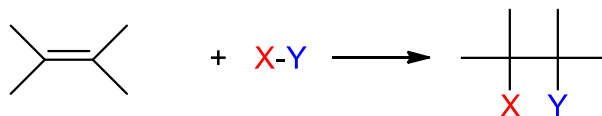# Reactions of Alkenes

Since σ bonds are **stronger** than π bonds, double bonds tend to react to convert the double bond into σ bonds

This is an <u>addition</u> reaction.   (Other types of reaction have been *substitution* and *elimination*).
Addition reactions are typically exothermic.

<u>Electrophilic Addition</u>
The π bond is localized above and below the C-C σ bond. The π electrons are relatively far away from the nuclei and are therefore <u>loosely</u> bound.
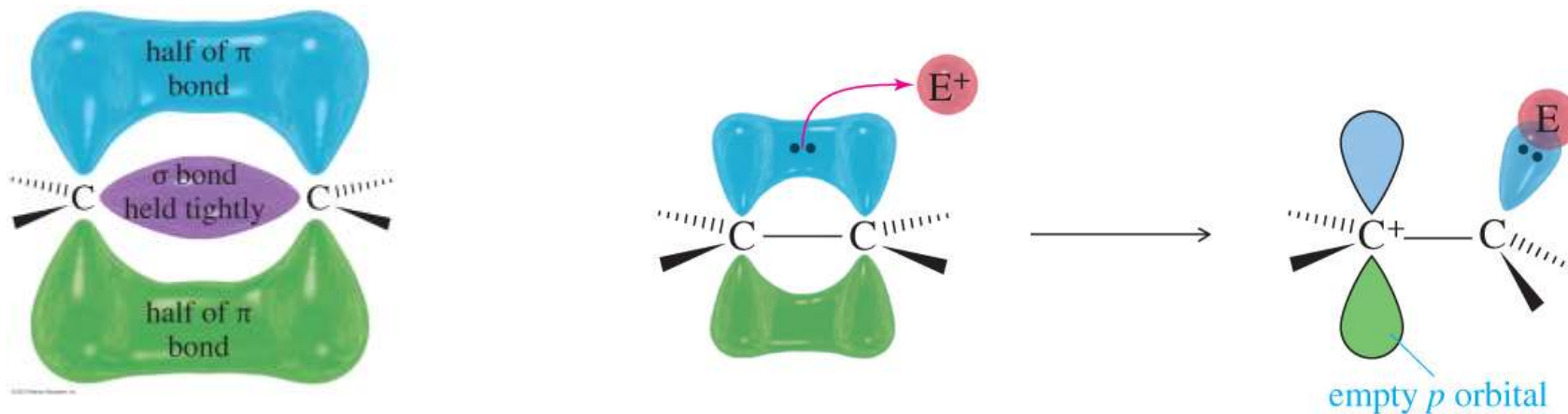
An **electrophile** will attract those electrons, and can pull them away to form a new bond.
This leaves one carbon with only 3 bonds and a +ve charge (carbocation).

The double bond acts as a **nucleophile** (attacks the electrophile).

In most cases, the cation produced will react with another nucleophile to produce the final overall electrophilic addition product.
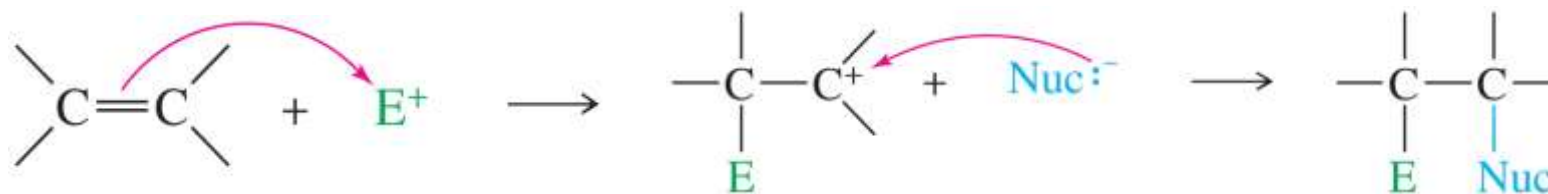
Electrophilic addition is probably the most common reaction of alkenes.

Consider the electrophilic addition of H-Br to but-2-ene:
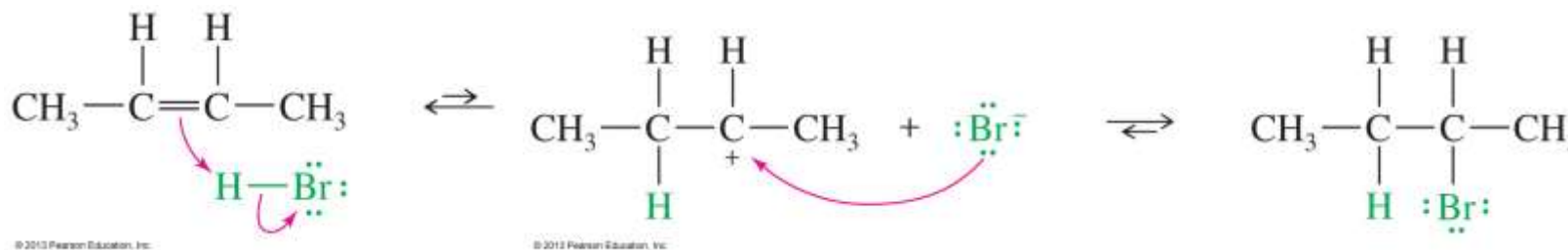
The alkene abstracts a **proton** from the HBr, and a carbocation and bromide ion are generated.

The bromide ion quickly attacks the cationic center and yields the final product.

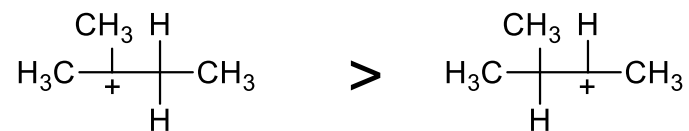In the final product, H-Br has been added across the double bond.

Orientation of Addition

Consider the addition of H-Br to 2-methylbut-2-ene:
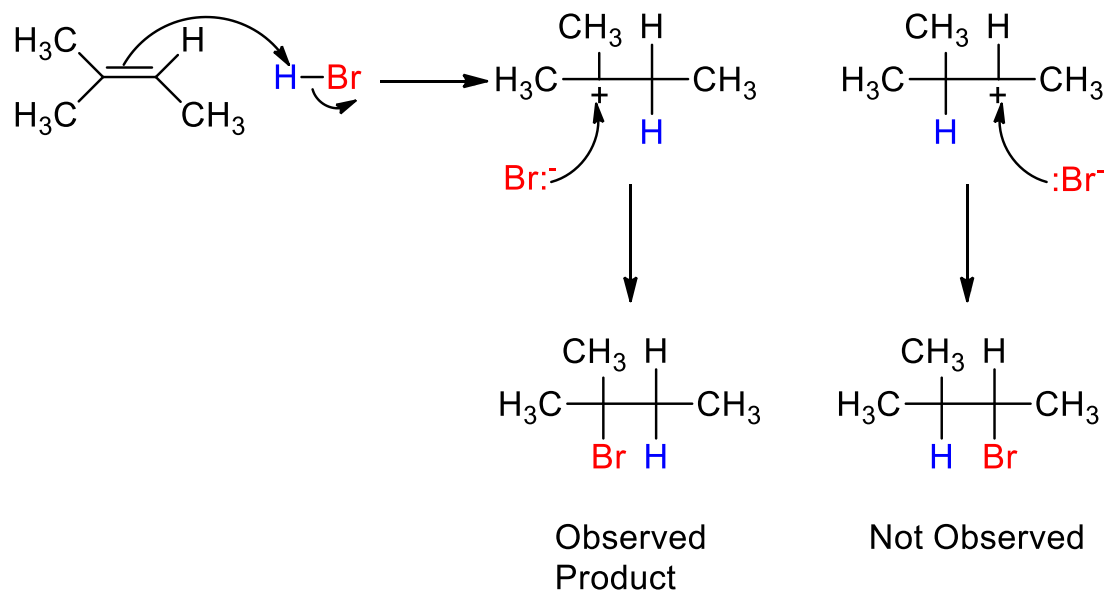
There are *two* possible products arising from the two different ways of adding H-Br across the double bond. But only one is observed.

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

Tertiary carbocations are more stable than secondary.

The protonation occurs at the least highly substituted end so that the cation produced is at the most highly substituted end (and therefore more stable).

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.

(More generally: In an electrophilic addition to an alkene, the electrophile adds in such a way that it generates the most stable intermediate).

Reactions that give such products are said to have Markovnikov orientation, and are Markovnikov products.

The electrophilic addition of HBr is said to be **regiospecific**, since it only gives one orientation of addition.
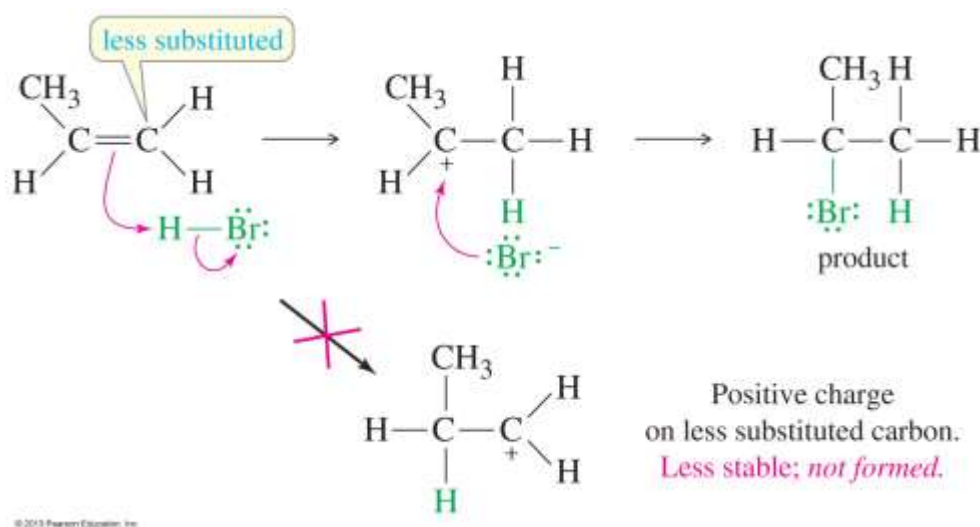
(HCl and HI perform analogous electrophilic addition reactions).

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.

The free radical initiators change the mechanism of addition from *electrophilic addition* to *free radical addition*.
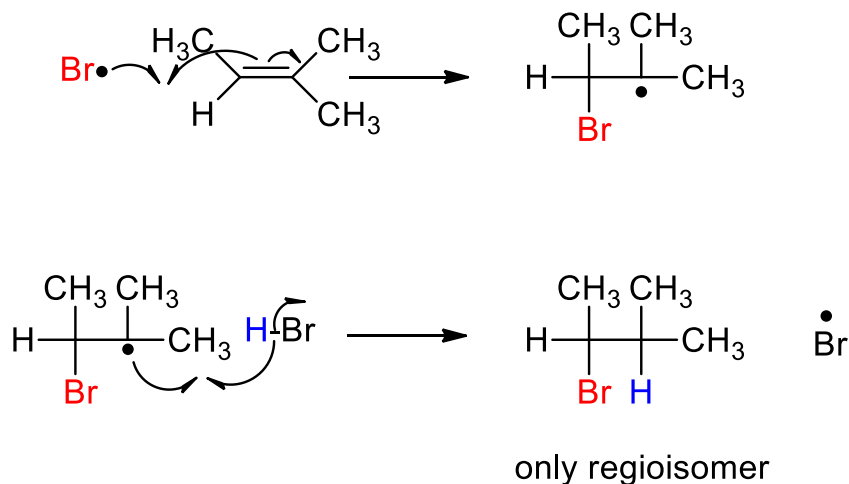
This change of mechanism gives rise to the opposite regiochemistry.

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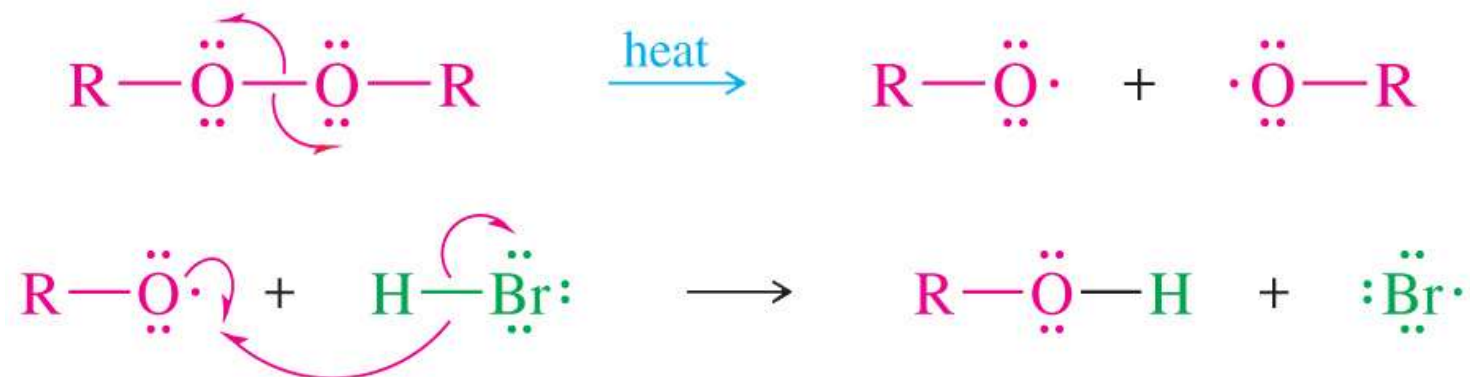
The oxygen-oxygen bond is weak, and is easily homolytically cleaved to generate two alkoxy radicals, which in turn abstract hydrogen to generate bromine radicals.

Propagation:

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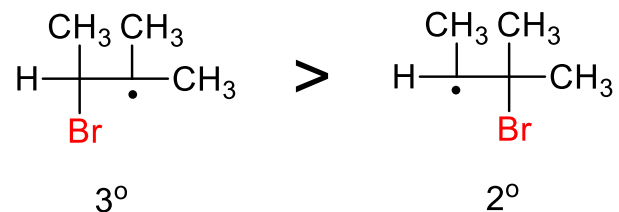
This radical then abstracts hydrogen from a molecule of H-Br, giving the product, and another bromine radical. (Chain process).

The orientation of this reaction is **anti Markovnikov**.

The reversal of regiochemistry through the use of peroxides is called the **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.

$$
\begin{array}{ccc}
\underset{\text{Br}}{\underset{|}{\underset{\bullet}{\text{H}-\overset{\overset{\text{CH}_3}{|}}{\underset{}{\text{C}}}-}}}\text{CH}_3 & > & \underset{\text{Br}}{\underset{|}{\underset{}{\text{H}-\overset{\overset{\text{CH}_3}{|}}{\underset{\bullet}{\text{C}}}-}}}\text{CH}_3
\end{array}
$$

3°   2°

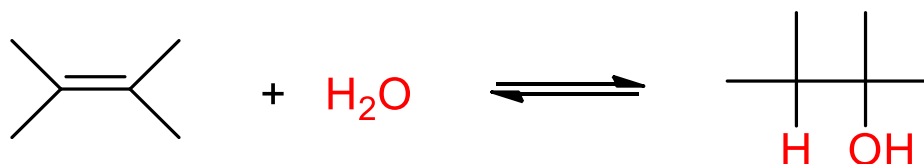Tertiary radicals are more stable than secondary radicals.

The reaction goes through the most stable intermediate. (It still follows the expanded Markovnikov rules, but the orientation is anti Markovnikov).

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

Addition of Water

Alkenes can be converted to alcohols.

It is the *reverse* reaction of the dehydration of alcohols to give alkenes.

$$\diagdown\hspace{-0.5em}\diagup C=C\diagdown\hspace{-0.5em}\diagup \quad + \quad H_2O \quad \rightleftharpoons \quad \overset{\ \ }{\underset{H \ \ OH}{\text{—C—C—}}}$$

The principle of **microscopic reversibility** states that a forward reaction and a reverse reaction taking place under the same conditions must follow the **same** reaction pathway in microscopic detail.

(Logically, it seems sensible that the lowest energy T.S.'s and intermediates for the forward reaction would be the same for the reverse reaction but in the opposite order).

So it is no surprise that the mechanism for hydration of alkenes is identical to that of dehydration of alcohols, but in the reverse order of steps.
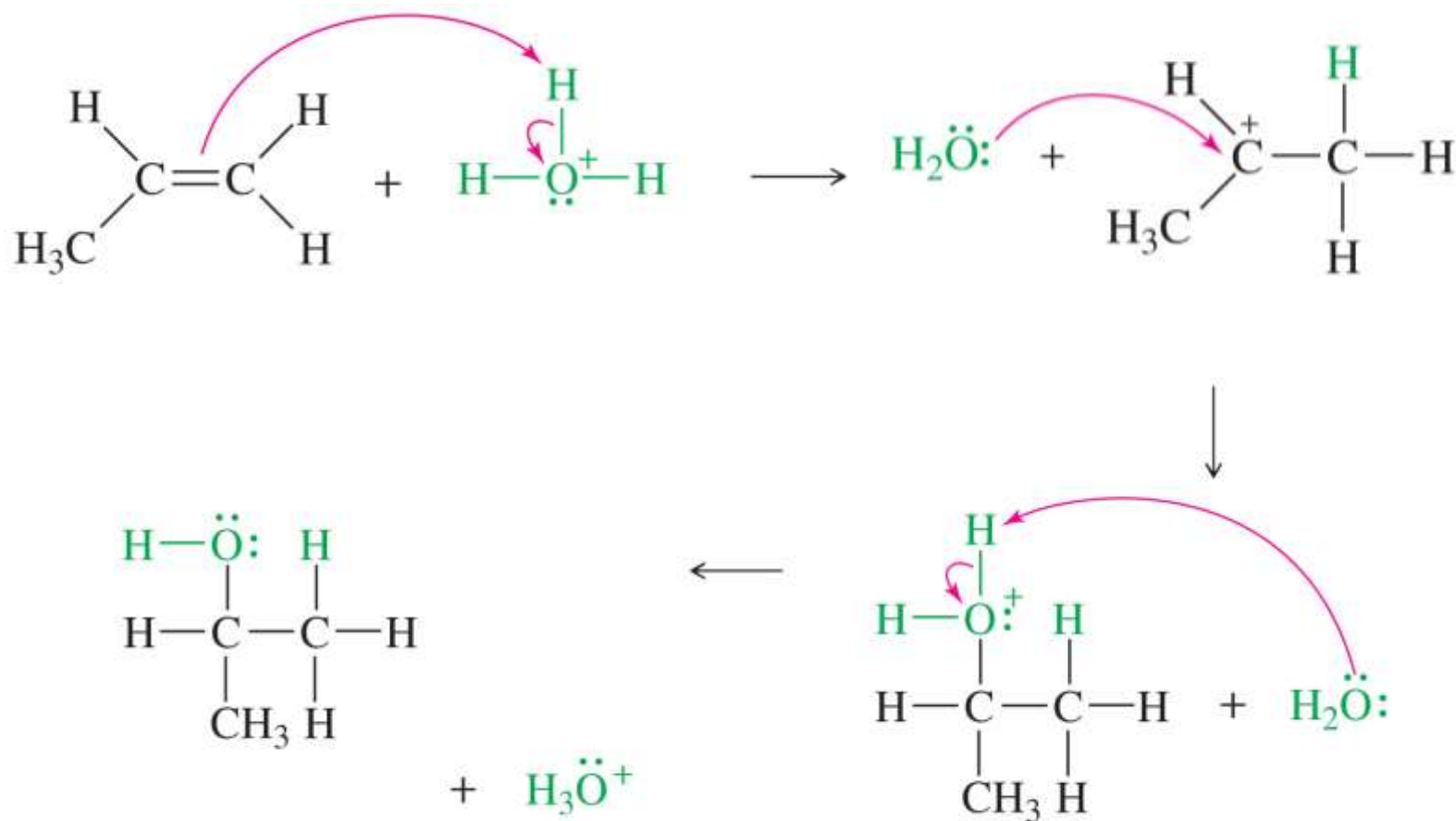
The first step is the protonation of the double bond to generate a carbocation, which in turn is attacked by water (a nucleophile).

The final step is quick proton removal to generate the product.

The hydration of alkenes is **regiospecific**.

The orientation is Markovnikov since the proton has added to the least highly substituted end, and the hydroxyl to the most highly substituted end.

The regiochemistry is explained by the intermediate carbocation:


$$2^o \qquad\qquad 1^o$$
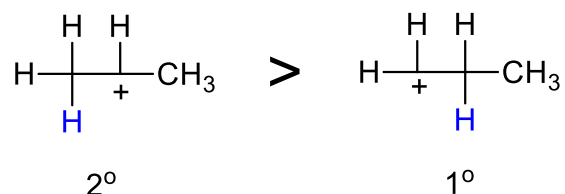
The secondary carbocation is more stable than the primary carbocation.

The reaction of dilute acid to hydrate alkenes is not a fantastic practical route due to insolubility problems, and typically two other indirect approaches are used.

(1) Addition of sulfuric acid followed by hydrolysis
(2) Oxymercuration-demercuration
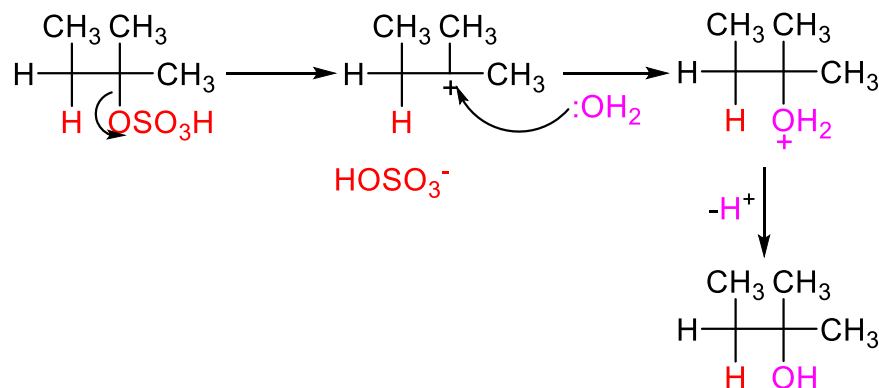
Addition of Sulfuric Acid followed by Hydrolysis
The alkene reacts with conc. sulfuric acid to give an alkyl hydrogen sulfate, which then in turn is hydrolyzed to give the alcohol.

alkene   alkyl hydrogen   alcohol
                    sulfate
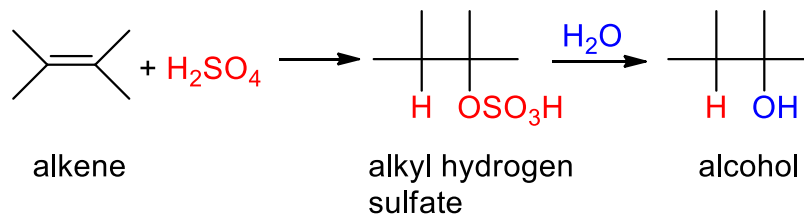
The formation of the alkyl hydrogen sulfate arises from initial protonation on the double bond, and the intermediate carbocation is trapped by the bisulfate anion. (Markovnikov addition).

HO_3S-O-H H_3C CH_3 / H CH_3 → CH_3 CH_3 / H—| |—CH_3 / H $^-$:OSO_3H

CH_3 CH_3 / H—| |—CH_3 / H OSO_3H
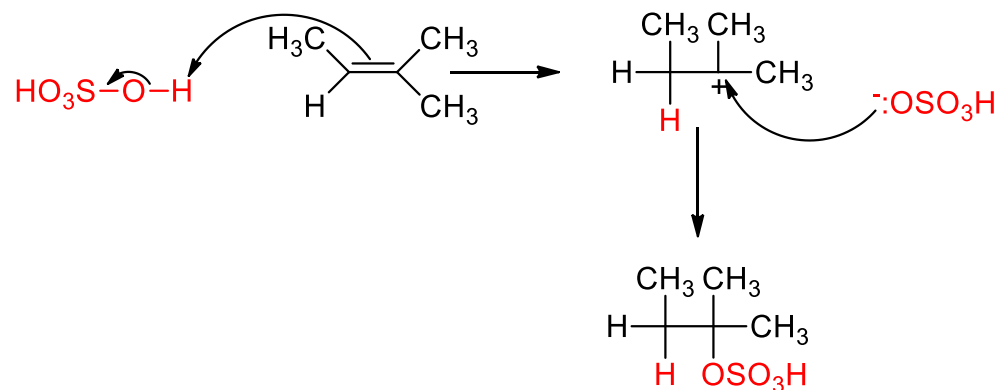
The alkyl hydrogen sulfate can be converted to an alcohol by boiling in water.
This proceeds usually by S_N1 substitution where water is the nucleophile and bisulfate is the leaving group.

CH_3 CH_3 / H—| |—CH_3 / H OSO_3H → CH_3 CH_3 / H—| |—CH_3 / H :OH_2 $HOSO_3^-$ → CH_3 CH_3 / H—| |—CH_3 / H OH_2 (+)

$-H^+$

CH_3 CH_3 / H—| |—CH_3 / H OH

The product has the same regiochemistry as an alcohol formed by direct hydration of the same alkene.
(*Markovnikov orientation*).

Oxymercuration-Demercuration

This is another alternative for converting alkenes to alcohols with Markovnikov orientation. This method has the advantage of not involving free carbocationic species, and thus removes the possibility of **rearrangements**.


(Markovnikov orientation)
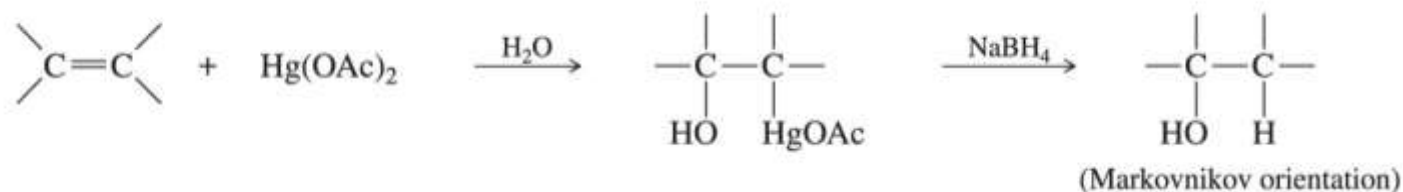
The reagent is called mercuric acetate, and is usually abbreviated to $Hg(OAc)_2$. In solution it ionizes into acetate ion and a positively charged mercury species which is very **electrophilic**.

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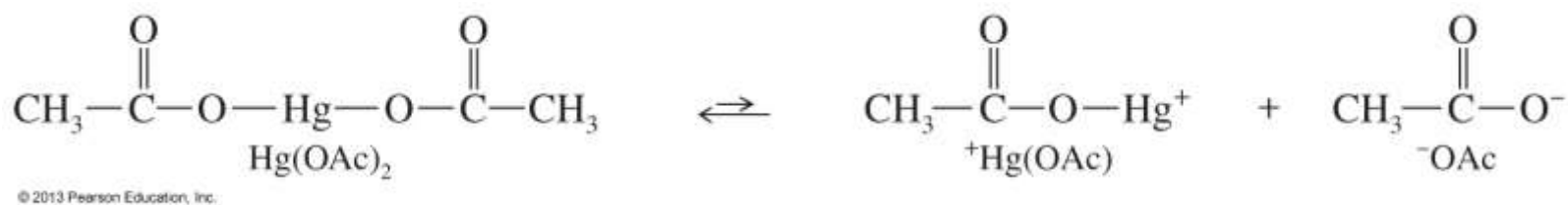
Oxymercuration is the electrophilic attack of this species on a double bond, giving a 3 membered ring compound called a mercurinium ion.


mercurinium ion

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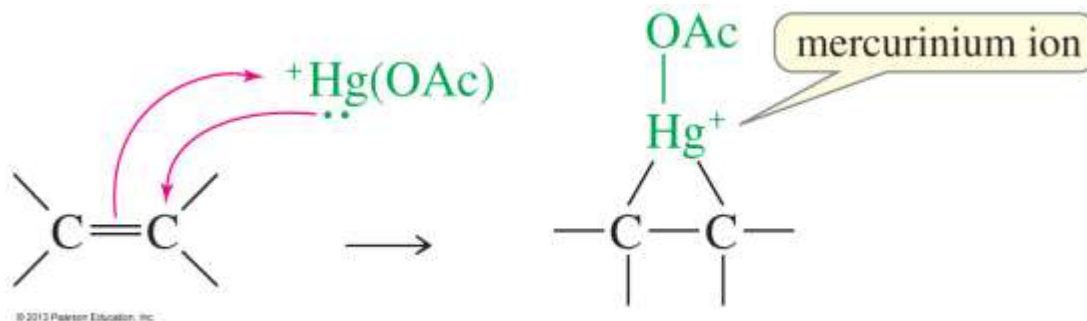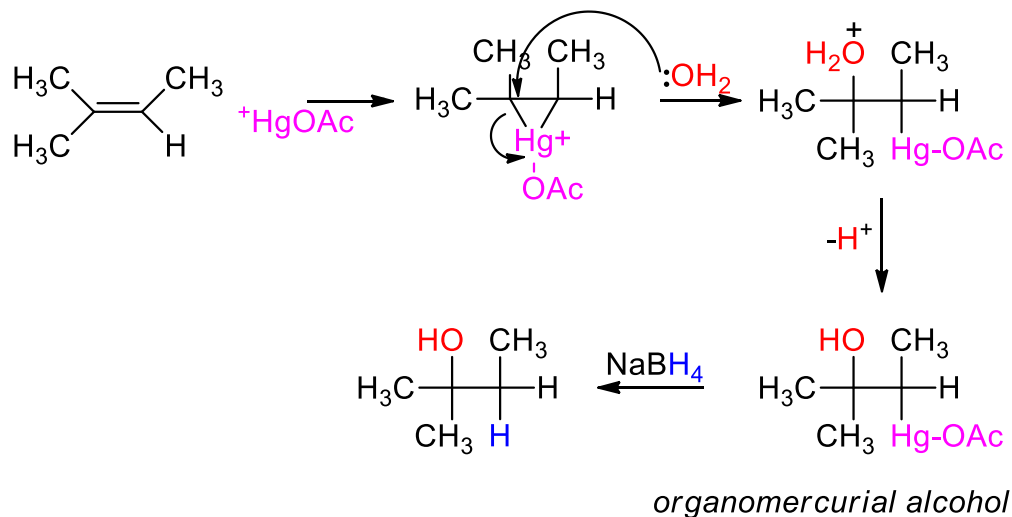
When water is present, the nucleophilic oxygen will open the mercurinium ring, and generate an organomercurial alcohol.

Demercuration is the removal of the mercury containing species, which is achieved by reaction with Sodium borohydride, a powerful reducing agent, which replaces the mercury species with a **hydrogen** atom – giving the desired alcohol.

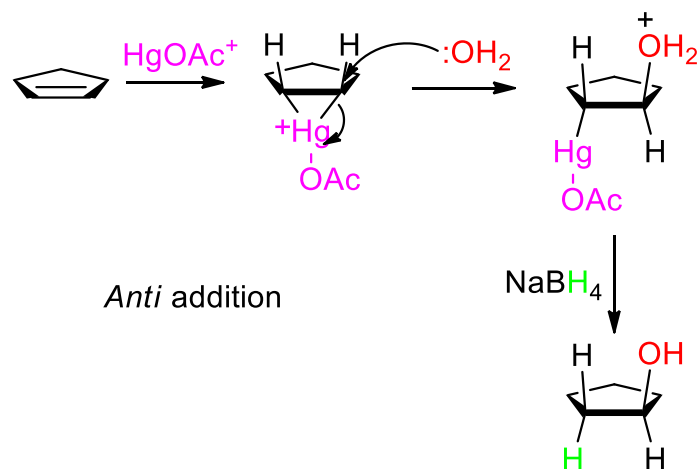Oxymercuration-demercuration also gives Markovnikov orientation of the alcohol.
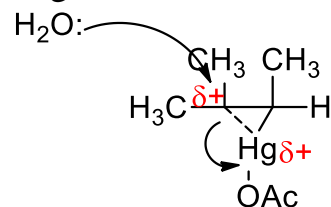
The water molecule attacks the carbon with **most** positive charge (most *electrophilic* carbon).
The electrophile $^+$HgOAc remains bound to the less highly substituted carbon.

The stereochemistry of the product is also important: the new H and OH groups are on the opposite sides of what was the double bond - this is called **anti** addition.

(Addition to the same side of a double bond is called **syn** addition).

This is easier to see in cyclopentene:

Anti addition

Oxymercuration-Demercuration gives better chemical yields than the other 2 methods, uses less harsh conditions and does not allow the possibility of carbocation rearrangements.
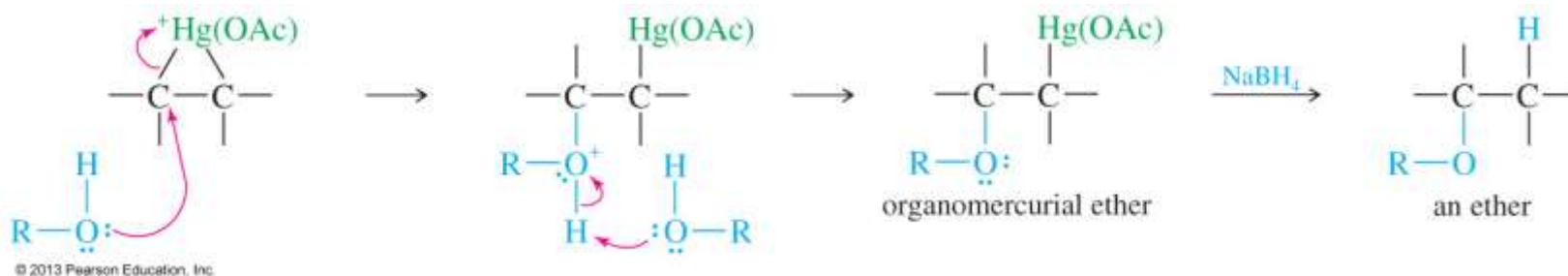
Alkoxymercuration-Demercuration

This is an extension of the previous reaction, where the reaction is performed in the presence of an **alcohol** rather than water.
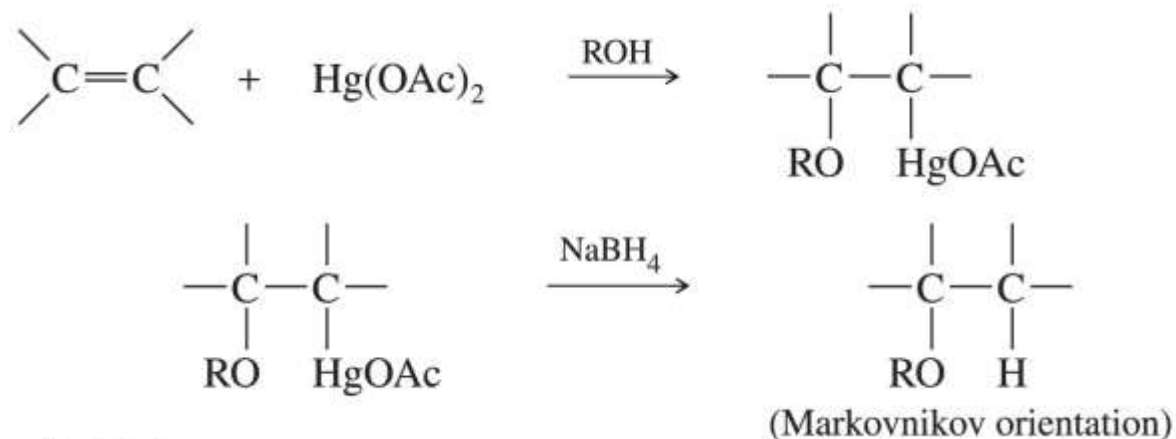
(Markovnikov orientation)

The alcohol opens the mercurinium ring, and the final product is an **ether**.
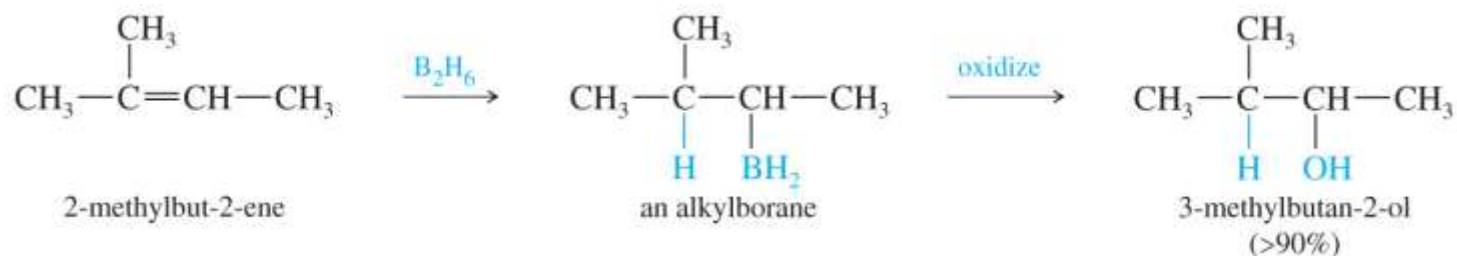
Hydroboration of Alkenes

We have studied three ways of hydrating alkenes to give <u>Markovnikov</u> orientated alcohols.

There is also a way to obtain <u>anti-Markovnikov</u> oriented alcohols: hydroboration.

2-methylbut-2-ene   an alkylborane   3-methylbutan-2-ol (>90%)

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

Borane (BH_3) itself is unstable, and exists either as a dimer or as a complex with THF.

diborane   borane

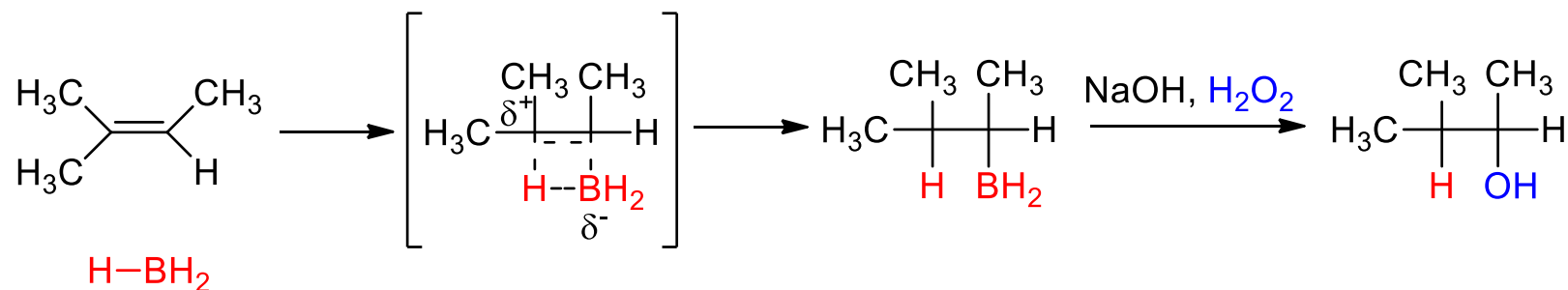tetrahydrofuran (THF)   diborane   borane–THF complex   = $BH_3 \cdot THF$
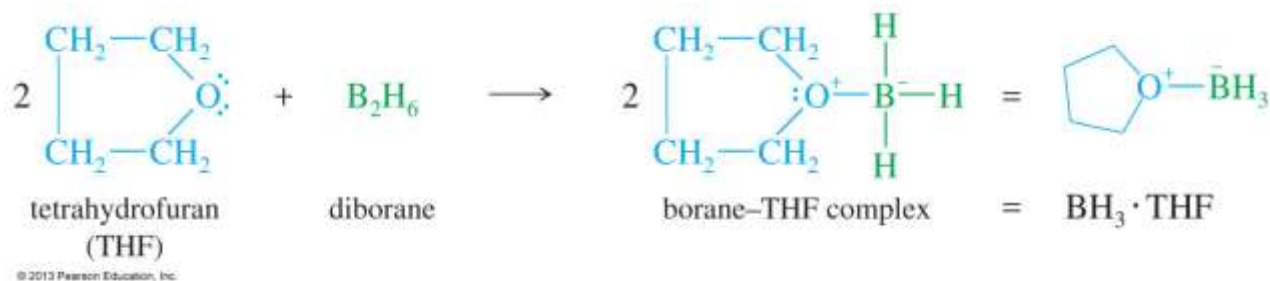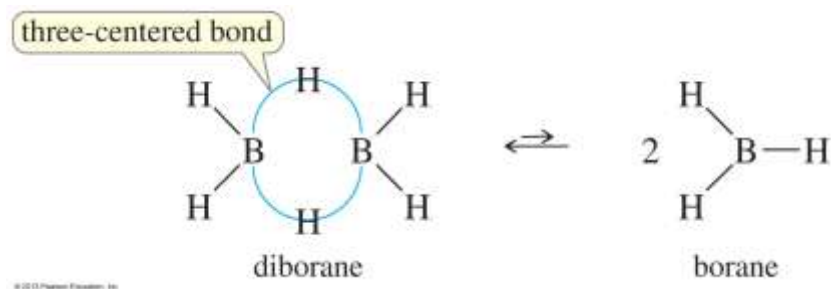
Mechanism of Hydroboration

Borane has only six valence electrons and is very electron **deficient**.

Borane is an electrophilic molecule, and reacts with double bonds in a one step process to generate an alkylborane.

The boron atom adds to the least highly substituted end of the double bond. This places partial positive charge on the more highly substituted end of the double bond (which is more stable).
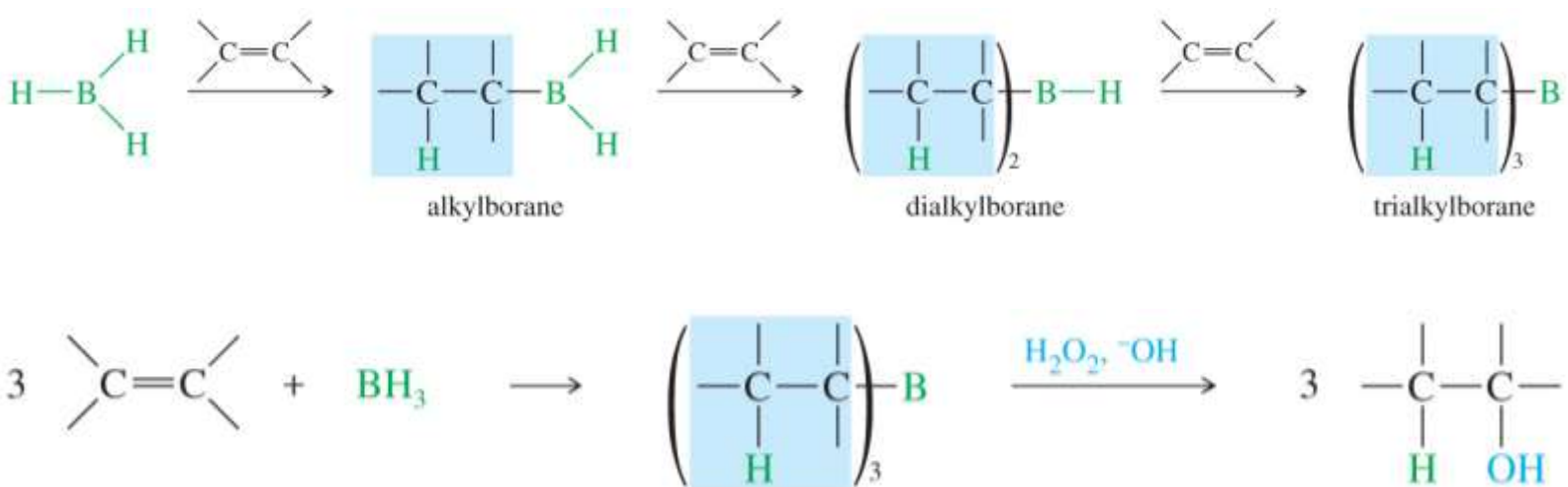
Hydroboration also gives **syn** addition of the boron and hydrogen (and therefore the –OH and –H).
This is a **stereospecific** reaction.

H$_3$C H

H$_3$C H

H$_3$C H

H--BH$_2$

H BH$_2$

H$_3$C H

H$-$BH$_2$

Syn addition

H$_2$O$_2$, $^-$OH

H$_3$C H

H OH
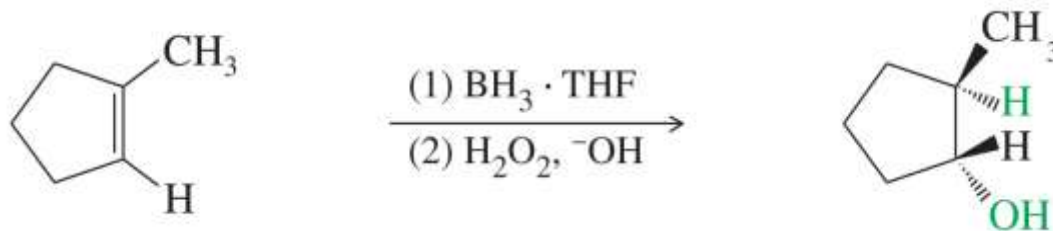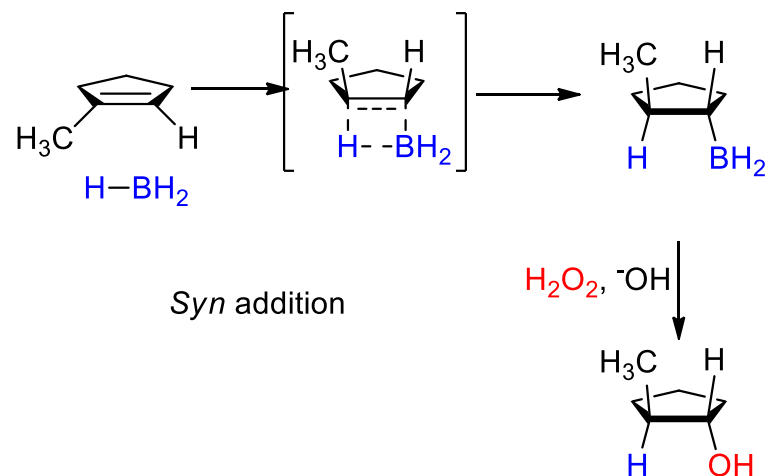
Stoichiometry of the Reaction
In reality, each B-H bond can add across a double bond.

H$-$B   C=C   —C—C—B   C=C   (—C—C—)$_2$B—H   C=C   (—C—C—)$_3$B

alkylborane   dialkylborane   trialkylborane

3 C=C + BH$_3$ ⟶ (—C—C—)$_3$B   H$_2$O$_2$, $^-$OH   3 —C—C—
                                                                H OH

The di- and tri-alkyl boranes behave just as the alkylboranes, but for simplicity they are often written as mono alkylboranes.

Catalytic Hydrogenation

This is the addition of a hydrogen molecule to a compound using a (usually Pt, Pd, Ni) catalyst.
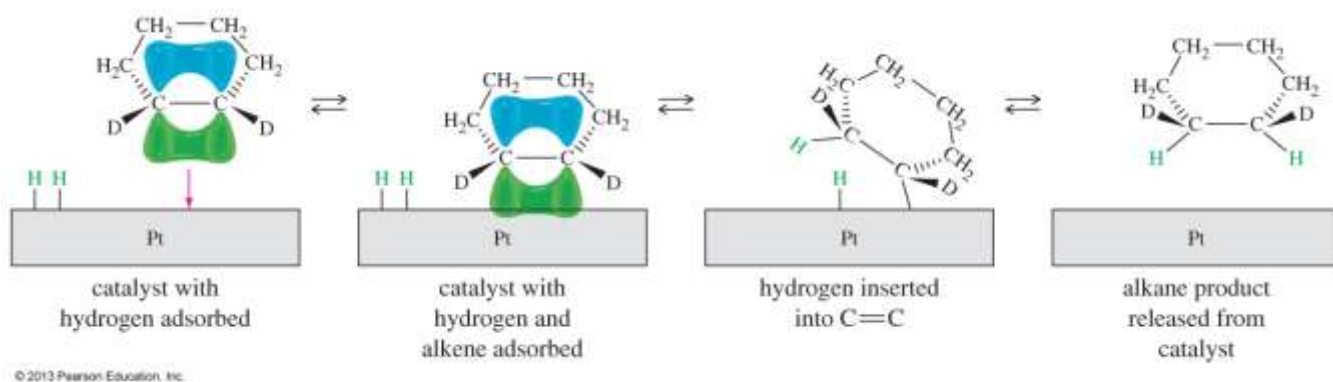
When the catalyst is in a different physical state to the other reactants it is called <u>Heterogeneous</u> catalysis (E.g. a solid catalyst with a liquid and a gas).

In contrast a liquid catalyst in a reaction solution is an example of <u>homogeneous</u> catalysis (acid catalyzed alcohol dehydration).

During catalytic hydrogenation, the hydrogen adsorbs onto the surface of the metal catalyst, and they add syn to the double bond.
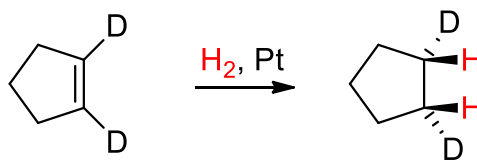

One face of the π system binds to the catalyst, then the bound hydrogen inserts into the π bond, and the product is liberated from the catalyst.

catalyst with hydrogen adsorbed

catalyst with hydrogen and alkene adsorbed

hydrogen inserted into C=C

alkane product released from catalyst

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Addition of Carbenes

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

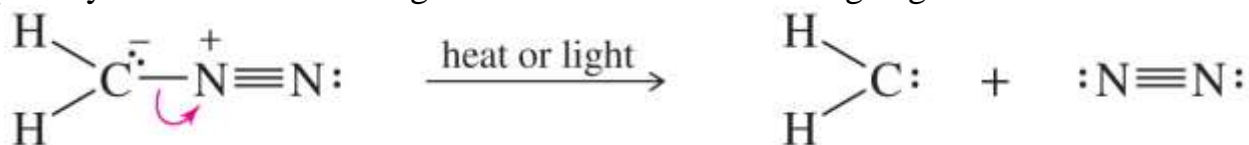alkene   methylene   cyclopropane
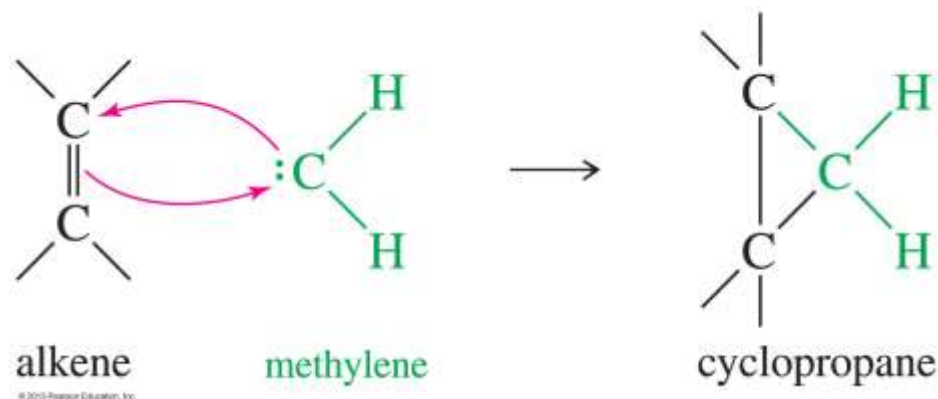
Carbenes are potent electrophiles and react with double bonds to form 3 membered rings (cyclopropanes).

There are 3 classical ways to generate carbenes:
- (1) diazomethane
- (2) Simmons-Smith Reaction
- (3) Alpha Elimination from Haloforms

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.

Simmons-Smith Reaction

The reaction of diiodomethane with zinc metal in the presence of Cu(I) salts generates a <u>carbenoid</u> species ICH_2ZnI. (It behaves like a carbene).
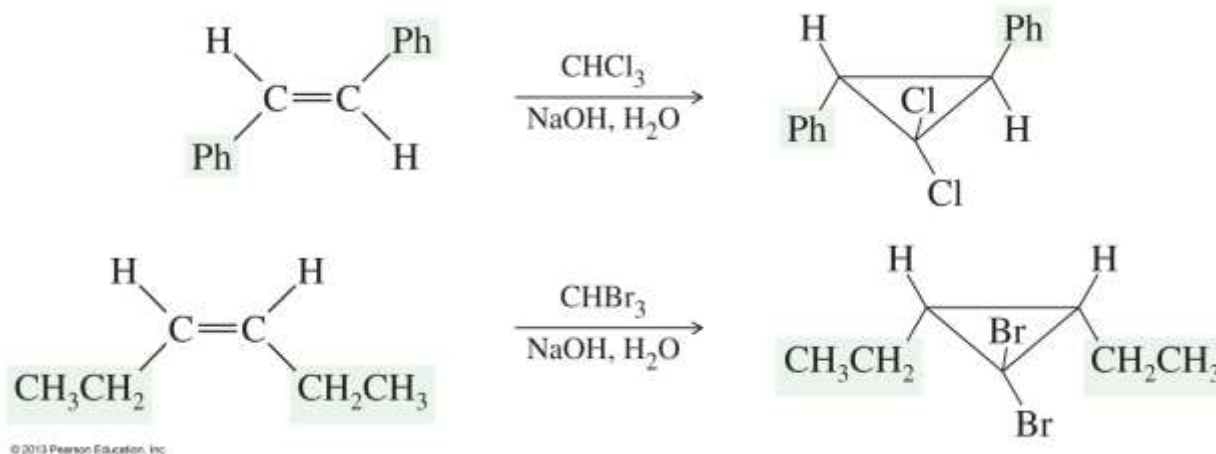
$$CH_2I_2 + Zn(Cu) \rightarrow ICH_2ZnI$$

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.
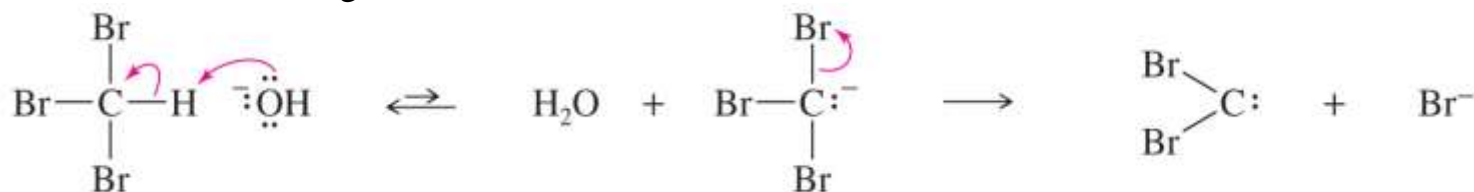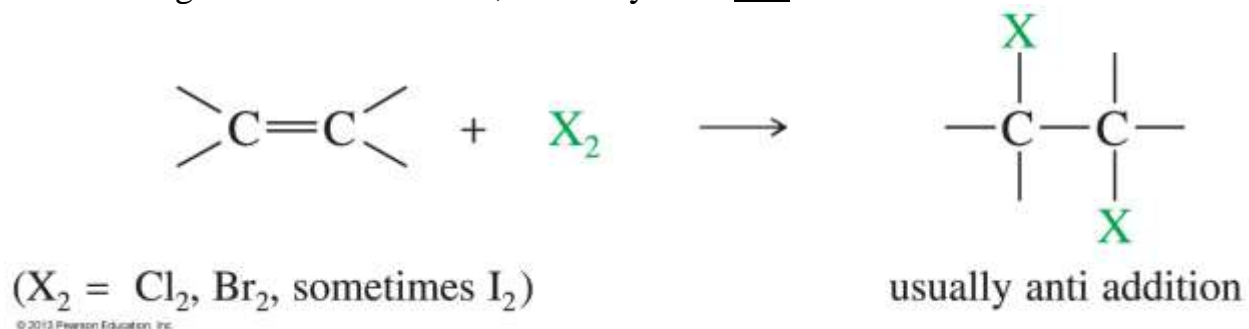

This type of carbene reacts with **retention** of stereochemistry of the reactants.

Addition of Halogens to Alkenes

Halogens add to alkenes to give vicinal dihalides, normally with <u>anti</u> addition.

$$>C=C< \quad + \quad X_2 \quad \longrightarrow$$

$(X_2 = Cl_2, Br_2, \text{sometimes } I_2)$

usually anti addition

Mechanism

The halogen molecule (X_2) is electrophilic – a nucleophile will attack one end, and displace a halide ion.

bromonium ion

Typically, a π bond will attack the bromine molecule kicking out bromide ion and generating a **bromonium** ion. (3 membered positively charged ring containing bromine).

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


X⁻ attacks from the back side
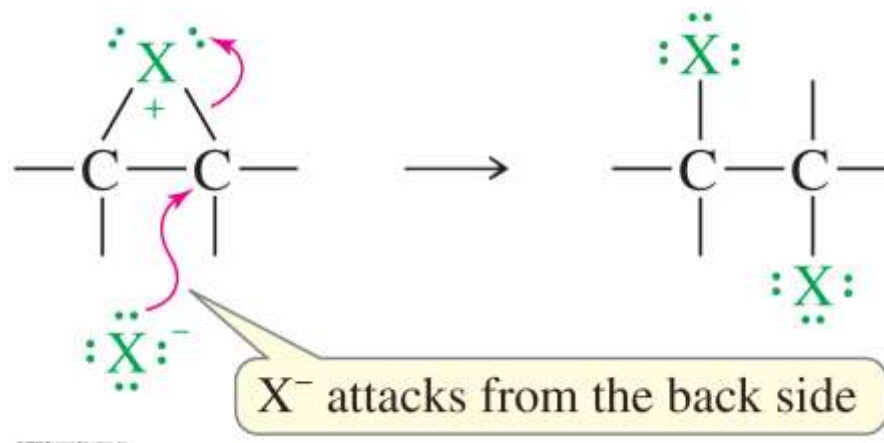
The halogen addition reaction is stereospecific, it gives <u>anti</u> addition.

but not

Halohydrin Formation

When the halogenation reaction takes place in the presence of a nucleophilic solvent, a nucleophile **different** from the halide can open the halonium ring.

back-side attack

halohydrin
Markovnikov orientation
anti stereochemistry
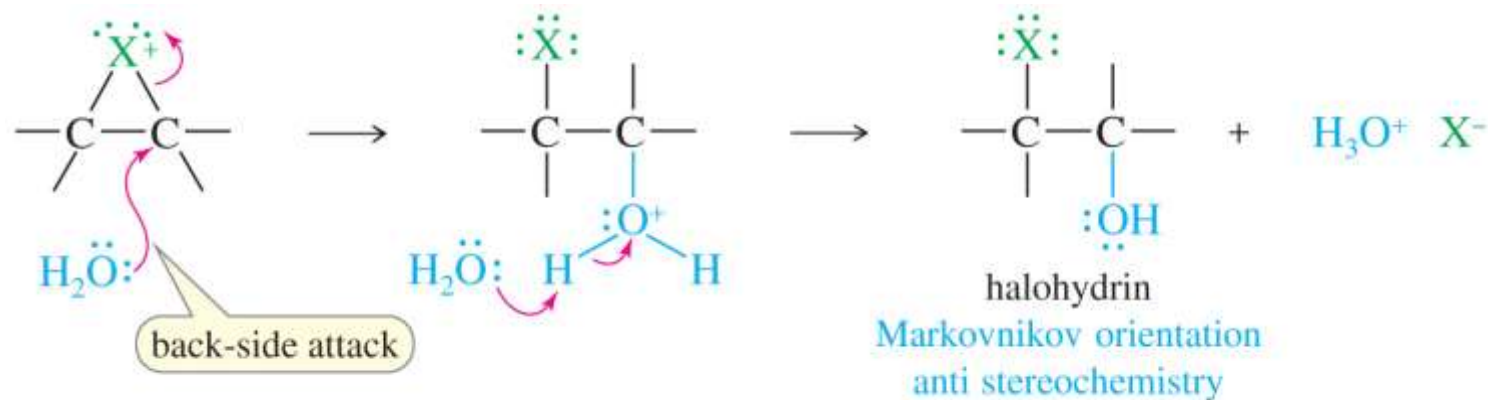
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If the reaction is performed in the presence of water, **Halohydrins** are produced.

The stereochemistry of the intermediate bromonium ring determines that the final product must be of **anti** addition, since ring opening must occur via backside attack.

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.
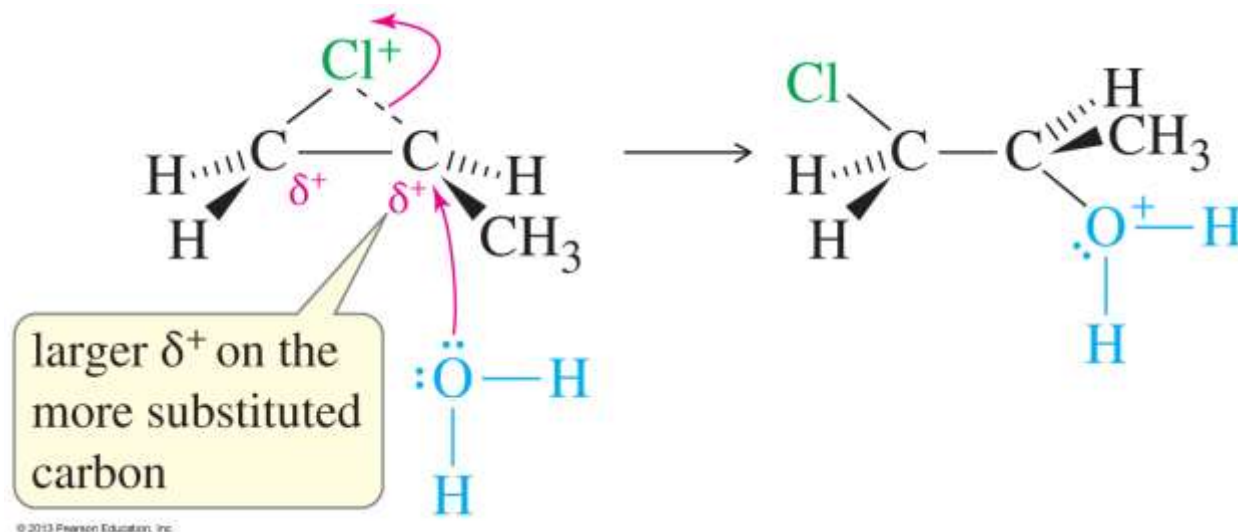

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In the halonium ring, the halogen is bound to both carbon atoms, which carry some partial positive charge. The more highly substituted carbon can bear more partial positive charge than the less highly substituted carbon.

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 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 (epoxidation, hydroxylation and oxidative cleavage).

Epoxidation of Alkenes
An epoxide (oxirane) is a three membered ring containing an oxygen. (Heterocyclic version of a cyclopropane).

alkene   peroxyacid   epoxide (oxirane)   acid
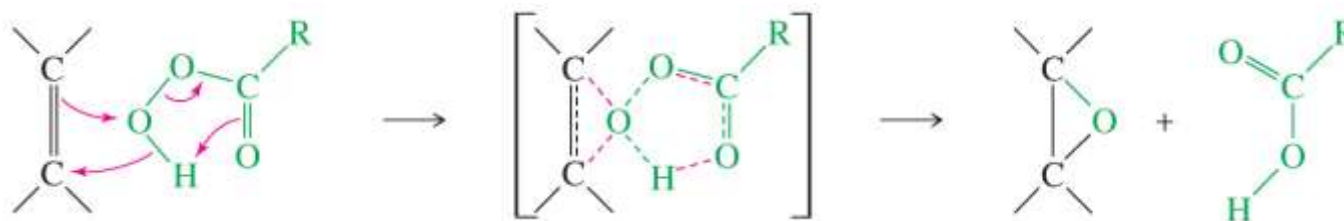
© 2013 Pearson Education, Inc.
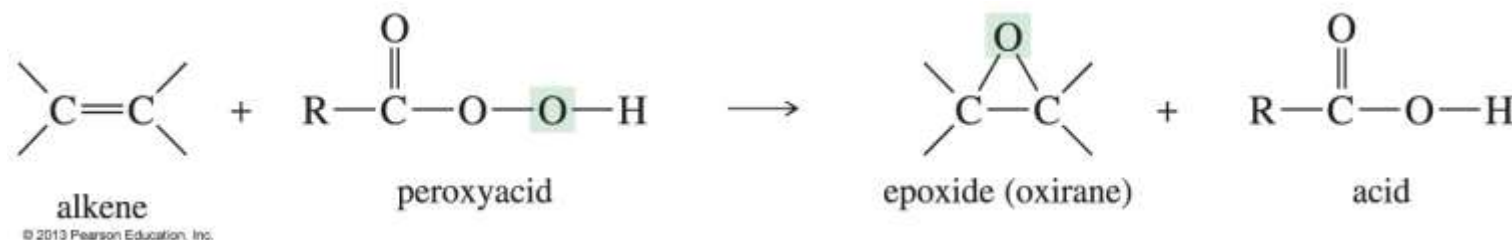
The most common reagent to convert an alkene to an epoxide is a peroxyacid. (Carboxylic acid but with an extra O).
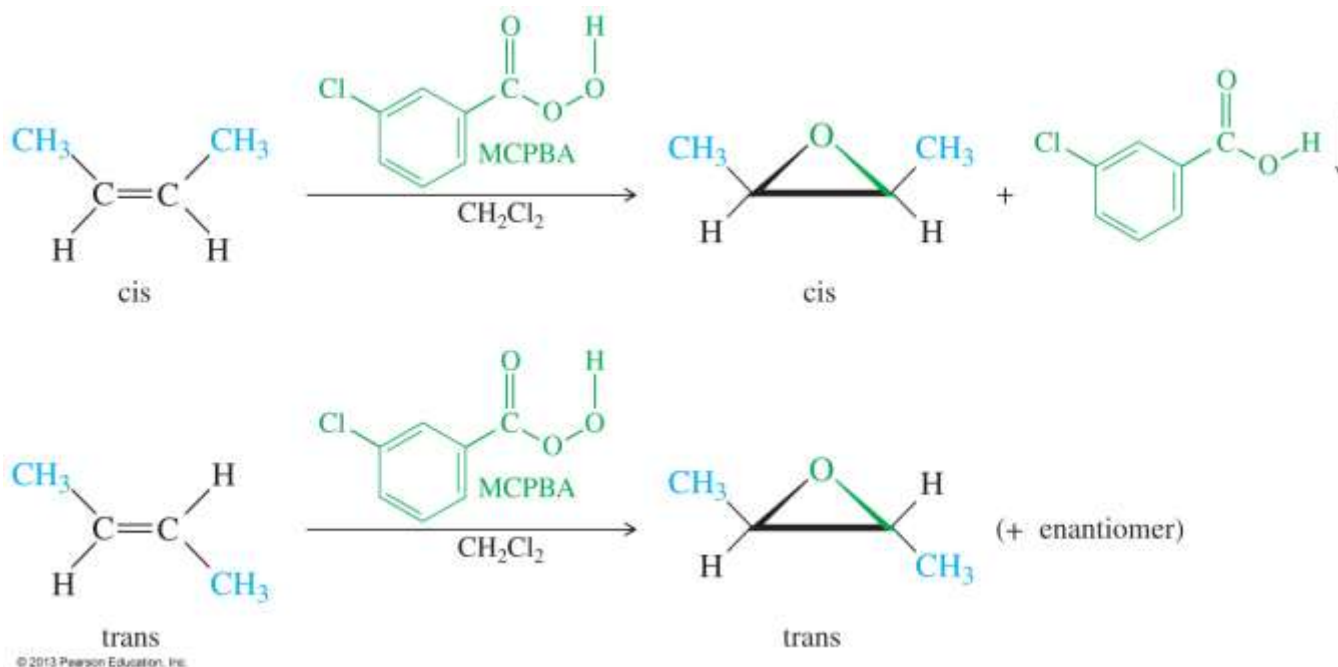
It is the oxygen of the OH which is transferred in this oxidation.

Mechanism

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

The stereochemistry of the reactant has no time to rearrange in this one step reaction, and so any stereochemistry of the reactant is **maintained** in the product.

Acid catalyzed Ring Opening
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.
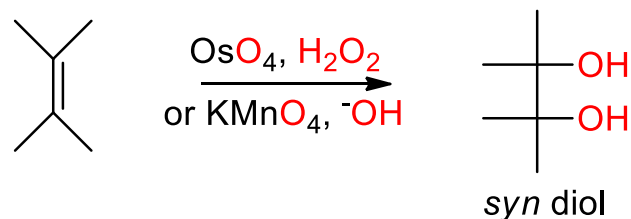

anti orientation
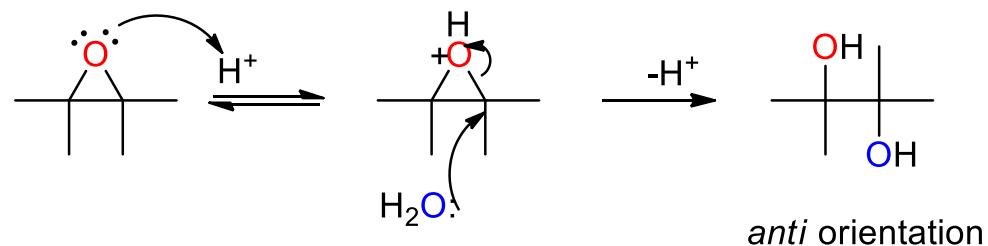
Mild acid reacts with epoxides to generate anti 1,2-diols (glycols).

cyclopentene oxide

trans-cyclopentane-1,2-diol
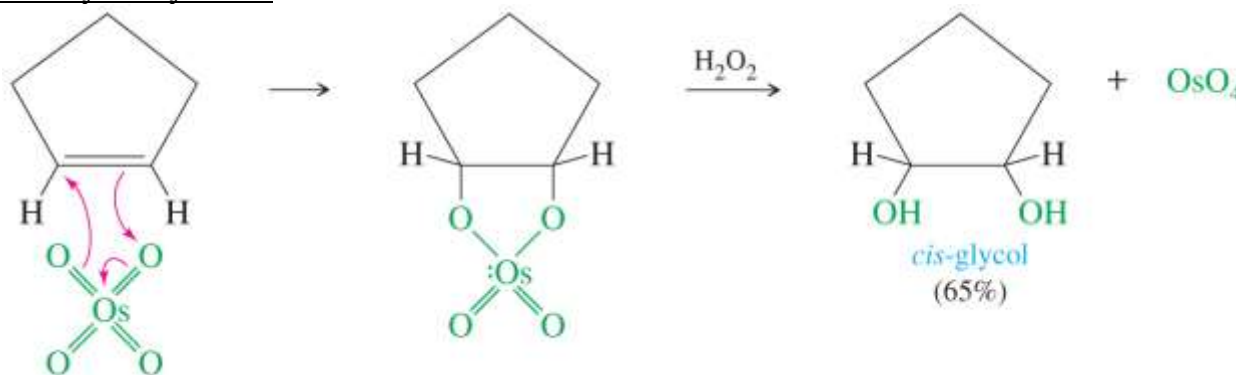(both enantiomers)
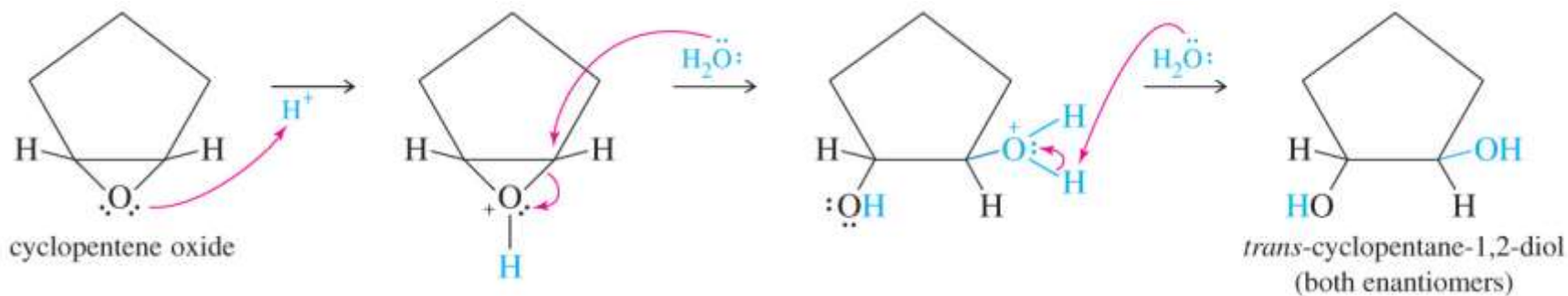
Syn 1,2-Diols   (*Recall - Epoxidation followed by acidic hydrolysis gives* <u>*anti*</u> *1,2-diols*).

Syn hydroxylation of alkenes gives syn 1,2-diols.

syn diol

The two most common methods use osmium tetroxide with hydrogen peroxide, or potassium permanganate and hydroxide ion.
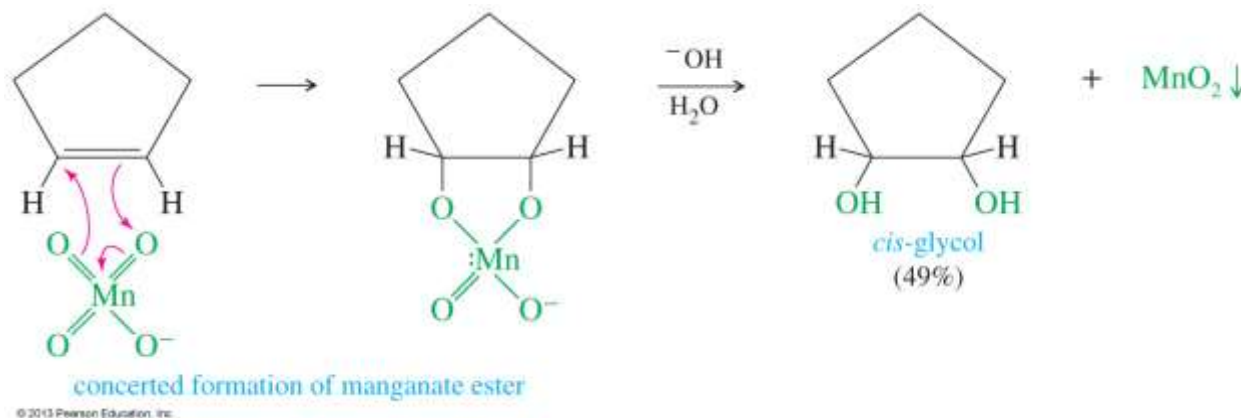
Osmium Tetroxide Hydroxylation

cis-glycol
(65%)

This reaction proceeds via a concerted electrophilic addition generating an osmate ester, which is hydrolyzed to a syn diol by hydrogen peroxide, which also reoxidizes the osmium catalyst.

The two C-O bonds are formed at the *same time* with the cyclic ester, and the oxygen atoms are added at the same face of the π bond – **syn** orientation.

Permanganate Hydroxylation

An alkaline, cold solution of potassium permanganate will do exactly the same transformation as osmium tetroxide.

concerted formation of manganate ester

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The intermediate cyclic ester again forces **syn** hydroxylation.

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

Oxidative Cleavage

If either acid or heat is used with permanganate, cleavage and further oxidation can occur producing ketones and/or aldehydes. The aldehydes further oxidize to carboxylic acids.
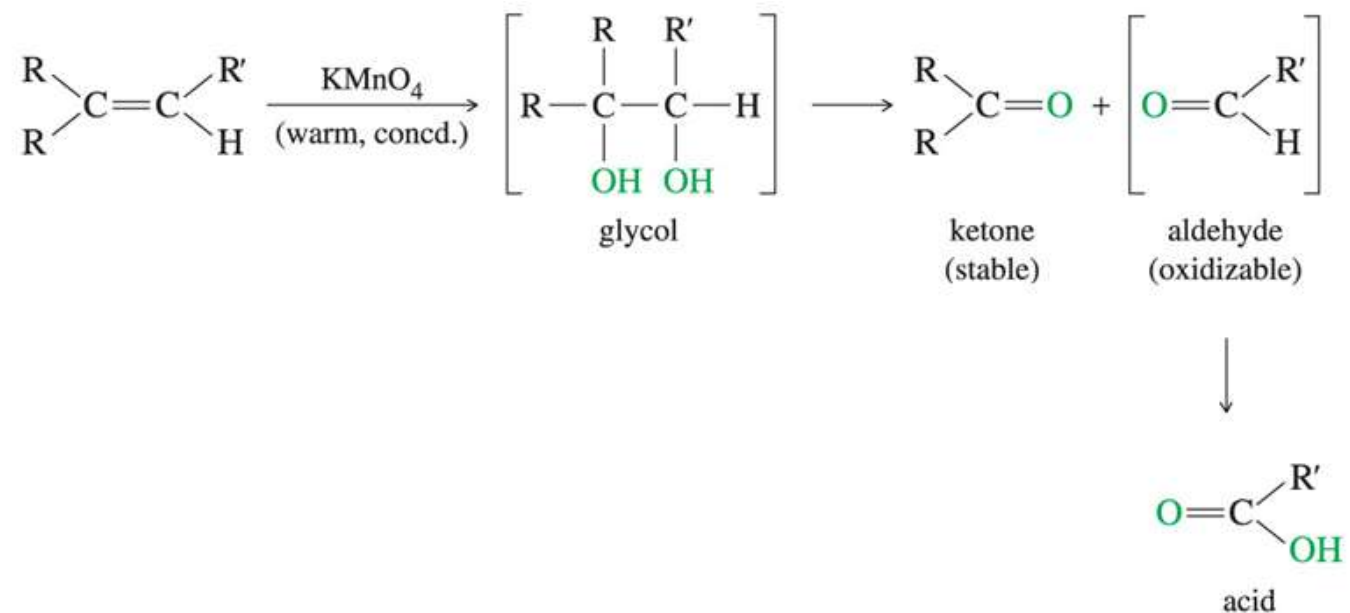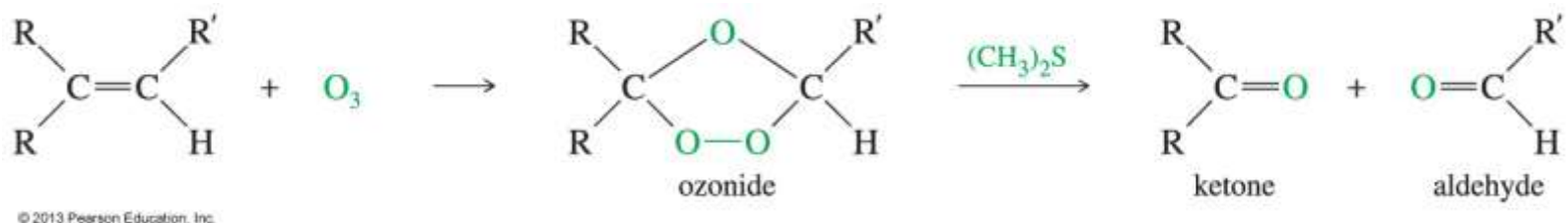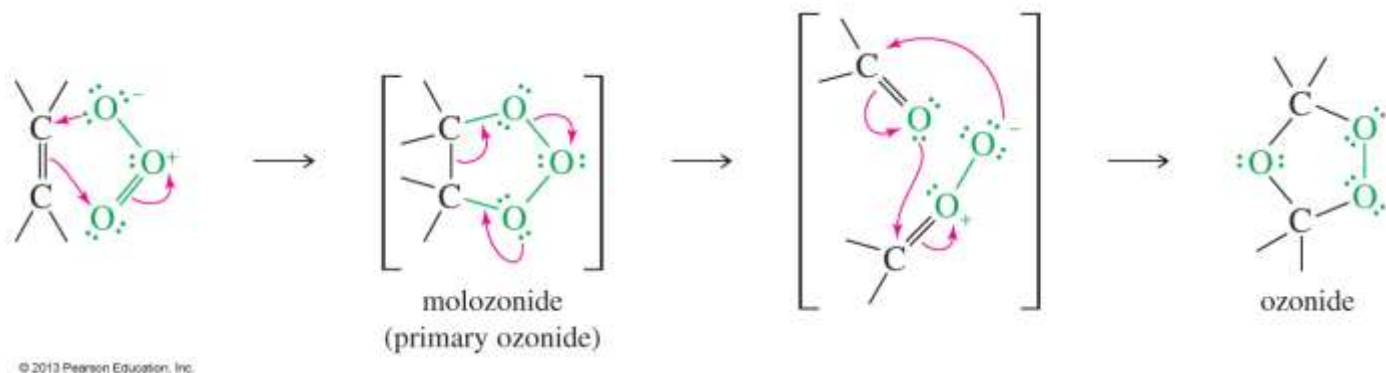

E.g.
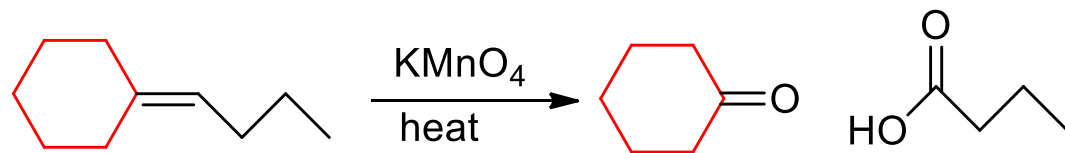
Ozonolysis

Ozone (O_3) also cleaves double bonds, but this milder reagent gives aldehyde and ketones as the products.

The intermediate ozonide reacts with reducing agents like dimethyl sulfide to produce DMSO and the carbonyl products.
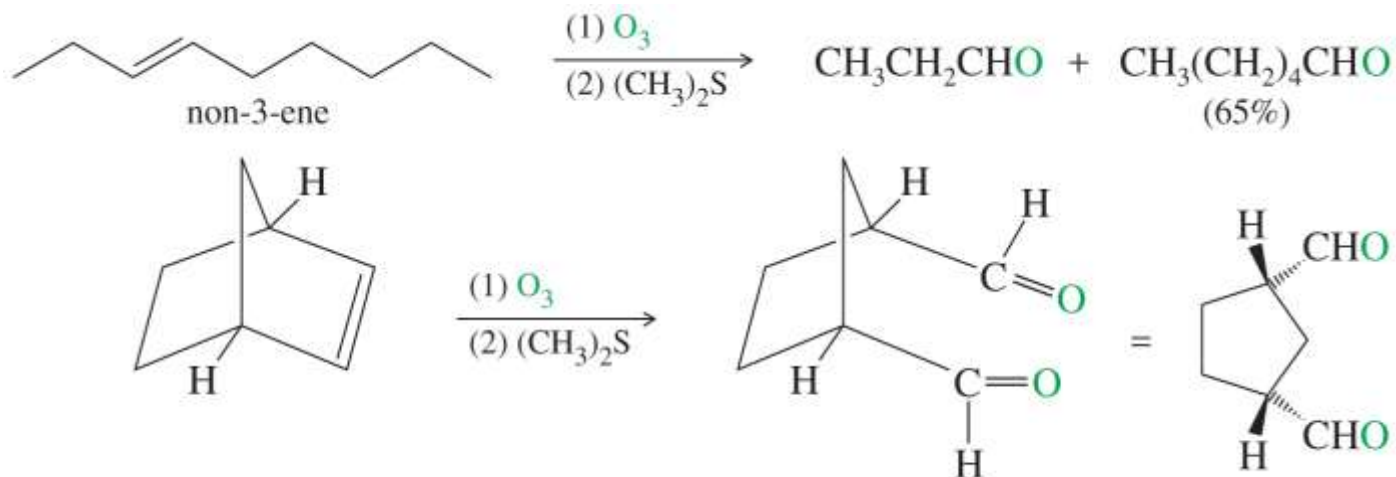

molozonide
(primary ozonide)

ozonide

Ozone reacts with the double bond to give an unstable molozonide (primary ozonide) which rearranges to an ozonide.

This cleavage reaction is often used to identify the positions of double bonds in alkenes.

E.g.

non-3-ene

$\xrightarrow[\text{(2) (CH}_3)_2\text{S}]{\text{(1) O}_3}$

$CH_3CH_2CHO \ + \ CH_3(CH_2)_4CHO$

(65%)

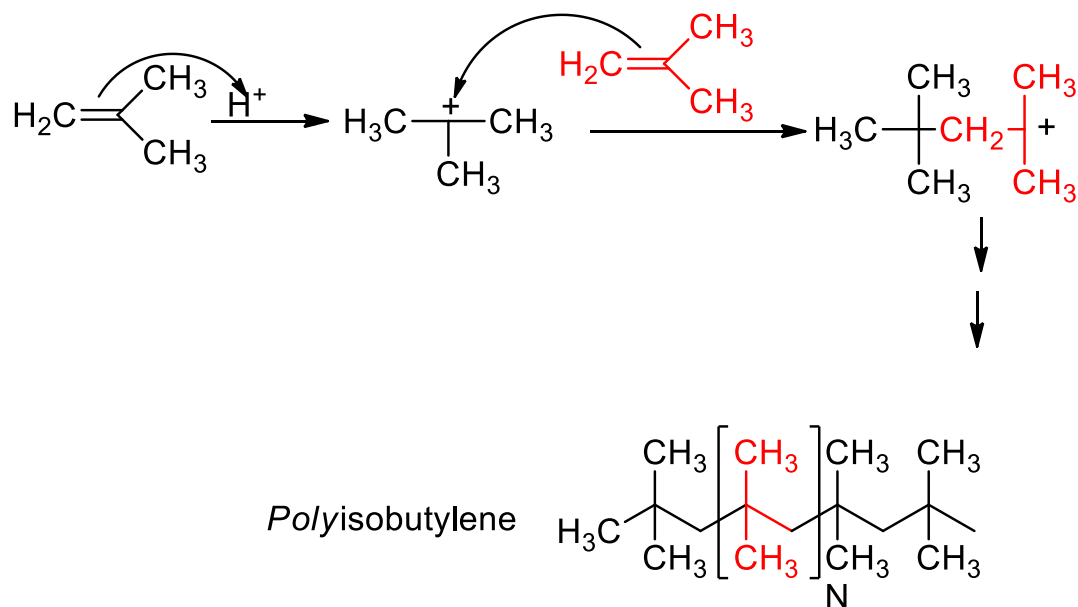$\xrightarrow[\text{(2) (CH}_3)_2\text{S}]{\text{(1) O}_3}$

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Dimerization and Polymerization of Alkenes

Alkenes in the presence of strong acids can be made to polymerize.

An electrophile (H^+) adds electrophilically to the double bond, and the carbocation is attacked by another alkene double bond.

*Poly*isobutylene

Depending on the reaction conditions either low molecular weight products (dimers trimers, etc) or high molecular products (polymers) are formed.