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ALKENE (UG)

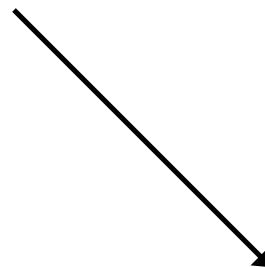
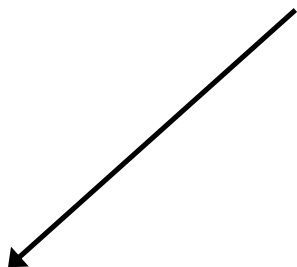
B.Sc-Ist Year

Unit-03

Hydrocarbons

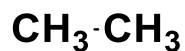


Composed of only carbon and hydrogen



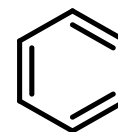
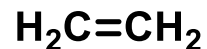
Saturated hydrocarbons

Alkanes



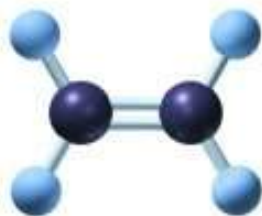
Unsaturated hydrocarbons

Alkenes, Alkynes & Aromatics

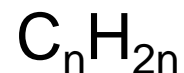
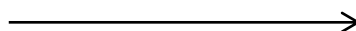


Unsaturated Compounds

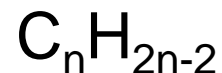
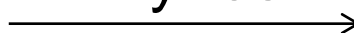
Alkenes and alkynes are said to be **unsaturated** because they are capable of adding hydrogen in the presence of a catalyst. An alkane is called as **saturated** because it cannot react with any more hydrogen.



Alkenes

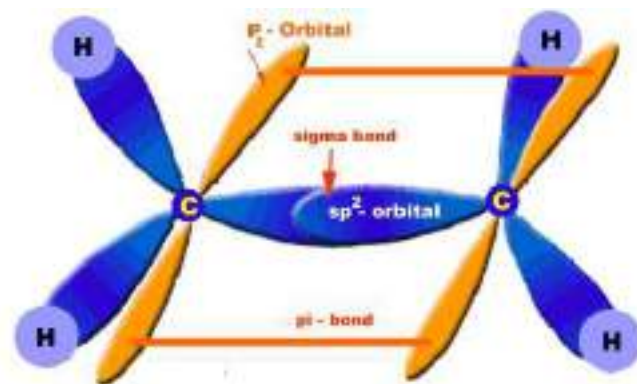
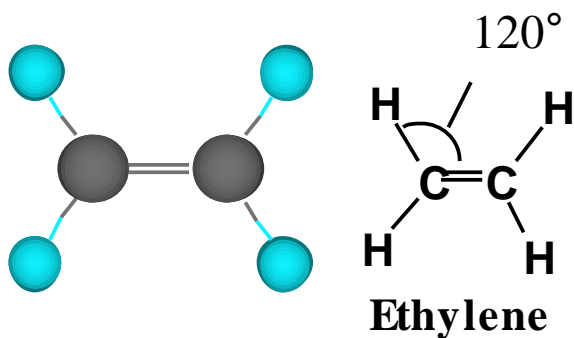


Alkynes



Geometry of Alkenes

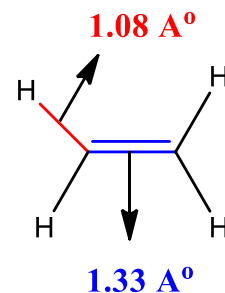
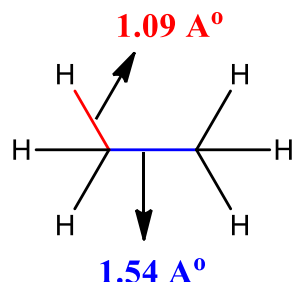
Hydrocarbons that contain carbon-carbon double bond are called **Alkenes** (also called as **Olefins**). It has three sp^2 orbitals that lie in a plane with angles of 120° . One of the carbon-carbon bonds in a double bond is σ -bond, formed by the overlap of a sp^2 orbital of one carbon with a sp^2 orbital 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.



Orbital Structure of ethylene

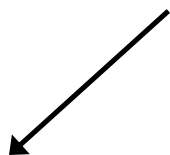
These two p -orbitals must be parallel to each other to achieve maximum orbital-orbital overlap. Therefore, all six atoms of the double-bond system are in the same plane. Since there is maximum side-to-side overlap, rotation about a double bond does not occur. Each C-H σ -bond is formed by overlap of a sp^2 hybrid orbital of carbon atom with the $1s$ 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.

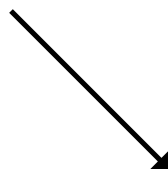


Nomenclature of alkenes

2 ways of naming compounds:



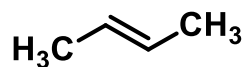
Common system



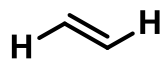
IUPAC system

Alkene names change the end **-ane to -ylene**.

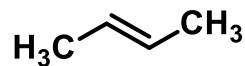
Alkene names change the end **-ane to -ene**.



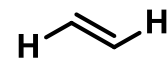
Butylene



Ethylene

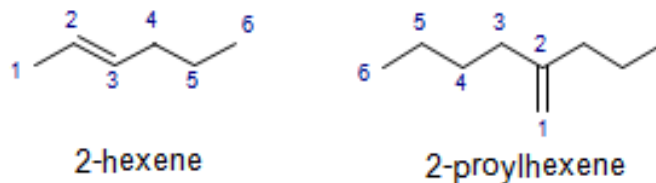


Butene

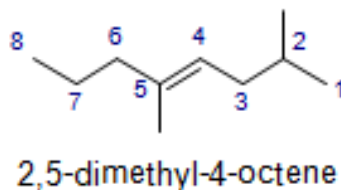


Ethene

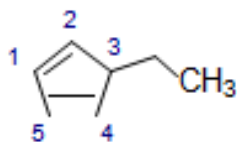
- Find the longest continuous chain of carbon atoms that includes the double bond and change the **-ane** ending of the parent alkane to **-ene**. The chain is numbered as the double bond having the lower possible numbers.



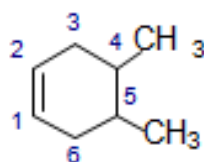
- If a chain has more than one substituent, the substituents are cited in alphabetical order. The prefixes *di*, *tri*, *sec*, and *tert* are not considered in alphabetizing, but *iso*, *neo*, and *cyclo* are considered. It should also contain the lowest substituent number.



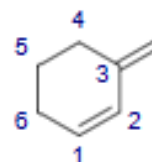
- The double bond should be in between carbon 1 and 2, while numbering the ring.



3-ethylcyclopentene

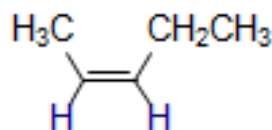


4,5-dimethylcyclohexene

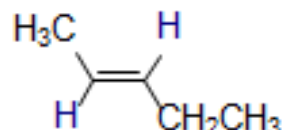


3-methylenecyclohexene

- 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.

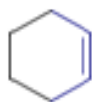


cis-2-pentene

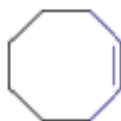


trans-2-pentene

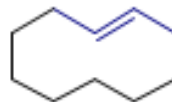
- Cycloalkenes are preferred to be *cis* unless the ring is large enough (at least eight carbon atoms) to be *trans*.



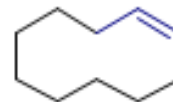
cyclohexene



cyclooctene

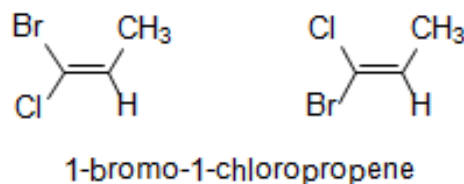


cis-cyclodecene

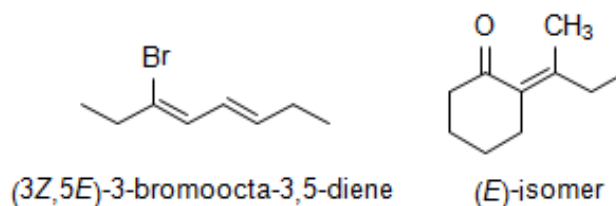
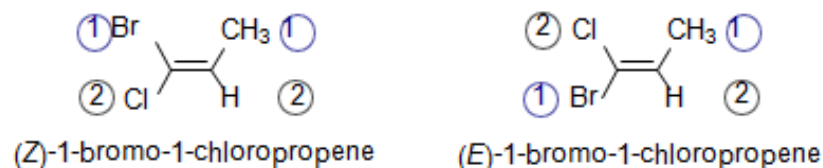


trans-cyclodecene

- *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.



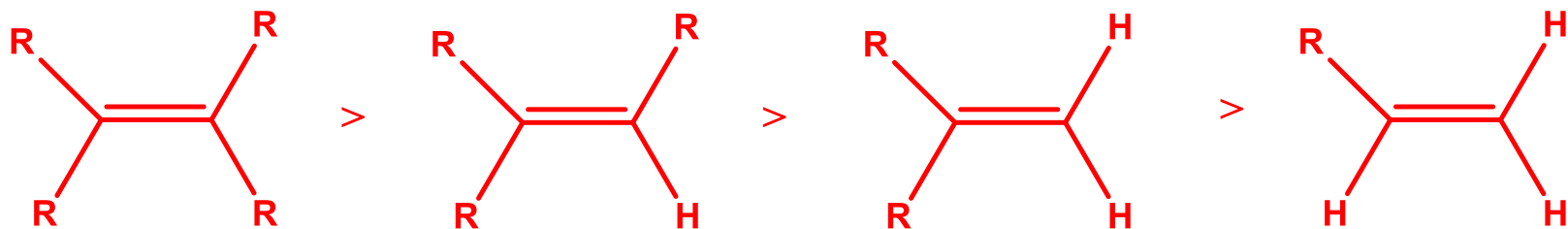
- Each end of the double bond should be considered separately. Assign first and second priorities to the two substituent groups on one end of the double bond. Do the same for the other end. If the two first-priority atoms are on the same side of the double bond, it is called as *Z* isomer. If the two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



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.

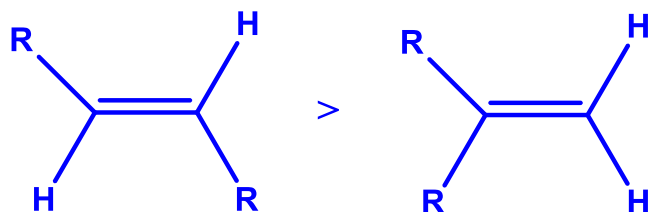
□ The difference in the stabilities of alkenes is the difference in their heats of hydrogenation. Alkene, which releases the most heat, must be the least stable and the alkene, which releases the least heat, must be the most stable. More substituted double bonds are usually more stable. In summary, the alkyl groups attached to the double bonded carbons and least heats of hydrogenation stabilize the alkene.



More stable

Less stable

□ The heats of hydrogenation show that *trans*-isomers are generally more stable than the corresponding *cis*-isomers.



□ For cyclodecene and larger cycloalkenes, the *trans*-isomer is nearly as stable as the *cis*-isomer.



cis-cyclodecene
(Less stable)

<



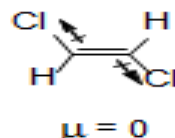
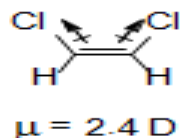
trans-cyclodecene
(More stable)

Physical properties of alkenes

- ❑ Alkenes are non polar compounds.
- ❑ All alkenes are insoluble in water, due to the weak van der Waal forces.
- ❑ alkenes are soluble in organic solvents like benzene or acetone because the van der Waal forces will be replaced by new ones, making alkenes fully soluble.
- ❑ The boiling points of alkenes depend on their molecular structure. The bigger their molecular chain the higher the boiling points. So the higher alkenes have very high boiling points.
- ❑ They are less dense than water
- ❑ Range of physical states:

✓ ≤ 4 C's are gases
✓ 5 - 17 C's are liquids
✓ ≥ 18 C's are solids

- ❑ The *cis*-isomer has higher dipole moment (μ) than that of the *trans*-isomer.



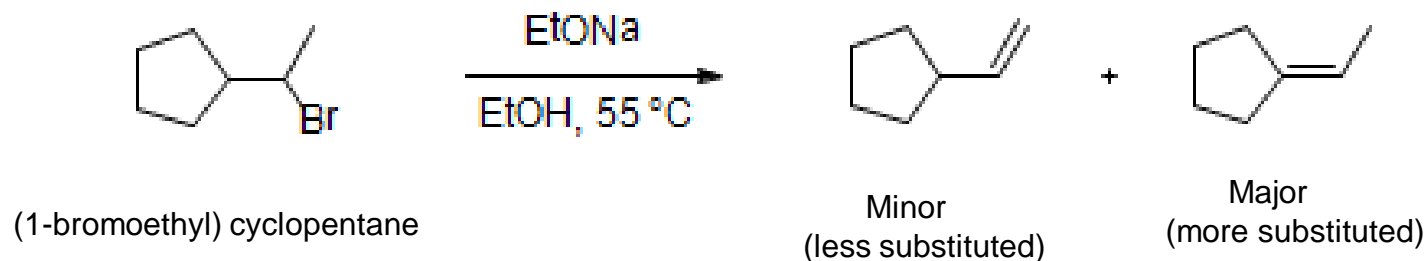
Synthesis of alkenes

□ Alkenes can be synthesized by elimination reactions.

□ **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.

OR

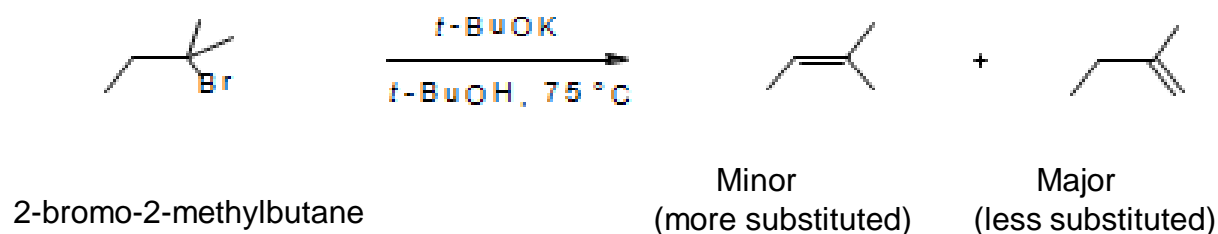
Hydrogen is preferably removed from the carbon with least no. of hydrogen.



Examples:



Hofmann's 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.



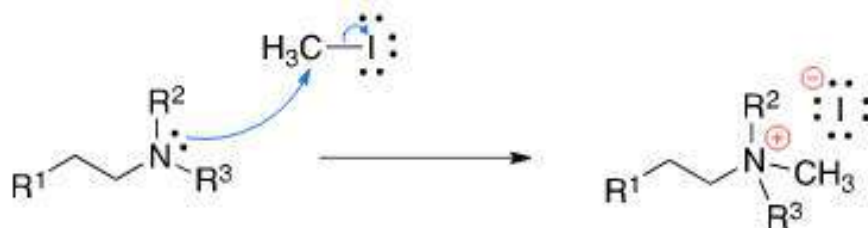
Hofmann elimination reaction

The Hofmann elimination is an organic reaction used to convert an amine with a β -hydrogen to an alkene using methyl iodide, silver oxide and water under thermal conditions. The mechanism begins with an attack of the amine on methyl iodide to form an ammonium iodide salt. The iodide then reacts with silver oxide to form silver iodide which is insoluble and precipitates out of solution and a silver oxide ion which deprotonates water to form a hydroxide ion.

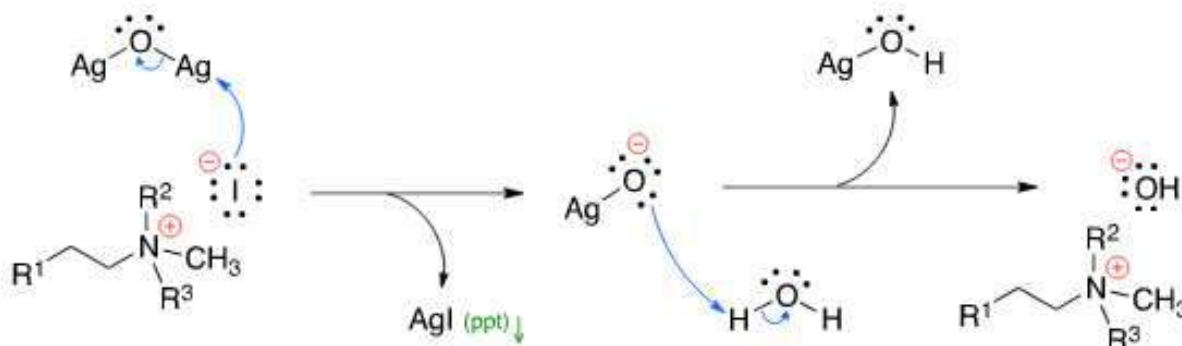
Heating the mixture facilitates an elimination reaction where the hydroxide picks up the β -hydrogen from the ammonium ion and releases an amine to afford the final olefin product.

Mechanism

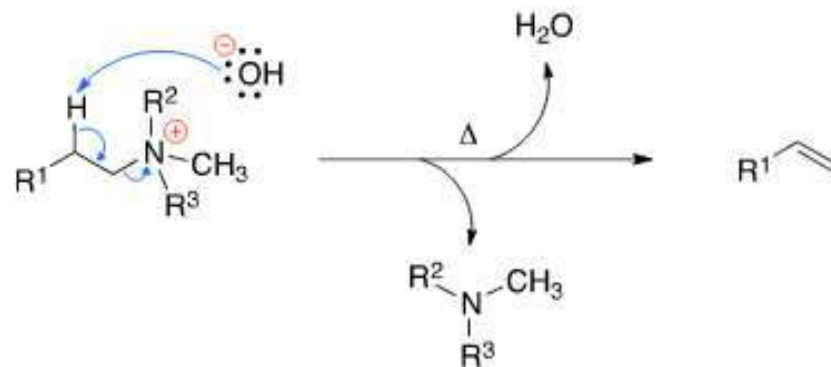
Step 1. Formation of the ammonium iodide salt



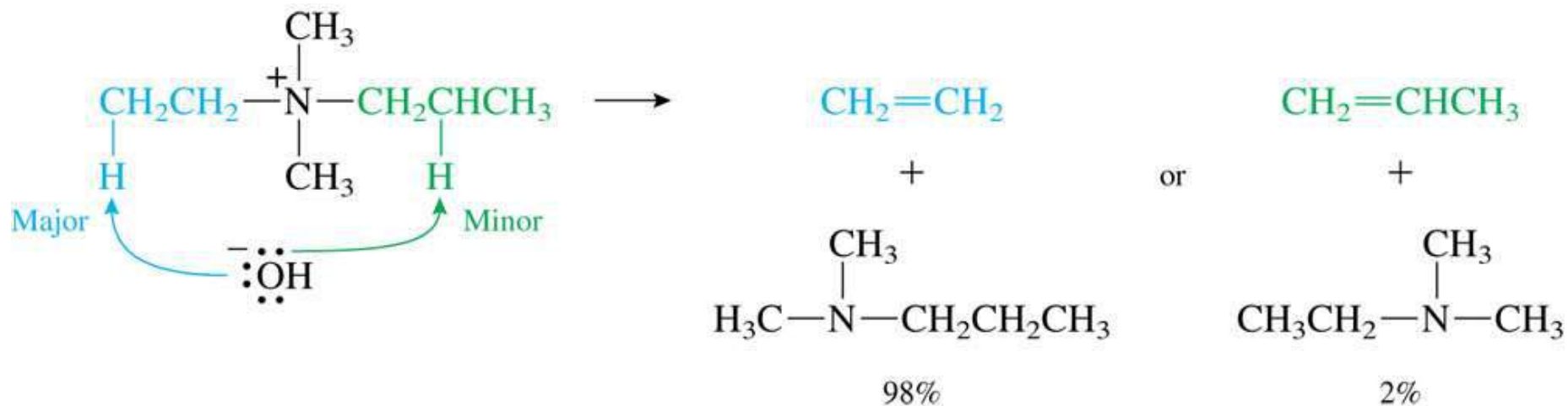
Step 2. Substitution of iodide anion with hydroxide



Step 3. Heat mediated elimination leading to product.

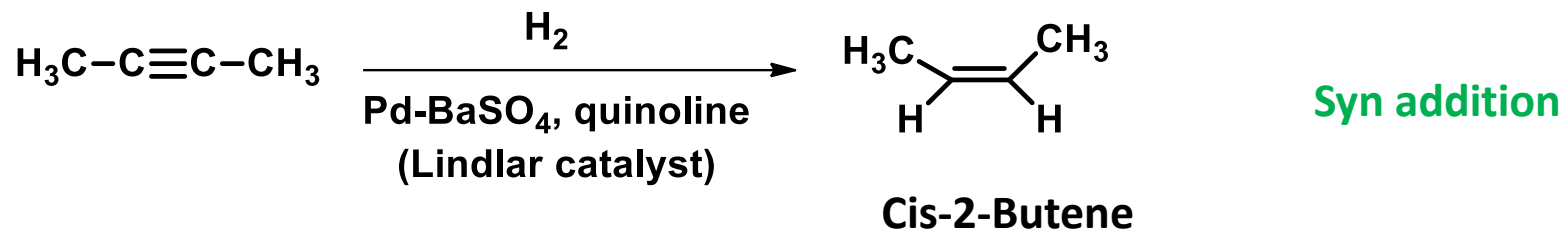


Examples:

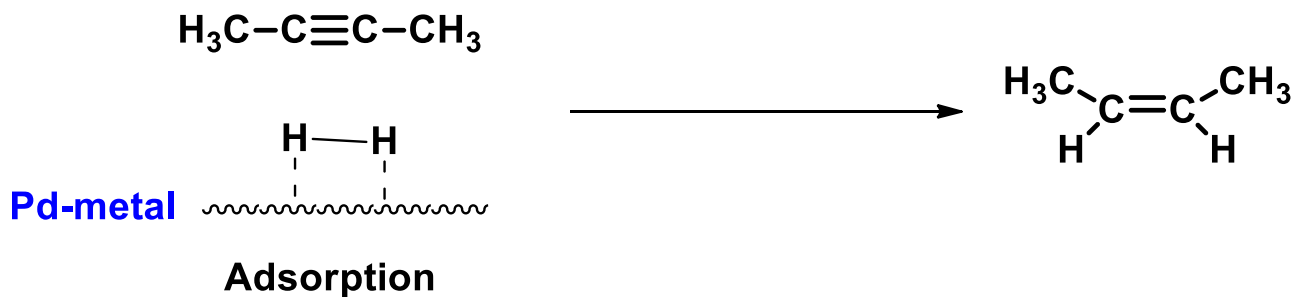


Synthesis of alkenes

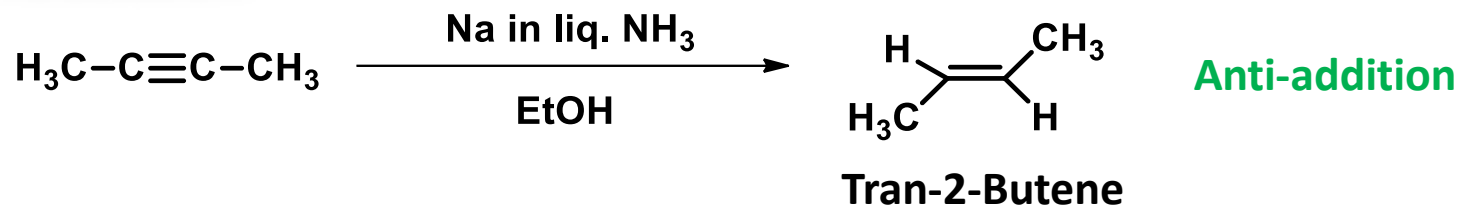
1) Catalytic hydrogenation of Alkynes



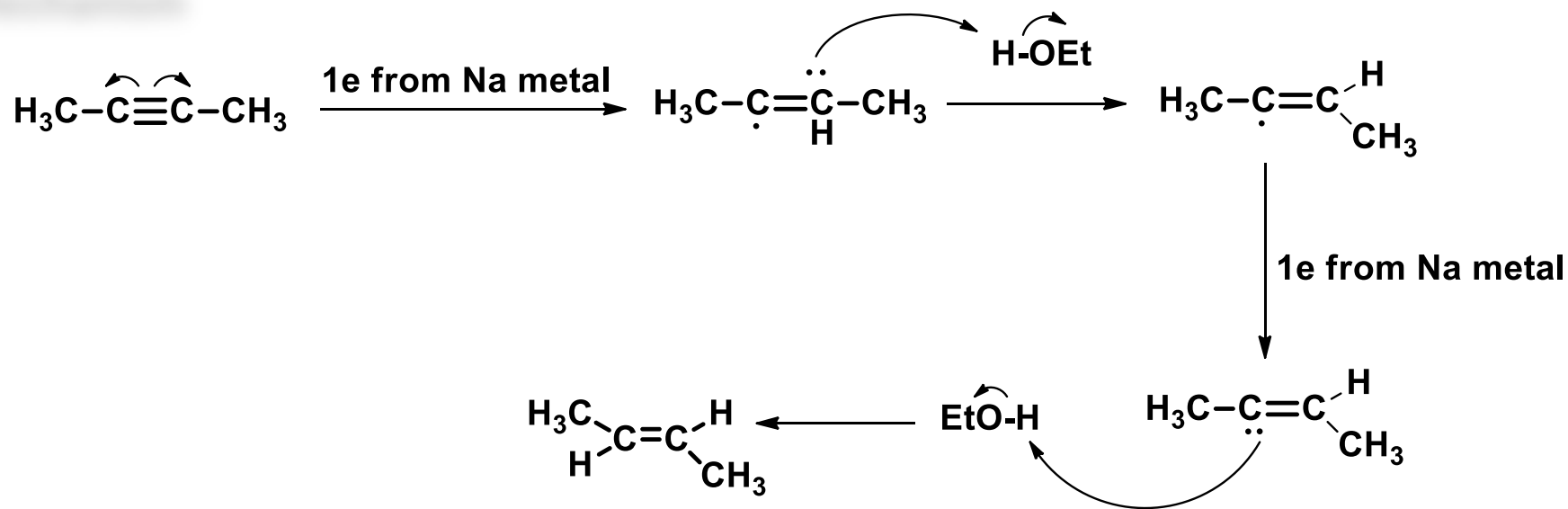
Mechanism



2) Birch Reduction

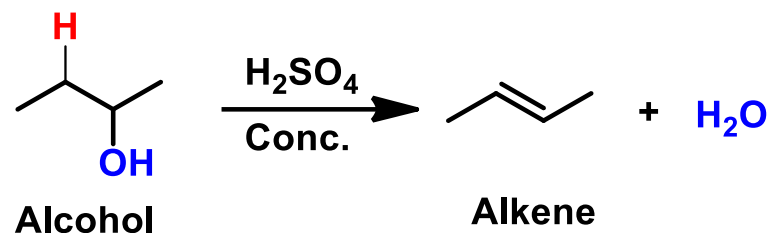


Mechanism

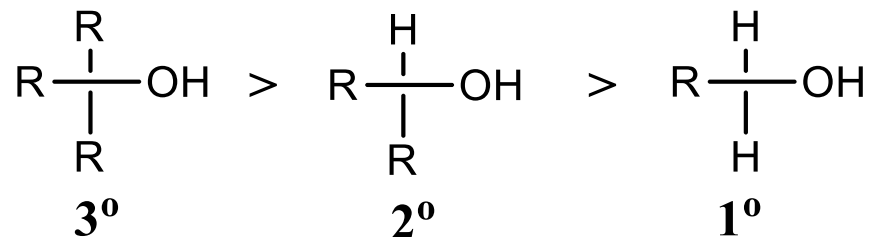


3) Dehydration of Alcohol

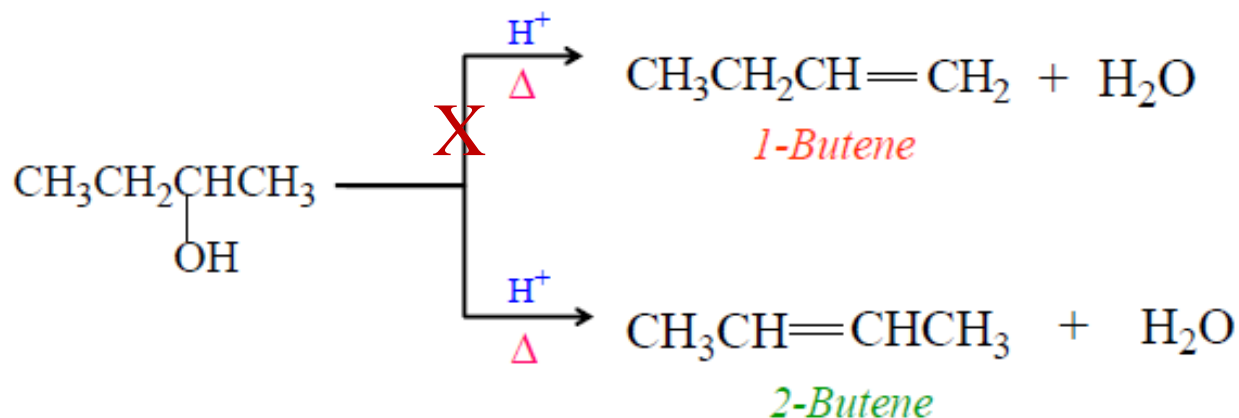
Alcohols undergo dehydration to form an alkene when heated with a strong acid. Concentrated sulfuric acid or concentrated phosphoric acid are often used as reagents.



Alcohols that form stable carbocations can easily undergo dehydration. Tertiary alcohol undergoes dehydration easily as it forms a relatively stable tertiary carbocation. The relative ease with which alcohols undergo dehydration is as follows:



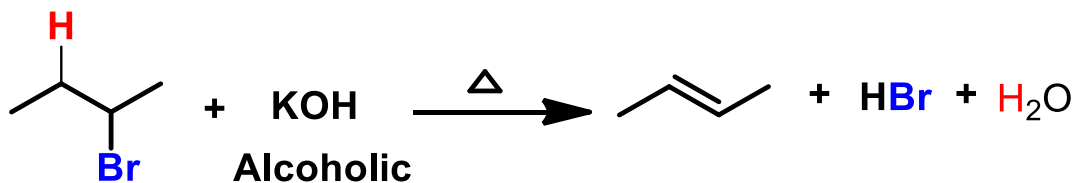
Which alkene Predominates?



Examples:

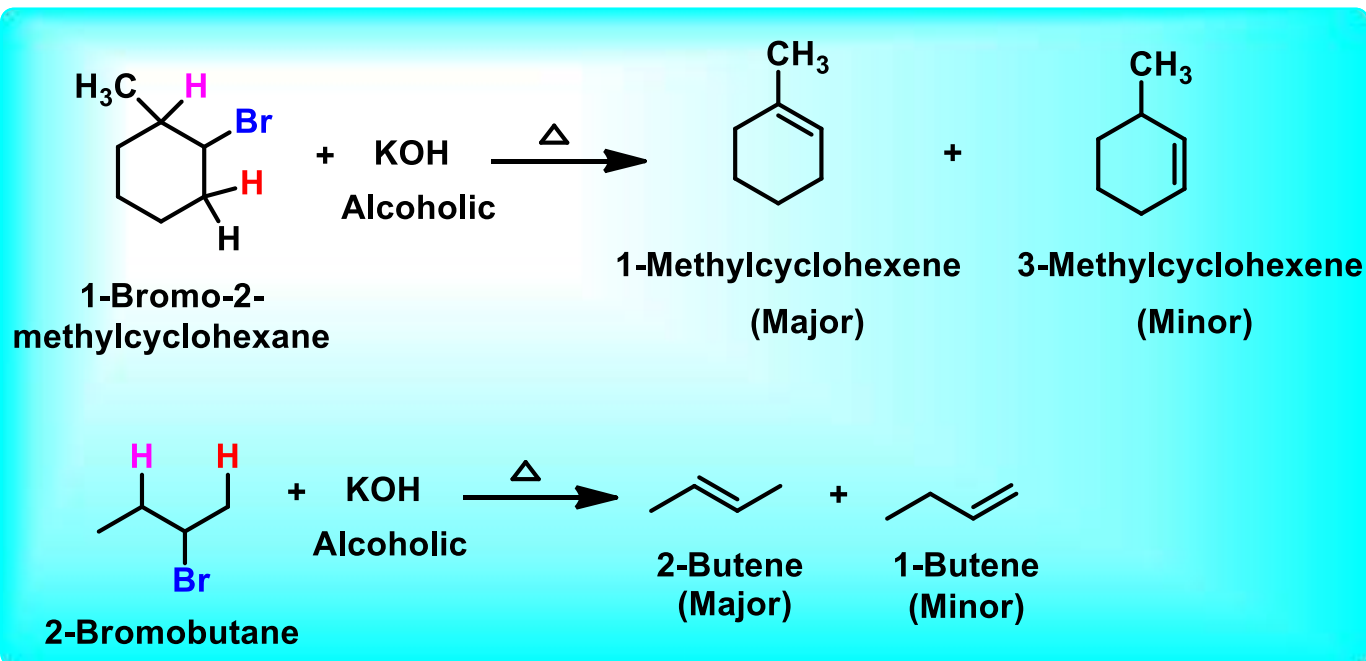


4) Dehydrohalogenation of alkyl halide

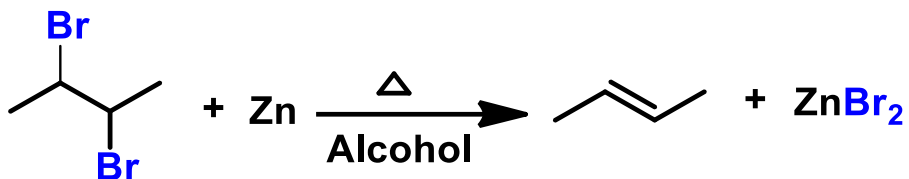


Examples:

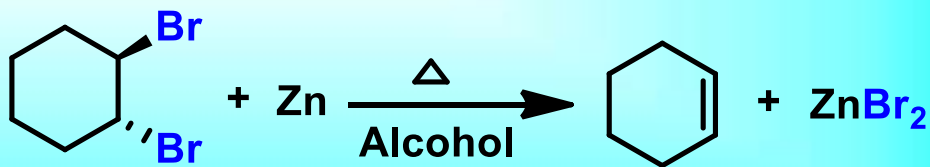
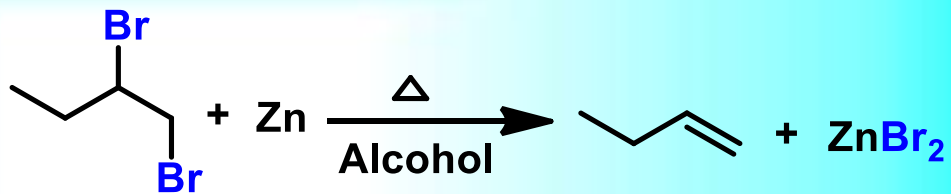
Saytzeff's rule applies.



5) Dehalogenation of vicinal dihalides



Examples:



Reaction of Alkenes

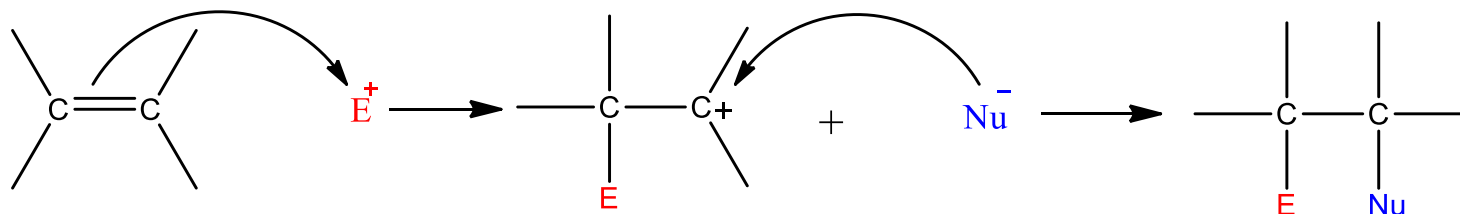
- 1- Addition reactions on the carbon-carbon double bond.
- 2- Substitution reactions on the saturated alkyl chain.

Addition reactions

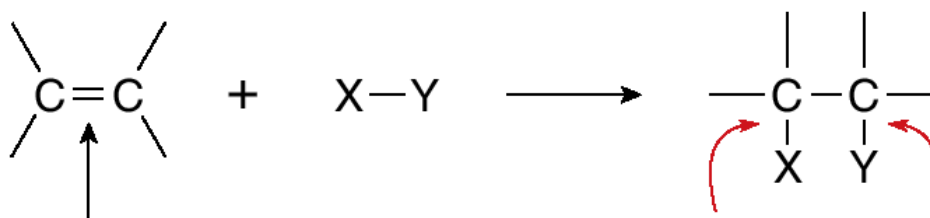
1. Addition of H_2
2. Addition of X_2
3. Addition of HX
4. Addition of HOSO_3H
5. Addition of H_2O
6. Addition of halohydrin XOH
7. Oxidation
8. Ozonolysis

Addition 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. 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.



Since σ bonds are stronger than π bonds, double bonds tend to react to convert the double bond into σ bonds. This is an addition reaction. Addition reactions are typically exothermic.

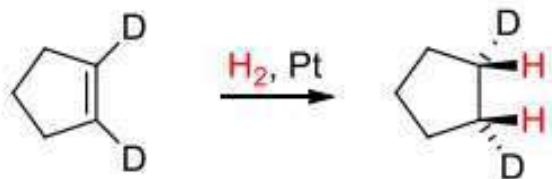


This π bond is broken.

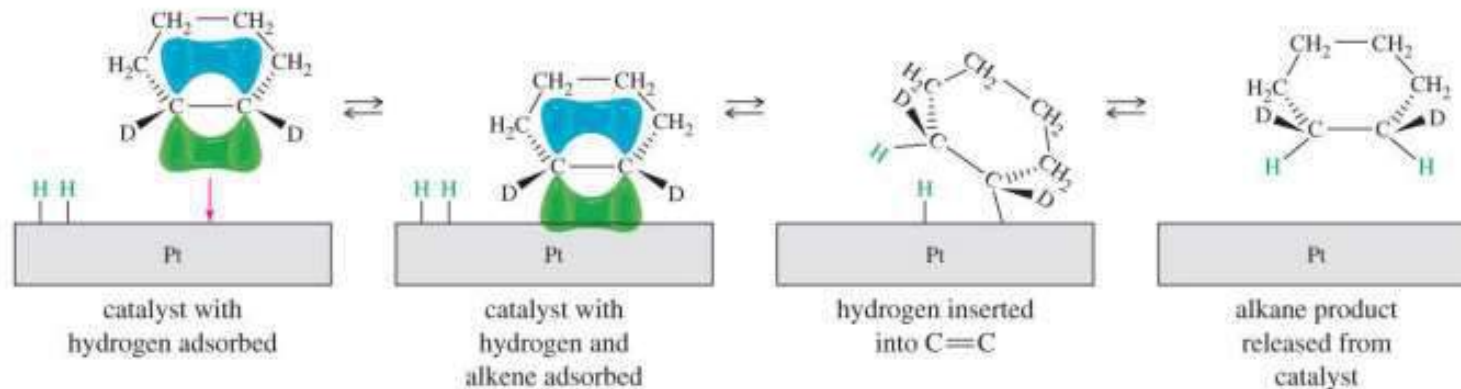
Two σ bonds are formed.

(1) Addition of Hydrogen: Catalytic Hydrogenation

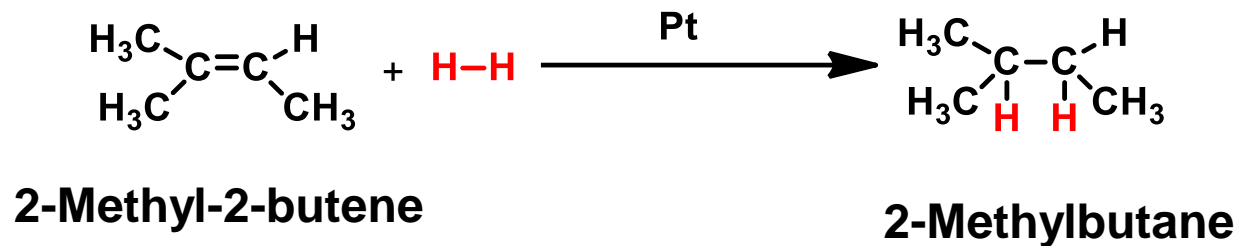
During catalytic hydrogenation, the hydrogen adsorbs onto the surface of the metal catalyst, and they add syn to the double bond. One face of the π system binds to the catalyst, then the bound hydrogen inserts into the π bond, and the product is liberated from the catalyst



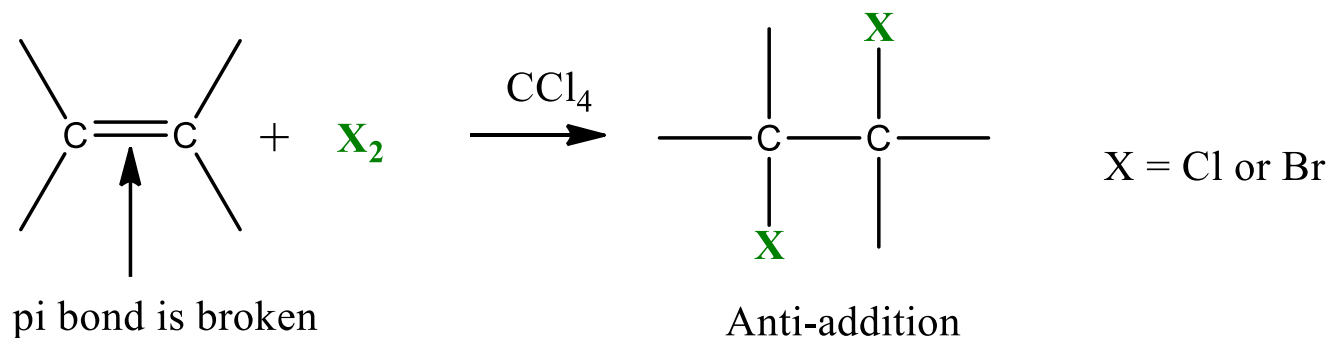
Mechanism



Example:

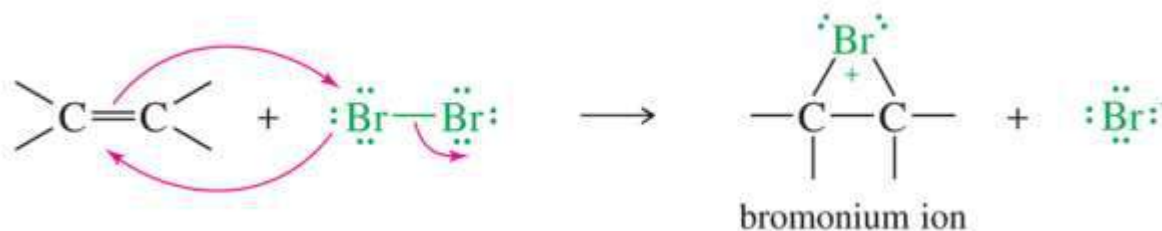


(2) Addition of Halogens: Halogenation

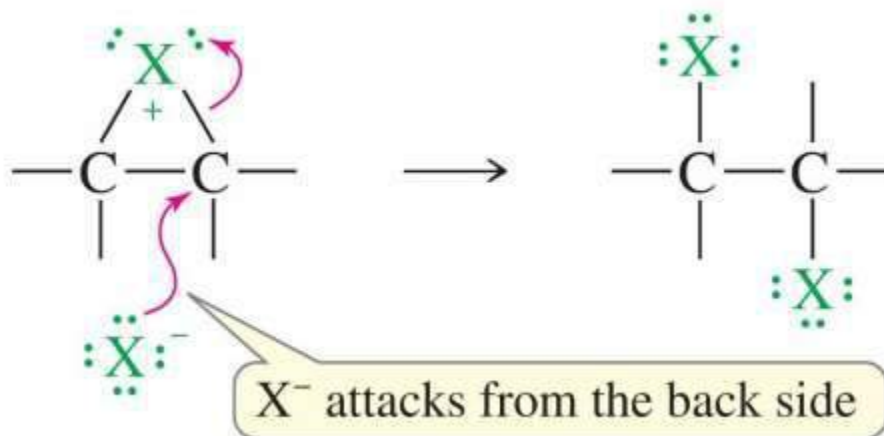


Mechanism

The halogen molecule (X_2) is electrophilic –a nucleophile will attack one end, and displace a halide ion. Typically, a π bond will attack the bromine molecule kicking out bromide ion and generating a bromonium ion.

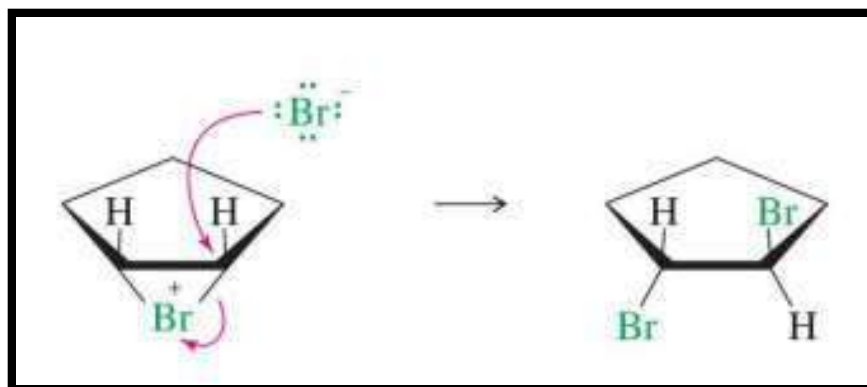
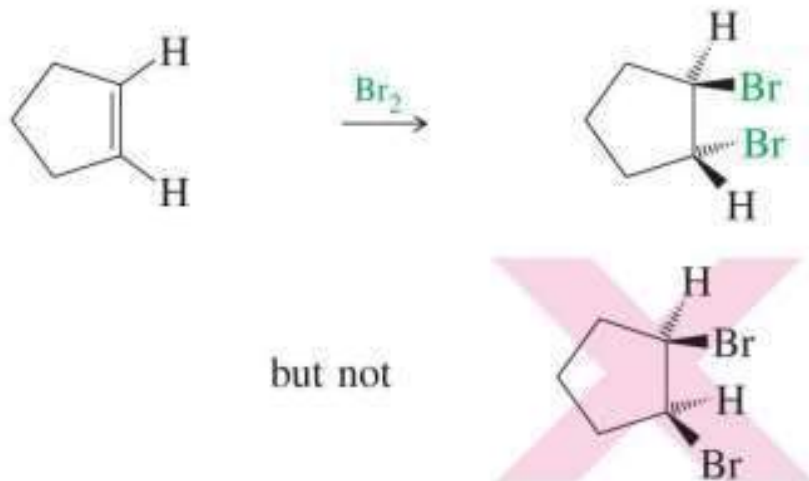


This halonium ring is then opened by back side attack of a nucleophile (often the halide) to give the final anti product.

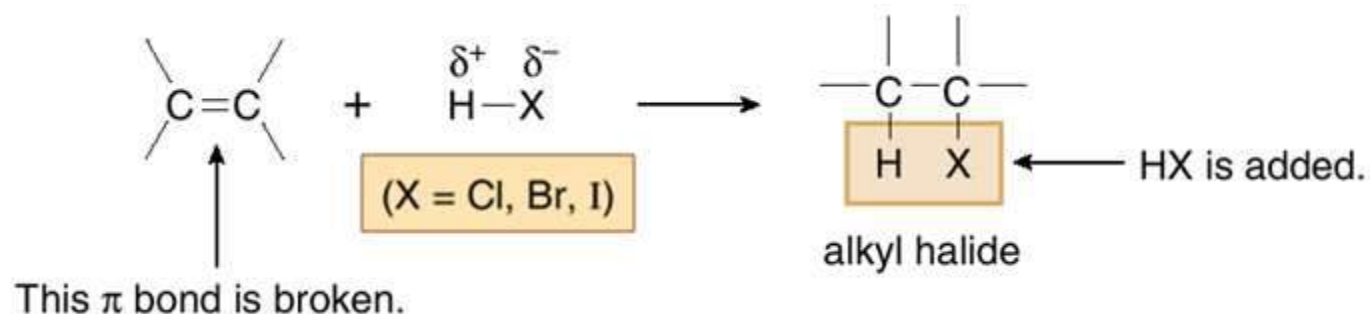


The halogen addition reaction is stereospecific, it gives anti addition

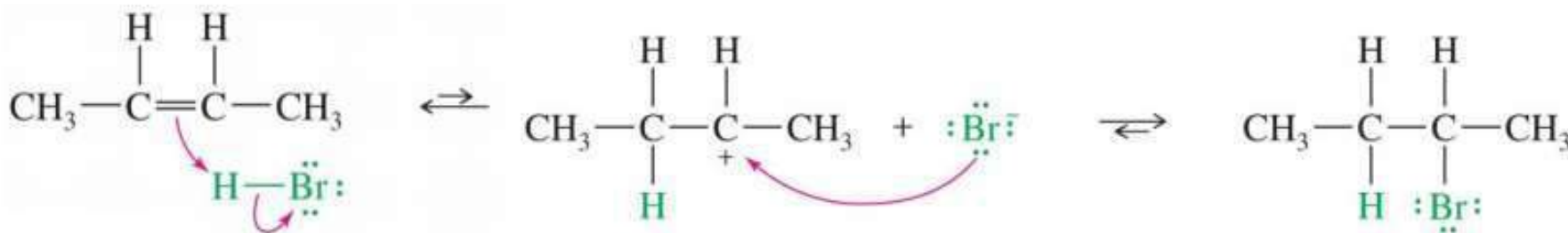
Examples:



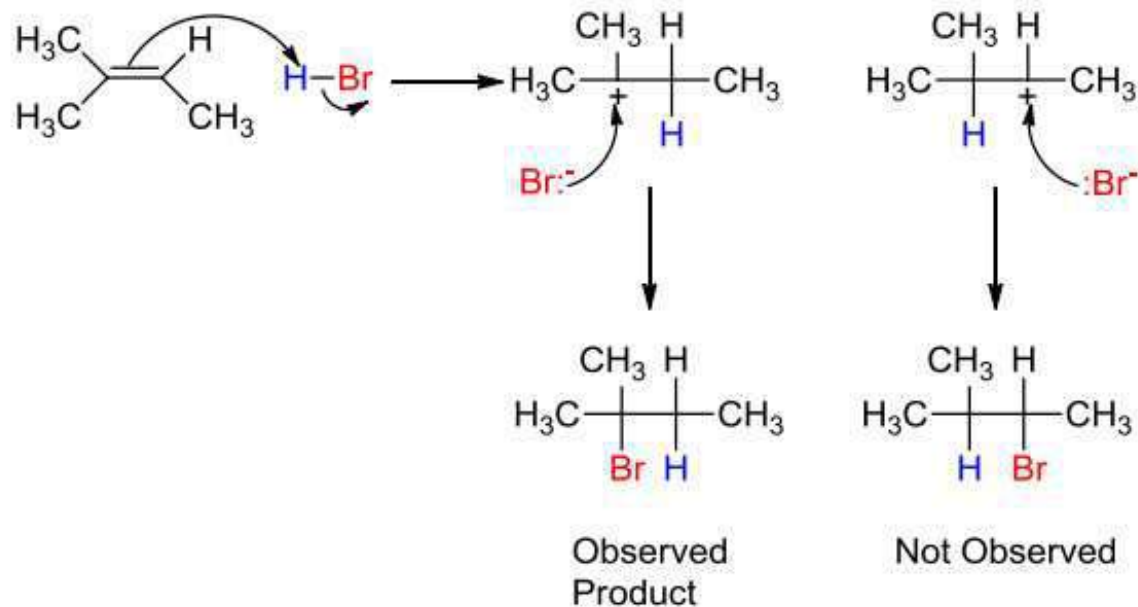
(3) Addition of Hydrogen Halides: Hydrohalogenation



The alkene abstracts a proton from the HBr , and a carbocation and bromide ion are generated. The bromide ion quickly attacks the cationic center and yields the final product. In the final product, $H-Br$ has been added across the double bond.



Mechanism



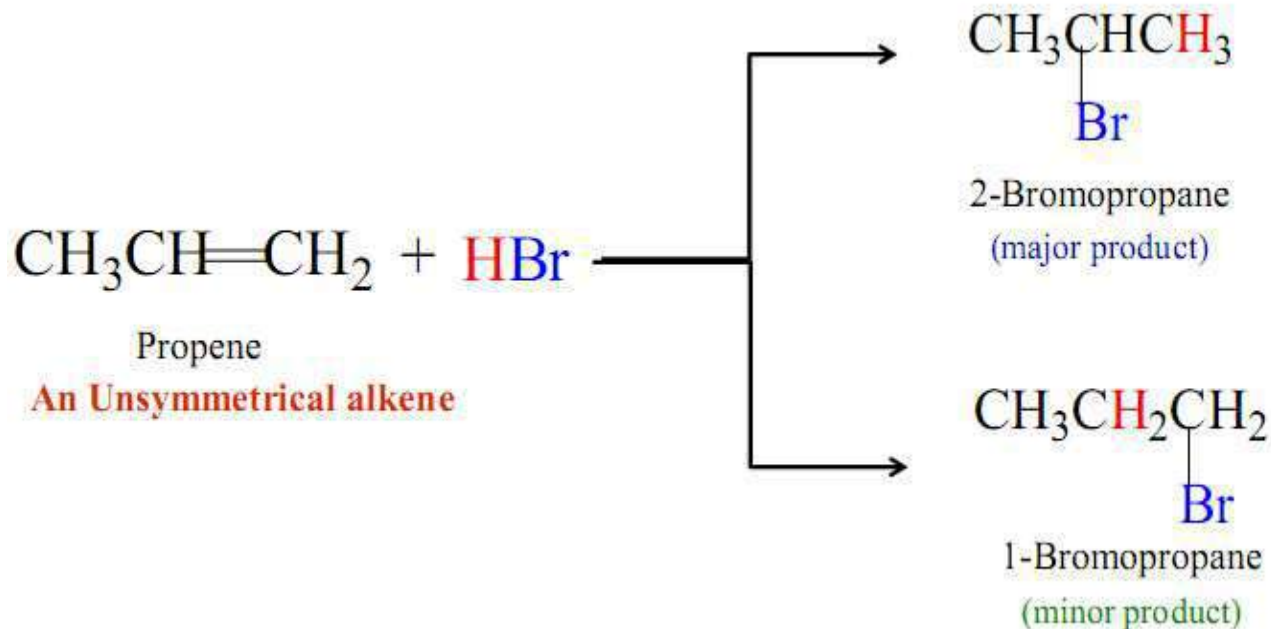
The observed product is the one resulting from the more stable carbocation intermediate



Tertiary carbocations are more stable than secondary.

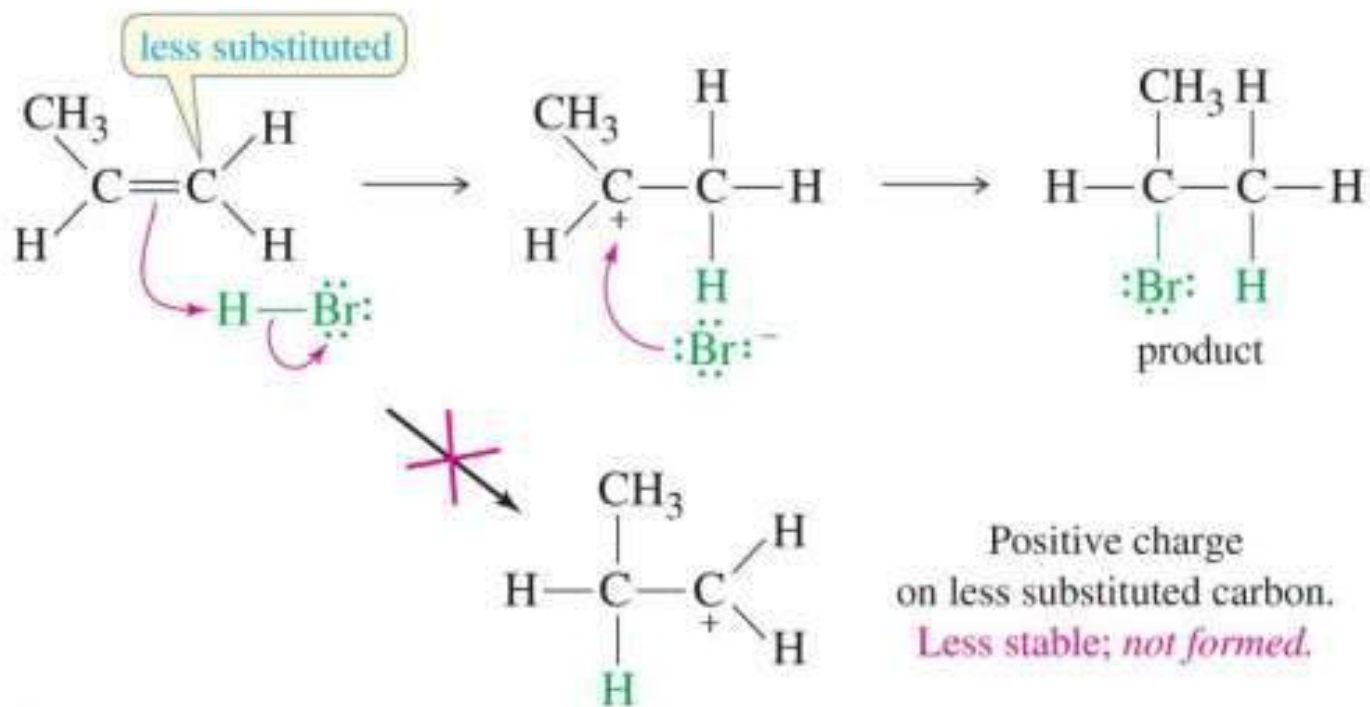
❑ **Markovnikov's Rule:** The addition of a proton acid to the double bond of an alkene results in a product with the acid hydrogen bound to the carbon atom that already has the greater number of hydrogens attached.

With unsymmetrical alkene



*Richer gets rich
Poor gets poorer*

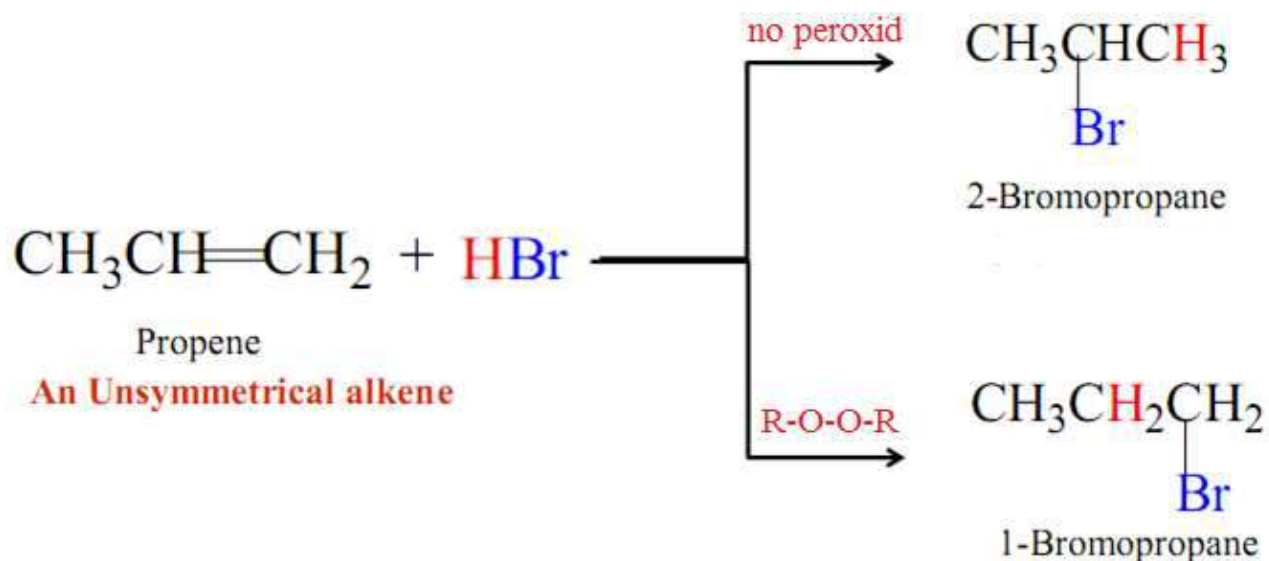
The electrophilic addition of HBr is said to be regiospecific, since it only gives one orientation of addition. Reactions that give such products are said to have Markovnikov orientation, and are Markovnikov products.



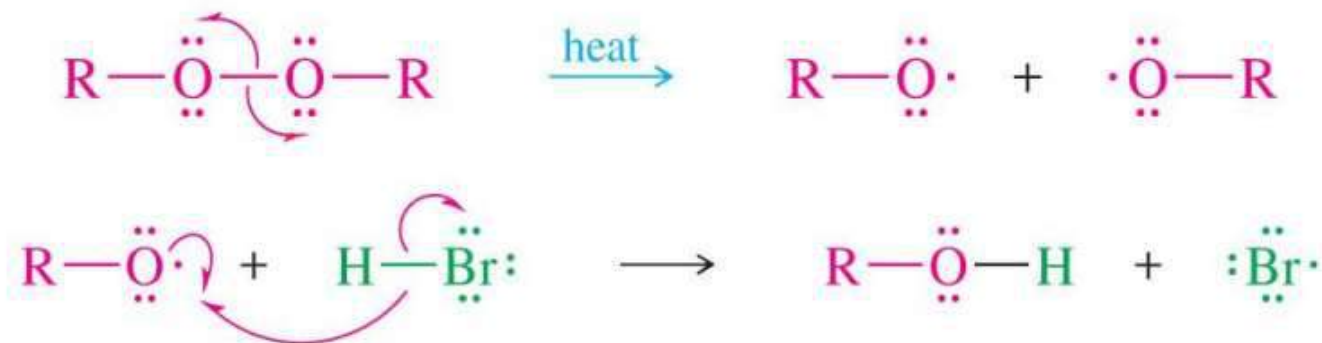
Free Radical addition to Alkenes

It is possible to obtain anti-Markovnikov products when HBr is added to alkenes in the presence of free radical initiators.

❑ **Anti-Markovnikov's Rule:** The addition of a proton acid to the double bond of an alkene in the presence of peroxide results in a product with the acid hydrogen bound to the carbon atom that has lowest number of hydrogen attached.



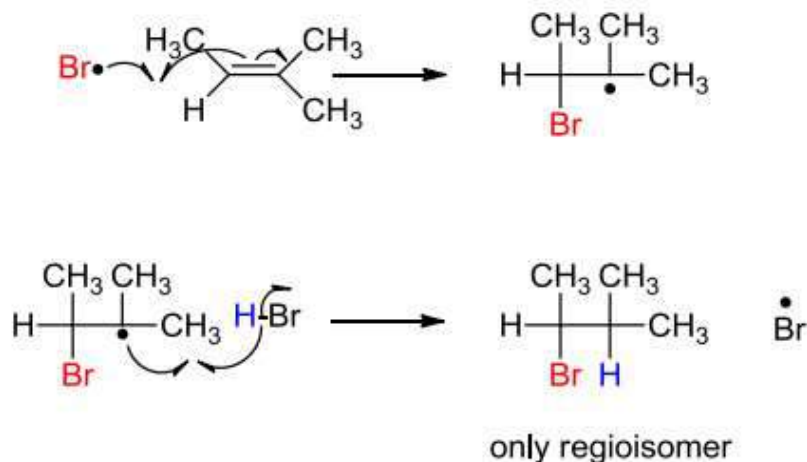
Initiation:



The oxygen-oxygen bond is weak, and is easily homolytically cleaved to generate two alkoxy radicals, which in turn abstract hydrogen to generate bromine radicals.

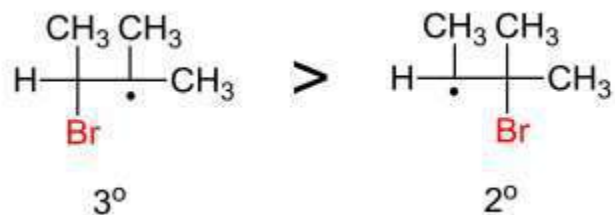
Propagation:

The bromine radical is electron deficient and electrophilic. The radical adds to the double bond, generating a carbon centered radical. This radical then abstracts hydrogen from a molecule of H-Br, giving the product, and another bromine radical. (Chain process). The orientation of this reaction is anti Markovnikov/ Peroxide effect.



To explain the different regiochemistry, we must look at the intermediates:

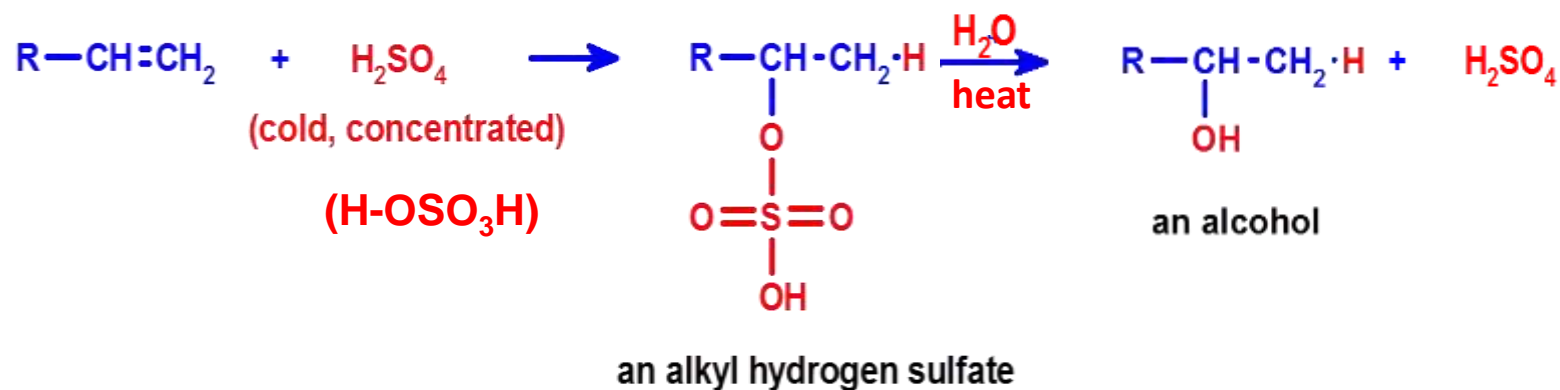
The electrophile adds to the least substituted end just like before, but this time the electrophile is a bromine radical (not a proton). This generates an intermediate radical.



Tertiary radicals are more stable than secondary radicals. The reaction goes through the most stable intermediate.

(Radical additions do not proceed with HCl or HI, only HBr)

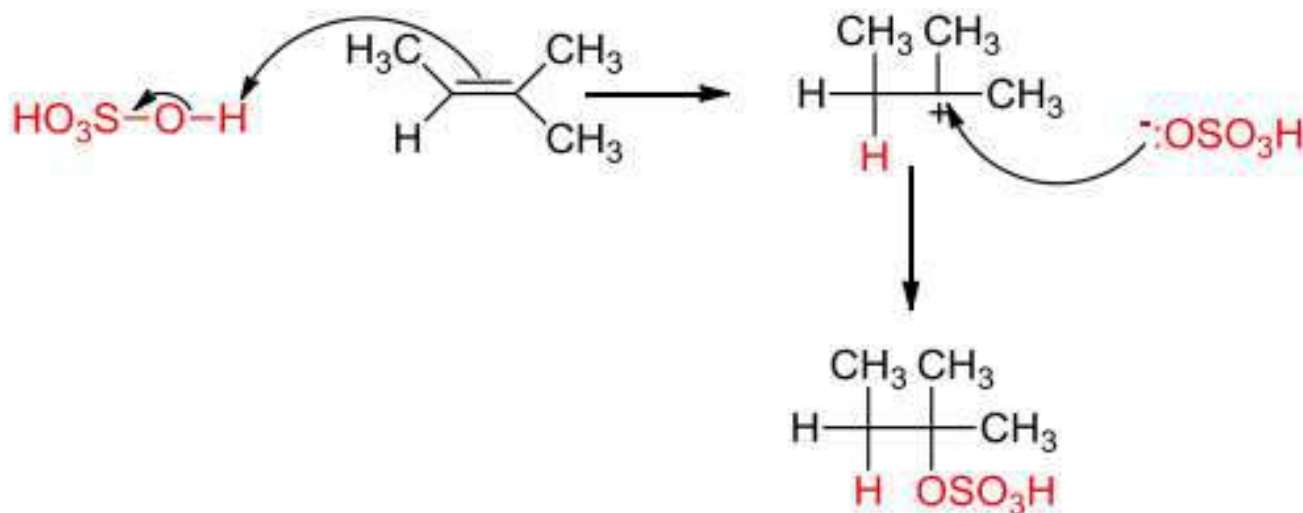
(4) Addition of Sulfuric acid



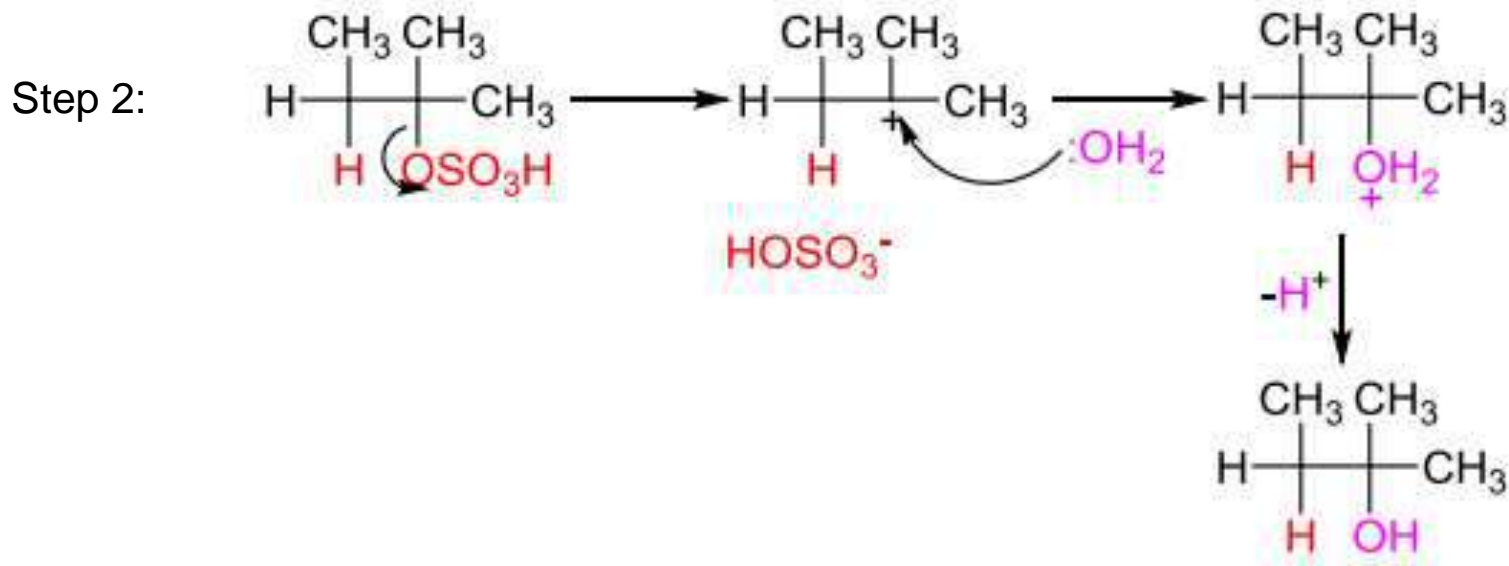
Follows Markovnikov's rule

Mechanism

Step 1:



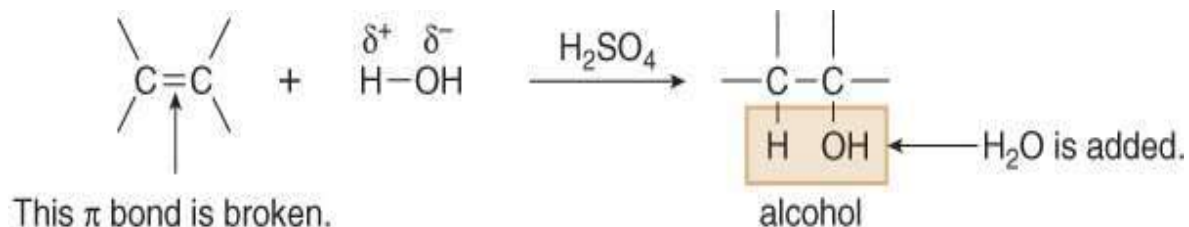
The alkyl hydrogen sulfate can be converted to an alcohol by boiling in water. This proceeds usually by S_N1 substitution where water is the nucleophile and bisulfate is the leaving group.



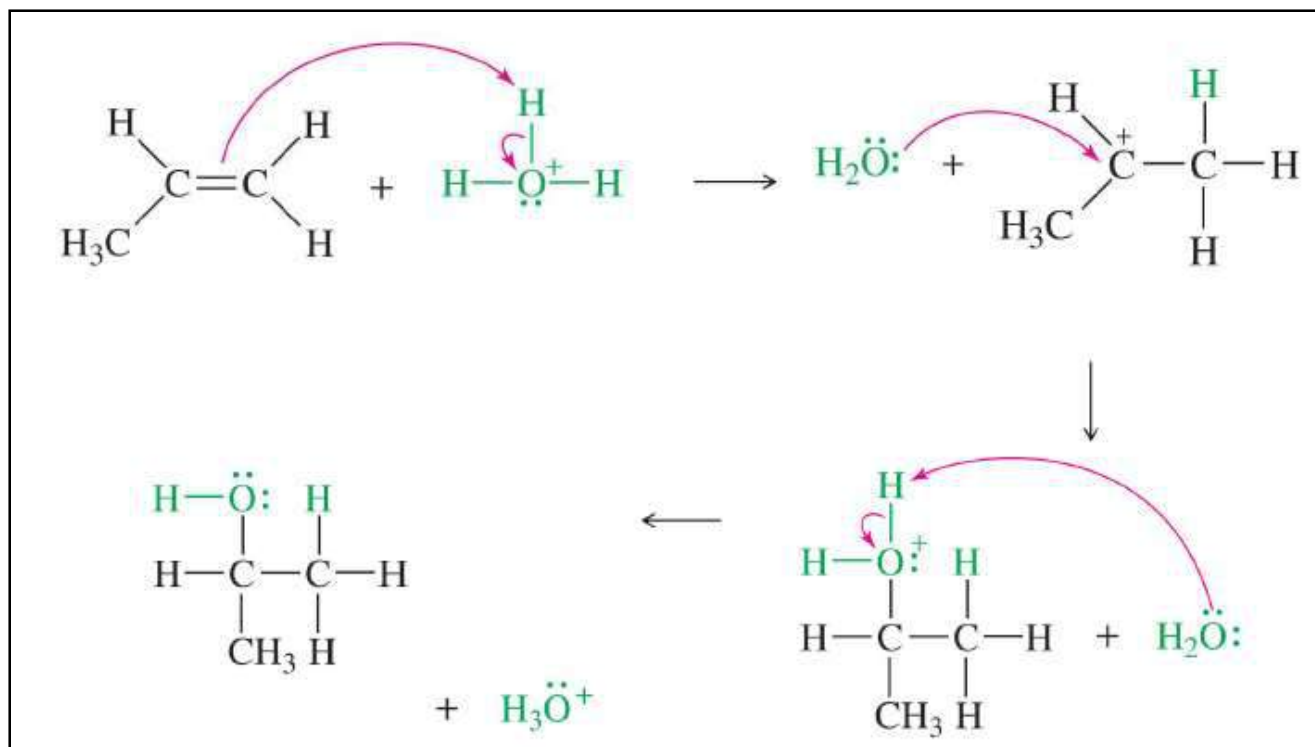
The product has Markovnikov orientation.

(5) Addition of Water : Hydration

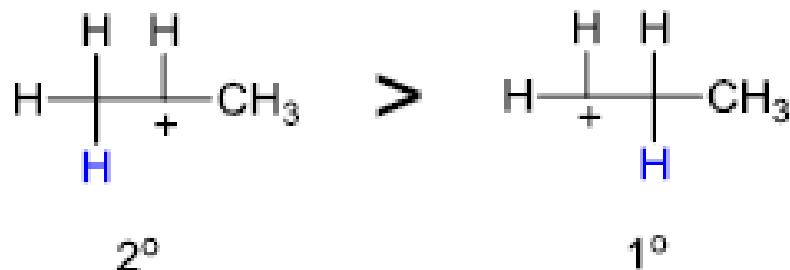
Follows Markovnikov's rule



Mechanism

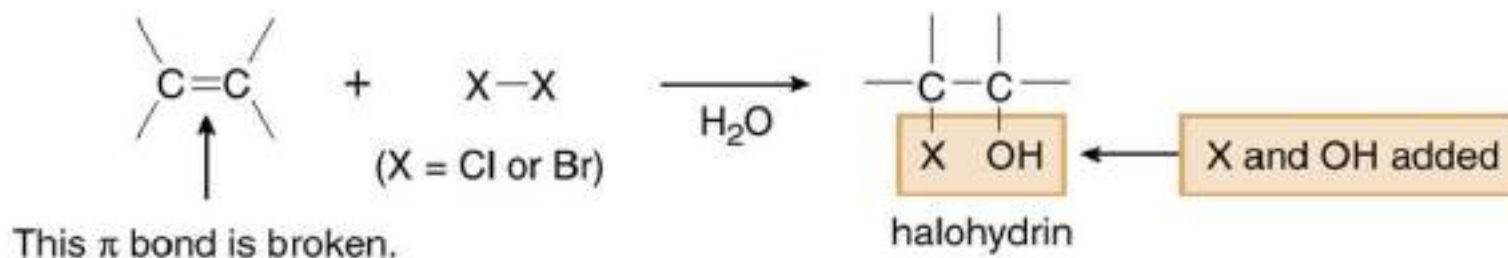


The hydration of alkenes is **regiospecific**. The regiochemistry is explained by the intermediate carbocation



The secondary carbocation is more stable than the primary carbocation.

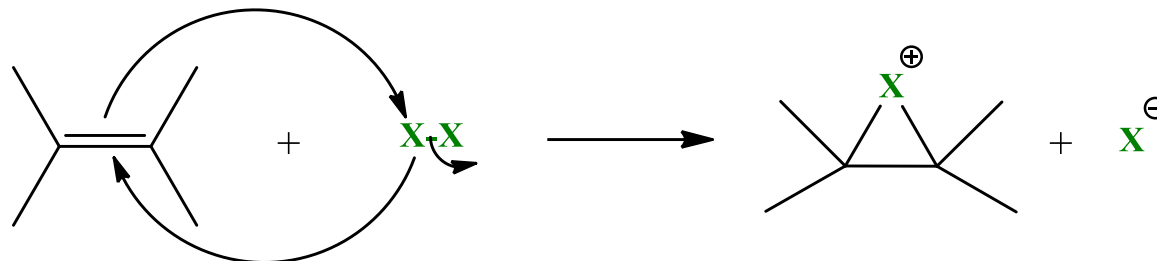
(6) Addition of HOX : Halohydrin Formation



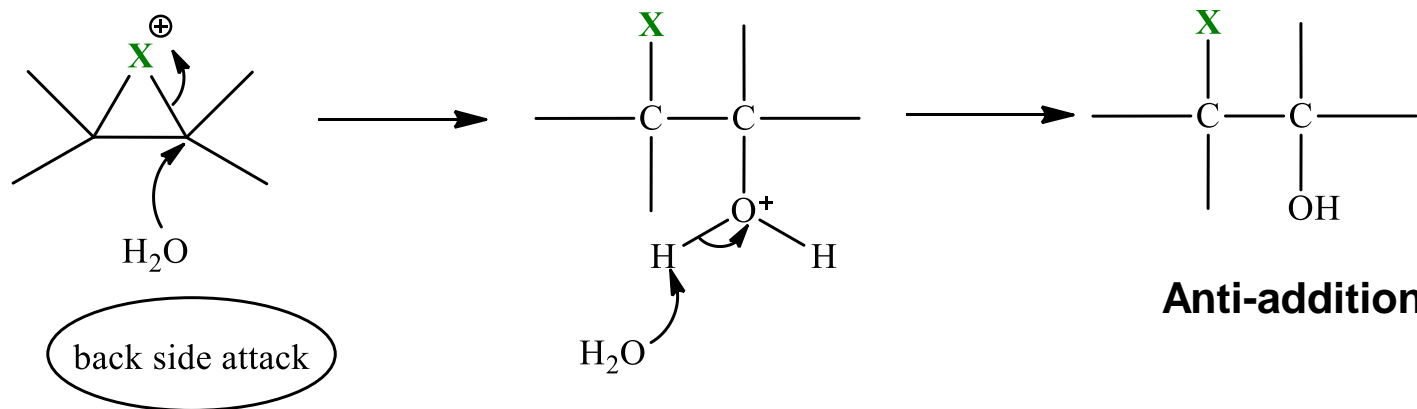
Mechanism

Follows Markovnikov's rule

Step 1:



Step 2:

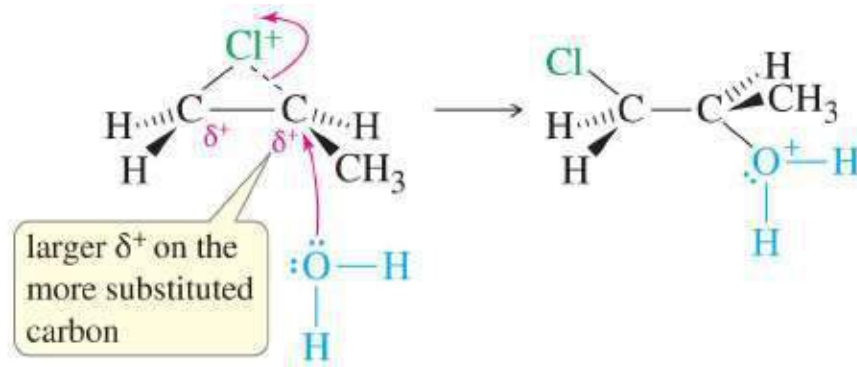


Orientation of Halohydrin Formation:

When propene reacts with chlorine water, the major product has the Cl bound to the less highly substituted carbon, and hydroxyl to the most highly substituted carbon.



In the halonium ring, the halogen is bound to both carbon atoms, which carry some partial positive charge. The more highly substituted carbon can bear more partial positive charge than the less highly substituted carbon. The nucleophile attacks the site of greatest partial positive charge, which is the more substituted carbon.



Since the electrophile (Cl) is bound to the least highly substituted carbon, and the nucleophile (OH) is bound to the most substituted carbon, this is **Markovnikov orientation**.

Oxidation reactions of Alkenes

- Addition of hydrogen is termed a chemical reduction.
- Addition of halogens across a double bond is called a **chemical oxidation**
- Oxidation is normally the formation of C-O bonds

There are three common methods for the introduction of oxygen containing functional groups into molecules via alkenes:

- 1) Epoxidation
- 2) Hydroxylation and
- 3) Oxidative cleavage

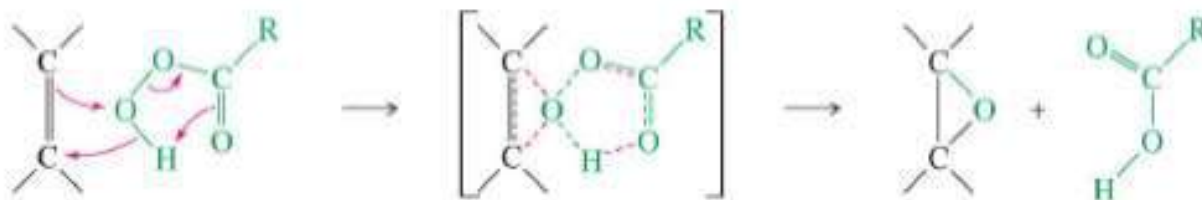
1) Epoxidation of Alkenes :

An epoxide (oxirane) is a three membered ring containing an oxygen. The most common reagent to convert an alkene to an epoxide is a peroxyacid.



Mechanism

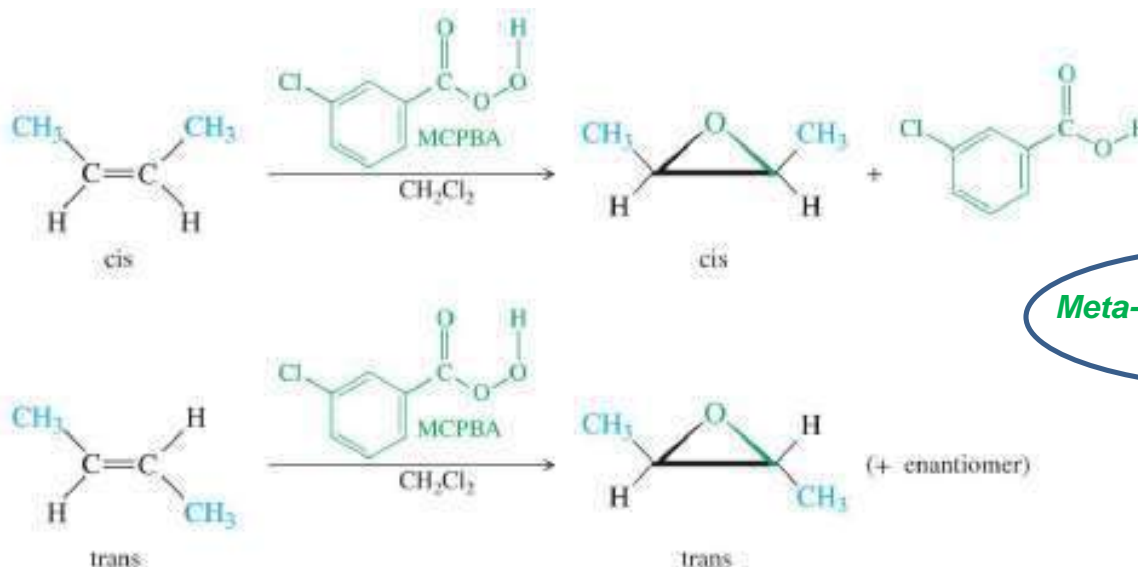
The epoxidation takes place in a concerted one step electrophilic process.



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.

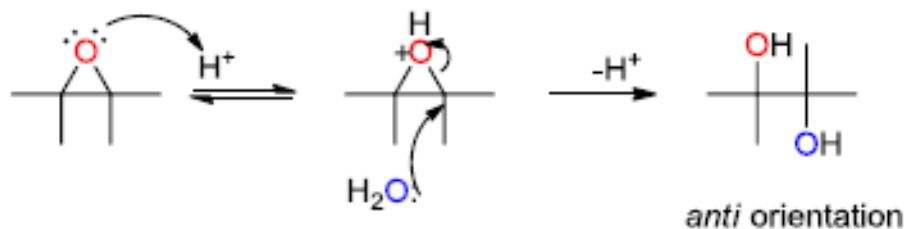
For example:



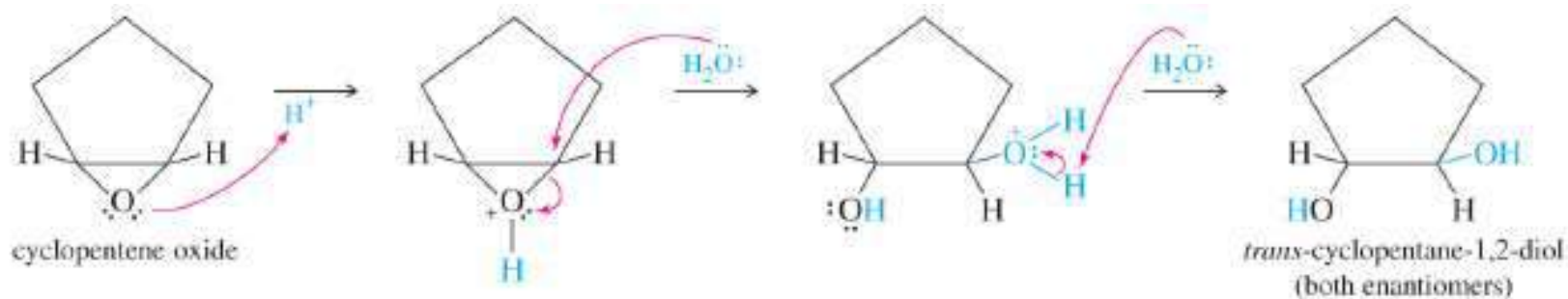
**Meta-chloroperbenzoic acid
(MCPBA)**

Acid catalyzed Ring Opening (anti hydroxylation)

Generally epoxides are stable compounds, but they can be easily ring opened. Moderate acids can protonate the ring oxygen (creating a good leaving group) and then any nucleophile can open the ring via back side attack to give anti orientation type products.



Mild acid reacts with epoxides to generate anti 1,2-diols (glycols).



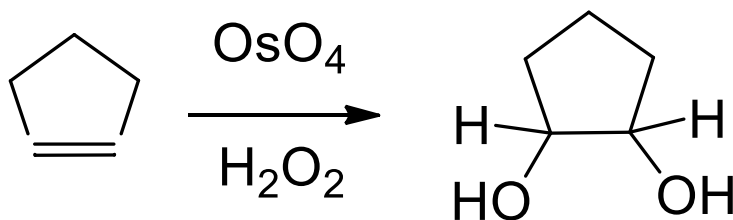
2) Hydroxylation of Alkenes (Syn hydroxylation)

Addition of a hydroxyl group to the double bond is called hydroxylation. The two most common methods for syn hydroxylation:

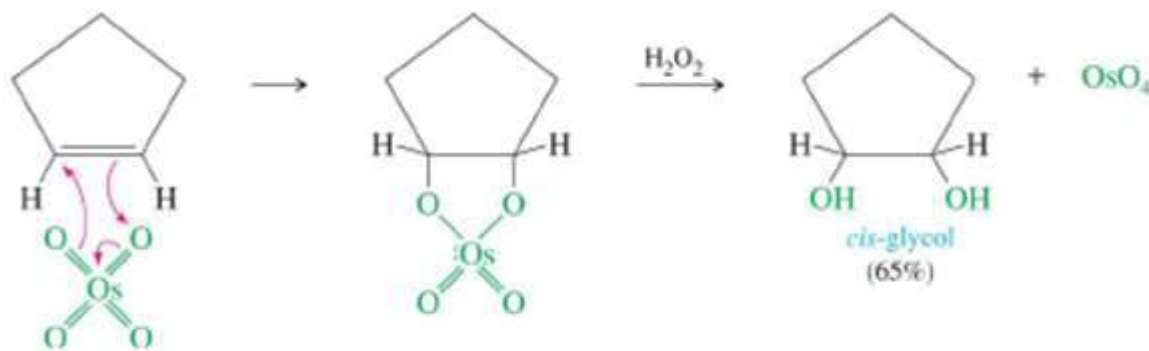
- a) Osmium tetroxide with hydrogen peroxide
- b) Potassium permanganate

a) Osmium tetroxide with hydrogen peroxide

Osmium tetroxide reacts with alkene in a concerted step to form a cyclic osmate ester which is hydrolyzed into syn diol by hydrogen peroxide, which also reoxidizes the osmium catalyst. The two carbon-oxygen bonds are formed simultaneously and the oxygen atoms add to the same face of the double bond (syn- addition).

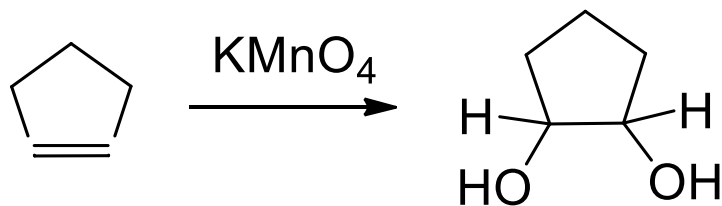


Mechanism

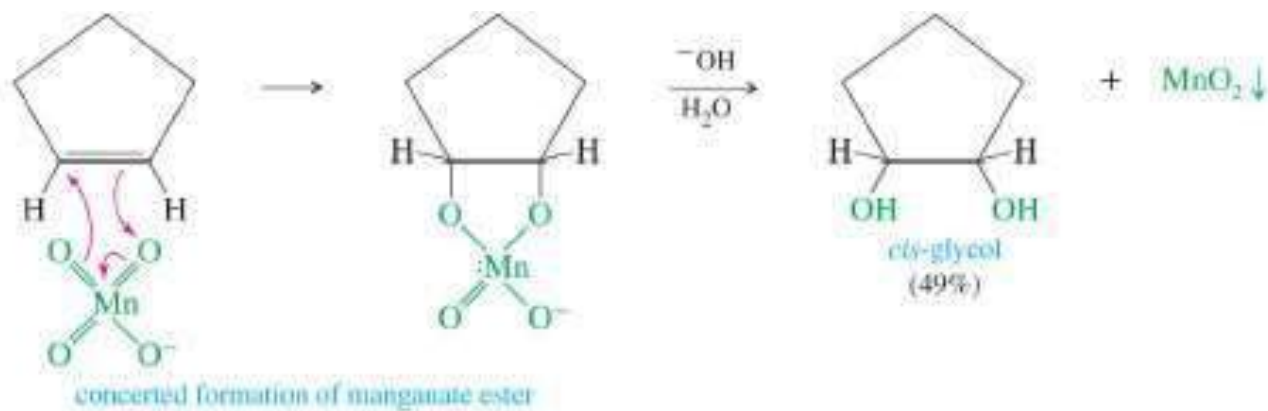


b) Potassium permanganate hydroxylation

An alkaline, cold solution of potassium permanganate will do exactly the same transformation as osmium tetroxide. The intermediate cyclic ester again forces syn hydroxylation.



Mechanism



Potassium permanganate is cheaper and less toxic than osmium tetroxide, but gives the product in slightly lower yield.

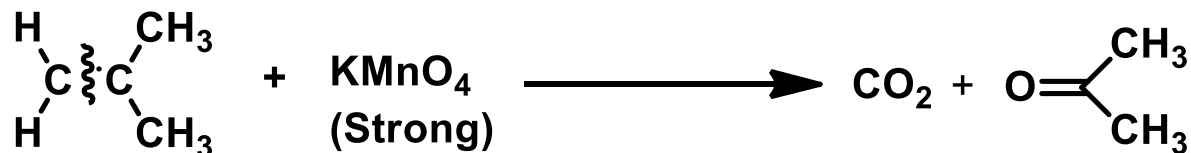
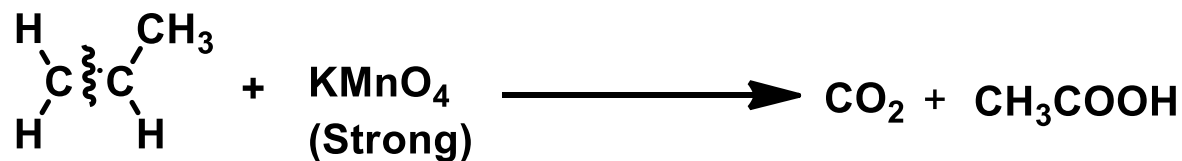
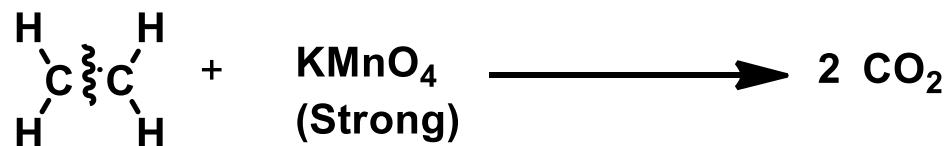
3) Oxidative Cleavage

The two most common methods for Oxidative Cleavage:

- Strong permanganate (KMnO_4)**
- Ozonolysis**

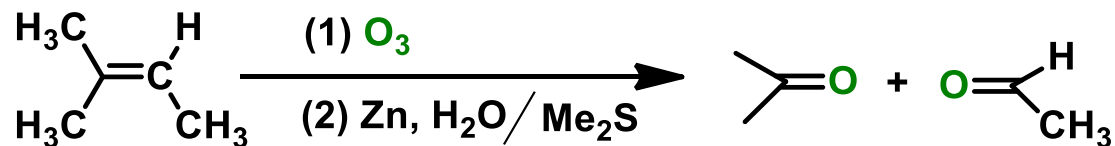
a) Strong permanganate (KMnO_4)

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. Disubstituted alkene carbons are oxidatively cleaved to ketones. Unsubstituted alkene carbons are oxidized to carbon dioxide.

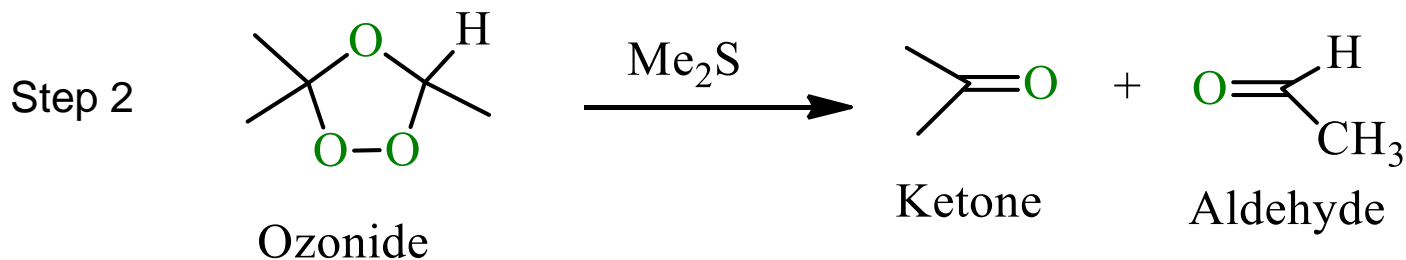
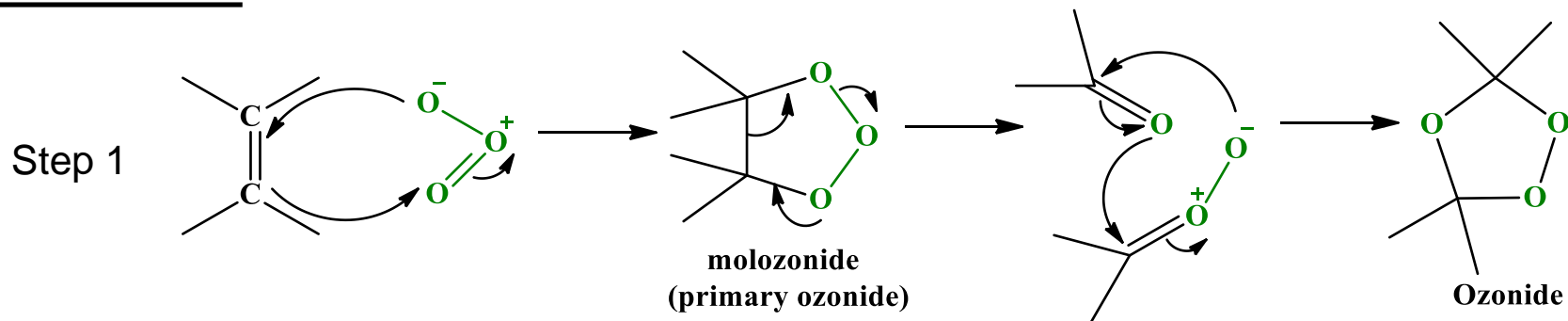


b) Ozonolysis

Ozone can cleave double bond to give ketones or aldehydes. The intermediate ozonide reacts with reducing agents like dimethyl sulfide/zinc, H_2O to produce DMSO and the carbonyl products.

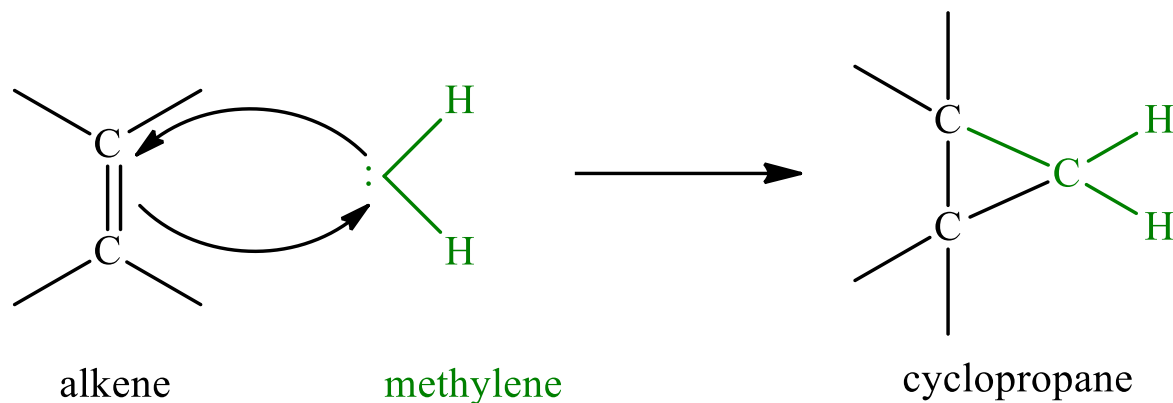


Mechanism



Addition of Carbenes

Carbenes are neutral, reactive intermediates with a divalent carbon and a lone pair.



Carbenes are potent electrophiles and react with double bonds to form 3 membered rings (cyclopropanes).

There are 3 classical ways to generate carbenes:

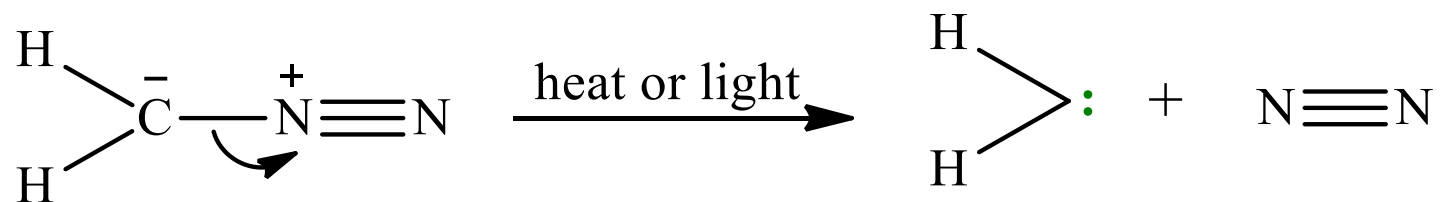
(1) diazomethane

(2) Simmons-Smith Reaction

(3) Alpha Elimination from Haloforms

1) Diazomethane

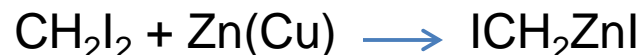
The heating or photolysis of diazomethane generates a carbene and nitrogen gas.



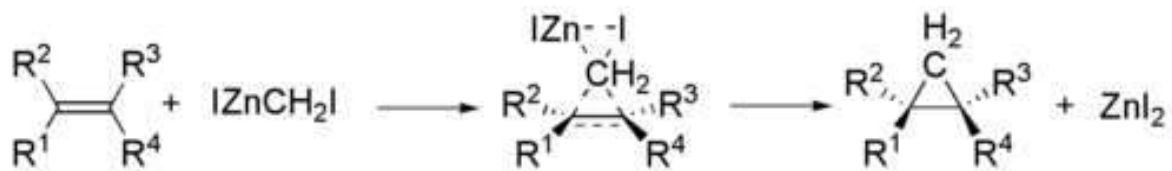
However, diazomethane is toxic and explosive, and it often forms carbenes that are so reactive that numerous side products are formed

2) Simmons-Smith Reaction

The reaction of diiodomethane with zinc metal in the presence of Cu(I) salts generates a carbenoid species ICH_2ZnI . (It behaves like a carbene).

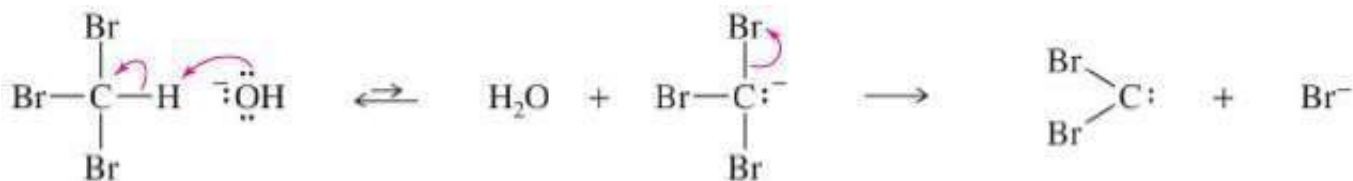


Mechanism

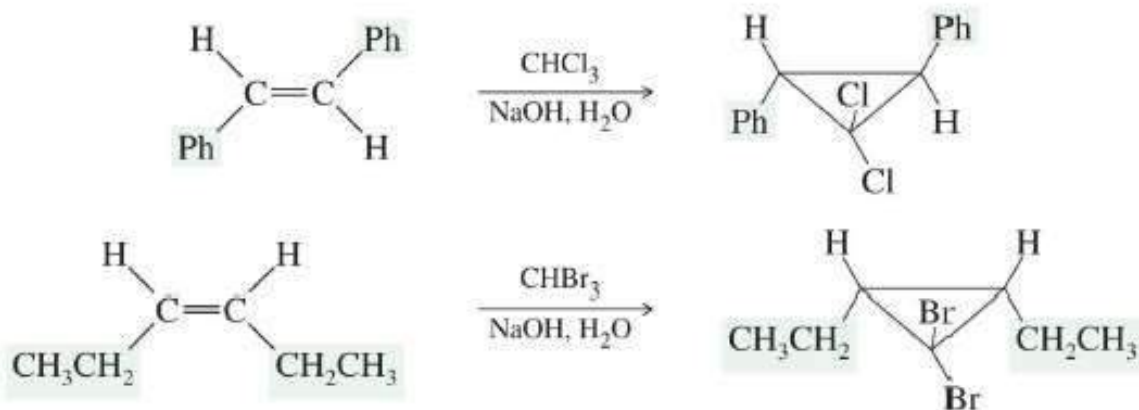


3) Alpha Elimination from Haloforms

In the presence of a strong enough base, Bromoform can have its proton removed, and the tribromomethyl anion will eliminate a bromide ion to generate dibromocarbene.

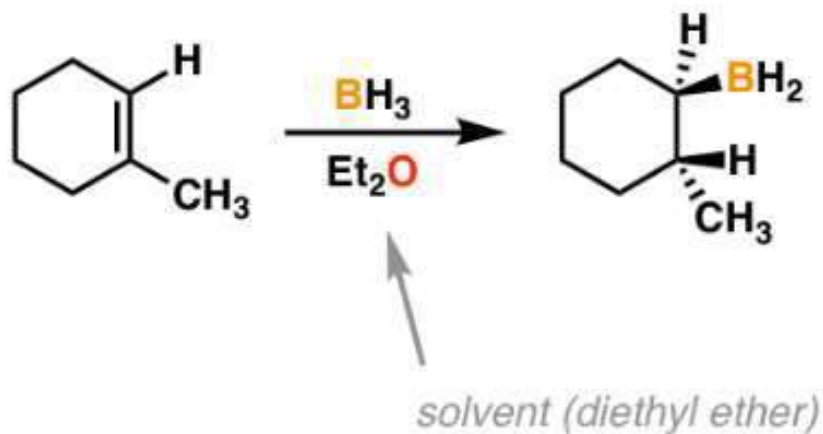
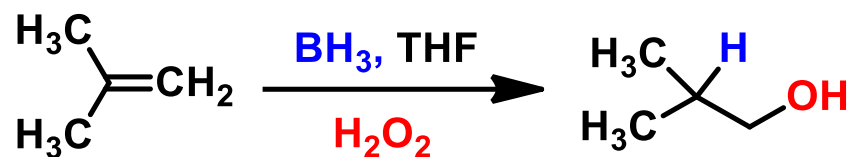


This type of carbene reacts with **retention of stereochemistry of the reactants**



Hydroboration-Oxidation reaction

Borane adds to alkenes with anti-Markovnikov orientation, and these alkylboranes can then be oxidized to alcohols .



Regiochemistry

"anti-Markovnikov"

H adds to carbon with fewest attached hydrogens

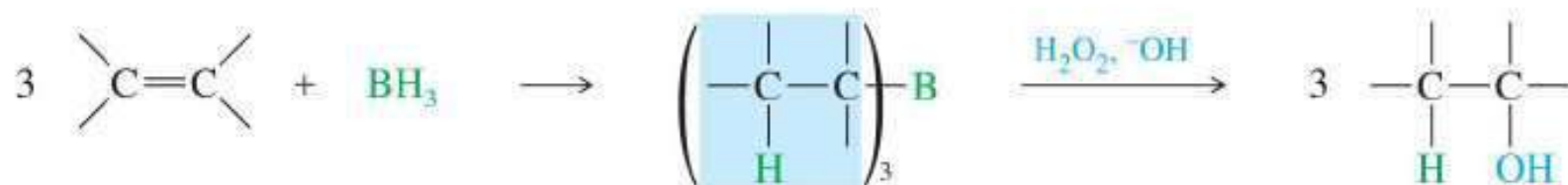
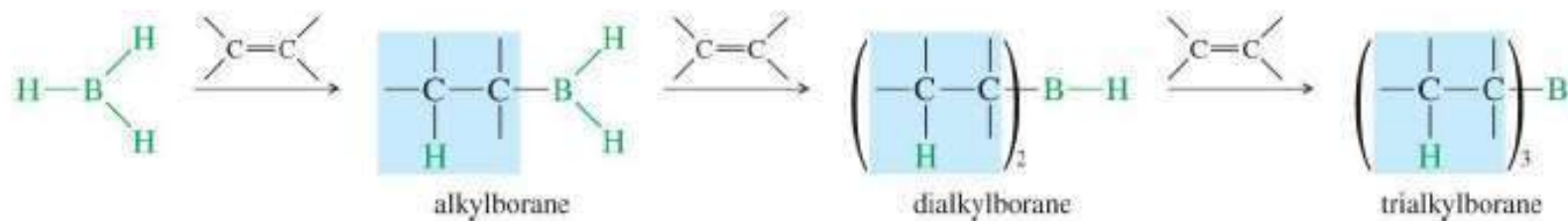
Stereochemistry

"Syn"

H and B add to same face of alkene

- No rearrangements observed
- Never observe incorporation of solvent

Stoichiometry of the Reaction



Mechanism

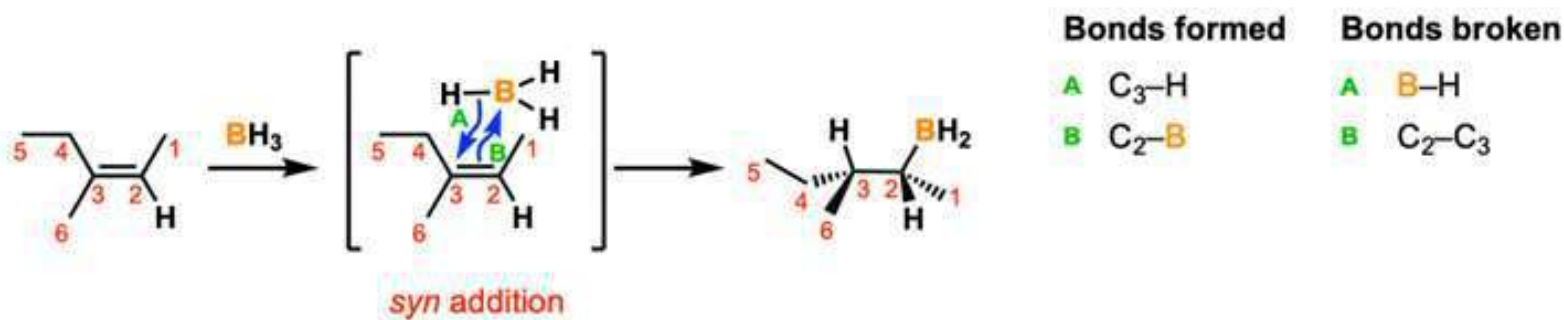
In reality, each B-H bond can add across a double bond.

- ❑ Borane is an electrophilic molecule, and adds to the least highly substituted end of the double bond in a one step process to generate an alkylborane.
- ❑ This places partial positive charge on the more highly substituted end of the double bond (which is more stable).

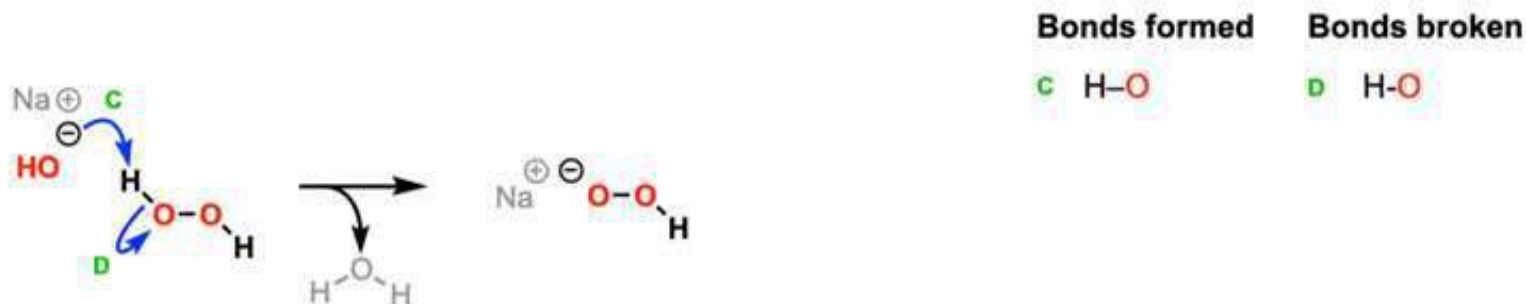
□ Hydroboration also gives syn addition of the boron and hydrogen (and therefore the –OH and –H).

□ This is a stereospecific reaction

Step 1: Hydroboration



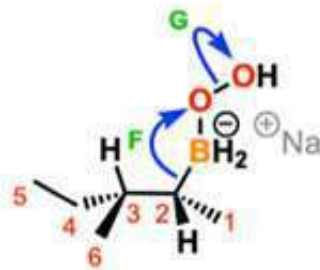
Step 2: Deprotonation of hydrogen peroxide



Step 3: Attack of NaOOH on boron



Step 4: Migration of C-B bond to oxygen



Bonds formed

E O-B

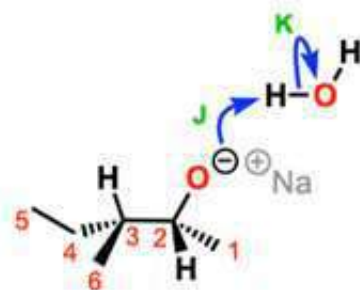
F C₂-O

Bonds broken

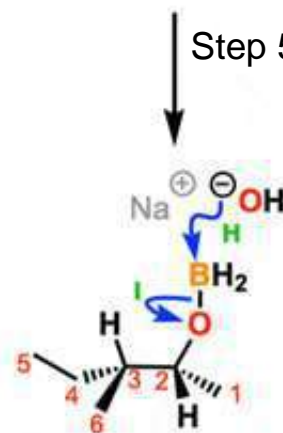
F C₂-B

G O-O

Step 6: Protonation of oxygen



Step 5: Attack of NaOH on OBH₂



Bonds formed

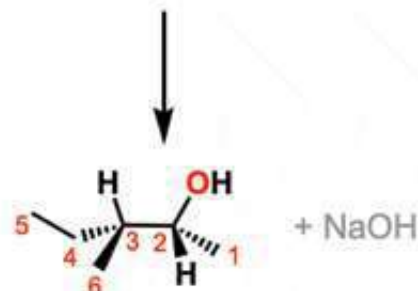
H O-B

J H-O

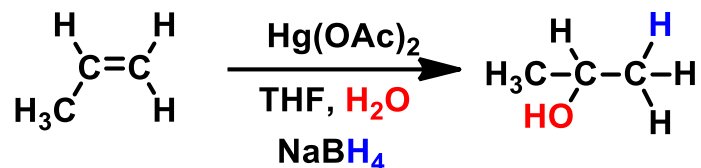
Bonds broken

I O-B

K H-O



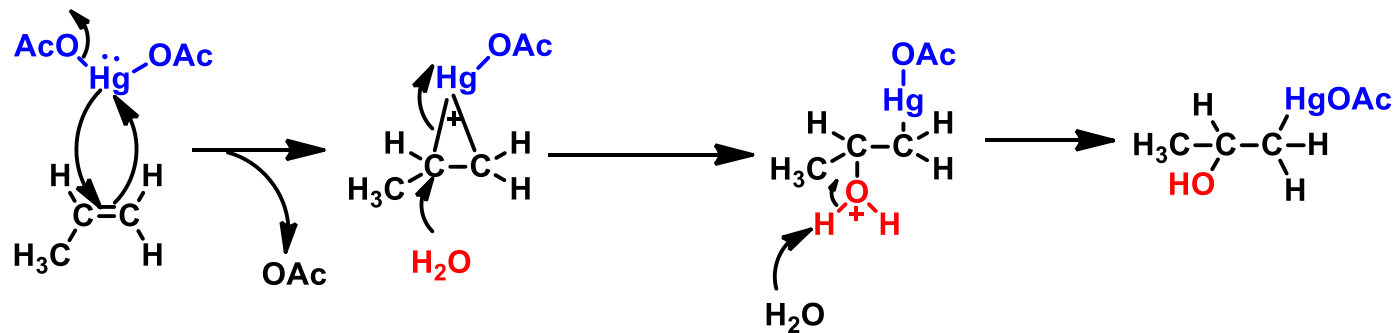
Oxymercuration-Demercuration



Follows Markovnikov's rule

Oxymercuration–demercuration process has two advantages over acid-catalyzed addition: (i) it does not require acidic conditions and (ii) no carbocation intermediate is involved, so that rearrangements do not occur.

OXYMERCURATION



DEMERCURATION

