Module 4 Alkenes and Alkynes
Lecture 7 Alkenes

4.1 Introduction

Hydrocarbons that contain carbon-carbon double bond are called **Alkenes** (also called as **Olefins**). Many alkenes are found in plant and animals. It has three *sp*^{2} orbitals that lie in a plane with angles of 120°. One of the carbon–carbon bonds in a double bond is σ-bond, formed by the overlap of a *sp*^{2} orbital of one carbon with a *sp*^{2} orbital of the other carbon. The second carbon–carbon bond in the double bond is formed from side-to-side overlap of the remaining *p*-orbitals of the carbons. These two *p*-orbitals must be parallel to each other to achieve maximum orbital-orbital overlap. Therefore, all six atoms of the double-bond system are in the same plane (Figure 1). Since there is maximum side-to-side overlap, rotation about a double bond does not occur.

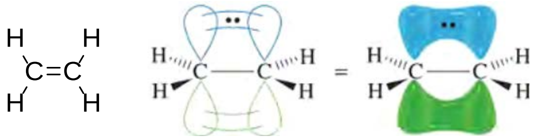


Figure 1

Each C-H σ-bond is formed by overlap of a *sp*^{2} hybrid orbital of carbon atom with the 1*s* orbital of a hydrogen atom. The C-H bond length in ethylene is slightly shorter than the C-H bond in ethane because the *sp*^{2} orbital in ethylene has more *s* character that attracts the electrons even more strongly. The C=C bond in ethylene is much shorter than the C-C bond in ethane, partly because the σ-bond of ethylene is formed from *sp*^{2} orbitals and partly because both σ- and π-bonds are attracting the atoms together (Figure 2).

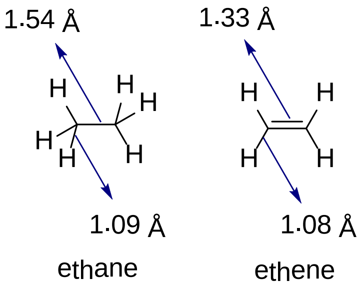
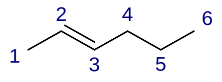


Figure 2

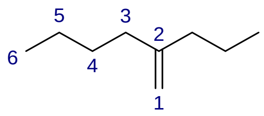
Alkenes are said to be **unsaturated** because they are capable of adding hydrogen in the presence of a catalyst. An alkane is called as **saturated** because it cannot react with any more hydrogen.

4.2 Nomenclature of Alkenes

- Find the longest continuous chain of carbon atoms that includes the double bond and change the **-ane** ending of the parent alkane to **-ene**. The chain is numbered as the double bond having the lower possible numbers.

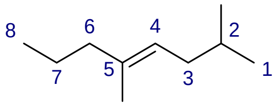


2-hexene



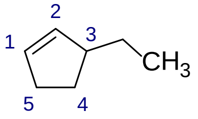
2-proylhexene

- If a chain has more than one substituent, the substituents are cited in alphabetical order. The prefixes *di, tri*, *sec*, and *tert* are not considered in alphabetizing, but *iso, neo,* and *cyclo* are considered. It should also contain the lowest substituent number.

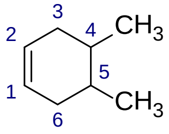


2,5-dimethyl-4-octene

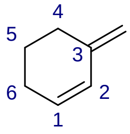
- The double bond should be inbetween carbon 1 and 2, while numbering the ring.



3-ethylcyclopentene

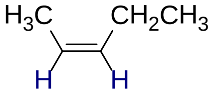


4,5-dimethylcyclohexene

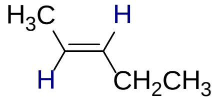


3-methylenecyclohexene

- Lack of rotation of carbon-carbon double bond gives rise to *cis-trans* isomerism, also called geometrical isomerism. In *cis*-isomer, two similar groups bonded on the same side of the double bond. If the similar groups are on opposite sides of the double bond, then the alkene is a *trans*-isomer.

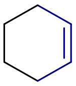


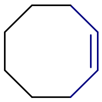
cis-2-pentene

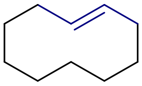


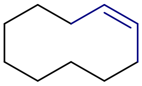
trans-2-pentene

- Cycloalkenes are preferred to be *cis* unless the ring is large enough (at least eight carbon atoms) to be *trans*.


cyclohexene


cyclooctene

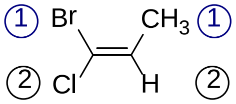

cis-cyclodecene


trans-cyclodecene

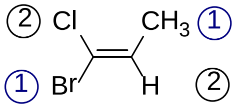
- *Cis-trans* nomenclature cannot be used for the alkenes having four different groups. For example, 1-bromo-1-chloropropene is not clearly *cis* or *trans* as there is no similar groups. Such alkene can be named using *E-Z* Nomenclature.

1-bromo-1-chloropropene

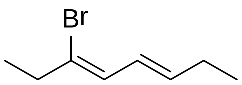
- Each end of the double bond should be considered separately. Assign first and second priorities to the two substituent groups on one end of the double bond. Do the same for the other end. If the two first-priority atoms are on the same side of the double bond, it is called as *Z* isomer. If the two first-priority atoms are on opposite sides of the double bond, it is then called as *E* isomer.



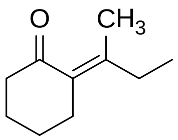
(*Z*)-1-bromo-1-chloropropene



(*E*)-1-bromo-1-chloropropene



(3*Z*,5*E*)-3-bromoocta-3,5-diene

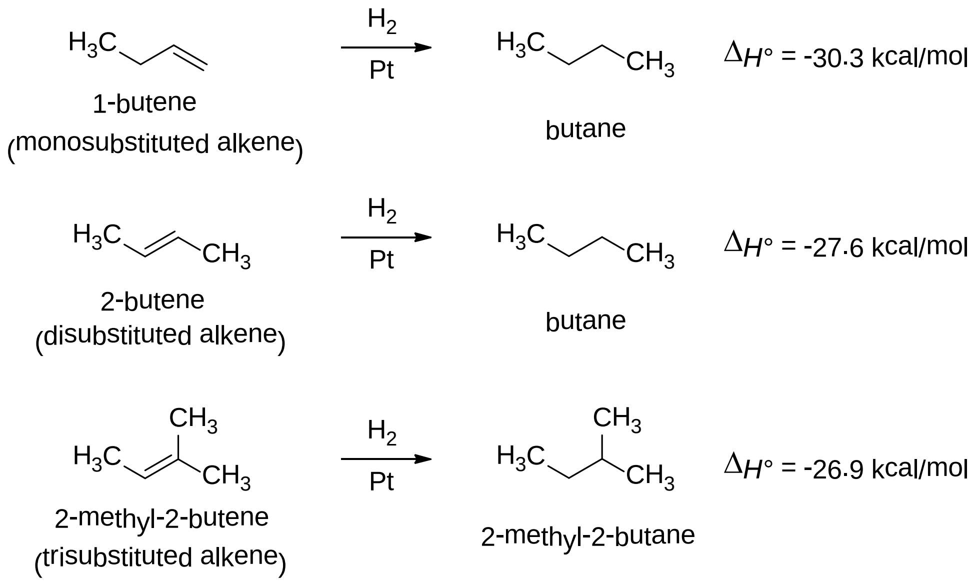


(*E*)-isomer

4.3 Stability of Alkenes

The stability of an alkene depends on its structure. The heat released in a hydrogenation reaction is called the **heat of hydrogenation**. When an alkene is treated with hydrogen in the presence of a platinum catalyst, hydrogen adds to the double bond, reducing the alkene to an alkane. Hydrogenation is exothermic, evolving about 20 to 30 kcal of heat per mole of hydrogen consumed.

The difference in the stabilities of alkenes is the difference in their heats of hydrogenation. While considering the hydrogenation of 1-butene (a monosubstituted alkene), 2-butene (a disubstituted alkene) and 2-methyl-2-butene (a trisubstituted alkene), 2-methyl-2-butene is more stable by 3.4 kcal/mol and 2-butene is stable by 2.7 kcal/mol (Scheme 1). More substituted double bonds are usually more stable. In other words, the alkyl groups attached to the double bonded carbons stabilize the alkene.

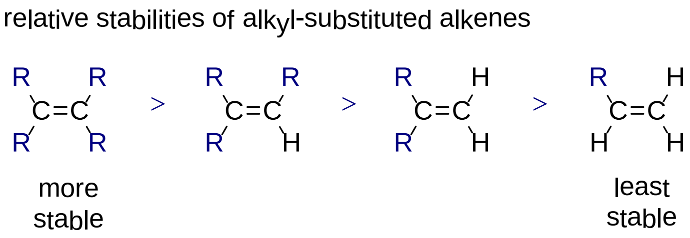


$$\Delta H^\circ = 30.3\ \text{kcal/mol} - 27.6\ \text{kcal/mol} = 2.7\ \text{kcal/mol}$$

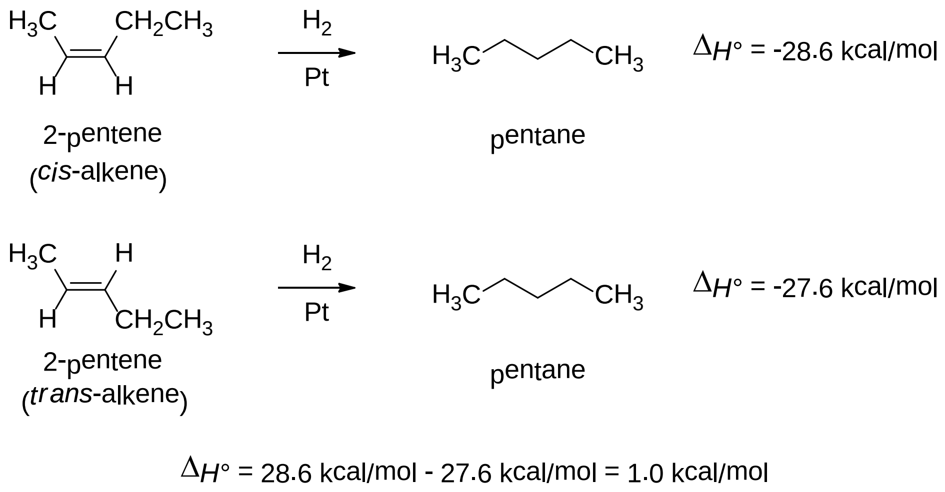
$$\Delta H^\circ = 30.3\ \text{kcal/mol} - 26.9\ \text{kcal/mol} = 3.4\ \text{kcal/mol}$$

Scheme 1

Alkene, which releases the most heat, must be the least stable. In contrast, the alkene, which releases the least heat, must be the most stable.



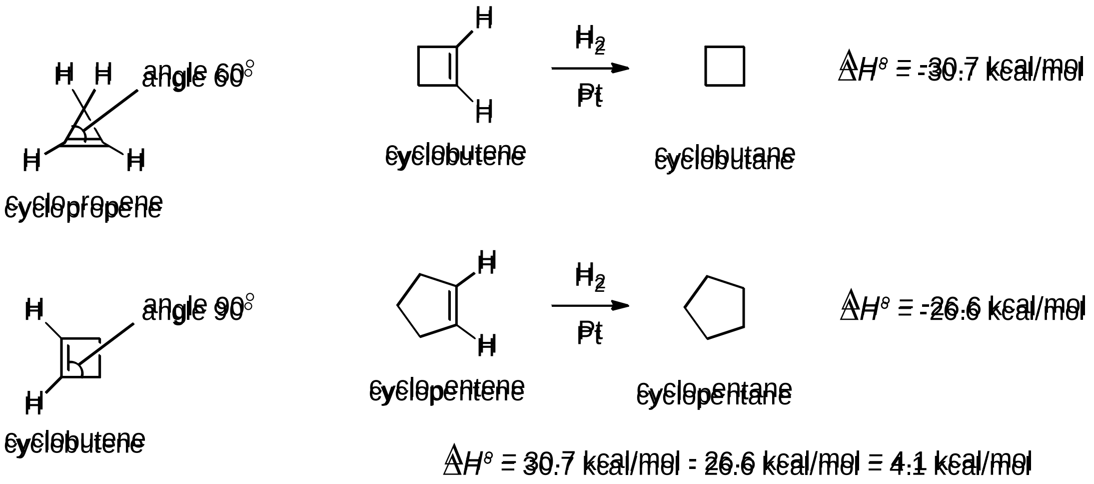
The heats of hydrogenation show that *trans*-isomers are generally more stable than the corresponding *cis*-isomers. Because the alkyl substituents are separated farther in *trans*-isomers than they are in *cis*-isomers. The greater stability of the *trans*-isomer is evident in the following example, which shows that the *trans*-isomer is stable by 1.0 kcal/mol (Scheme 2).



Scheme 2

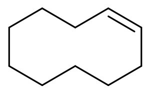
4.4 Stability of Cycloalkenes

Rings that are five-membered or larger can easily accommodate double bonds, and these cycloalkenes react much like acyclic alkenes. Three- and four-membered rings show evidence of ring strain. Cyclopropene is highly strained as it has bond angles of about 60°, compressing the bond angles of the carbon-carbon double bond to half their usual value of 120°. The double bond in cyclobutene, where the angle of sp^2 hybrid carbons is 90° instead the usual value of 120°, has about 4.1 kcal/mol of extra ring strain in addition to the ring strain in cyclobutane (Scheme 3). The extra ring strain in cyclopropene and cyclobutene makes the double bond more reactive than a typical double bond.

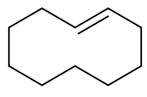


Scheme 3

Cycloalkanes usually have *cis*-isomer especially for small rings but the *trans*-isomers are possible for rings having more than eight carbon atoms. *Trans*-cyclohexene is too strained to be isolated, but *trans*-cycloheptene can be isolated at low temperatures. *Trans*-cyclooctene is stable at room temperature and its *cis*-isomer is still more stable. Cycloalkene containing at least ten or more carbon atoms can easily accommodate a *trans* double bond. For cyclodecene and larger cycloalkenes, the *trans*-isomer is nearly as stable as the *cis*-isomer.

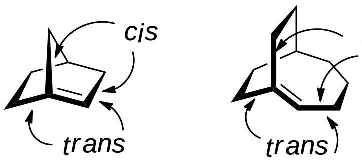


cis-cyclodecene



trans-cyclodecene

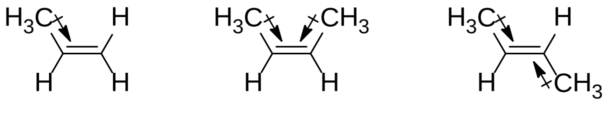
A bicyclic compound is one that contains two rings that share two carbons. A bridged bicyclic compound cannot have a double bond at a bridgehead position unless one of the rings contains at least eight carbon atoms. This principle is called **Bredt's rule**. A bridged bicyclic compound has at least one carbon atom in each of the three links between the bridgehead carbons. If there is a double bond at the bridgehead carbon of a bridged bicyclic system, one of the two rings contains a *cis* double bond and the other must contain a *trans* double bond. For example, norbornane contains a five-membered ring and a six-membered ring. If there is a double bond at the bridgehead carbon atom, an unstable arrangement results that contains a *cis* double bond in the five-membered ring and *trans* double bond in the six-membered. If the larger ring contains at least eight carbon atoms, then stable arrangement results that contain a *trans* double bond at the bridgehead (Figure 3).



unstable stable

Figure 3

The more weakly held electrons in the π-bond are more polarizable and the vinylic bonds tend to be slightly polar. Alkyl groups are slightly electron donating toward a double bond that slightly polarizes the vinylic bond, with a small partial positive charge on the alkyl group and a small negative charge on the double-bond carbon atom. For example, propene has a small dipole moment of 0.35 D. In a *cis*-disubstituted alkene, the vector sum of the two dipole moments is directed perpendicular to the double bond. In a *trans*-disubstituted alkene, the two dipole moments tend to cancel out. If an alkene is symmetrically *trans*-substituted, the dipole moment is zero. *Cis*-2-butene and *trans*-2-butene have similar van der Waals attractions, but only the *cis*-isomer has dipole-dipole attractions (Figure 4).



μ = 0.35D μ = 0.33 D μ = 0

Figure 4

The effect of bond polarity is even more apparent in the 1,2-dichloroethenes, where carbon-chlorine bonds are strongly polar. The *cis*-isomer has a large dipole moment (μ = 2.4 D), giving it a boiling point 12 degrees higher than that of the *trans*-isomer (Figure 5).

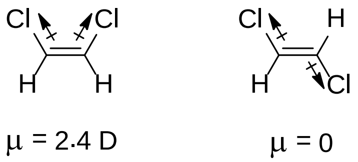
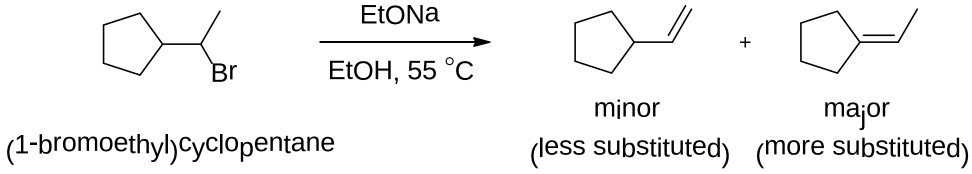


Figure 5

4.5 Synthesis of Alkenes

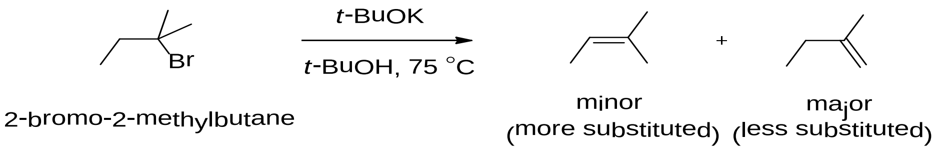
Alkenes can be synthesized by elimination reactions. Dehydrohalogenation of alkyl halides takes place by E1 or E2 elimination mechanisms. E2 elimination of dehydrohalogenation takes place in one step, in which base abstracts a proton from one carbon and leaving group leaves the adjacent carbon.

Zaitsev's Rule: A more substituted alkene is favored with small base. For example, (2-bromoethyl)cyclopentane in the presence of ethoxide (a small base) follows Zaitsev's rule to give more substituted alkene as major product (Scheme 4).



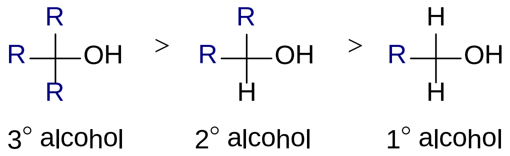
Scheme 4

Hoffman Rule: A less substituted alkene is favored with bulky base. Dehydrohalogenation with a bulky base such as *tert*-butoxide (*t*-BuOK) in *tert*-butyl alcohol (*t*-BuOH) favours the formation of less substituted alkene. The large *tert*-butoxide ion seems to have difficulty in removing a *β*-Hydrogen atom because of greater crowding (Scheme 5).

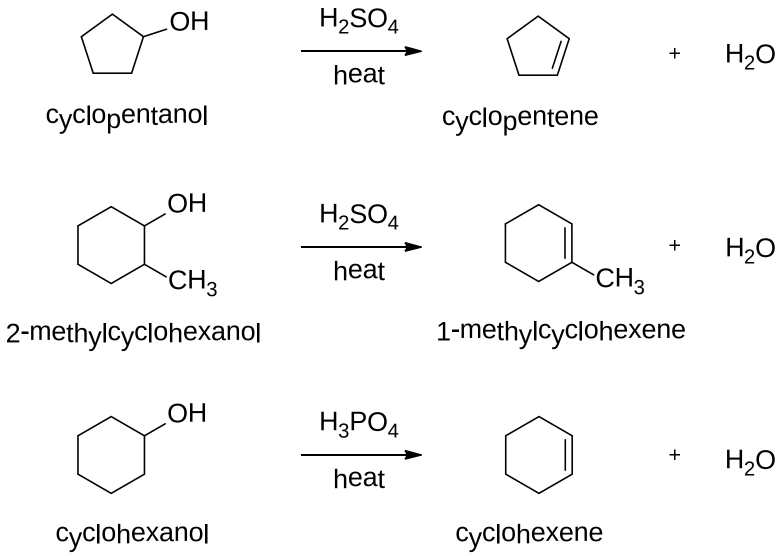


Scheme 5

Dehydration of alcohol is another method of making alkene. Most alcohols undergo dehydration to form an alkene when heated with a strong acid. Concentrated sulfuric acid or concentrated phosphoric acid are often used as reagents. Alcohols that form stable carbocations can easily undergo dehydration. The relative ease with which alcohols undergo dehydration is as follows:



Tertiary alcohol undergos dehydration easily as it form relatively stable tertiary carbocation. For example, cyclopentanol, 2-methylcyclohexanol and cycloxanol give the corresponding alkenes on dehydration (Scheme 6).



Scheme 6

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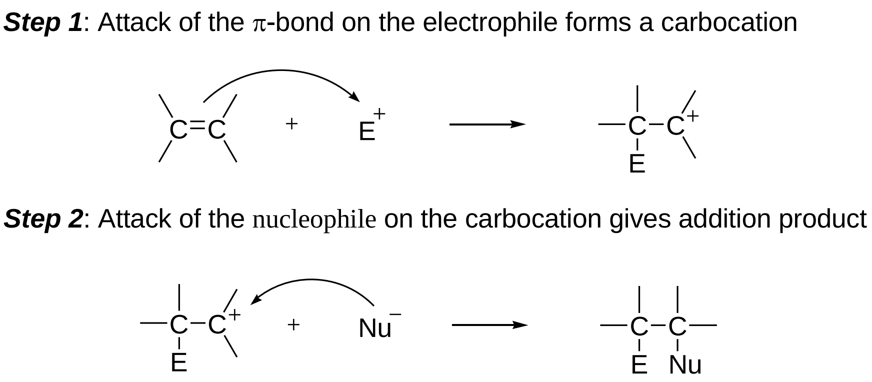
4.6 Reactions of Alkenes

Most alkene reactions fall into the class of electrophilic addition to alkenes. Many different reagents could add to the double bond to form more stable products. In some cases catalyst has to be added to have convenient reaction rates. The double bond in an alkene has loosely held π-bonding electrons which have affinity towards a strong electrophile. First, a strong electrophile attracts the loosely held electrons from the π-bond of an alkene and forms carbocation. The carbocation reacts with a nucleophile to form an addition product (Scheme 1).

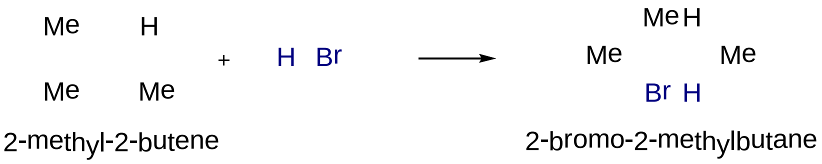

Step 1: Attack of the π-bond on the electrophile forms a carbocation

Step 2: Attack of the nucleophile on the carbocation gives addition product

Scheme 1

4.6.1 Addition of Hydrogen Halides

The proton in HBr is electrophilic; thus, it reacts with the alkene to form a carbocation. Bromide ion reacts rapidly with the carbocation to give a stable product in which the elements of HBr have added to the ends of the double bond. For example, 2-methyl-2-butene reacts with hydrogen bromide to give 2-bromo-2-methylbutane (Scheme 2).



Scheme 2

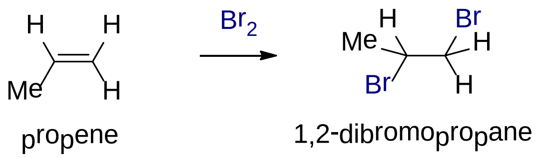
Markovnikov's Rule: when a hydrogen halide adds to an unsymmetrical alkene, the addition occurs in such a manner that the halogen attaches itself to the double-bonded carbon atom of the alkene bearing the lesser number of hydrogen atoms. When the proton adds to the secondary carbon, a tertiary carbocation results. When the proton adds to the tertiary carbon atom, a secondary carbocation results. The tertiary carbocation is more stable, so the corresponding product is favored (Figure 1).

tertiary carbocation secondary carbocation

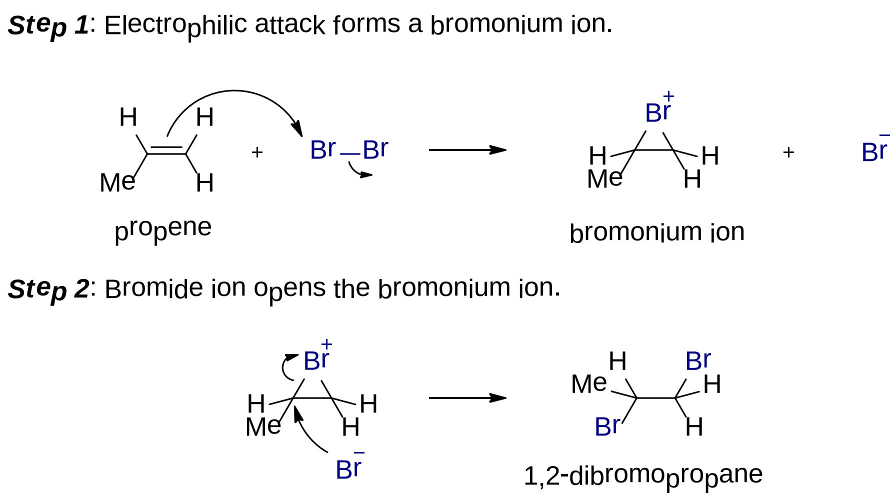
Figure 1

4.6.2 Addition of Halogens

Halogens add to alkenes to form vicinal dihalides. The nucleophilic alkene attacks the electrophilic nucleus of one halogen atom, and the other halogen serves as the leaving group, departing as halide ion. For example, the reaction of propene with bromine follows:



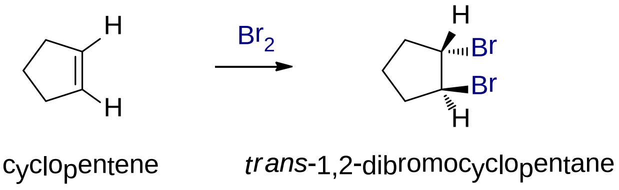
In first step, a bromonium ion results, containing a three-membered ring with a positive charge on the bromine atom. Unlike a normal carbocation, all the atoms in a halonium ion have filled octets. The three-membered ring has considerable ring strain, which makes the bromonium ion strongly electrophilic. Attack by a nucleophile, a bromide ion, opens the bromonium ion to give 1,2-dibromo derivative (Scheme 3**)**.


Step 1: Electrophilic attack forms a bromonium ion.

Step 2: Bromide ion opens the bromonium ion.

Scheme 3

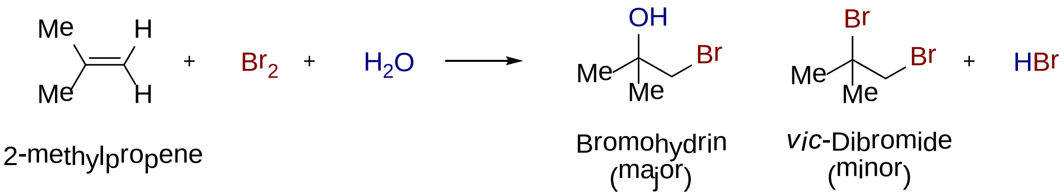
The addition of bromine to alkene is a **stereospecific reaction.** For example, the addition of bromine with cyclopentane gives, *trans*-1,2-dibromocyclopentane, an *anti*-addition product (Scheme 4).



Scheme 4

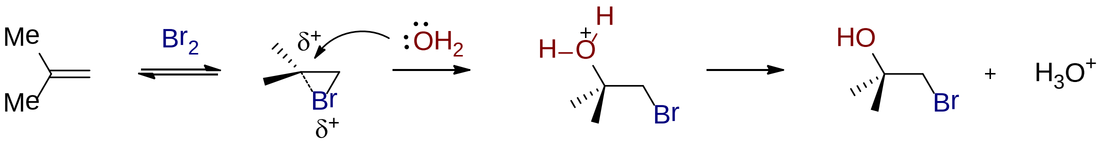
4.6.3 Halohydrin Formation

Halohydrin can be obtained when the halogenation of an alkene is carried out in aqueous solution. If the halogen is bromine, it is called a bromohydrin, and if chlorine, it is called as a chlorohydrin. For example, the reaction of 2-methylpropene with bromine in the presence of water gives bromohydrin along with a vicinal dibromide as a minor product (Scheme 5).



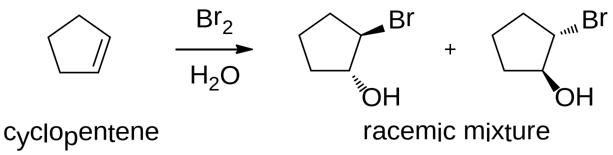
Scheme 5

The first step is the same as that the above described halogen addition reaction. In the second step, water acts as the nucleophile attacking the carbon atom of the bromonium ion to give the target bromohydrin (Scheme 6).



Scheme 6

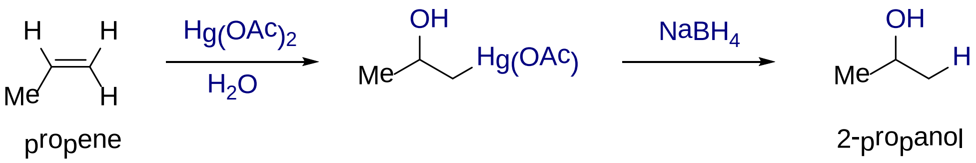
If the alkene is unsymmetrical, the bromine ends up on the carbon atom with the greater number of hydrogen atoms. The more highly substituted carbon atom bears the greater positive charge. Consequently, water attacks this carbon atom preferentially. But symmetrical alkenes usually give a racemic mixture (Scheme 7).



Scheme 7

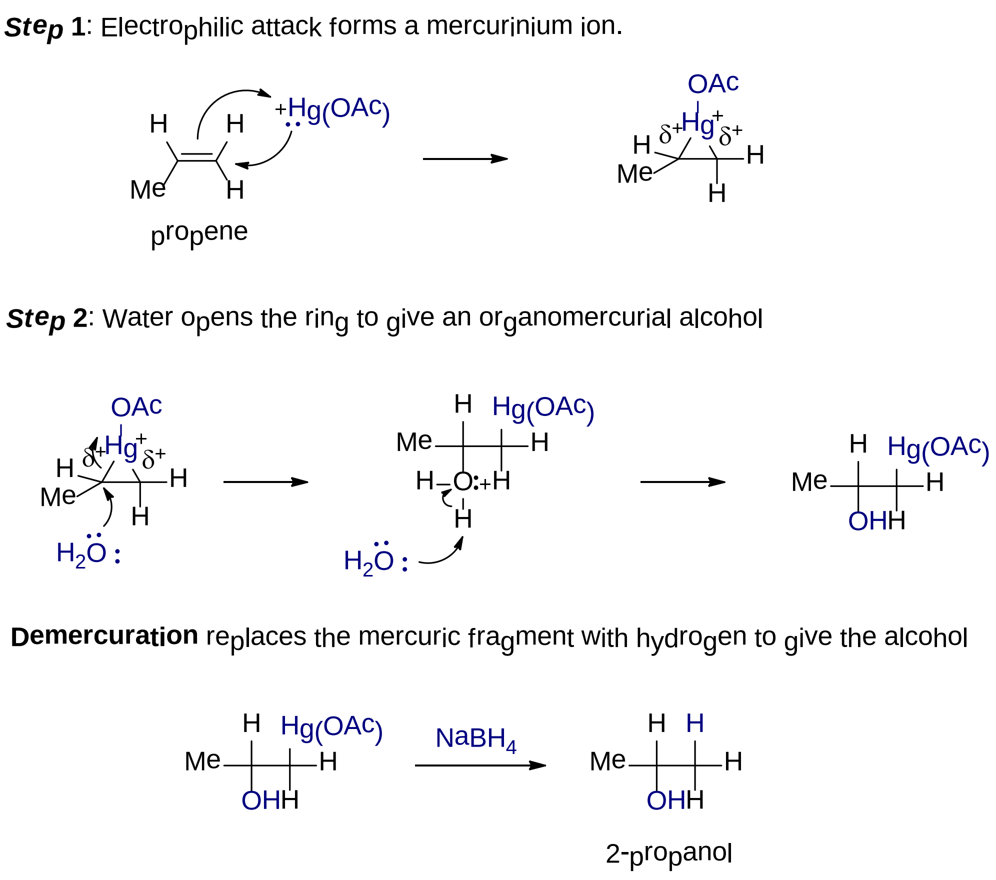
4.6.4 Oxymercuration–Demercuration

Oxymercuration-demercuration is another method for converting alkenes to alcohols. Many alkenes do not easily undergo hydration in aqueous acid. Some alkenes are nearly insoluble in aqueous acid, and others undergo side reactions such as rearrangement, polymerization. Thus, the use of oxymercuration–demercuration process has two advantages over acid-catalyzed addition: (i) it does not require acidic conditions and (ii) no carbocation intermediate is invovled, so that rearrangements do not occur. For example, the oxymercuration of propene with mercuric acetate gives the organomercurial alcohol, which is reduced to 2-propanol, called demercuration, by sodium borohydride (Scheme 8).



Scheme 8

Regarding the mechanism, the first step, the oxymercuration involves an electrophilic attack on the double bond by the positively charged mercury species to give mercurinium ion, an organometallic cation containing a three-membered ring. In the second step, water attacks the mercurinium ion to give an organomercurial alcohol. A subsequent reaction with sodium borohydride removes the mercuric acetate fragment with a hydrogen atom to give the alcohol (Scheme 9).



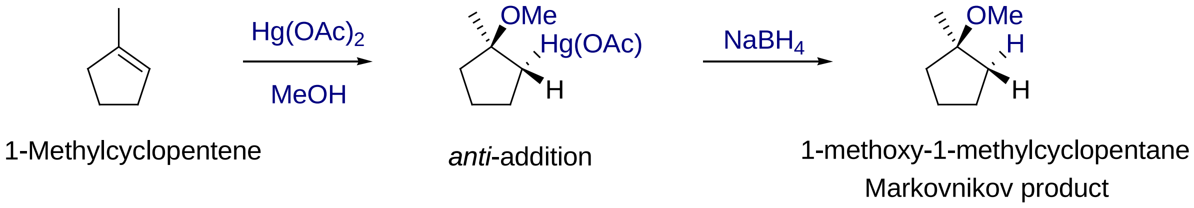
***Step* 1**: Electrophilic attack forms a mercurinium ion.

***Step* 2**: Water opens the ring to give an organomercurial alcohol

Demercuration replaces the mercuric fragment with hydrogen to give the alcohol

Scheme 9

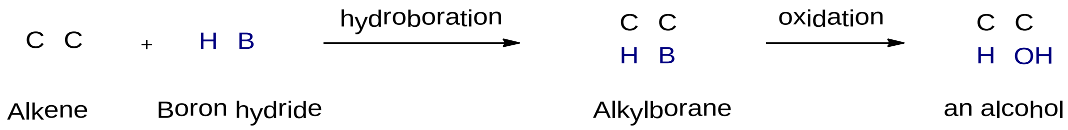
Unsymmetrical alkene generally gives Markovnikov orientation of addition, as shown by the oxymercuration of propene. The mercurinium ion has a considerable amount of positive charge on both of its carbon atoms, but there is more of a positive charge on the more substituted carbon atom, where it is more stable. Attack by water occurs on this more electrophilic carbon, giving Markovnikov orientation. The electrophile remains bonded to the less substituted end of the double bond. When mercuration takes place in an alcohol solvent, the alcohol serves as a nucleophile to attack the mercurinium ion. The resulting product contains an alkoxy (-OR) group. For example, oxymercuration-demercuration of 1-methylcyclopentene give 1-methoxy-1-methylcyclopentane where methanol has added across the double bond. In the first step mercuric acetate adds to the mercuric acetate to give mercurium ion which has a partial positive charge on the more substituted tertiary carbon. In the second step, methanol attacks this carbon from the opposite side, leading to *anti*-addition. Demercuration of this *anti*-addition product by sodium borohydride gives 1-methoxy-1-methylcyclopentane (Scheme 10).



Scheme 10

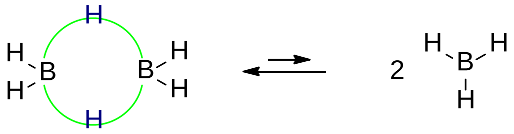
4.6.5 Hydroboration–Oxidation

Borane, a neutral molecule, is an electrophile because boron has only six shared electrons in its valence shell. Boron, therefore, readily accepts a pair of electrons in order to complete its octet. Thus, alkenes undergo electrophilic addition reactions with borane (serving as the electrophile). The addition of borane to an alkene, followed by reaction with hydroxide ion and hydrogen peroxide, is called **Hydroboration-Oxidation** (Scheme 11).



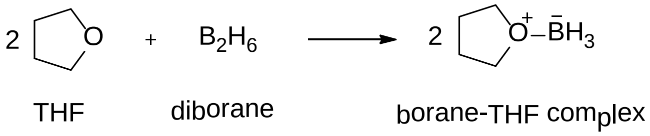
Scheme 11

Diborane (B_2H_6) is a dimer composed of two molecules of borane (BH_3). Diborane has three-centered two-electron (banana-shaped) bonds with protons in the middle of them. Diborane is in equilibrium with a small amount of borane (BH_3), a strong Lewis acid with only six valence electrons (Scheme 12).



Scheme 12

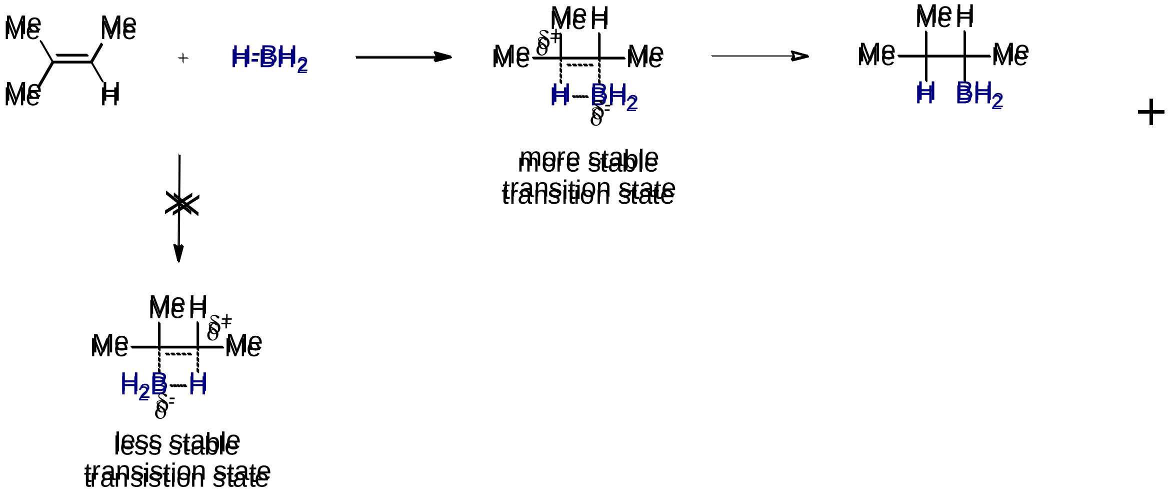
In the first step, the addition of a boron atom and hydrogen atom takes place to the double bond. In the second step, the oxidation followed by hydrolysis give the target alcohol and boric acid. Hydroboration can be accomplished with diborane (B_2H_6) or more conveniently with a reagent prepared by dissolving diborane in THF. When diborane is introduced to THF, it reacts to form a Lewis acid-base complex of borane and THF (represented as $BH_3{\cdot}THF$) (Scheme 13).



Scheme 13

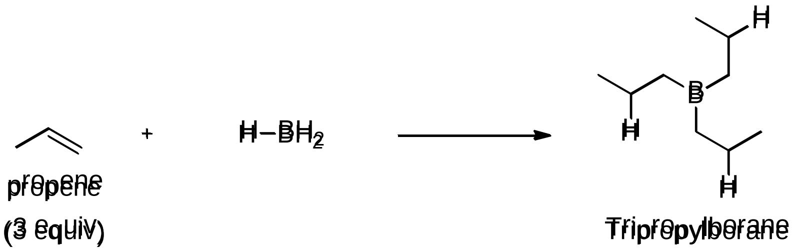
Mechanism

As an electron-deficient compound, BH_3 is a strong electrophile, capable of adding to a double bond. This hydroboration of the double bond occurs in one step, with the boron atom adding to the less substituted end of the double bond. In the transition state, the electrophilic boron atom withdraws electrons from the π-bond, and the carbon at the other end of the double bond acquires a partial positive charge. This partial charge is more stable on the more substituted carbon atom. The product shows boron bonded to the less substituted end of the double bond and hydrogen bonded to the more substituted end. Also, steric hindrance favors boron adding to the less hindered end of the double bond (Scheme 14).



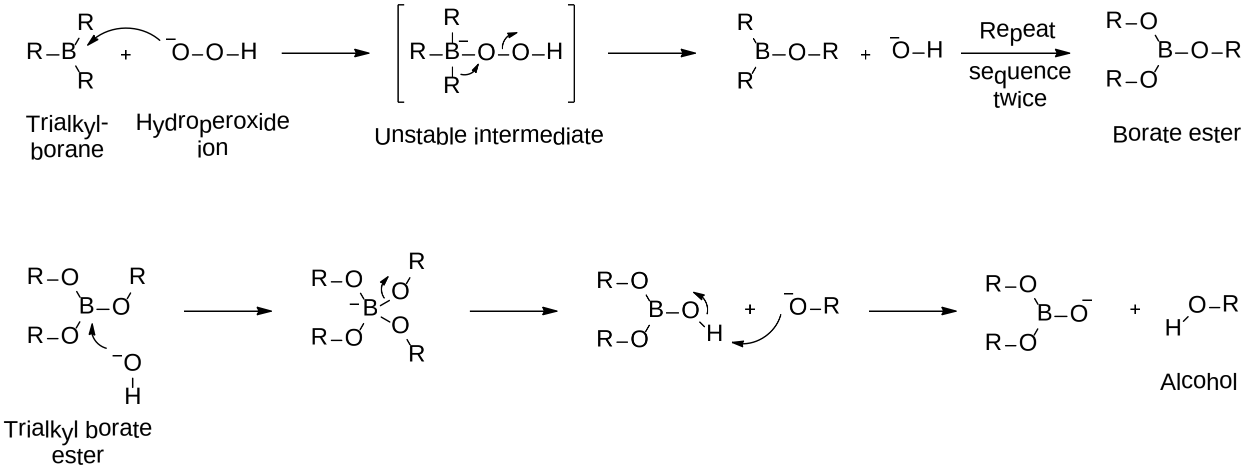
Scheme 14

When propene is treated with a solution containing BH_3.THF, the boron hydride adds successively to the double bonds of three molecules of the alkene to form a trialkylborane (Scheme 15).



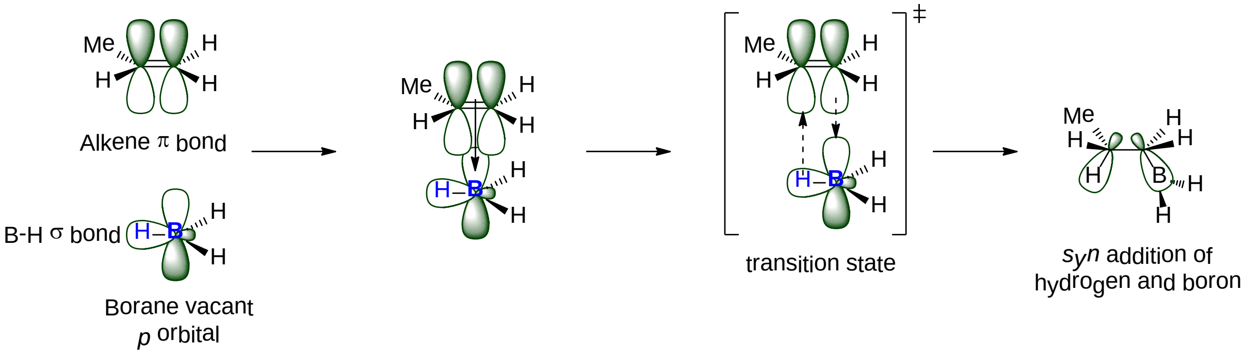
Scheme 15

In the oxidation step, hydroperoxide anion (HOO-) adds to the trivalent boron atom and forms an unstable intermediate that has a formal negative charge on the boron. Migration of an alkyl group with a pair of electrons from the boron to the adjacent oxygen leads to neutralization of the charge on boron and displacement of a hydroxide anion. The alkyl migration takes place with retention of configuration at the migrating carbon. Repetition of the hydroperoxide anion addition and migration steps occurs twice more until all of the alkyl groups have become attached to oxygen atoms, resulting in a trialkyl borate ester, $B(OR)_3$. The borate ester then undergoes basic hydrolysis to produce three molecules of the alcohol and an inorganic borate anion (Scheme 16).



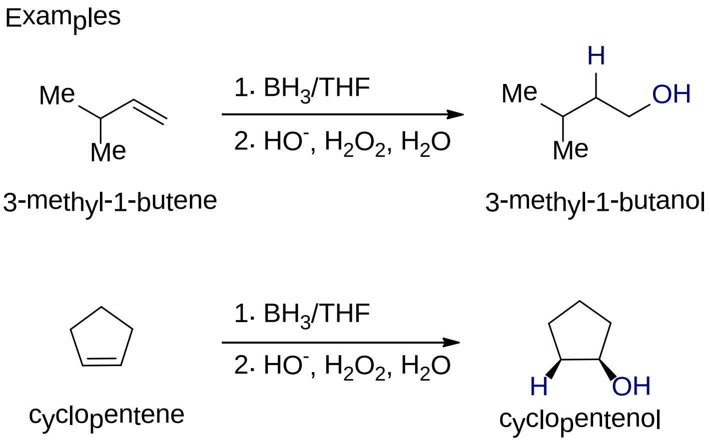
Scheme 16

The simultaneous addition of boron and hydrogen to the double bond leads to a ***syn*-addition**: Boron and hydrogen add across the double bond on the same side of the molecule. The stereochemistry of the hydroboration-oxidation of propene is shown (Scheme 17). Boron and hydrogen add to the same face of the double bond (*syn*) to form a trialkylborane. Oxidation of the trialkylborane replaces boron with a hydroxyl group in the same stereochemical position.



Scheme 17

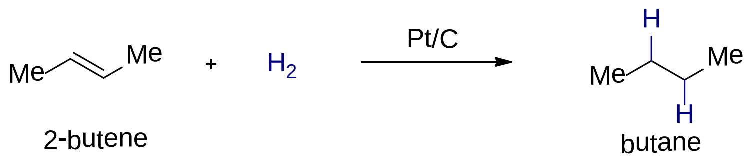
Hydroboration of alkenes is another example of a **stereospecific reaction**, in which different stereoisomers of the starting compound react to give different stereoisomers of the product. It is also regioselective and gives ***anti*-Markovnikov** product (Scheme 18).



Scheme 18

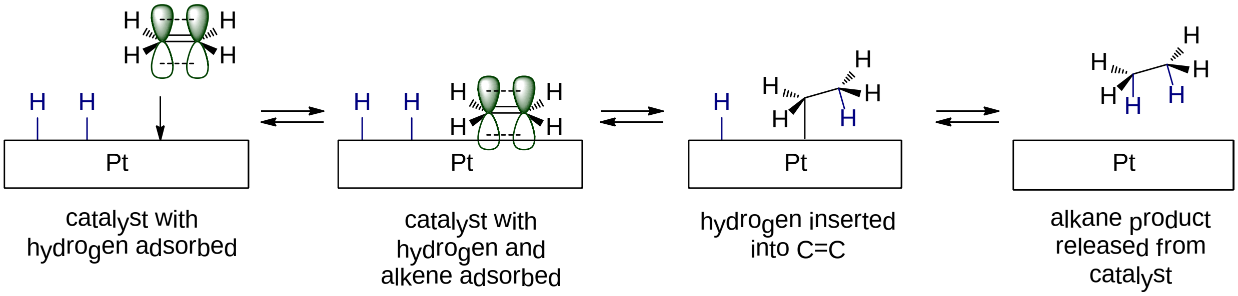
4.6.6 Addition of Hydrogen

Metal catalyst such as platinum, palladium, or nickel, can be used to add hydrogen to the double bond of an alkene to form an alkane. The H-H bond is so strong so that the energy barrier to the reaction would be enormous that can be decreased by the catalyst and breaks H-H bond. Platinum and palladium are used in a finely divided state adsorbed on charcoal (Pt/C, Pd/C). Addition of hydrogen occurs to the double bond of 2-butene in the presence of platinum charcoal to give butane (Scheme 19).



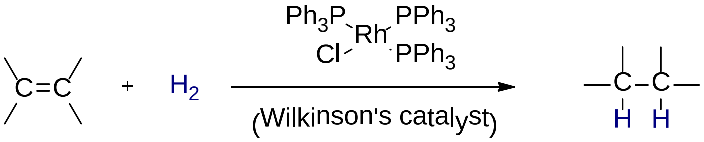
Scheme 19

Since the metal catalysts are insoluble in the reaction mixture, they are classified as **heterogeneous catalysts**, which can easily be separated from the reaction mixture by filtration. One face of the alkene π-bond binds to the catalyst, which has hydrogen adsorbed on its surface. Hydrogen inserts into the π-bond, and the product is released from the catalyst. The two hydrogen atoms add with ***syn*** stereochemistry (Scheme 20).



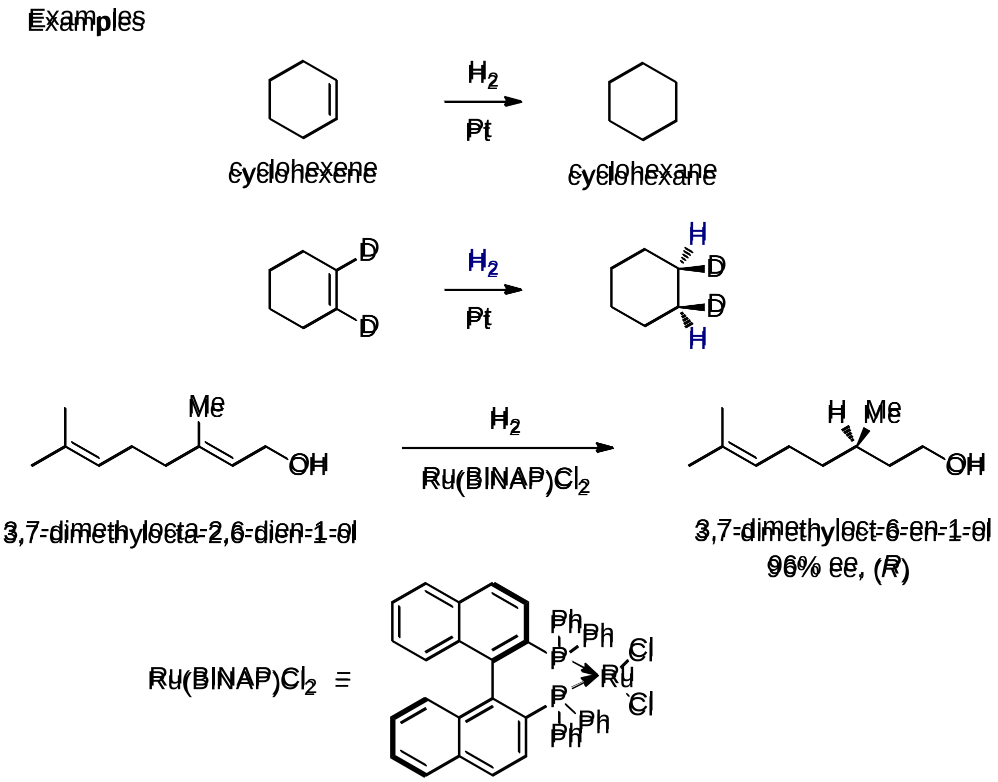
Scheme 20

Homogeneous catalysts, such as Wilkinson's catalyst, also catalyze the hydrogenation of carbon-carbon double bonds (Scheme 21).



Scheme 21

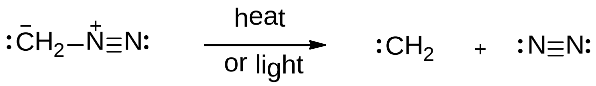
Wilkinson's catalyst adds a hydrogen molecule across the double bond of an alkene with *syn*-stereochemistry where hydrogenation of deutriated cyclohexene leads to *syn*-additon to give *syn*-deutriated cyclohexane. Wilkinson's catalyst is not chiral, but can be converted into a chiral catalyst by replacing its triphenylphosphine (PPh_3) groups with chiral phosphines. This chiral Wilkinson’s catalyst is capable of converting optically inactive starting materials to optically active products. Such a process is called **asymmetric induction or enantioselective synthesis.** For example, hydrogenation of optically inactive 3,7-dimethylocta-2,6-dien-1-ol with chiral Wilkinson’s catalyst gives, 3,7-dimethyloct-6-en-1-ol, an optically active compound (Scheme 22).



Scheme 22

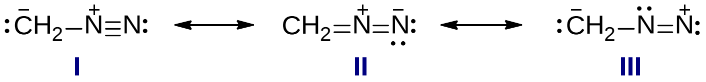
4.6.7 Addition of Carbenes

The simplest carbene is methylene (:CH_2), which is uncharged and very reactive intermediate. The reactions of carbenes are especially interesting because, in many instances, the reactions show a remarkable degree of stereospecificity. Methylene is a very poisonous yellow gas that can be prepared by the decomposition of diazomethane (CH_2N_2).

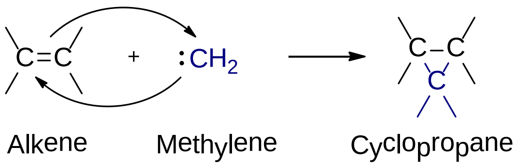


$$:\overset{-}{C}H_2-\overset{+}{N}\equiv N: \xrightarrow[\text{or light}]{\text{heat}} :CH_2 + :N\equiv N:$$

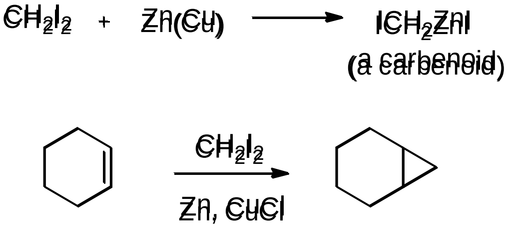
The structure of diazomethane is a resonance hybrid of three structures:



Methylene reacts with alkenes by adding to the double bond to form cyclopropanes.

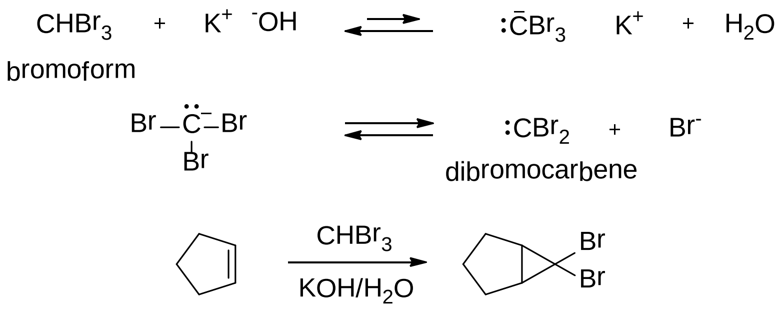


The Simmons-Smith reaction is one of the best ways of making cyclopropanes. The Simmons-Smith reagent is made by adding methylene iodide to the "zinc-copper couple" (zinc dust that has been activated with an impurity of copper). The reagent probably resembles iodomethyl zinc iodide, ICH_2Znl. This kind of reagent is called a carbenoid because it reacts much like a carbene (Scheme 23)



Scheme 23

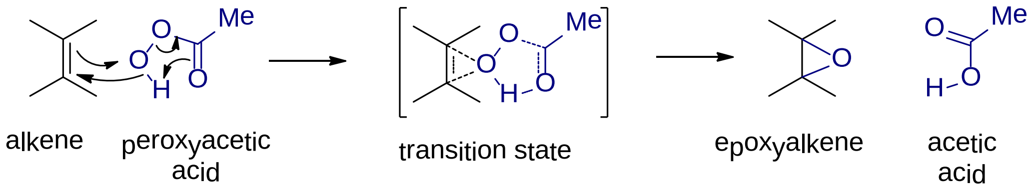
Dibromocarbene formed from $CHBr_3$ can add to a double bond to form a dibromocyclopropane (Scheme 24).



Scheme 24

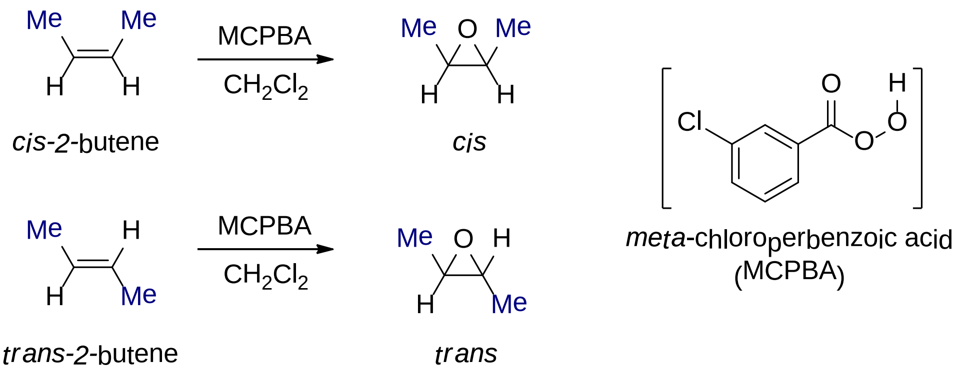
4.6.8 Epoxidation

An epoxide is a three-membered cyclic ether, also called an oxirane. An alkene is converted to an epoxide by a peroxyacid. The epoxidation takes place in one step as shown below (Scheme 25).



Scheme 25

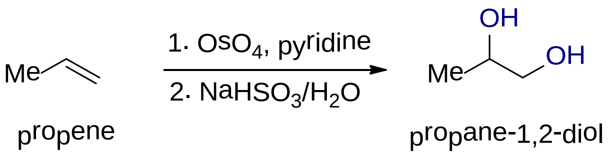
Alkene molecule cannot rotate and change its *cis* or *trans* geometry during the reaction. So the epoxide retains whatever stereochemistry is present in the alkene. For example, epoxidation of *cis*-2-butene and *trans*-2-butene retains its stereochemistry when reacts with *meta*-chloroperbenzoic acid (Scheme 26).



Scheme 26

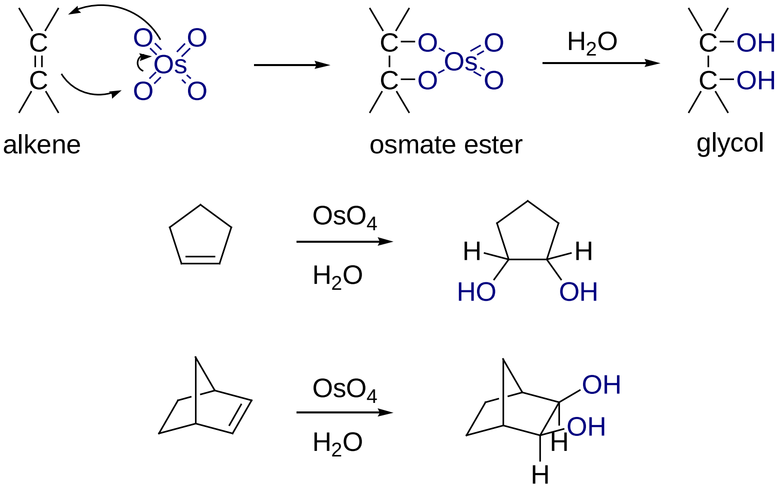
4.6.9 Dihydroxylation of Alkenes

Addition of a hydroxyl group to the double bond is called hydroxylation. For example, the hydroxylation of propene gives propane-1,2-diol in the presence of osmium tetroxide (Scheme 27).



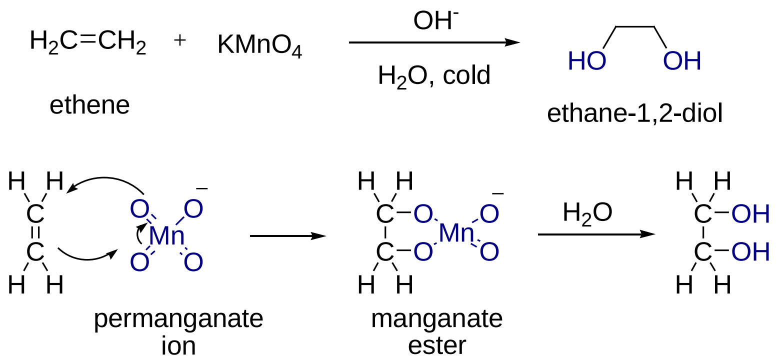
Scheme 27

Osmium tetroxide reacts with alkene in a concerted step to form a cyclic osmate ester which is hydrolyzed into cis-1,2-diol. The two carbon-oxygen bonds are formed simultaneously and the oxygen atoms add to the same face of the double bond (*syn*-addition) (Scheme 28).



Scheme 28

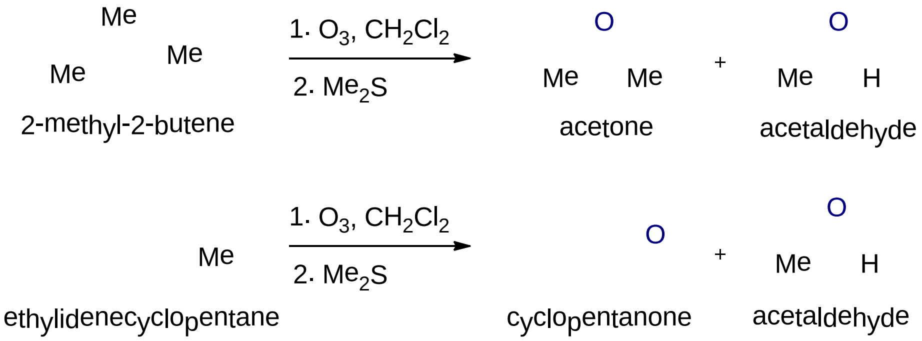
A cold, dilute solution of potassium permanganate ($KMnO_4$) can also hydroxylate alkenes with *syn* stereochemistry (Scheme 29).



Scheme 29

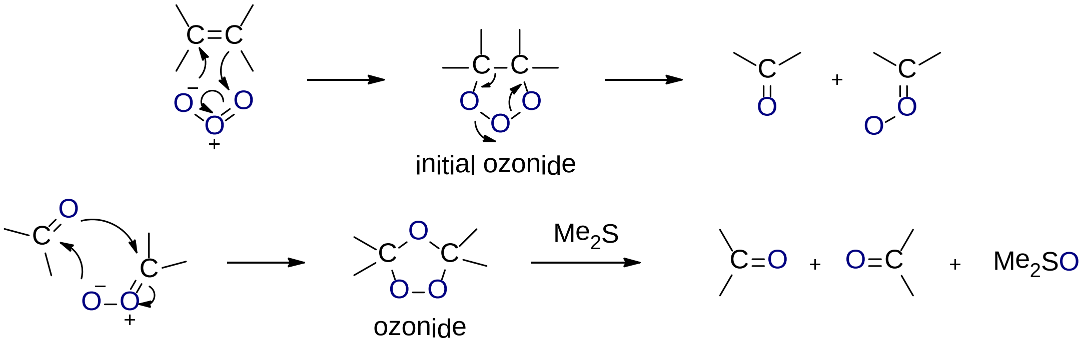
4.6.10 Cleavage with Ozone

Ozone can cleave double bond to give ketones or aldehydes (Scheme 30).



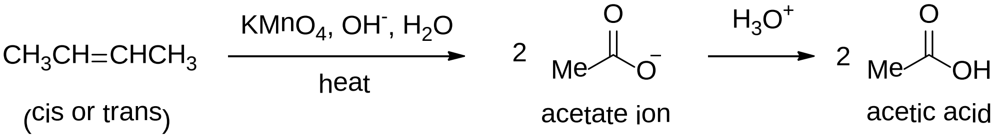
Scheme 30

Regarding the mechanism, ozone reacts with an alkene to form a cyclic compound called a primary ozonide which has peroxy (-O-O-) linkages, so it is quite unstable. It rearranges rapidly to form an ozonides that could be reduced by reducing agents such as dimethyl sulfide (Scheme 31).



Scheme 31

Treatment of an alkene with hot basic potassium permanganate oxidatively cleaves the double bond. Monosubstituted double bond carbon of an alkene is oxidatively cleaved to salts of carboxylic acids (Scheme 32). Disubstituted alkene carbons are oxidatively cleaved to ketones. Unsubstituted alkene carbons are oxidized to carbon dioxide.



Scheme 32

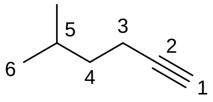
Module 4 Alkenes and Alkynes
Lecture 9 Alkynes

4.7 Introduction

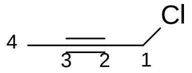
Alkynes are hydrocarbons that contain carbon-carbon triple bonds. Many of the reactions of alkynes are similar to the corresponding reactions of alkenes because both involve π-bonds between two carbon atoms. Like the π-bond of an alkene, the π-bonds of an alkyne are also electron rich, and readily undergo addition reactions.

4.8 Nomenclature of Alkynes

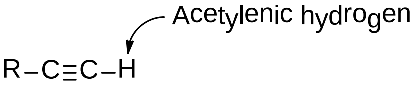
- Find the longest continuous chain of carbon atoms that includes the triple bond and change the **-ane** ending of the parent alkane to **-yne**.
- The chain is numbered to give the carbon atoms of the triple bond the lower possible numbers.
- The hydrogen attached to the carbon of the triple bond is called the acetylenic hydrogen atom.
- The anion obtained when the acetylenic hydrogen is removed is known as an alkynide ion or an acetylide ion.



5-methylhex-1-yne



1-chlorobut-2-yne



$R-C\equiv C^{-}$

acetylide ion

Alkynes are relatively nonpolar and quite soluble in most organic solvents. Acetylene, propyne, and the butynes are gases at room temperature. Alkynes have one σ-bond and two π-bonds. Hybridization of the *s* orbital with one *p*-orbital gives two linear *sp* hybrid orbitals that are used to form the σ-bond with each carbon atoms and with the hydrogen s orbitals. Two π-bonds result from overlap of the two remaining unhybridized *p*-orbitals on each carbon atom (Figure 1).

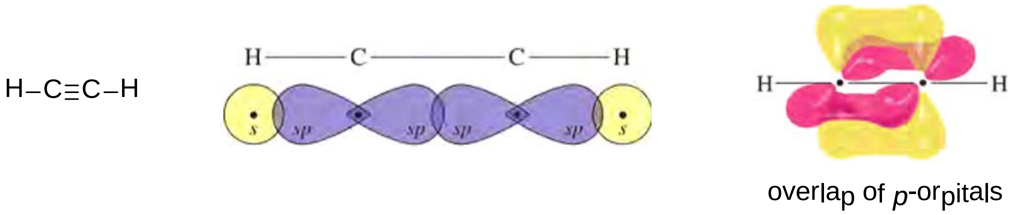


Figure 1

The triple bond is relatively short because of the high *s* character of the *sp* hybrid orbitals which also account for the slightly shorter C-H bonds in acetylene compared to ethylene and ethane (Figure 2).

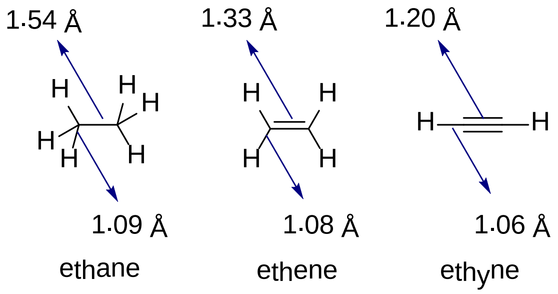
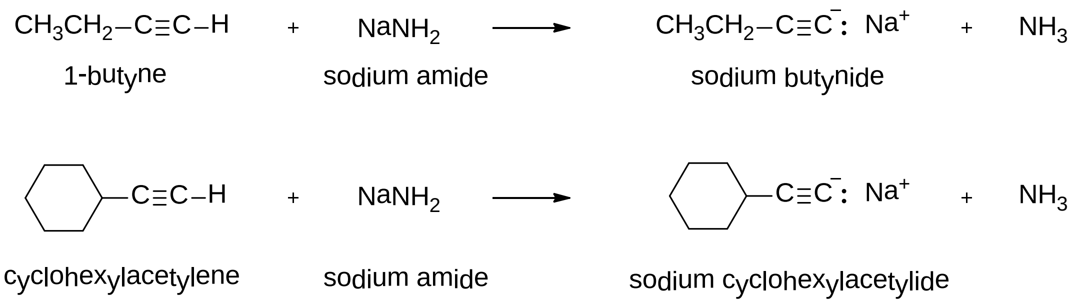


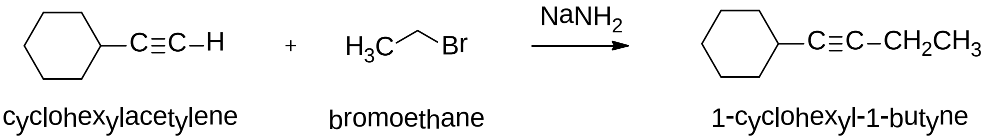
Figure 2

Terminal alkynes are much more acidic than other hydrocarbons. Abstraction of an acetylenic proton gives a carbanion that has the lone pair of electrons in the *sp* hybrid orbital. Hydroxide ion and alkoxide ions are not strong enough bases to deprotonate alkynes but very strong bases such as sodium amide, deprotonate terminal acetylenes to form acetylide ions (Scheme 1).



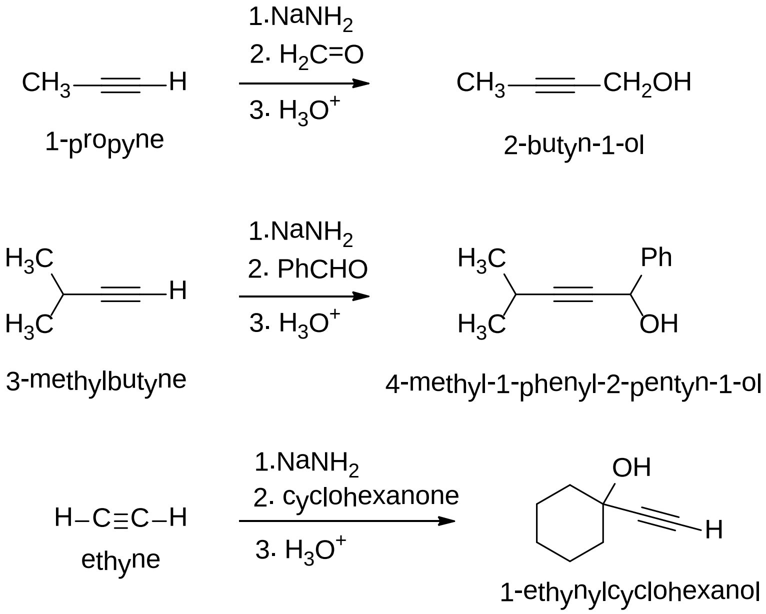
Scheme 1

An acetylide ion is a good nucleophile that can displace a halide ion from an alkyl halide to give substituted acetylene (Scheme 2).



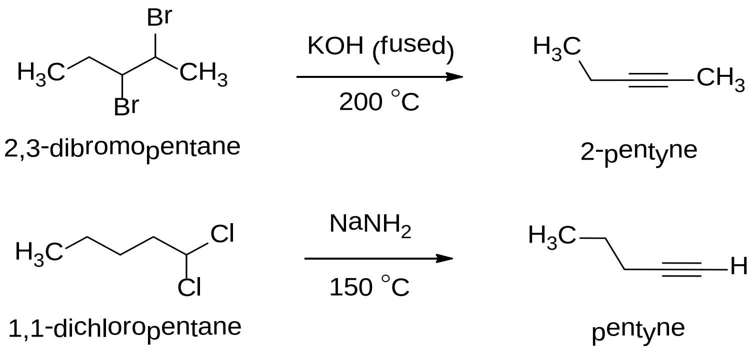
Scheme 2

Acetylide ion can also add to carbonyl compounds. A primary alcohol can be synthesized by adding an acetylide to formaldehyde but other aldehydes give a secondary alcohol. Addition of an acetylide ion to ketones gives a tertiary alcohol (Scheme 3).



Scheme 3

Carbon-carbon triple bond can be generated by eliminating two molecules of HX from a dihalide under strong basic conditions. In the first step vinyl halide is formed by dehydrohalogenation of a geminal or vicinal dihalide. Second dehydrohalogenation occurs only under strong basic conditions since it involves dehydrohalogenation of a vinyl halide. Dihalide is usually heated to 200 °C with strong base such as fused KOH or alcoholic KOH. Sodium amide can also be used for the double dehydrohalogenation that can take place at a lower temperature (Scheme 4).



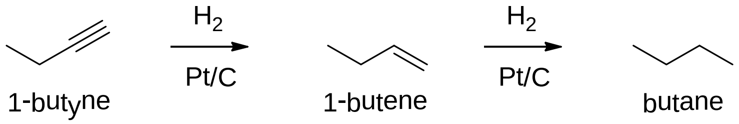
Scheme 4

4.9 Reactions of Alkynes

Many addition reactions of alkynes are similar to the corresponding reactions of alkenes since both involve π-bonds. Reagents add across the triple bonds of alkynes just as they add across the double bonds of alkenes and the reaction is usually exothermic.

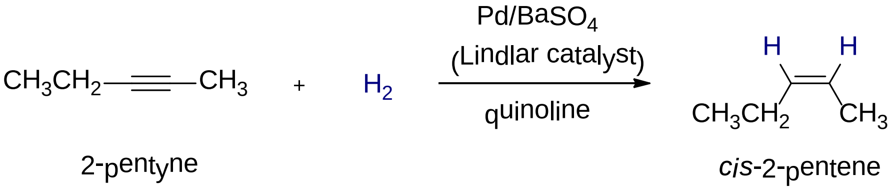
4.9.1 Addition of Hydrogen

In the presence of a catalyst, hydrogen adds to alkynes to give alkanes. For example, when either of the 1-butyne isomers reacts with hydrogen in the presence of a platinum catalyst, *n*-butane is formed. Platinum, palladium, and nickel catalysts are commonly used for this transformation (Scheme 5).



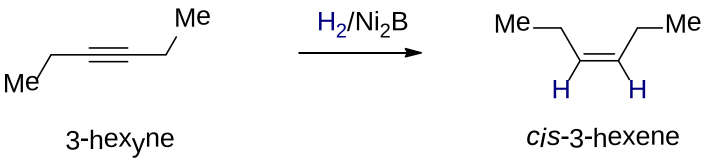
Scheme 5

Lindlar's catalyst is a poisoned palladium catalyst, composed of powdered barium sulfate coated with palladium. The catalytic hydrogenation of alkynes is similar to the hydrogenation of alkenes, and both proceed with *syn* stereochemistry. In this process, the face of a π-bond contacts the solid catalyst, and the catalyst weakens the π-bond, allowing two hydrogen atoms to add on the same face of the alkyne ensures *syn* stereochemistry (Scheme 6).



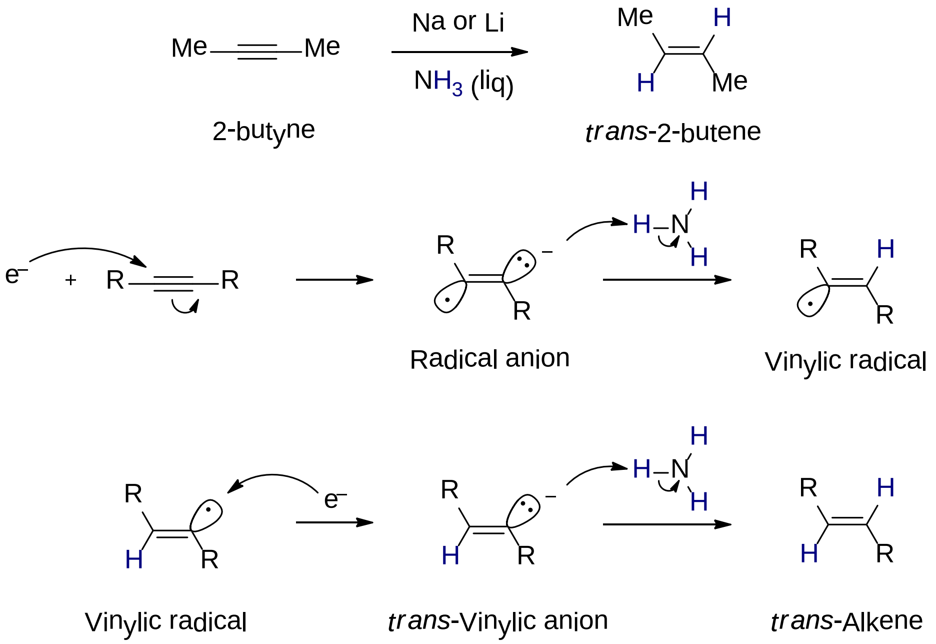
Scheme 6

Nickel boride (Ni_2B) is an alternative to Lindlar's catalyst that can be more easily made to give often better yields (Scheme 7).



Scheme 7

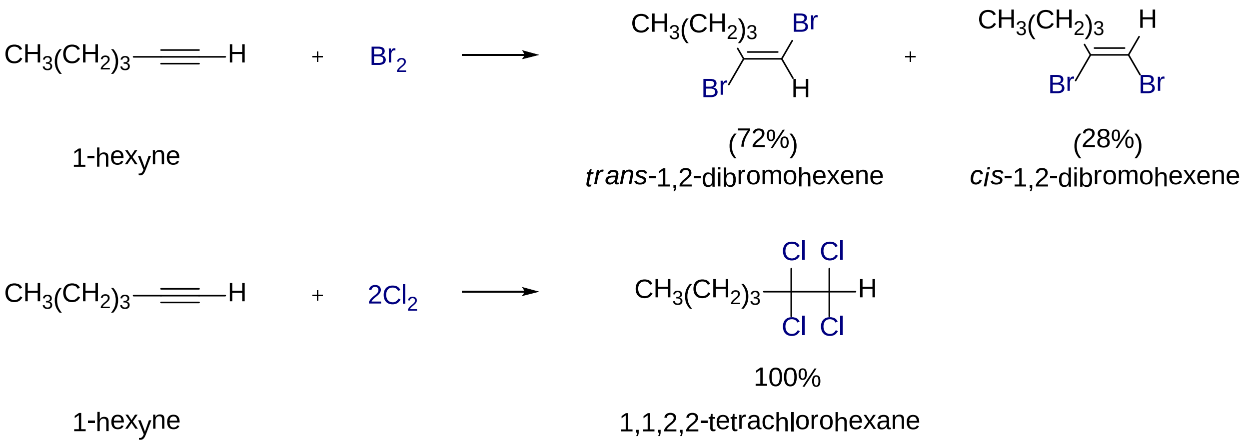
On the other hand, *anti*-addition of hydrogen to the triple bond of alkynes occurs when they are treated with lithium or sodium metal in ammonia or ethylamine at low temperatures (Scheme 8). In this process, sodium in liquid ammonia produces solvated electrons that can reduce the alkyne to *trans*-alkene. The *anti*-stereochemistry results from the greater stability of the vinyl radical in the *trans*-configuration, where the alkyl groups are farther apart.



Scheme 8

4.9.2 Addition of Halogens

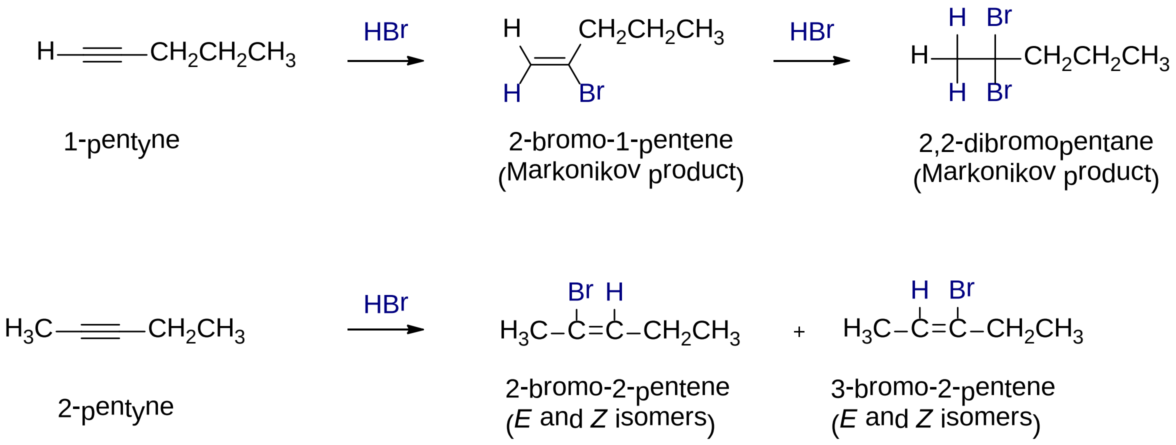
Bromine and chlorine can add to alkynes just as they add to alkenes. If 1 mole of halogen adds to 1 mole of an alkyne, the product is a dihaloalkene. The stereochemistry of addition may be either *syn* or *anti*, and the products are often mixtures of *cis* and *trans* isomers. If 2 moles of halogen add to 1 mole of an alkyne, a tetrahalide results (Scheme 9).



Scheme 9

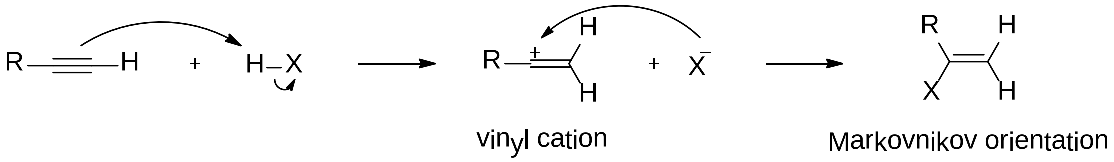
4.9.3 Addition of Hydrogen Halide

When a hydrogen halide adds to a terminal alkyne, the product has the orientation predicted by Markovnikov's rule. When two moles of a hydrogen halide add to an alkyne, the second mole also adds with the same orientation as the first. The reaction of an internal alkyne, such as 2-pentyne, gives a mixture of products (Scheme 10).



Scheme 10

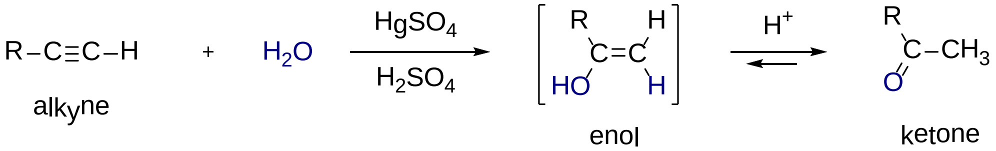
The mechanism is similar to the mechanism of hydrogen halide addition to alkenes. The vinyl cation, formed in the first step, is more stable with the positive charge on the more highly substituted carbon atom. Attack by halide ion gives Markovnikov product (Scheme 11).



Scheme 11

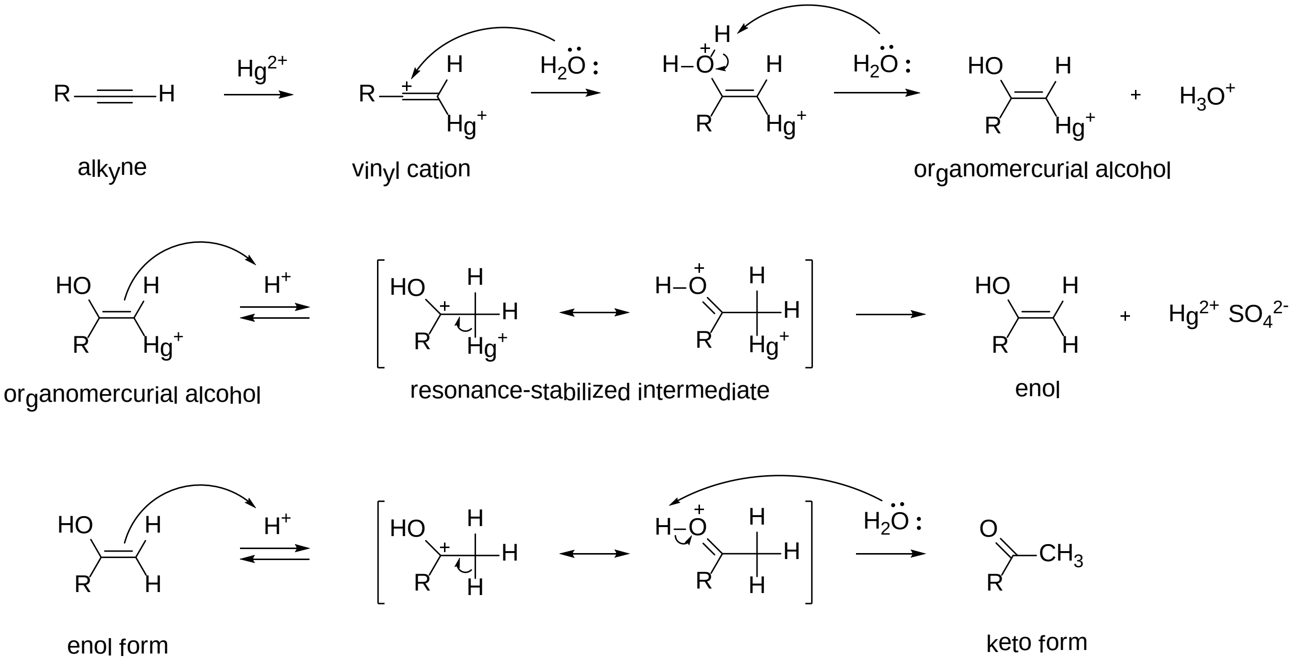
4.9.4 Hydration of Alkynes

Alkynes undergo acid-catalyzed addition of water across the triple bond in the presence of a mixture of mercuric sulfate in aqueous sulfuric acid. The hydration of alkynes also goes with Markovnikov's orientation (Scheme 12).



Scheme 12

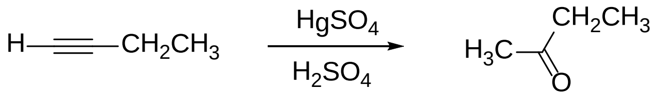
Electrophilic addition of mercuric ion gives a vinyl cation, which reacts with water and loses a proton to give an organomercurial alcohol. Under acidic conditions, mercury is replaced by hydrogen to give an enol which is unstable and isomerizes to the ketone (Scheme 13).



Scheme 13

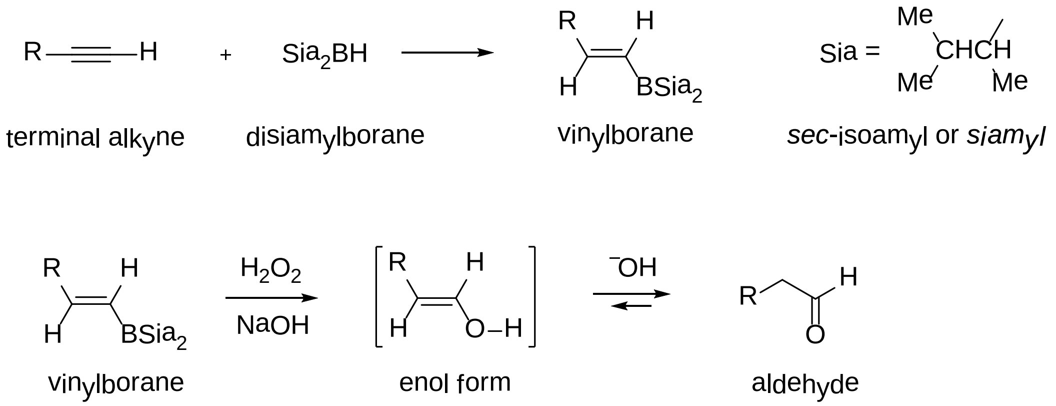
The hydroxyl proton in the enol is lost, and a proton is regained at the methyl position, while the π-bond shifts from the C = C position to the C = O position. This type of equilibrium is called as **tautomerism**.

Example:



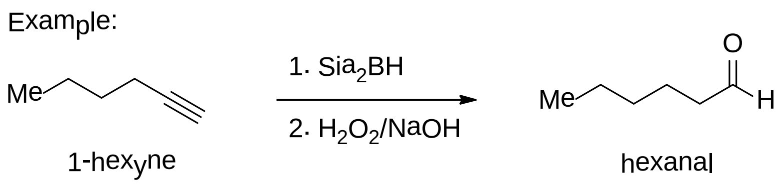
4.9.5 Hydroboration-Oxidation

We know that hydroboration-oxidation adds water across the double bonds of alkenes with *anti*-Markovnikov's orientation. A similar reaction too takes place with alkynes, but a hindered dialkylborane is used to prevent addition of two molecules of borane across the triple bond. Oxidation of the vinylborane with hydrogen peroxide gives an enol, resulting from *anti*-Markovnikov addition of water across the triple bond, which tautomerizes to its more stable keto form. In case of a terminal alkyne, the keto product is an aldehyde (Scheme 14).



Scheme 14

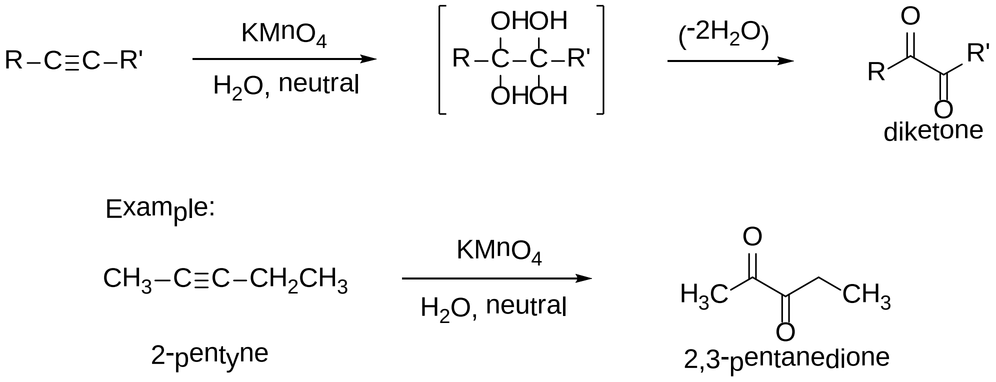
Under basic conditions, the mechanism of keto-enol tautomerism is quite different (Scheme 15). The proton is first removed from its old position in the OH group, and then replaced on carbon. In contrast, in acidic conditions, the proton was first added on carbon, and then removed from the hydroxyl group.



Scheme 15

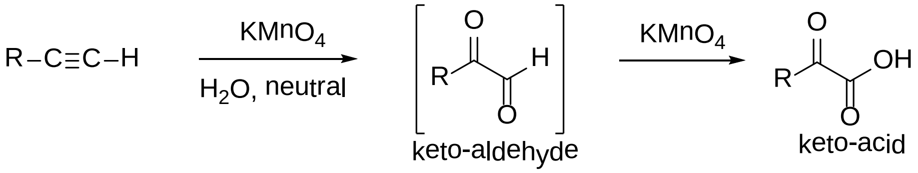
4.9.5 Oxidation

When an alkyne is treated with cold, aqueous potassium permanganate under neutral conditions, the formation of diketone is observed (Scheme 16).



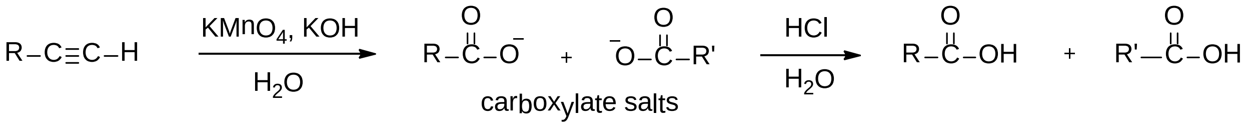
Scheme 16

Terminal alkynes give a keto-aldehyde that quickly oxidizes to an acid (Scheme 17).



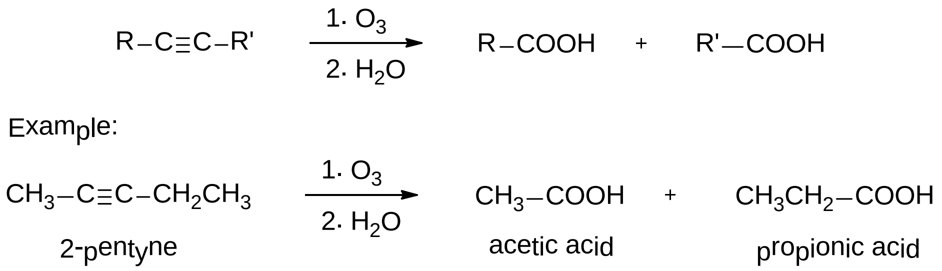
Scheme 17

If the reaction mixture becomes warm or too basic, the diketone undergoes oxidative cleavage to carboxylic acids (Scheme 18).



Scheme 18

Ozonolysis of an alkyne cleaves the triple bond to give two carboxylic acids (Scheme 19). This process can be used to determine the position of the triple bond in an unknown alkyne.



$$R-C\equiv C-R' \xrightarrow[\text{2. } H_2O]{\text{1. } O_3} R-COOH + R'-COOH$$

Example:

$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow[\text{2. } H_2O]{\text{1. } O_3} CH_3-COOH + CH_3CH_2-COOH$$

Scheme 19