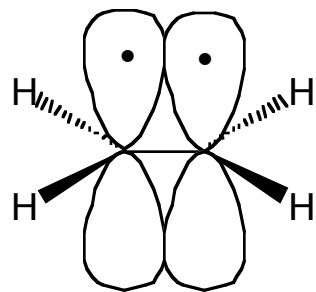


Review of an Alkene



two sp² hybridized carbon atoms

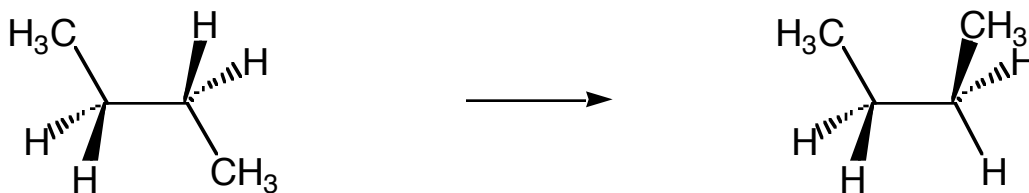
1	σ	bond	83	Kcal/mol
1	π	bond	63	Kcal/mol

a π bond is much lower in energy than a σ bond

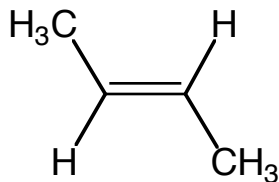
therefore even though carbon-carbon σ bonds rarely react the π bond reacts readily

Double Bond Prevents Rotation

a carbon-carbon single bond has conformational flexibility

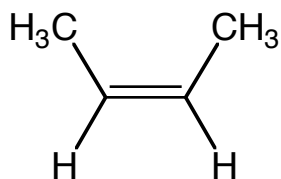


the carbon-carbon double bond prevents this rotation because the π bond would have to break for rotation to occur



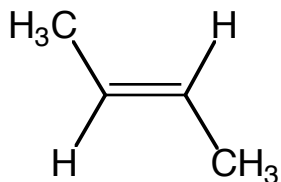
This Lack of Rotation Causes Geometric Isomers

- if substituents are on the same side of the double bond called CIS



cis-2-butene

- if substituents are on opposite sides of the double bond called TRANS



trans-2-butene

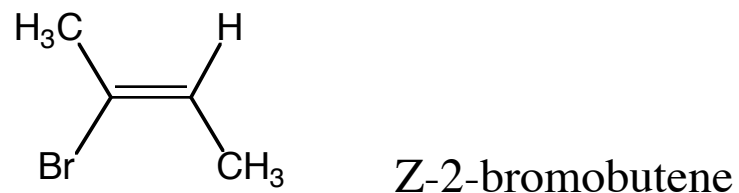
If there are more than two substituents with geometric isomers use Z and E naming

- substituents are prioritized

(same rules as already learned for R and S designation)

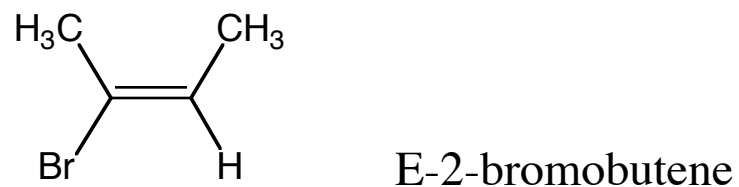
- if the highest priorities are on the same side called Z

(Z; zusammen - together)



- if the highest priorities are on opposite sides called E

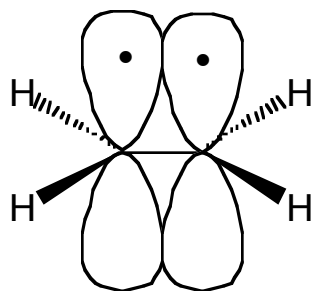
(E; entgegen - opposite)



Stability of Alkenes

We have already seen Zaitsev's rule which implies that as the number of alkyl substituents increases the stability of the alkene increases
(structure is of lower energy)

we can rationalize this by considering an alkene as two adjacent radical sites

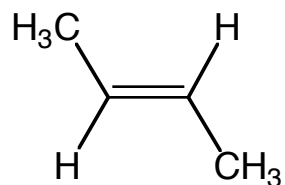


radicals are electron deficient

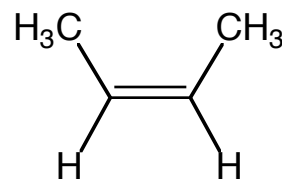
therefore anything that stabilizes electron deficient sites will stabilize an alkene
(and by inductive and hyperconjugation more
alkyl substituents stabilizes electron deficient sites)

Stability also changes between disubstituted alkenes

consider again cis- versus trans-2-butene

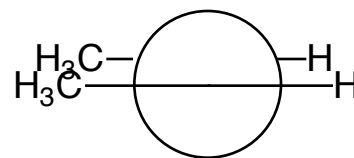
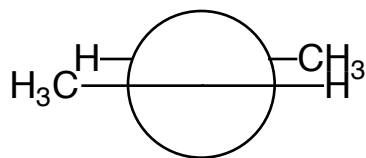


trans-2-butene



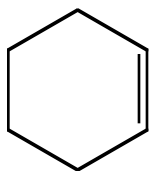
cis-2-butene

the cis isomer has higher nonbonded strain



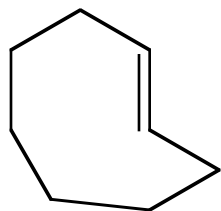
Ring Strain

a small ring requires a cis geometry

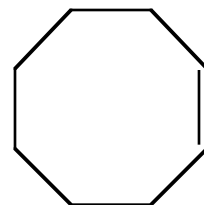


cyclohexene

with a ring system a trans alkene is too high in energy until the ring is 8 carbons or more



trans-cyclooctene



cis-cyclooctene

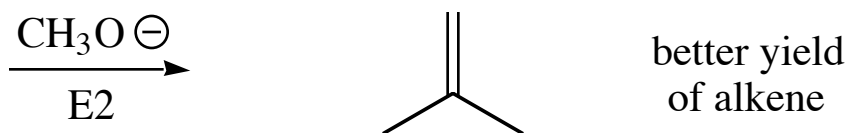
because of this geometric requirement alkenes are assumed to be cis in a ring
(do not need to write cis)

Synthesis of Alkenes

we have already learned two ways to synthesize an alkene:

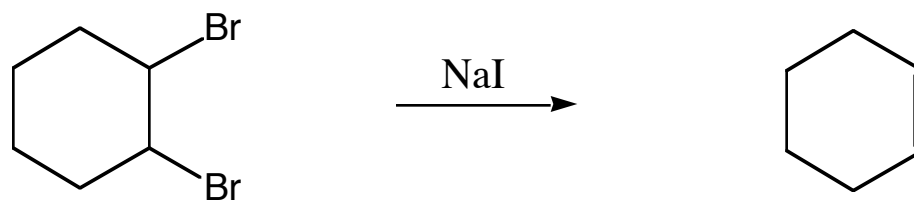
1) dehydrohalogenation (either E1 or E2)

- eliminate a hydrogen and halogen from a alkane to generate a double bond



2) dehalogenation

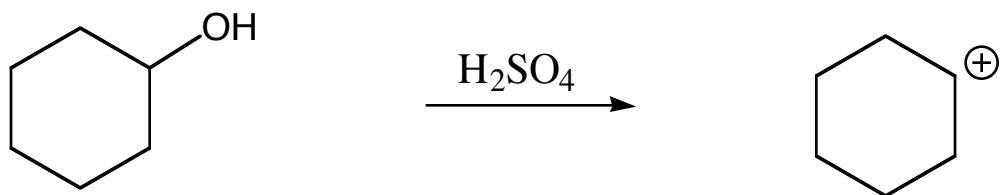
eliminate two adjacent bromines from an alkene with iodide ion



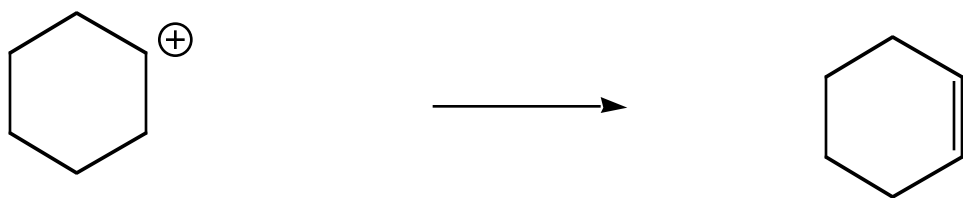
goes through an anti-coplanar elimination
similar to a E2 mechanism

A third route to alkenes is through a dehydration of alcohol

under acidic conditions an alcohol can leave to generate a carbocation

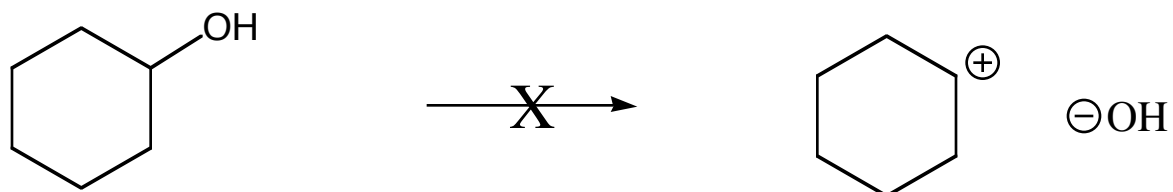


this carbocation can react similar to E1 reactions studied earlier with alkyl halides

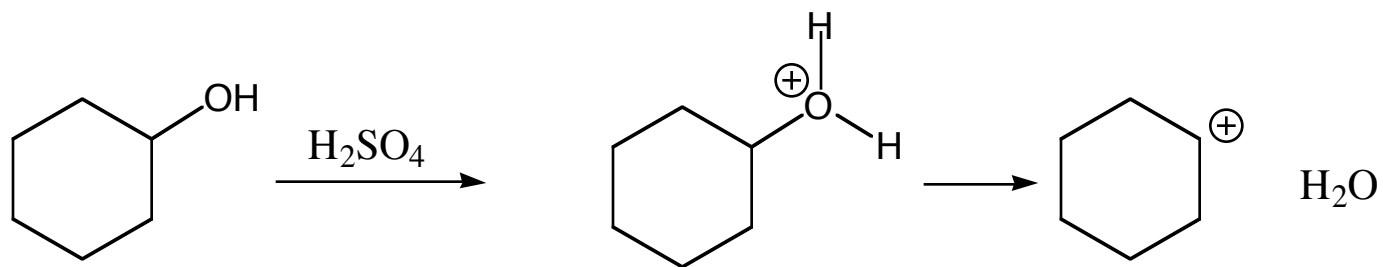


Acidic conditions are necessary to make the alcohol a good leaving group

without acid catalysis a hydroxy group is the leaving group
(remember this is a BAD leaving group and will not work)



with acid catalysis the hydroxy group becomes protonated BEFORE departing

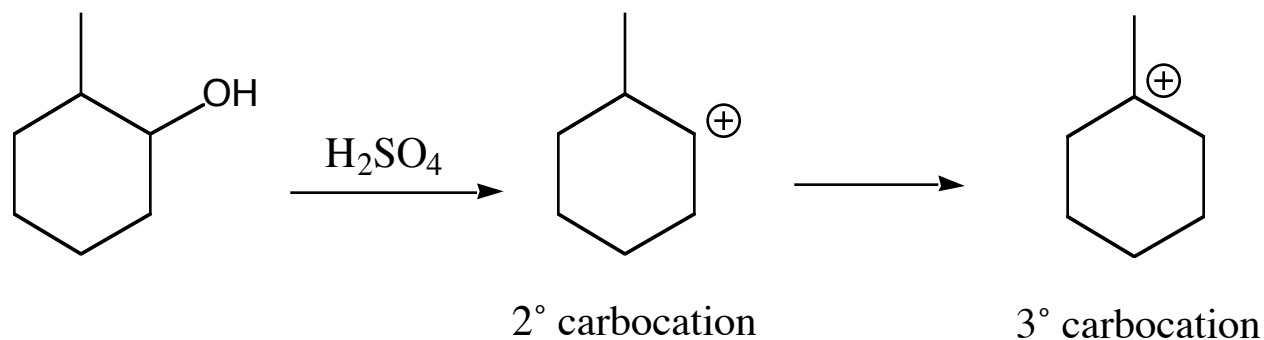


For acidic dehydration the same rules and trends we learned for alkyl halides apply

- a 3° site will be more reactive than a 2° and so forth

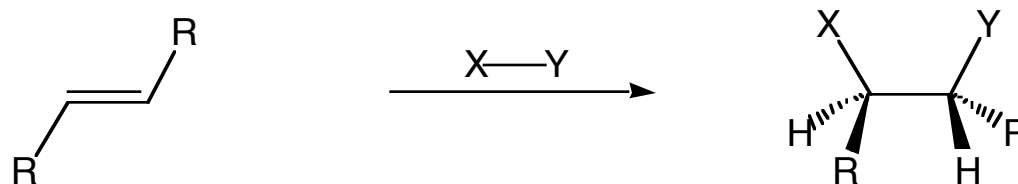
(a carbocation will be generated which is stabilized with electron donating substituents)

- after dehydration the carbocation can rearrange to form a more stable carbocation

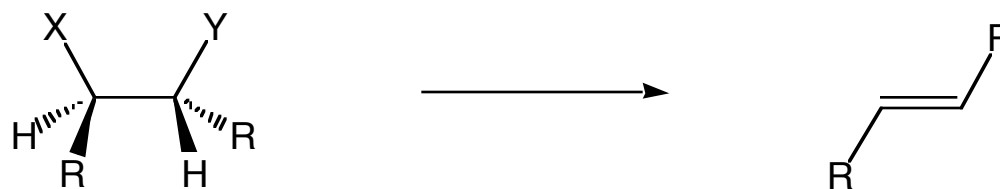


Reactions Of Alkenes

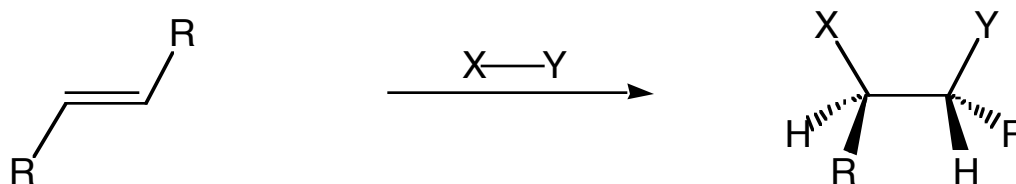
alkenes generally react in an addition mechanism
(addition - two new species add to a molecule and none leave)



realize this is the REVERSE of an elimination mechanism



There are three questions to ask for any addition reaction



1) what is being added

(what is the electrophile? the $X-Y$ group can change)

2) what is the regiochemistry (if any)

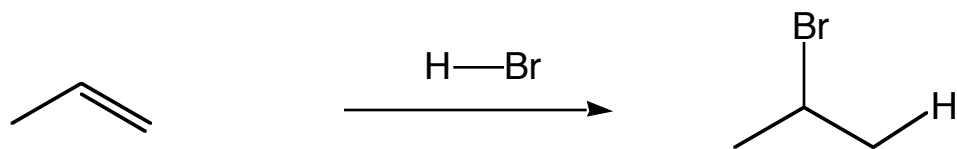
- do the reagents add with the X group to the left or right

3) what is the stereochemistry (if any)

- do X and Y both add to the same side of the double bond or to opposite sides

Addition of Hydrogen Halide

when an alkene and a molecule of hydrogen bromide react the H-Br adds to the two ends of the double bond

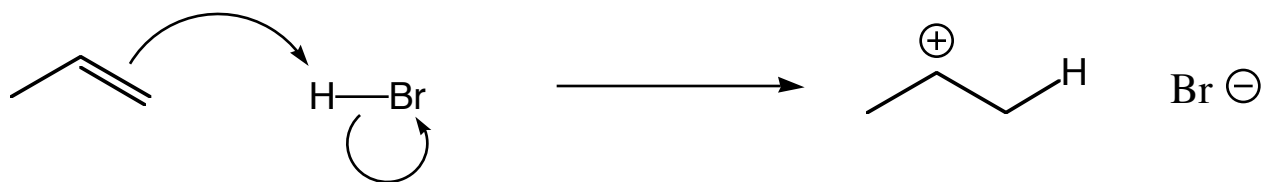


the same reaction will occur with hydrogen chloride and hydrogen iodide

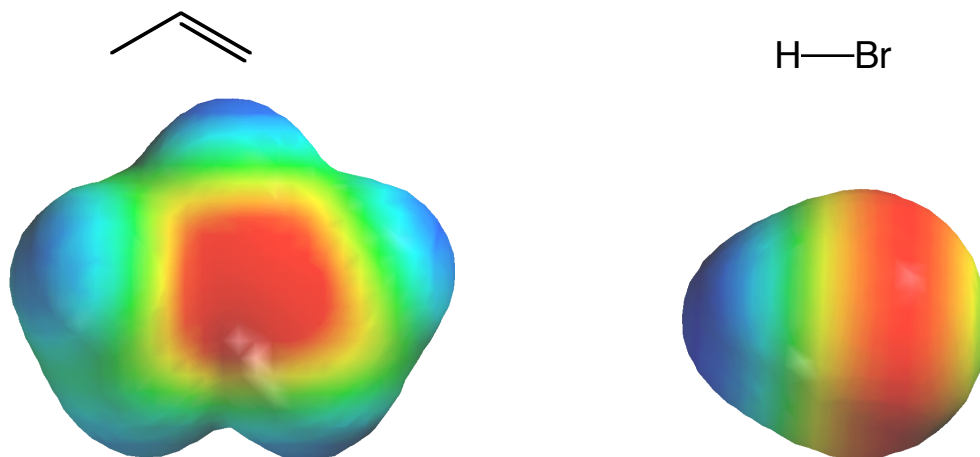
the two electrons involved in the π bond are the nucleophilic source
of an alkene addition

the difference in alkene additions therefore are the source of the electrophile

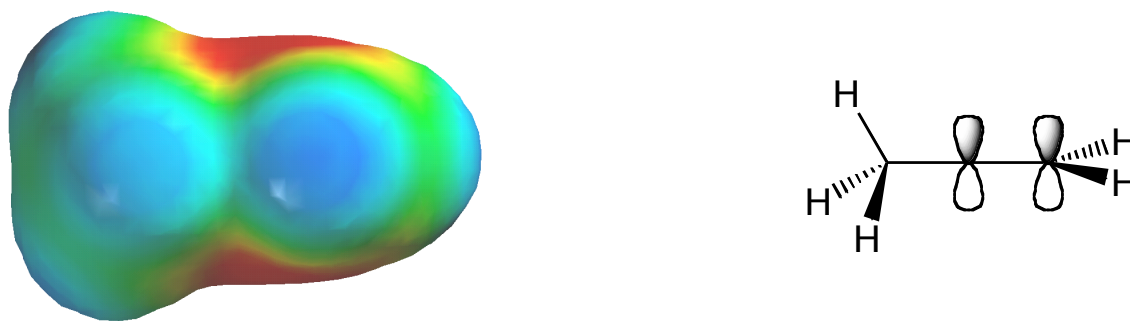
- for hydrogen bromide the electrophile is the proton



Again we can see why this reaction occurs by seeing the electron density plots

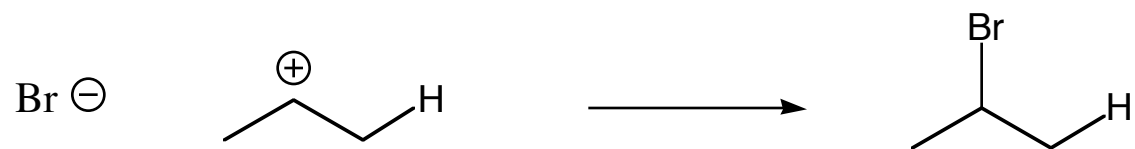


realize that the electron density of the alkene is located in the p bond which resides above and below the plane of the s bond



side view of 1-propene

the electron rich bromide can then react with the remaining carbocation



the mechanism therefore involves an electron rich alkene reacting with an electrophile
which generates a reactive carbocation

the carbocation then combines with any nucleophile (strong or weak) to complete the
addition reaction

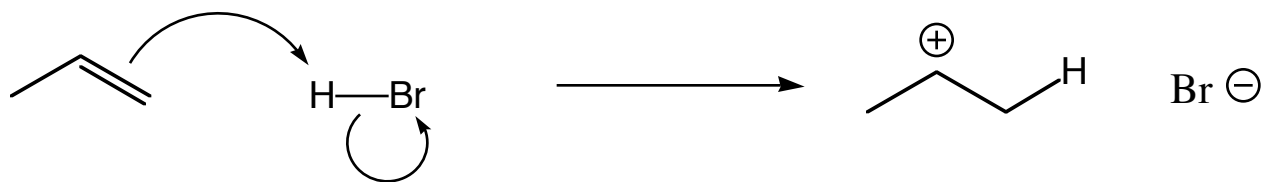
Regiochemistry

the hydrogen halide reactions with alkenes follow Markovnikov addition

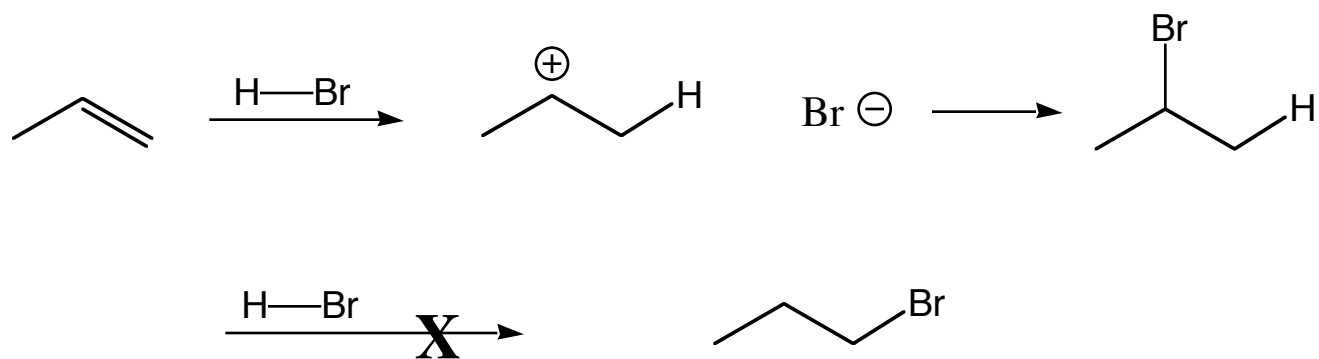
Markovnikov addition: in an electrophilic addition to an alkene, the electrophile adds in such a way as to generate the most stable intermediate

what does this imply for a hydrogen halide reaction

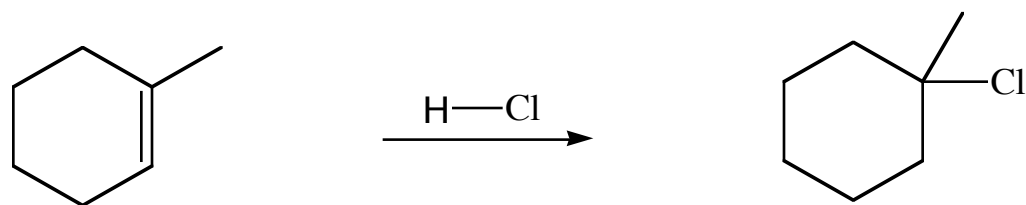
- remember that the first step is the creation of a carbocation



therefore want to generate the most stable carbocation intermediate

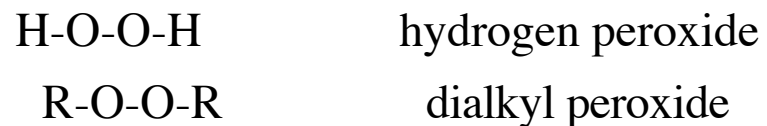


follow same rules of carbocation stability we have already learned

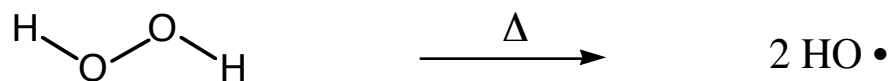


if peroxides are added the mechanism can be changed

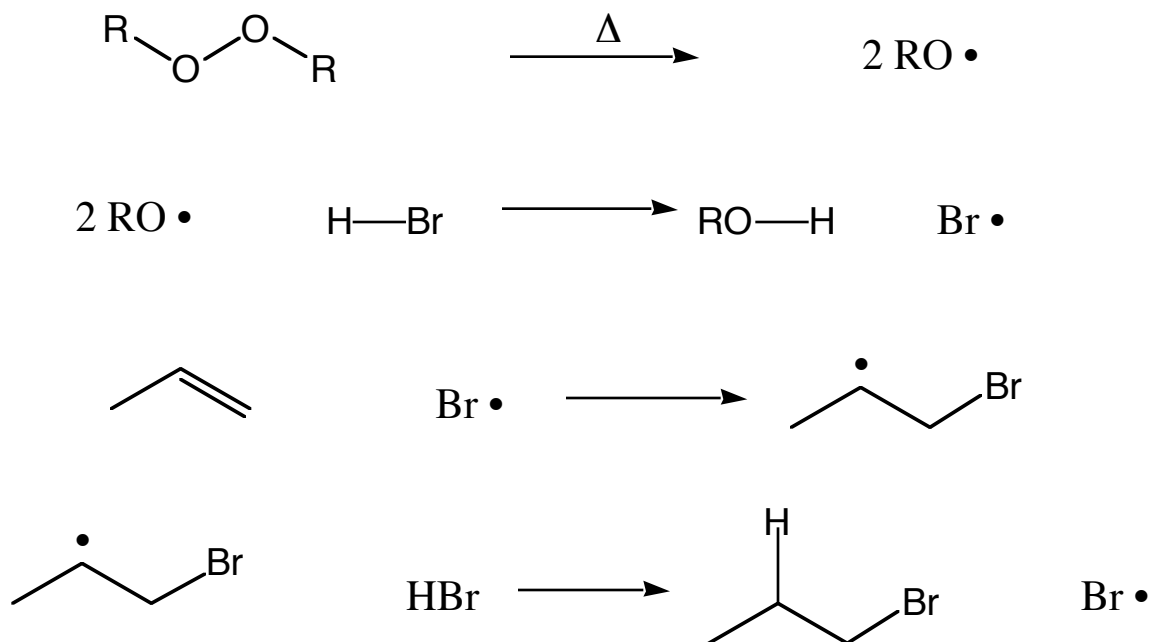
peroxide refers to compounds that contain an oxygen-oxygen (O-O) single bond



a oxygen-oxygen single bond is very weak and breaks homolytically



if a peroxide is added to a hydrogen bromide addition a radical pathway occurs



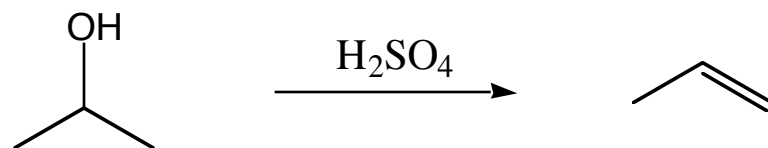
still get addition of HBr across a double bond but the REGIOCHEMISTRY is opposite

the halogen is at the least substituted carbon of the double bond

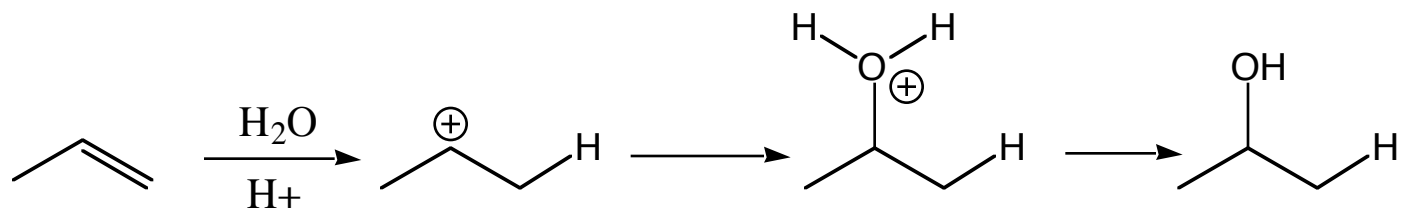
other species can be added besides hydrogen halides

Formation of Alcohols

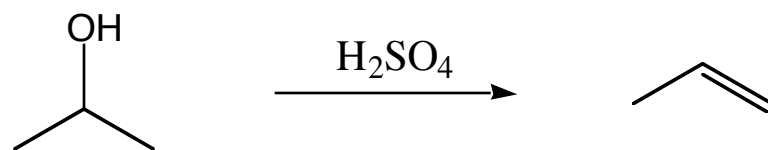
we saw how acidic conditions can be used to form alkenes from alcohols



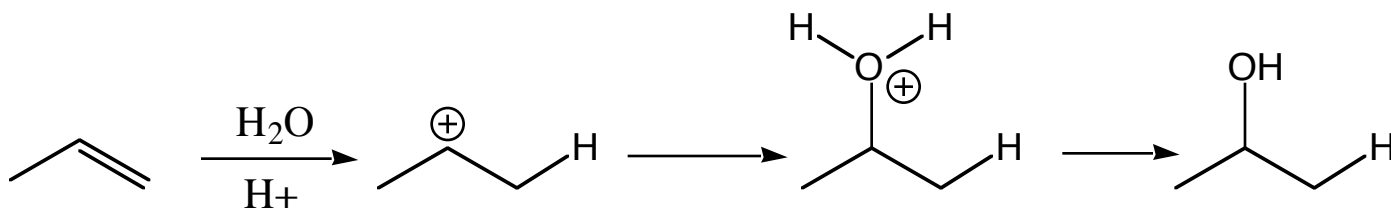
the reverse reaction can also occur



the reaction can be driven either direction by the conditions used



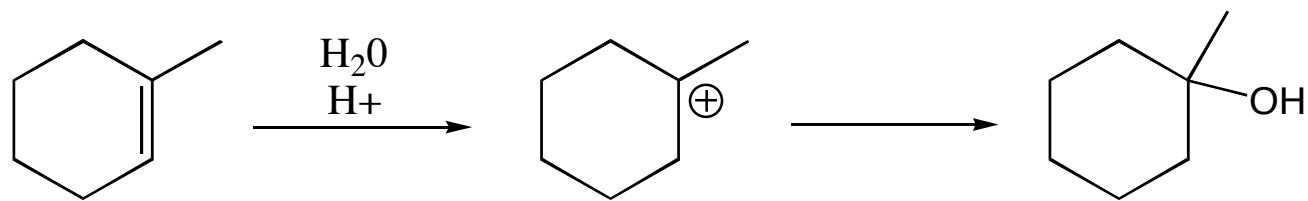
- need strong acid that is a good dehydrator



- take advantage of LeChatelier's principle, use an excess of water

Regiochemistry of Hydration

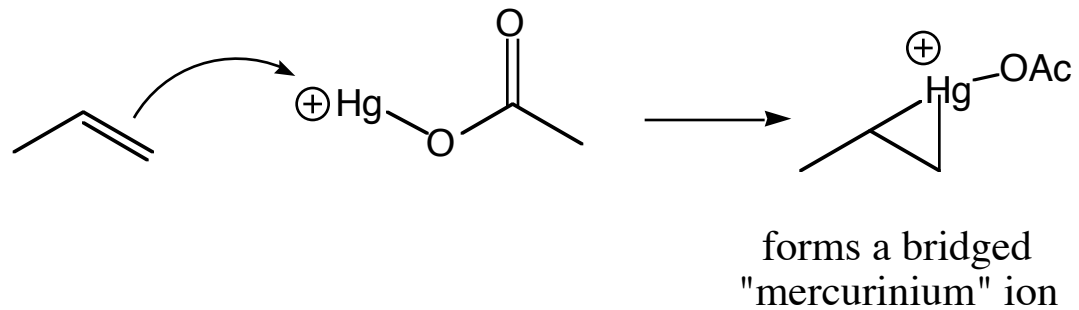
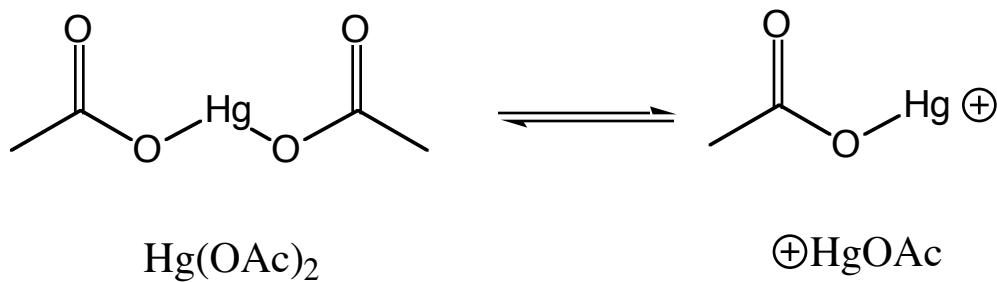
again follow Markovnikov addition



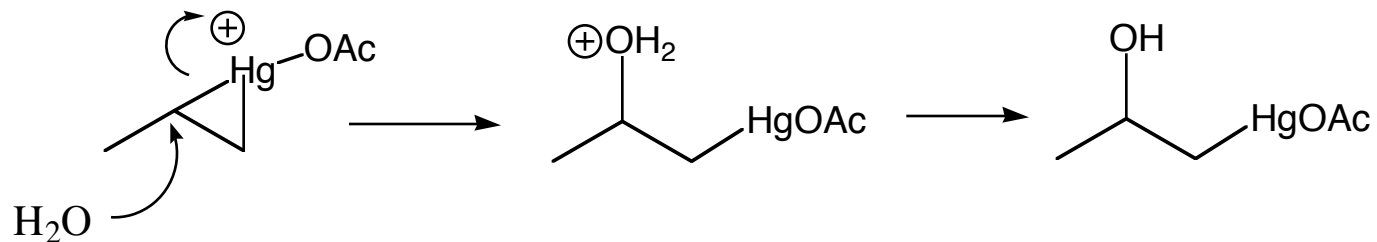
- alcohol will form at the more stable carbocation site

again in this case the electrophile is the proton

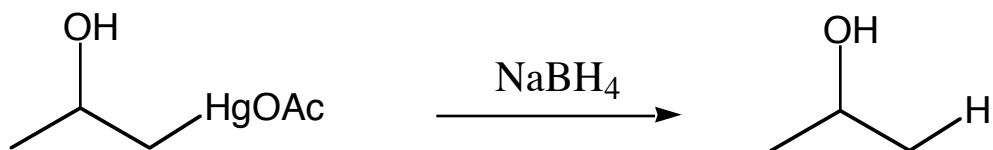
instead of a proton as the electrophile can use mercury compounds



water (which is generally the solvent) can attack the mercurinium ion

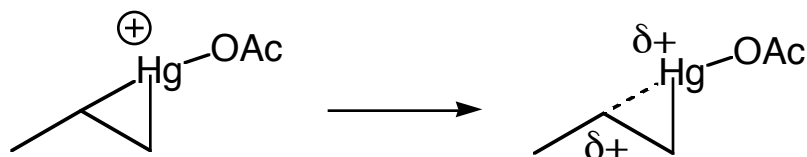


the mercury can be cleaved off using sodium borohydride (NaBH₄)

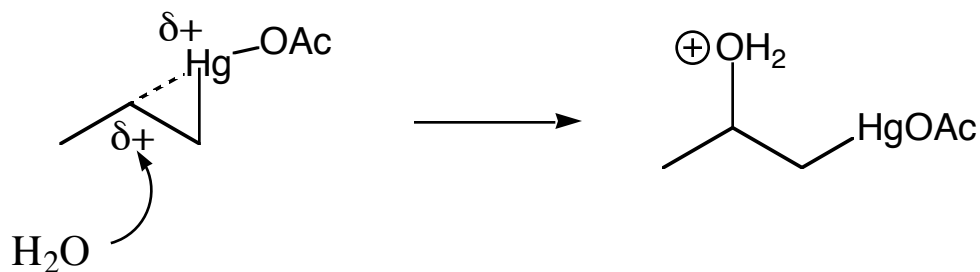


Regiochemistry

the water that attacks preferentially attacks the more substituted carbon
(one bond of the mercurinium ion is partially broken leaving a partial positive charge
- this charge is more stable at the more substituted carbon)

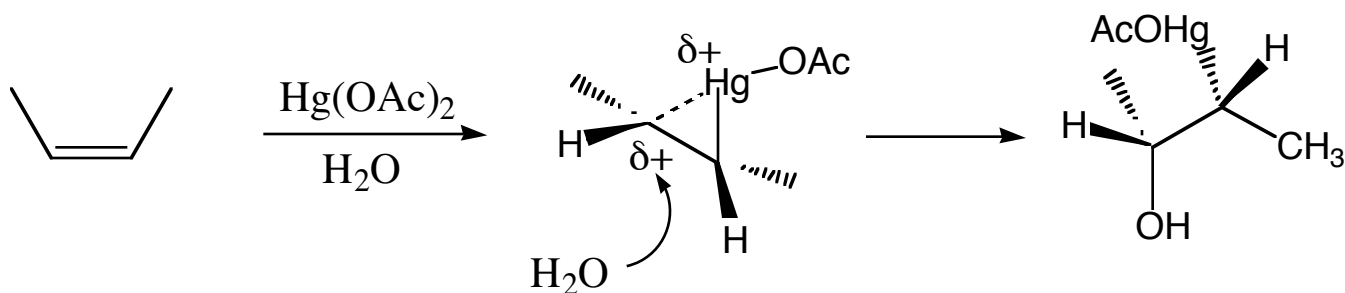


the water (which is acting as a nucleophile) will thus attack this more substituted carbon



Stereochemistry

since the mercury species forms this mercurinium ion the water must attack from the opposite side of the double bond

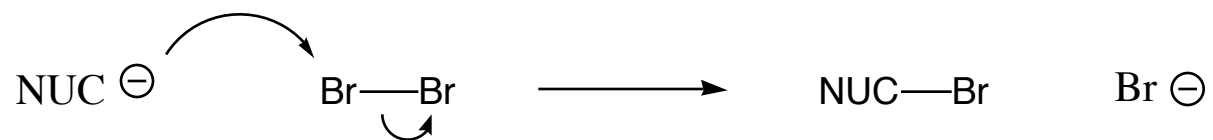


gives an anti addition to the double bond

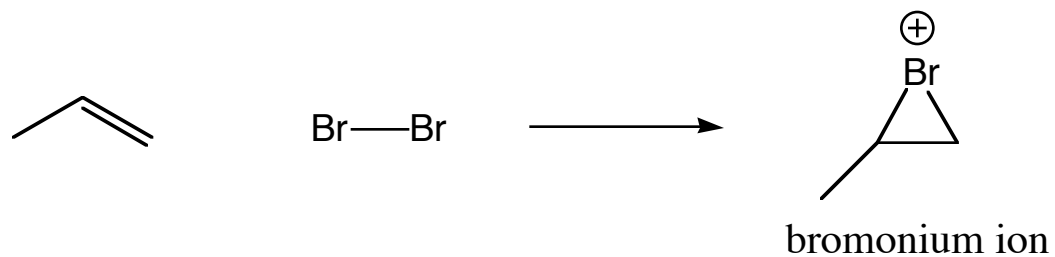
- the two new species have added to opposite sides of the double bond

Addition of Halogens

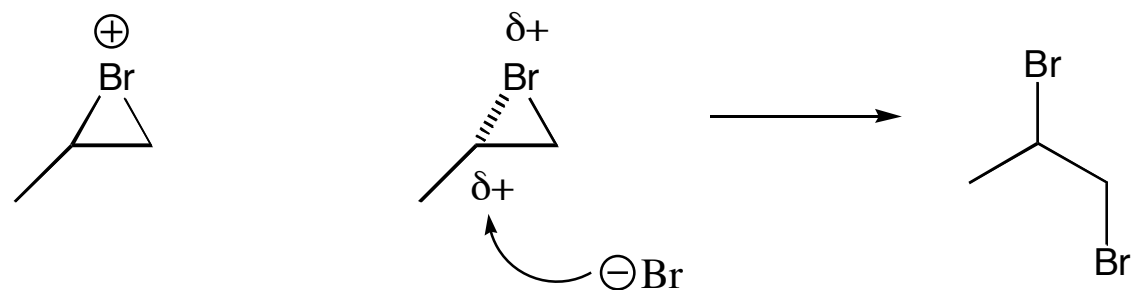
dihalides can also be used as an electrophile



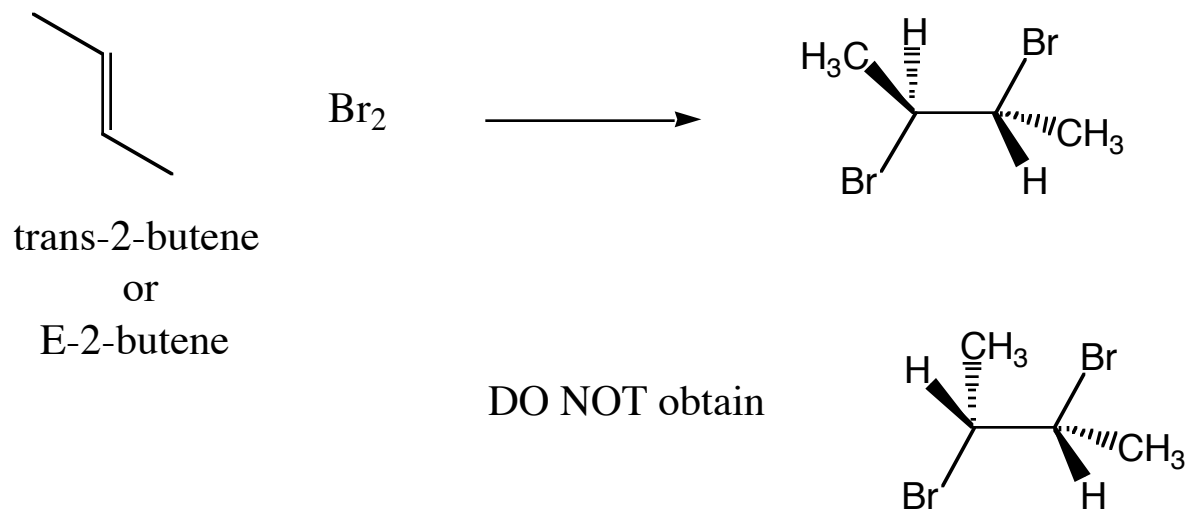
an alkene will form another 3-centered ring intermediate



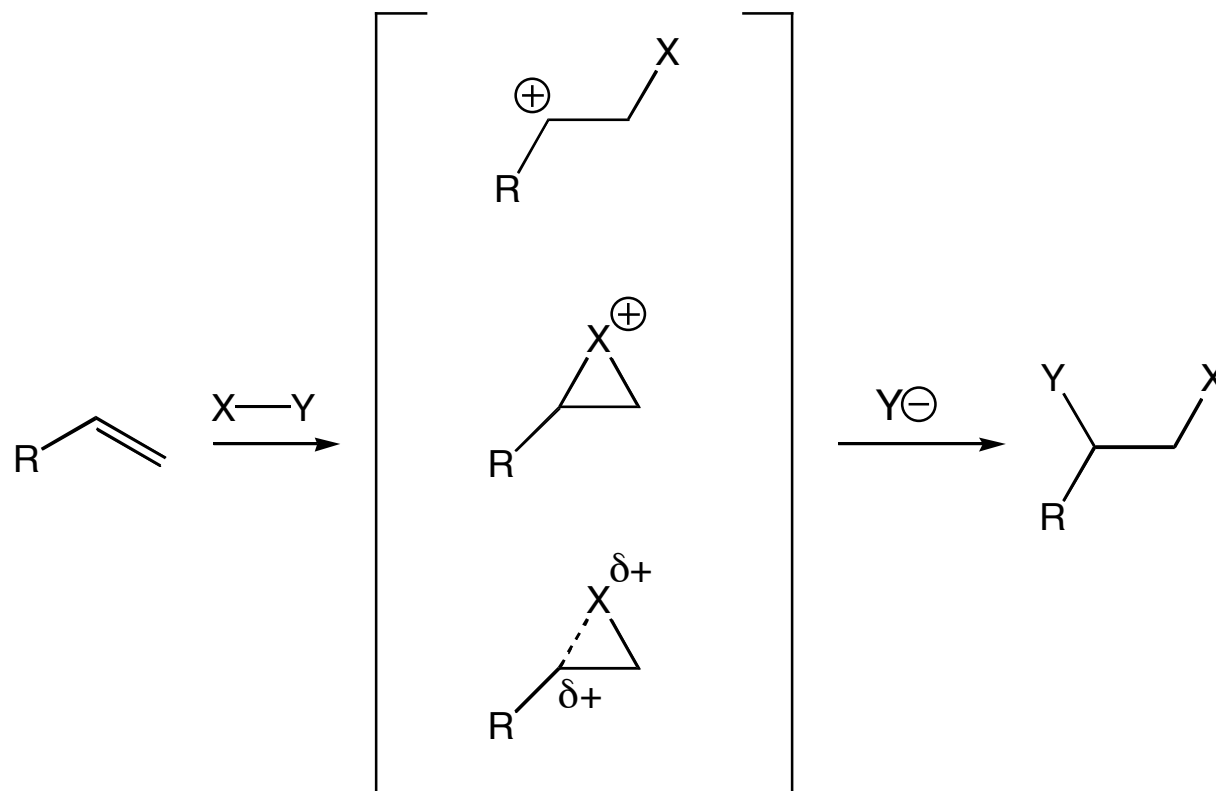
the bromonium ion then reacts with the bromide present to yield a dihalogen compound



due to the 3-centered intermediate dihalogen additions occur in an anti fashion



Considerations in Alkene Reactions

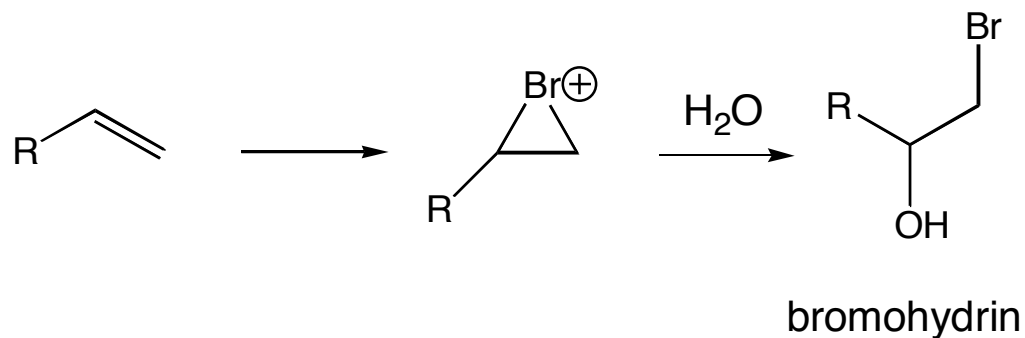


Questions:

- 1) what is the electrophile (what is X)?
- 2) what is the regiochemistry (does X bind to less or more substituted carbon)?
- 3) what is the stereochemistry (is X and Y addition syn or anti)?

Formation of Halohydrins

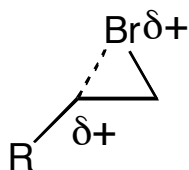
When water is present when a dihalogen is added to a double bond, then water can react with the halonium ion



the halohydrin is named according to which halogen is present
(bromohydrin, chlorohydrin, iodohydrin)

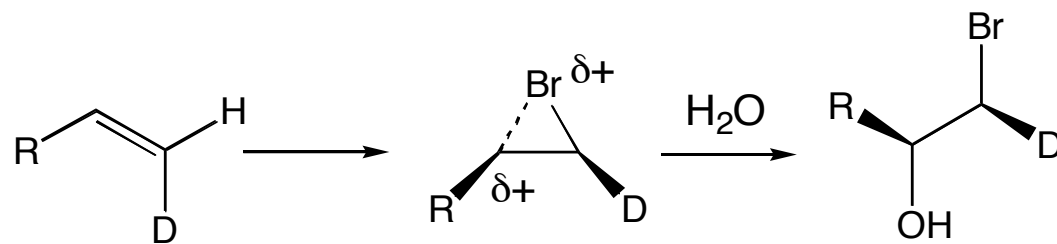
Regio- and Stereochemistry

As observed in the formation of mercurinium ions, the halogen actually forms one partial bond to the original carbon-carbon double bond



- the partial bond will form at the more substituted carbon atom
(partial charge is more stable)

this structure defines both the regio- and stereochemistry



get anti addition and nucleophile adds to more substituted carbon
(or carbon that can better accommodate a positive charge)

Boron is Another Potential Electrophile

- boron is to the left of carbon in the periodic table

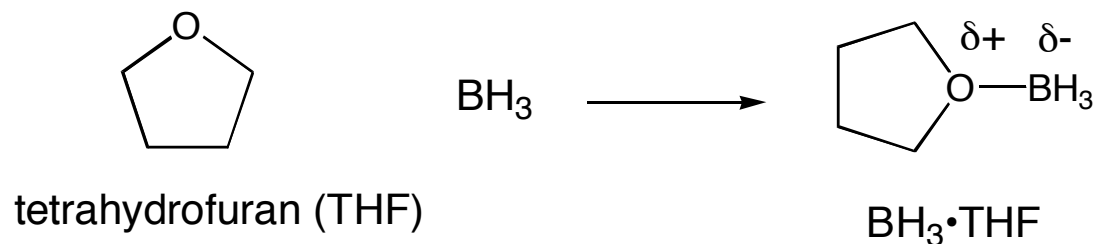


*hence boron is electropositive compared to carbon

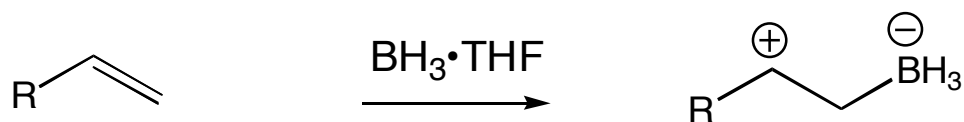
in fact the neutral form of boron, BH_3 , is unstable

(it only has 6 electrons in the outer shell)

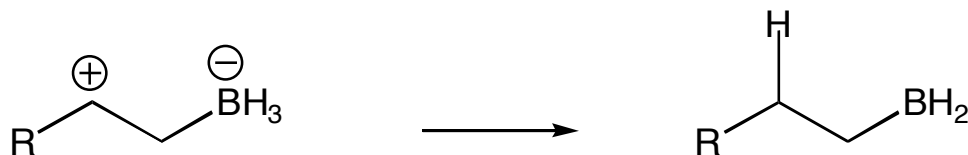
often boron is complexed with an oxygen containing species to offer stability



Due to the electropositive character of BH_3 ,
it will act as an electrophile in alkene reactions



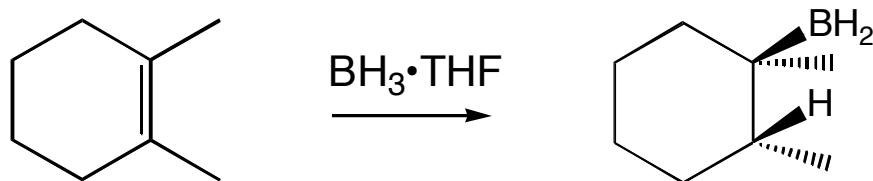
this complex will immediately shift a hydride (if not concerted)
to form an alkyl borane



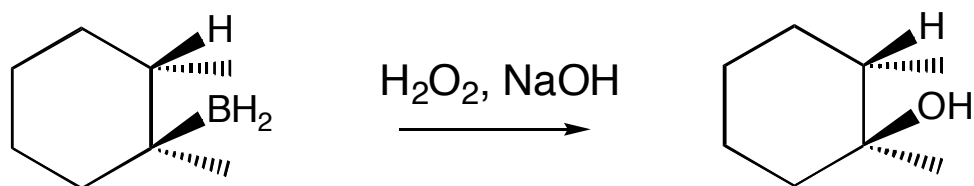
the borane therefore adds to the LEAST substituted carbon position!

Stereochemistry

- due to the hydride shift is faster than bond rotation,
both the borane and hydrogen add to the same face of the double bond
(SYN addition)



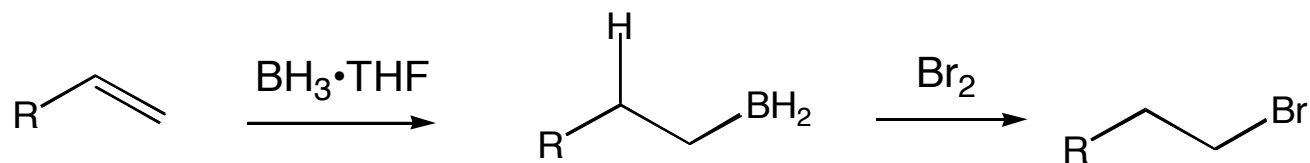
- the borane can now be removed



an alcohol can be formed by reacting the alkyl borane with basic hydrogen peroxide

-the hydroxy is added to the same face as the borane
therefore the hydrogen and hydroxy have added in a SYN addition

- the borane can also be replaced by a halogen

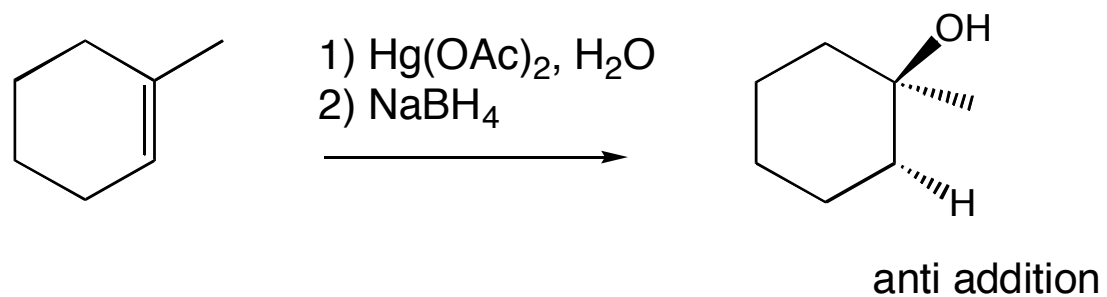


both the hydroxy and halogen reactions place the substituent
in the LEAST substituted position

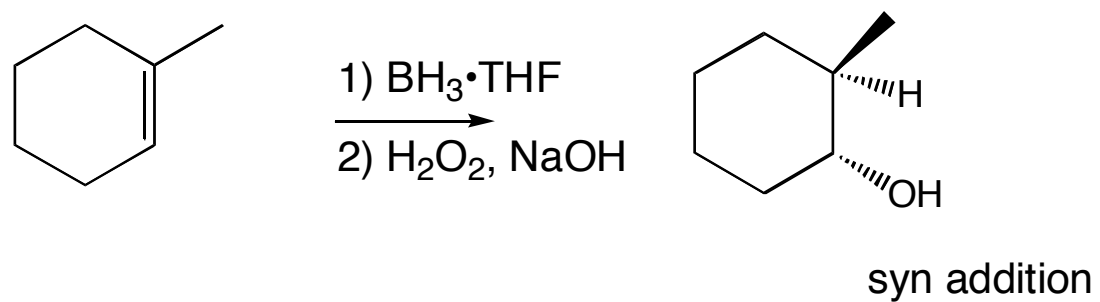
- In contrast to direct Markovnikov addition!

Compare two methods to generate alcohols from alkenes

Markovnikov addition



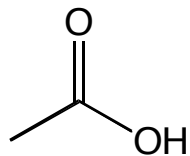
anti-Markovnikov addition



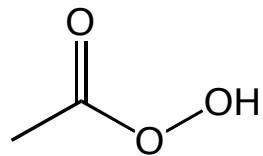
Adding Oxygen Directly as the Electrophile

Previously we have observed oxygen acting as a nucleophile
and reacting with carbocation sites

- a peroxy acid (or peracid) is a source of electrophilic oxygen

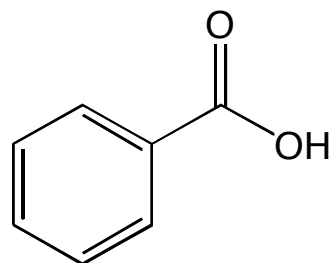


carboxylic acid

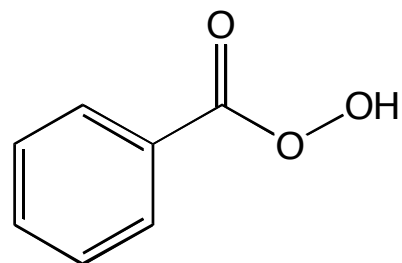


peroxy acid

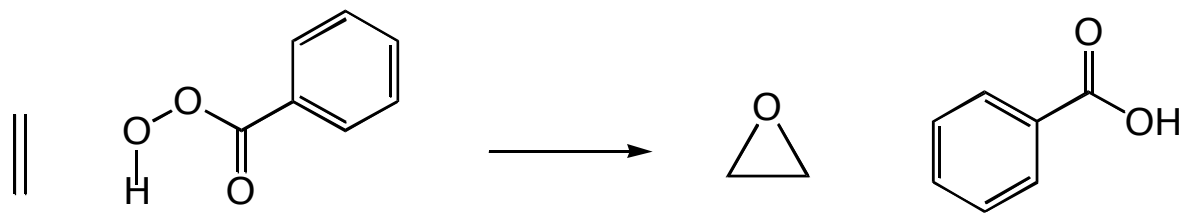
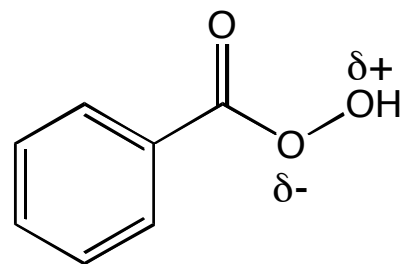
when added to an alkene the peroxy acid forms an epoxide



benzoic acid

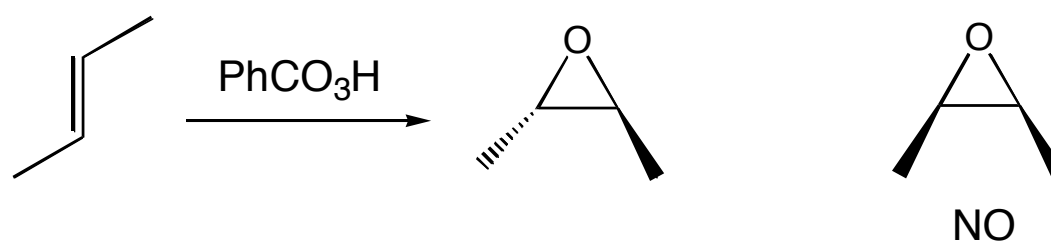
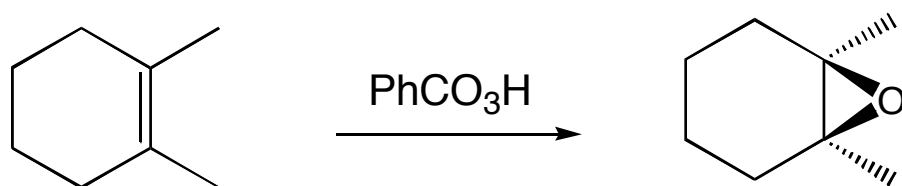


perbenzoic acid

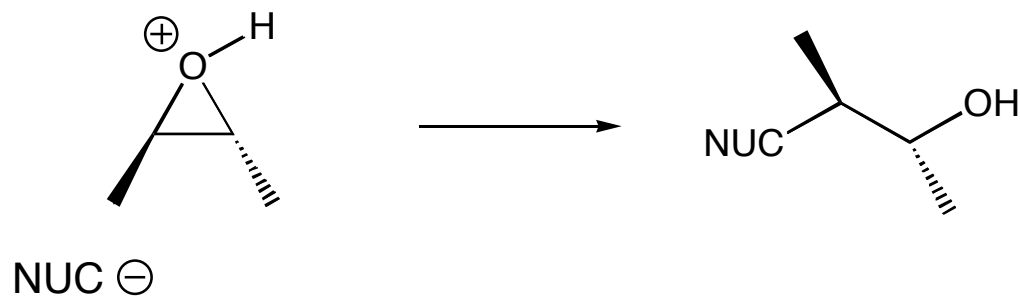


a three membered ring with one oxygen atom is called an epoxide

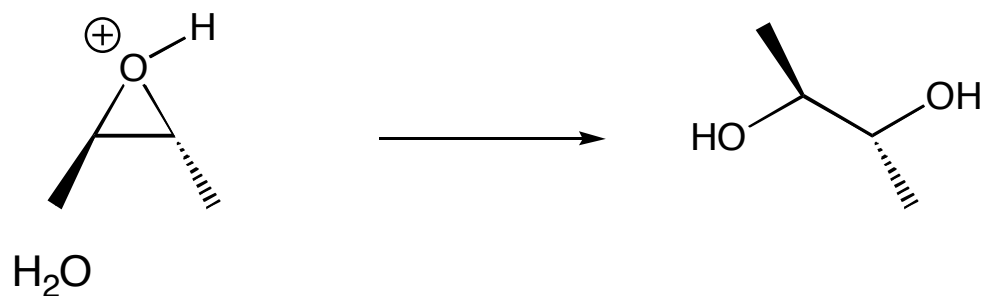
due to the cyclic nature of the transition state the epoxide is added in a SYN fashion



Nucleophiles can open epoxides
(especially in acidic media)



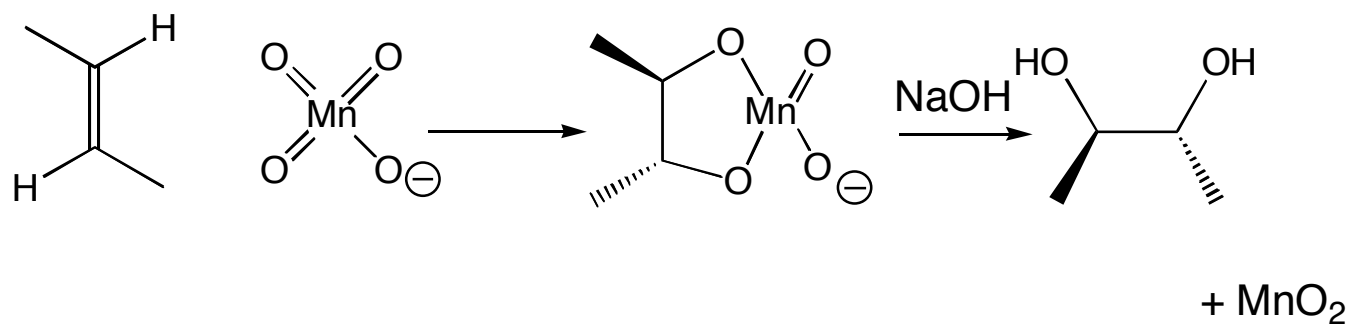
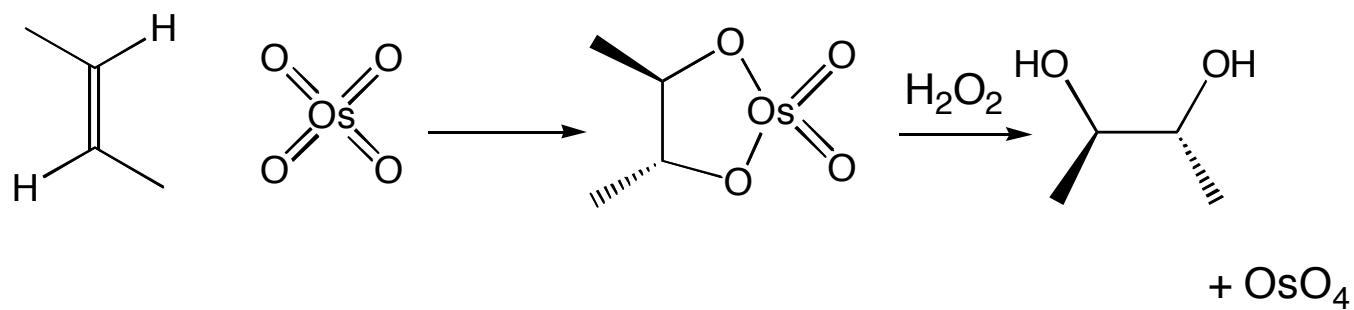
therefore in acidic aqueous conditions a glycol (1,2-dihydroxy compound) is formed



these conditions give an anti dihydroxy compound

SYN dihydroxylation requires both OH groups to be delivered from the same face

There are two common reagents for SYN dihydroxy addition to alkenes

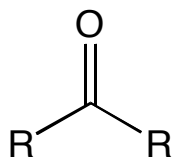


Carbonyl Nomenclature

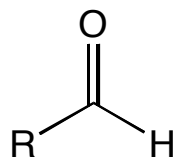
A carbon oxygen double bond is a common, and useful, functional group in organic chemistry

- called a carbonyl group (the carbon is called a carbonyl carbon)

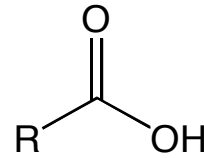
the nomenclature changes depending upon the substituents on the carbonyl carbon



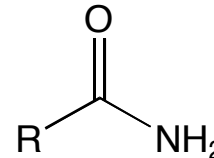
ketone



aldehyde

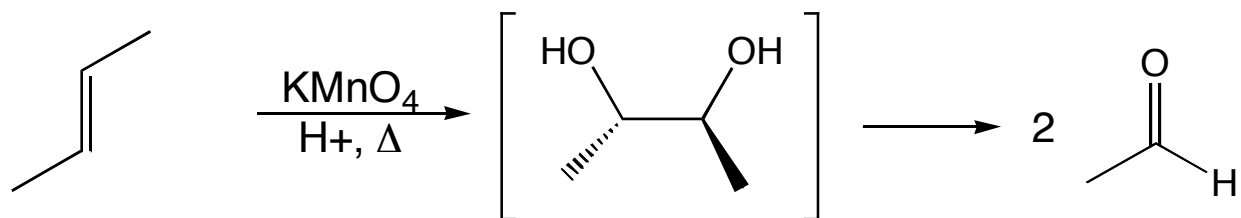


carboxylic acid



amide

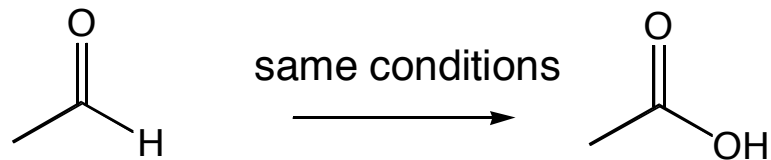
the dihydroxy compounds (glycols) can also be cleaved



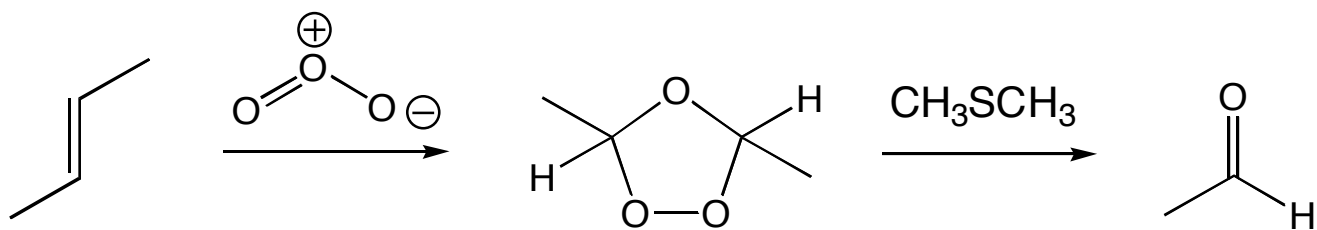
under acidic potassium permanganate conditions the glycol is cleaved to generate two carbonyl groups

if the resulting carbonyl group is a ketone, it is stable

-but if the resulting carbonyl group is an aldehyde it will be further oxidized to the carboxylic acid



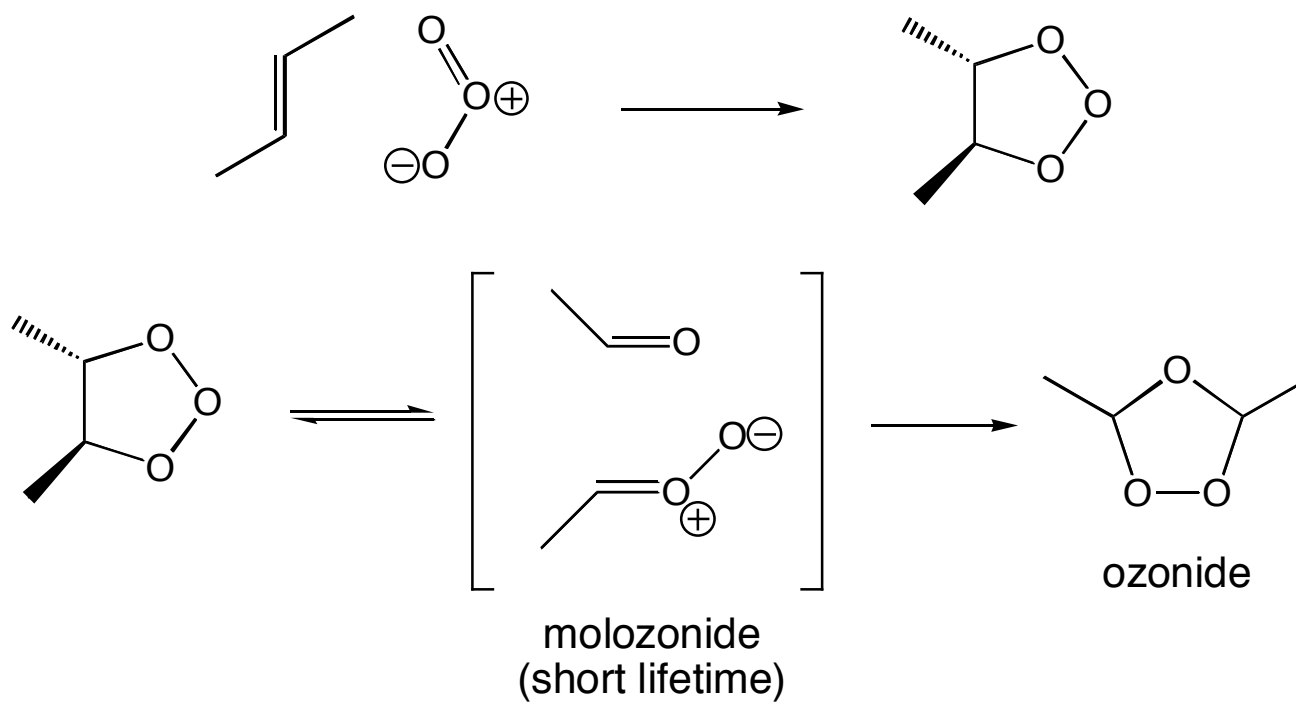
To prevent this "overoxidation" alkenes can be treated with ozone



The aldehyde is stable under these conditions

-in essence whatever is bonded at the carbon-carbon bond
becomes a carbonyl under ozonolysis

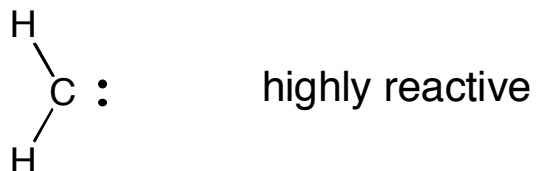
Mechanism of Ozonolysis



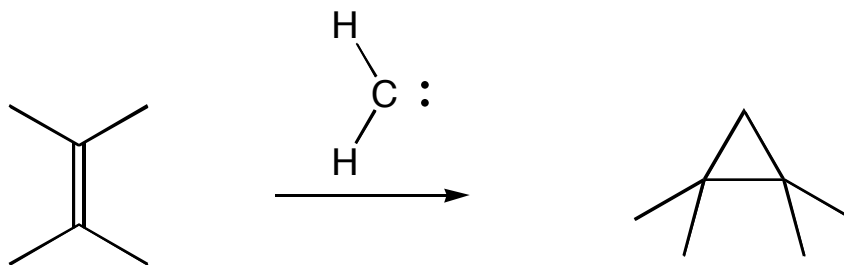
Other Reactions of Alkenes

Carbenes

A carbene refers to a carbon atom containing only 6 electrons in the outer shell
(two covalent bonds and an extra two electrons)

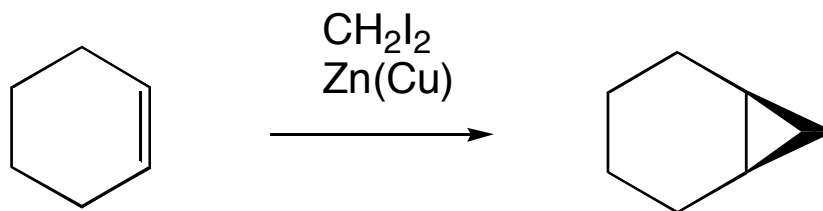


this compound will react quickly with alkenes to form a cyclopropane



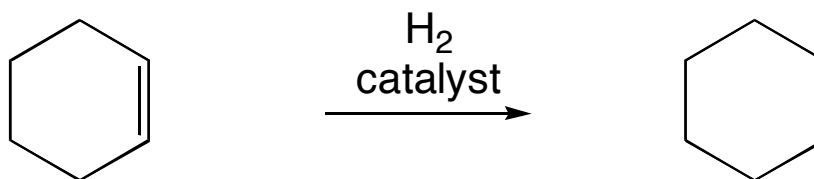
Generation of Carbenes

The most useful means is by reacting diiodomethane with a Zn(Cu) couple



Reacts in a SYN fashion

An alkene can also be reduced to an alkane

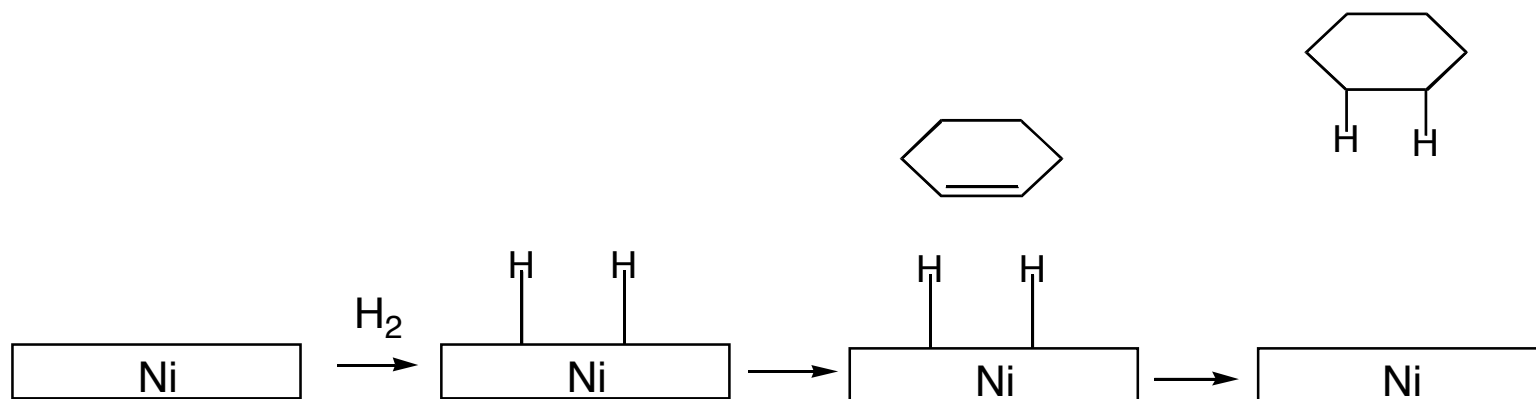


The catalyst is required for this process

Reaction occurs on the metal surface of the catalyst (Pt, Pd, Ni)

The hydrogens add in a SYN fashion

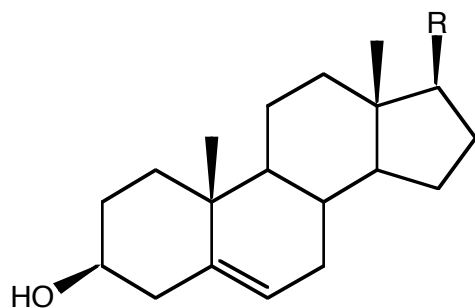
Both hydrogens are added to the same face of the alkene
as the alkene approaches the metal surface



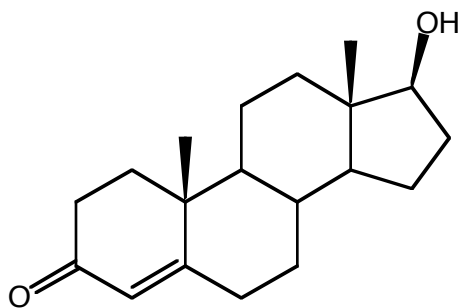
How Alkene Reactions are Important Biologically

- the same reactions we have been studied (and in not any more complexity!)
are used in biosynthetic pathways

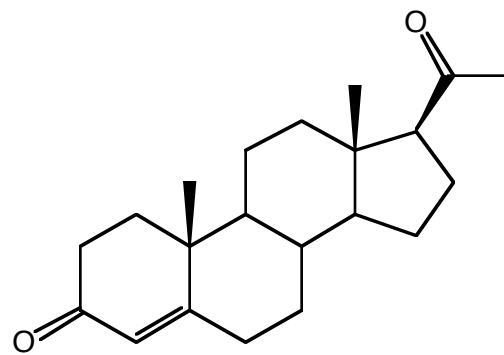
- especially important in the synthesis of steroids



cholesterol



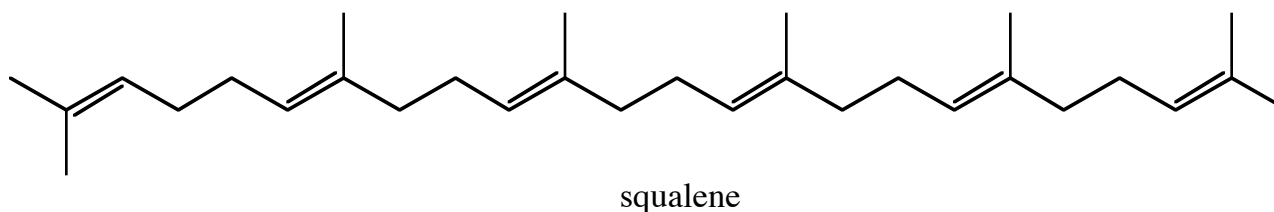
testosterone



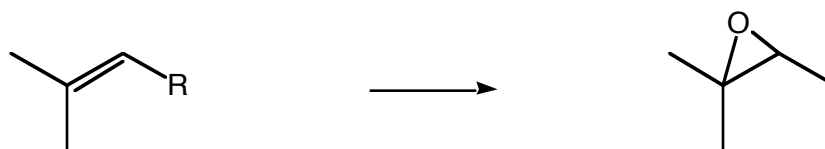
progesterone

the body produces these 6-6-6-5 ring structures
through an exquisite alkene reaction pathway

the body first produces an alkene (squalene)



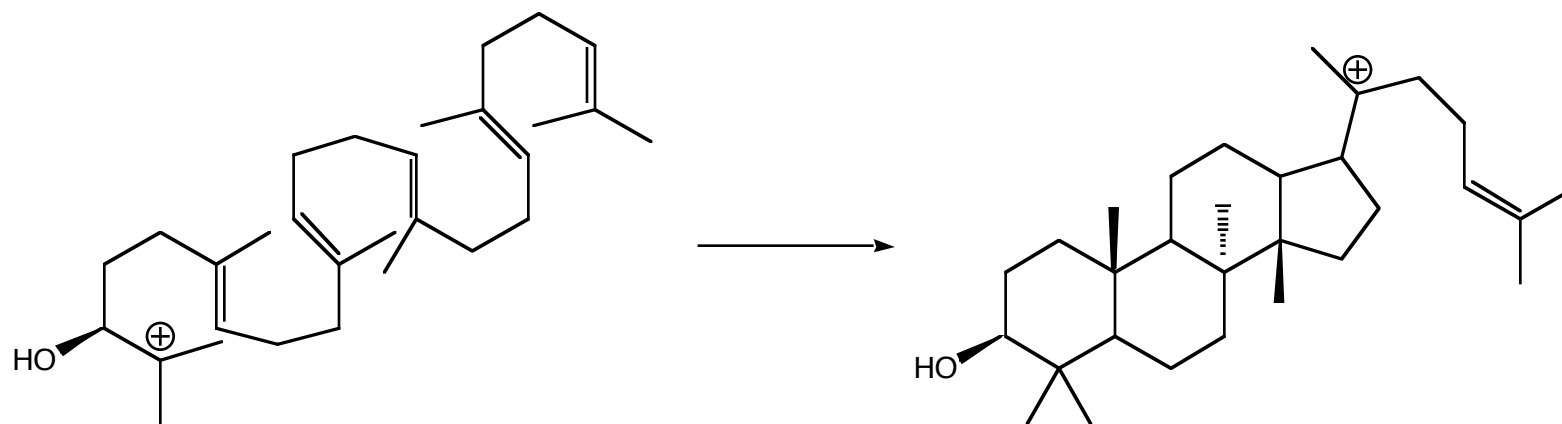
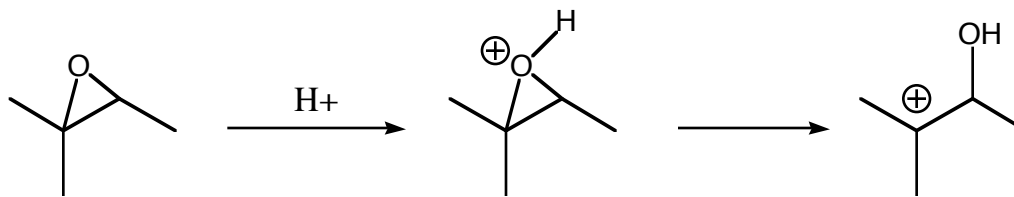
an enzyme then oxidizes a terminal alkene to an epoxide
(just like any peroxyacid we studied would)



the enzyme now supplies a proton

(in a proton shuttle mechanism - to be seen in biochemistry class if so inclined)

- important to realize that this proton will cause the protonated oxygen to leave to generate the MORE stable carbocation

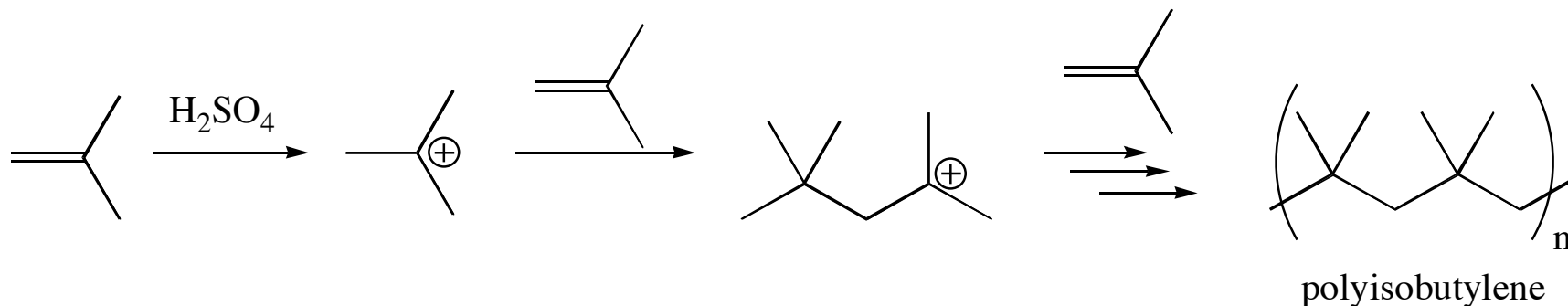


Polymerizations

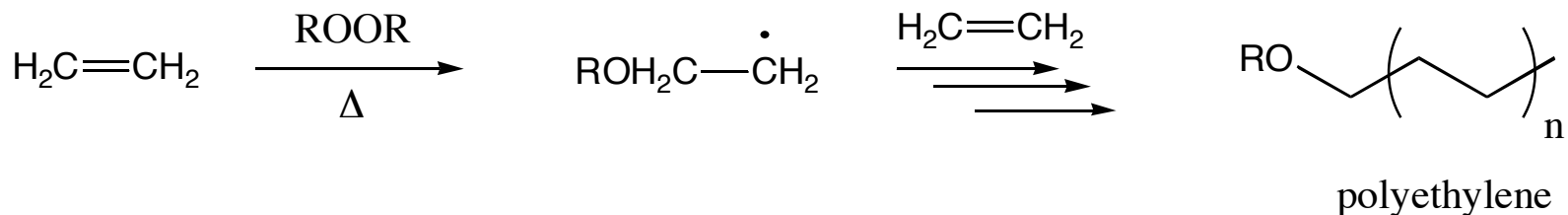
Similar to squalene reacting to form steroids, short alkenes can react to form polymers
(suffix -mer comes from Greek word meros, meaning "part";)

Routes:

Cationic polymerizations - carbocations are generated which react with other alkenes



Radical polymerization - radical sites are generated which react with other alkenes



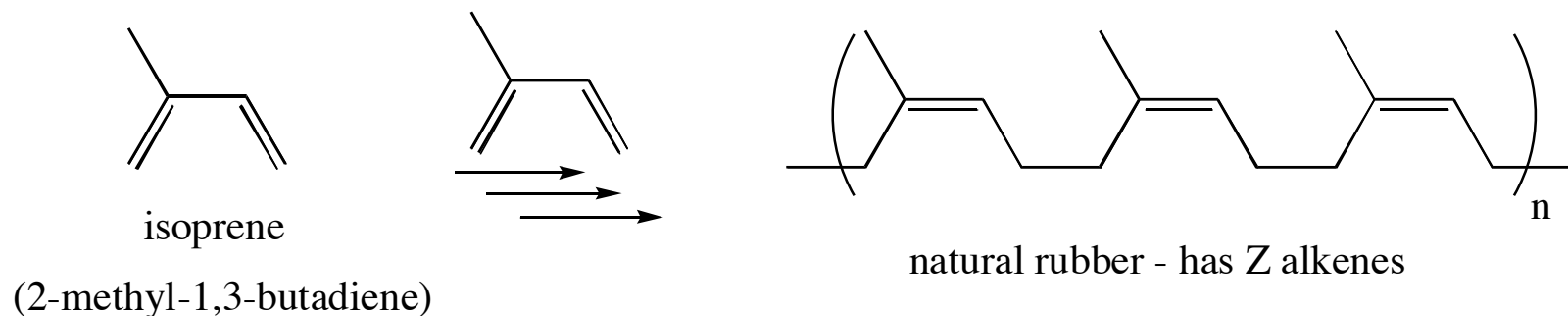
can also do anionic polymerization - anions react with alkene sources

Natural Rubber

Natural rubber is an alkene polymer produced by many sources,
most common being the rubber tree

Originally named by Joseph Priestley (discoverer of oxygen fame) due to its ability to
"rub" out pencil marks, therefore rubber is named due to its eraser properties

Natural rubber is a result of a diene polymerizing



natural rubber obtained from tree is called latex, it is too soft and is later hardened by a
process called vulcanization (heating with sulfur) to cross link the chains

double bonds in product are key for the rubber to be deformed and return to original
shape - they cause "kinks" in polymer so neighboring chains have difficulty packing