens to alkenes. In the presence of water, this reactive intermediate undergoes nucleophilic addition of water by an $S_N2$ mechanism giving an anti-orientation of the halide and hydroxyl group.
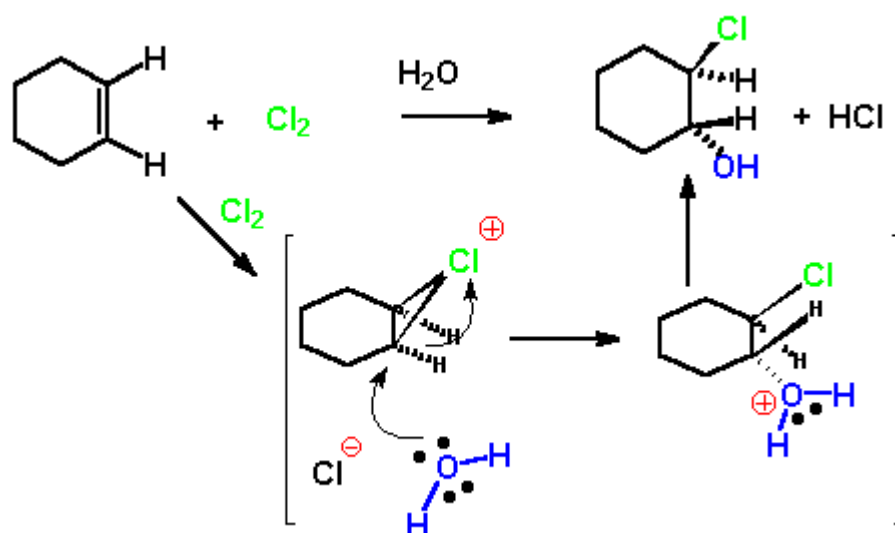
The reaction of halohydrins with base produces epoxides by an $S_N2$ mechanism. Base forms the hydroxide anion and the trans-arrangement of nucleophile and leaving group favors the $S_N2$ process.