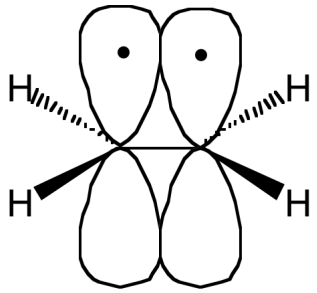
Review of an Alkene



Two sp^2 hybridized carbon atoms

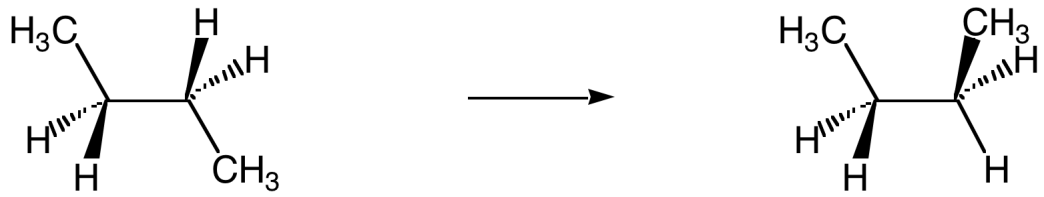
1 σ bond	83 Kcal/mol
1 π bond	63 Kcal/mol

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

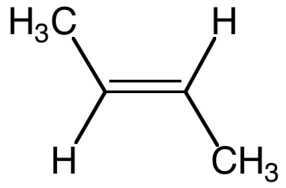
Therefore even though a carbon-carbon σ bond rarely reacts,
the π bond reacts readily

Double Bond Prevents Rotation

A carbon-carbon single bond has conformational flexibility

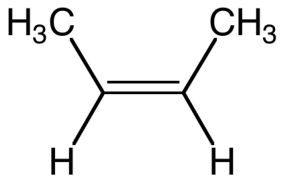


The carbon-carbon double bond prevents this rotation because the π bond would have to break for rotation to occur



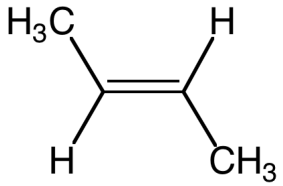
This Lack of Rotation Causes Geometric Isomers

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



cis-2-butene

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

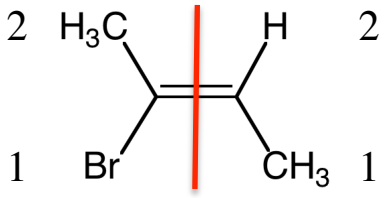


trans-2-butene

If there are more than two substituents on alkene use Z and E nomenclature

-substituents are prioritized
(same rules as already learned for R and S designation)

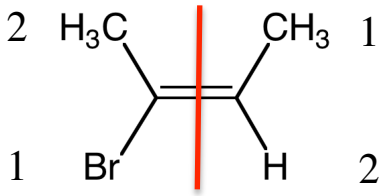
-if the highest priorities are on the same side called Z



Z – zusammen – “together”

Z-2-bromo-2-butene

-if the highest priorities are on the opposite side called E



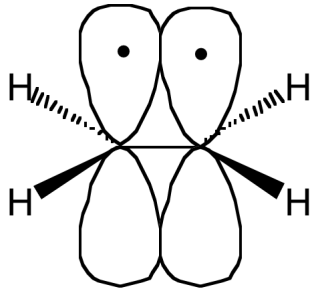
E – entgegen – “opposite”

E-2-bromo-2-butene

Stability of Alkenes

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

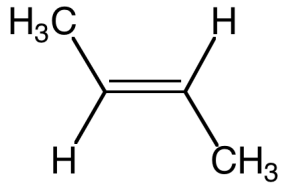
We can rationalize this by considering an alkene as two adjacent carbon radicals



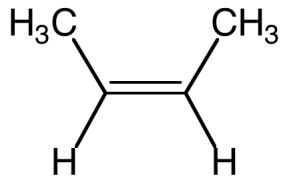
Radicals are electron deficient
Therefore anything that stabilizes electron deficient sits will stabilize an alkene
(carbon-carbon bonds are electron donating through inductive and hyperconjugation effects)

Stability also changes between disubstituted alkenes

Consider again cis- versus trans-2-butene

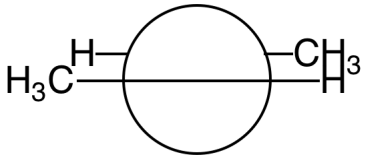


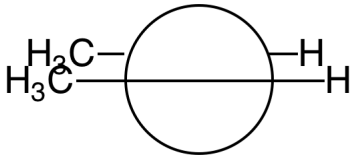
trans-2-butene



cis-2-butene

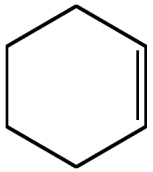
The cis isomer has higher nonbonded strain





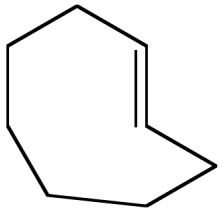
Ring Strain

A small ring requires a cis geometry

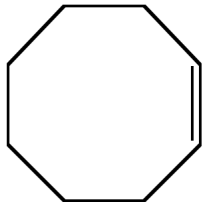


cyclohexene

In a ring structure, a trans alkene is too high in energy until at least an eight membered ring



trans-cyclooctene



cis-cyclooctene

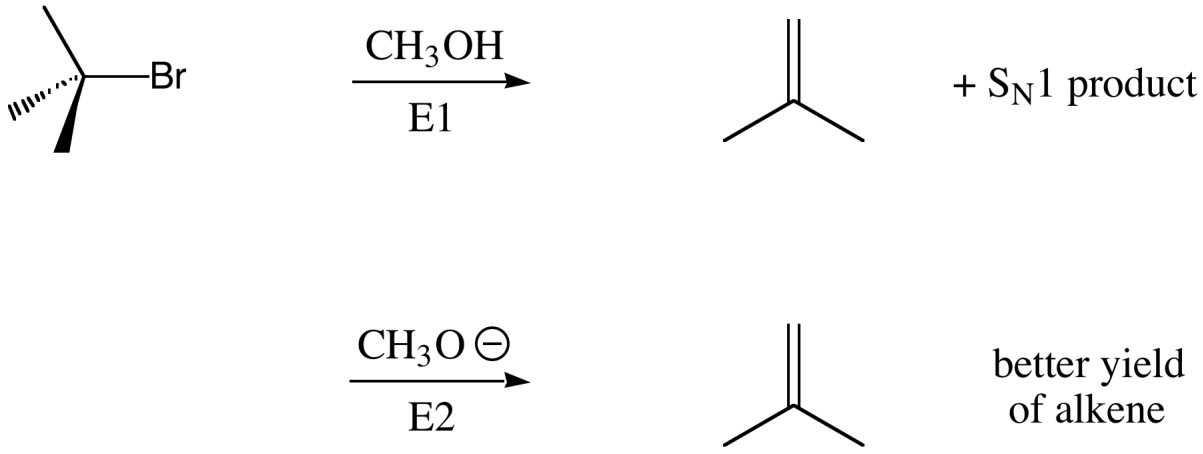
In smaller rings therefore any alkene in a ring is assumed to be cis
(do not need to write cis)

Synthesis of Alkenes

We have already learned two ways to synthesize an alkene:

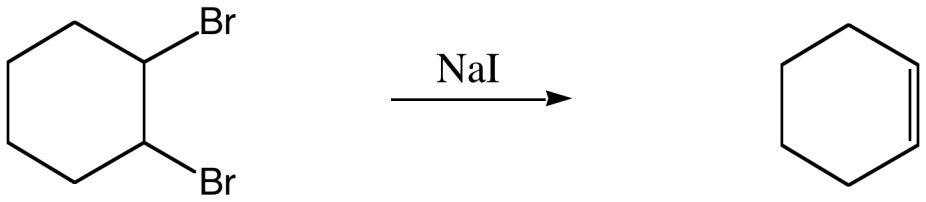
1) Dehydrohalogenation (either E1 or E2)

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



2) dehalogenation

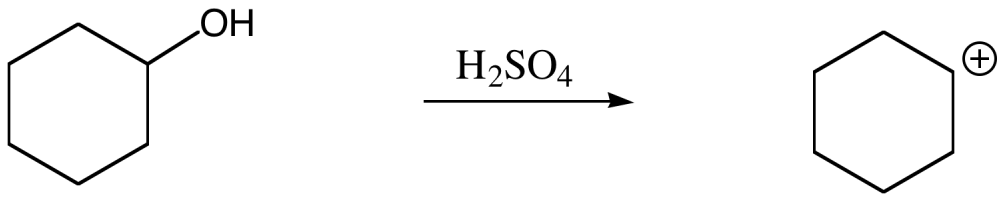
Eliminate two adjacent bromines from an alkane with iodide ion



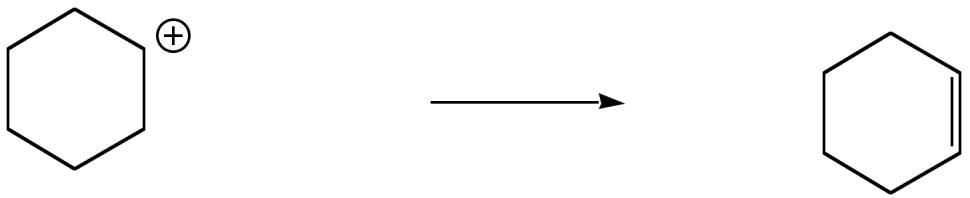
Goes through an anti-coplanar elimination
similar to an E2 mechanism

A third route to alkenes is through a dehydration of an alcohol

Under acidic conditions an alcohol can leave to generate a carbocation

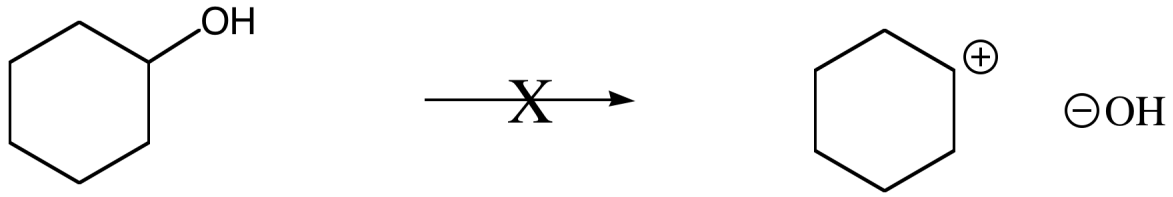


This carbocation can react similar to E1 reactions studied earlier to generate an alkene

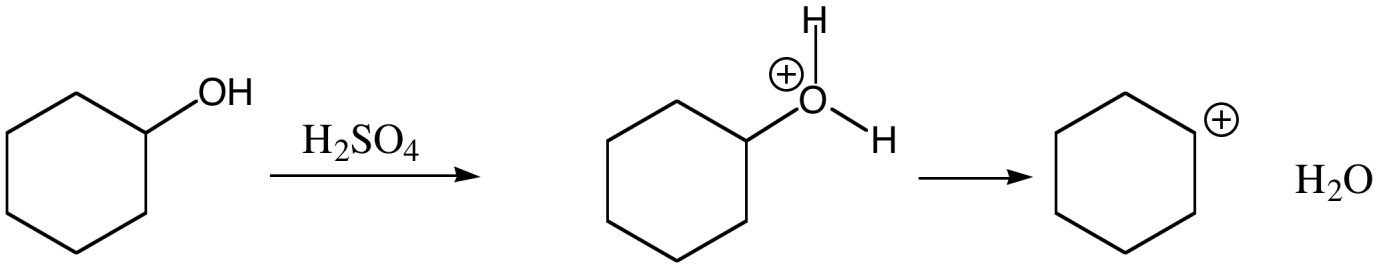


Acidic conditions are necessary to make the alcohol a good leaving group

Without acid catalysts a hydroxide would be the leaving group
(remember this is a BAD leaving group and will not work)



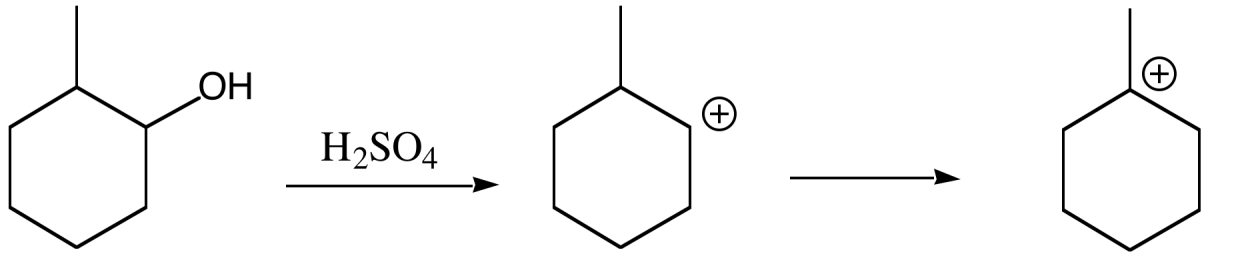
With acid catalysts the hydroxy group becomes protonated BEFORE departing as water



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

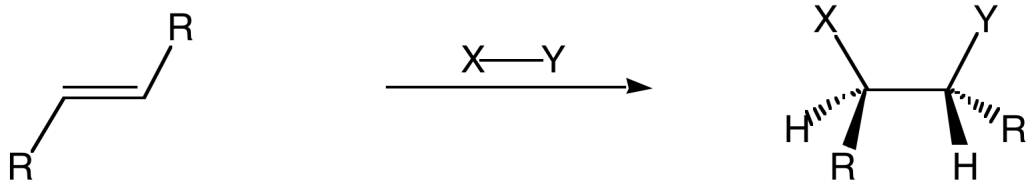
-a 3° site will be more reactive than a 2° and so forth
(a carbocation will be generated which is stabilized with electron donating substituents)

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

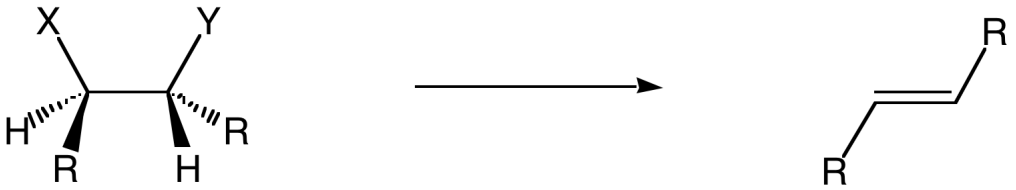


Reactions of Alkenes

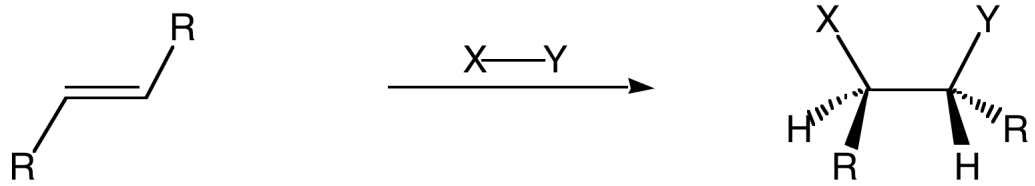
Alkenes generally react in an addition mechanism
(addition – two new species add to a molecule and none leave)



Realize this is the REVERSE of an elimination mechanism



There are three questions to ask for any addition reaction



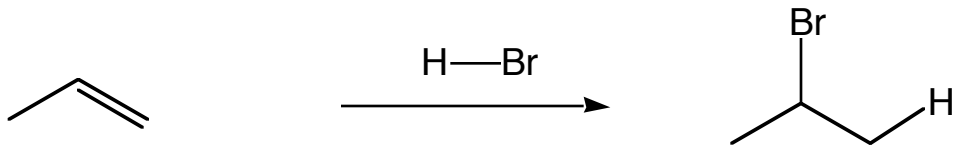
1) What is being added?
(what is the electrophile?)

2) What is the regiochemistry?
(do the reagents add with the X group to the left or right?)

3) What is the stereochemistry?
(do both the X and Y groups add to the same side of the double bond or 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 initial double bond

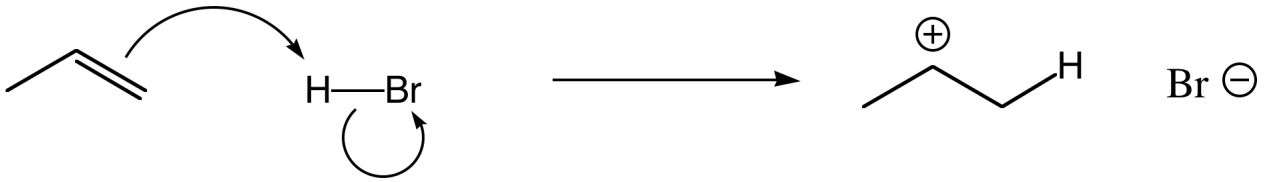


The same reaction will occur with hydrogen chloride and hydrogen iodide

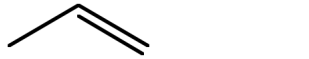
The two electrons involved in the π bond are the nuclophilic source of an alkene addition

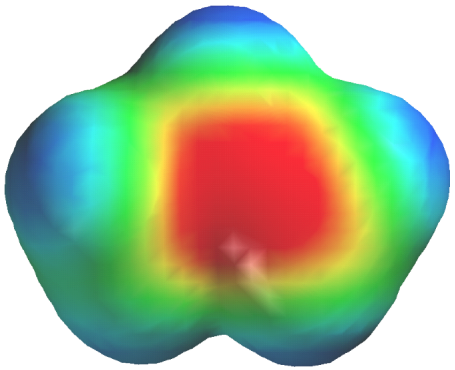
The difference in alkene additions therefore are the source of electrophiles

-for hydrogen bromide the electrophile is the proton

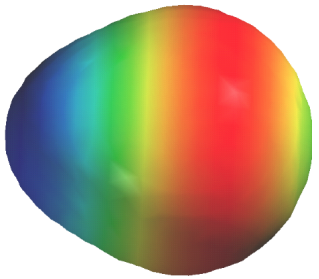


We can see why this reaction occurs by looking at the electron density plots

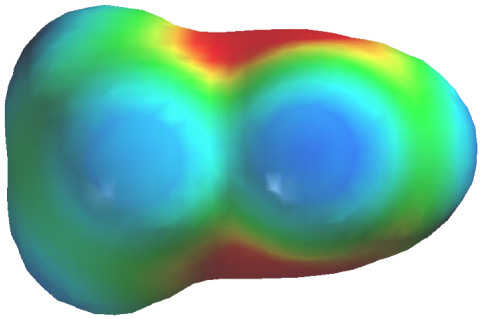


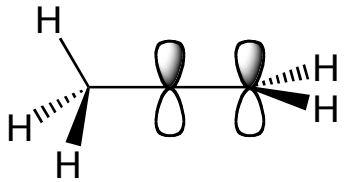


H—Br



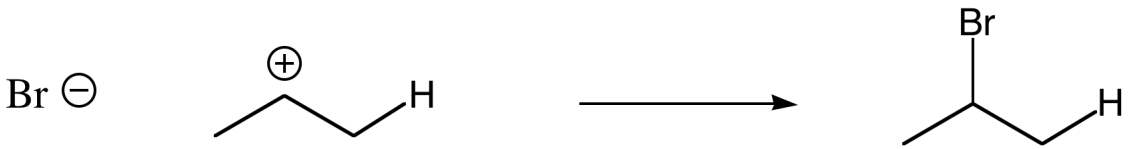
Realize that the electron density of the alkene is located in the π bond which resides above and below the plane of the σ bond





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

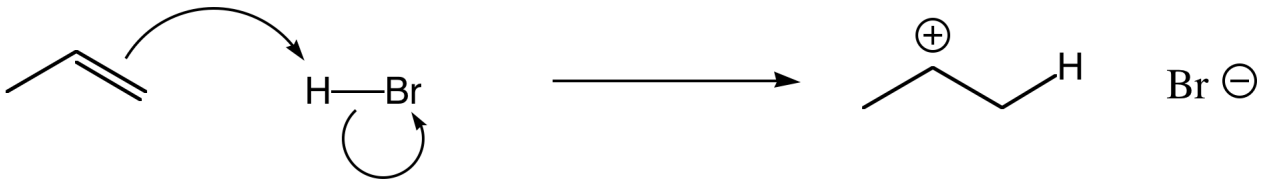
Regiochemistry

The hydrogen halide reactions with alkenes follow “Markovnikov” addition

Markovnikov addition – in an electrophilic addition, the heavier atom adds to the more substituted carbon

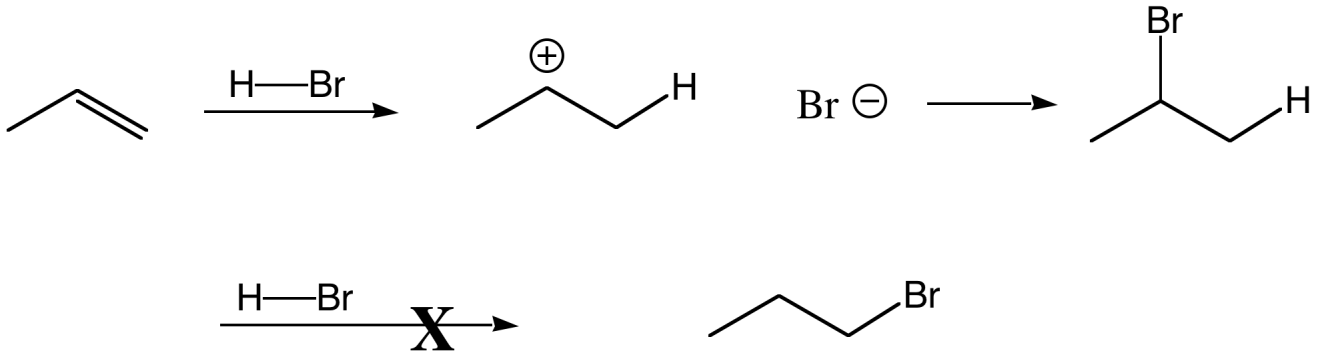
The physical meaning behind the Markovnikov addition is the electrophile adds in such a way to generate the most stable intermediate

What does this imply for a hydrogen halide reaction?
(remember that the first step is the creation of a carbocation)



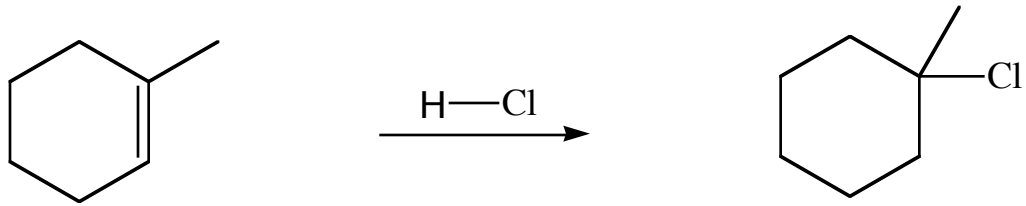
Therefore want to generate the most stable carbocation intermediate

With propene, obtain 2-bromopropane not 1-bromopropane



The heavier bromine atom has thus added to the more substituted carbon
(Markovnikov addition)

With any alkene therefore follow same rules of carbocation stability already learned
(3° > 2° > 1°)



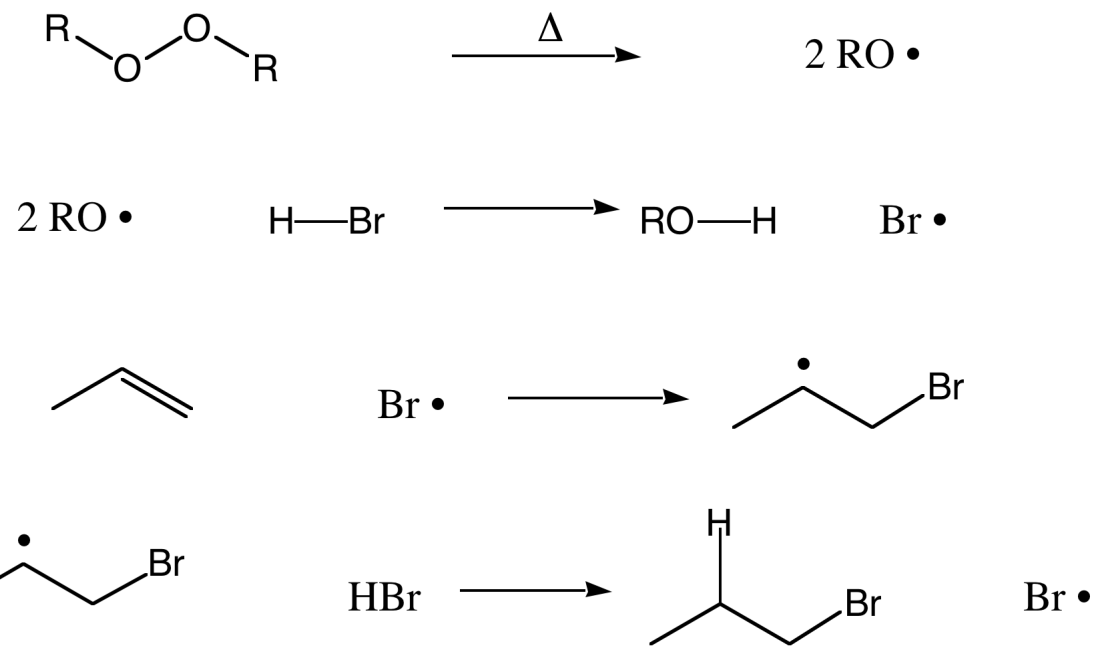
If peroxides are added the mechanism can be changed

Peroxides refer to compounds that contain an oxygen-oxygen (O-O) single bond

HO-OH	hydrogen peroxide
RO-OR	dialkyl peroxide

An 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 different

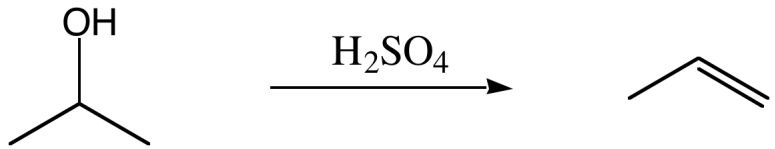
The halogen is at the least substituted carbon of the double bond

Called anti-Markovnikov product

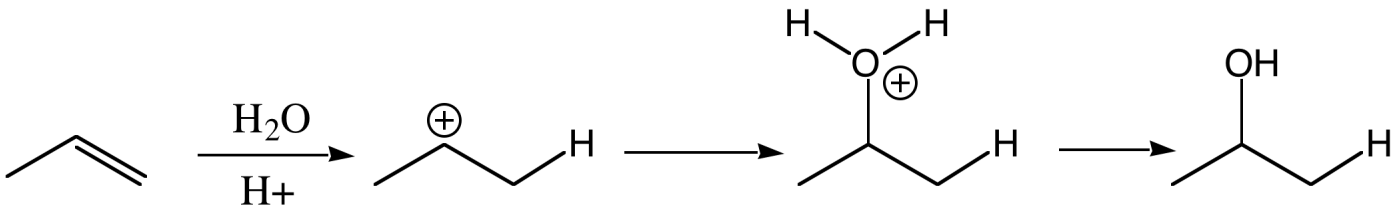
Many other species can be added to double bonds besides hydrogen halides

Formation of Alcohols

We saw how acidic conditions can be used to form an alkene from alcohols

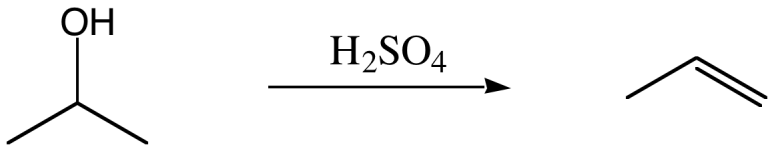


The reverse reaction can occur to form alcohols from alkenes

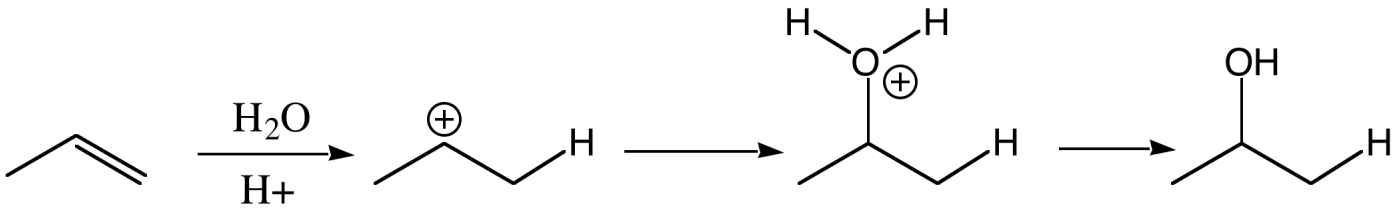


The reaction can be driven either direction by the conditions used

To form alkene need a strong acid that is also a good dehydrator
(common acids include H_2SO_4 and H_3PO_4)

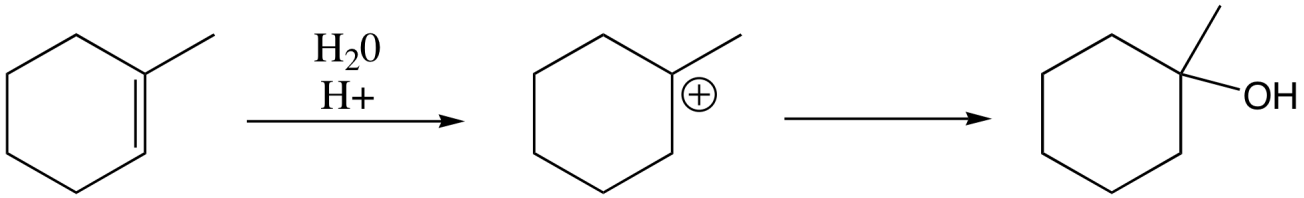


To form alcohol take advantage of LeChatelier's principle and use excess water



Regiochemistry of Hydration

Will follow Markovnikov addition

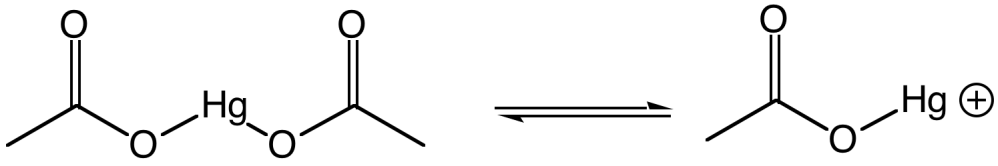


Alcohol will form at the more stable carbocation site

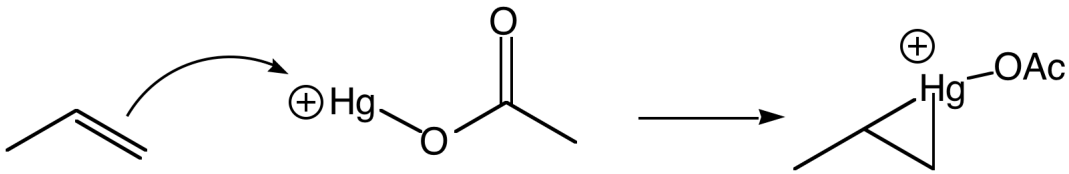
This is another example where the electrophile is the proton

Can also hydrate an alkene by using mercury as the electrophile

Common reagent is $Hg(OAc)_2$

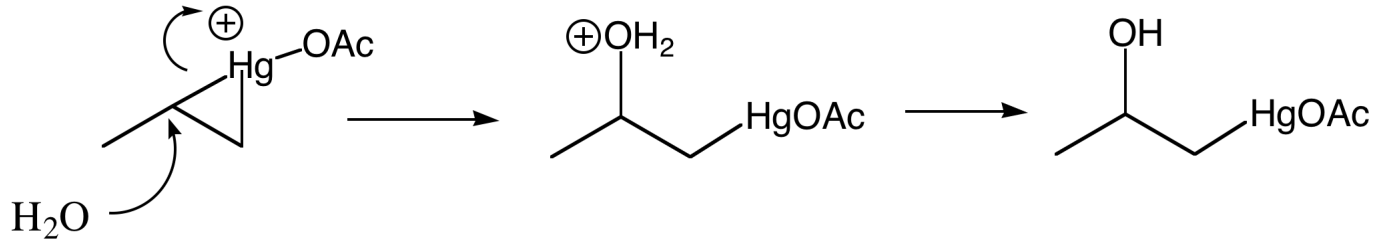


$Hg(OAc)_2$ ⊕HgOAc

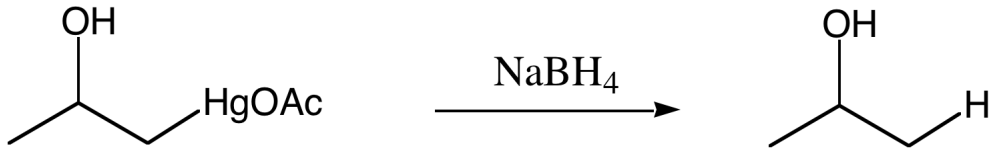


forms a bridged
"mercurinium" ion

Water (which is generally the solvent in this reaction) can attack the mercurinium ion

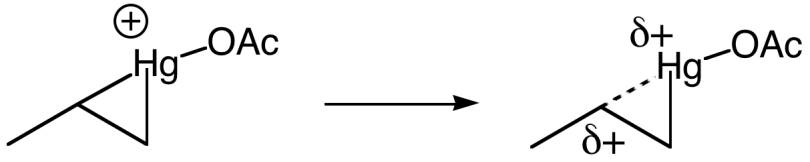


The mercury can then be cleaved off using sodium borohydride ($NaBH_4$)

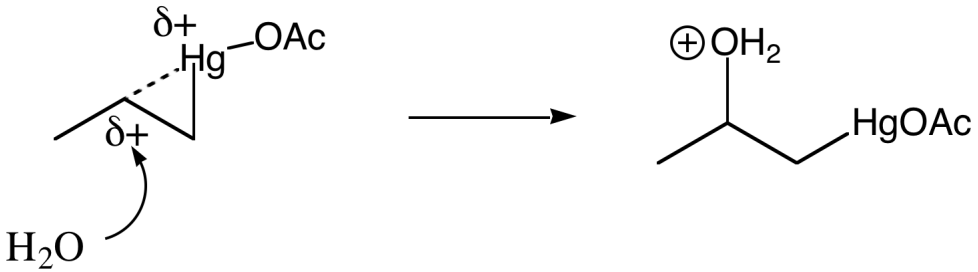


Regiochemistry

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)

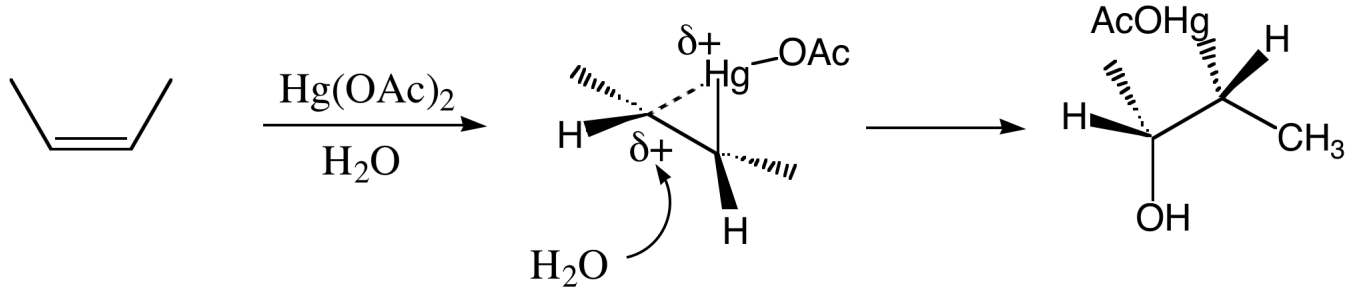


The water (which is acting as a nucleophile) will thus attack this more substituted carbon



Stereochemistry

Since the mercury atom forms this mercurinium ion,
the water must attack from the opposite side of the double bond

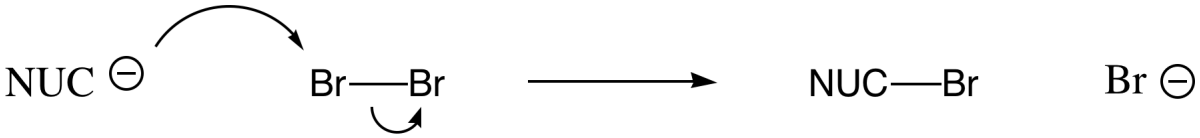


Gives an anti addition to the double bond
-two new species have added to opposite sides of the double bond

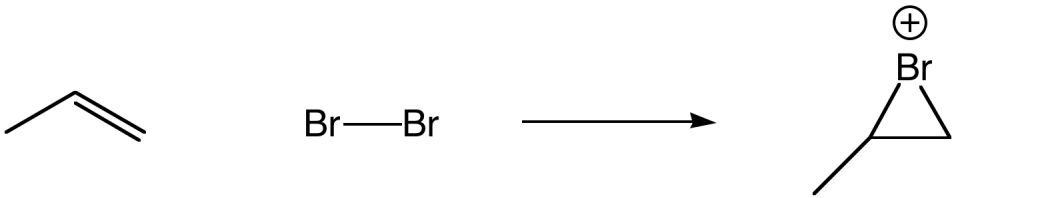
Stereochemistry is due to not forming a planar carbocation as an intermediate

Addition of Halogens

Dihalogens can also be used as an electrophile

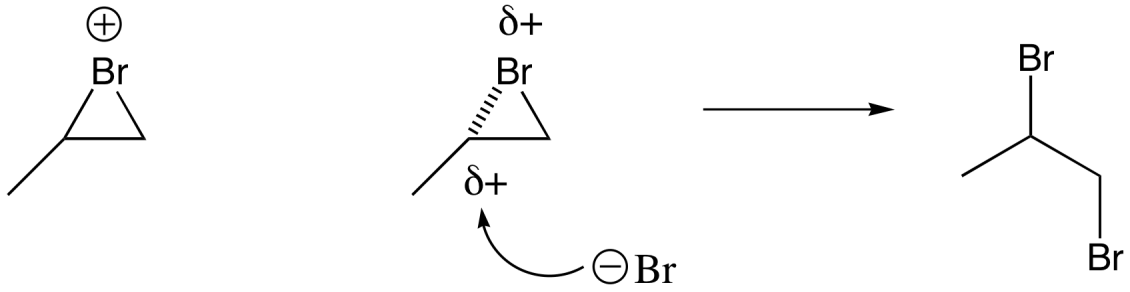


An alkene will form another 3-centered ring intermediate
(called a bromonium ion)



bromonium ion

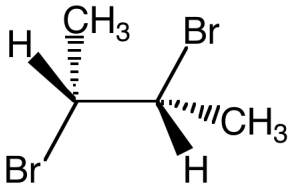
The bromonium ion also forms a partial bond to the carbon that can best stabilize a positive charge which will then react with the bromide nucleophile



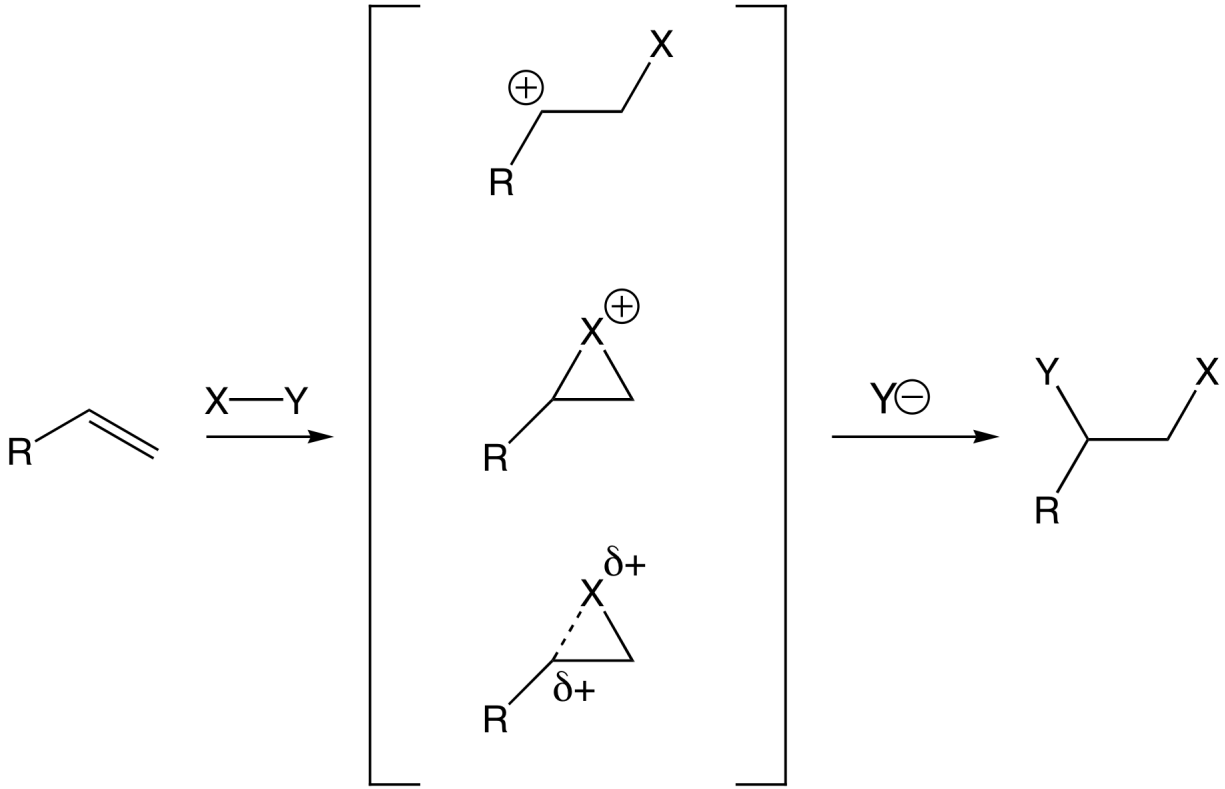
Due to the 3-centered intermediate, dihalogen additions occur with an anti addition

trans-2-butene
or
E-2-butene

DO NOT obtain



Considerations in Alkene Reactions



Questions:

1) What is the electrophile? (what is X?)

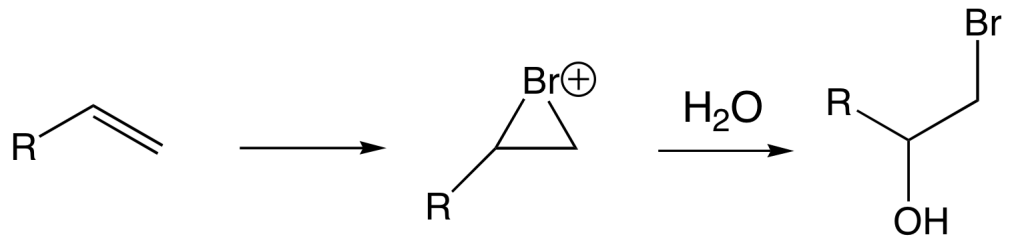
2) What is the regiochemistry? (does X bind to the less or more substituted carbon?)

3) What is the stereochemistry? (do X and Y add syn or anti to the double bond?)

All of these questions can be answered by knowing the intermediate structure

Formation of Halohydrins

When water is present a dihalogen is added to a double bond,
then water can react as the nucleophile with the halonium (e.g. bromonium) ion

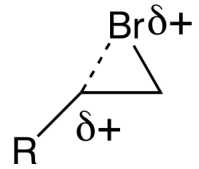


bromohydrin

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

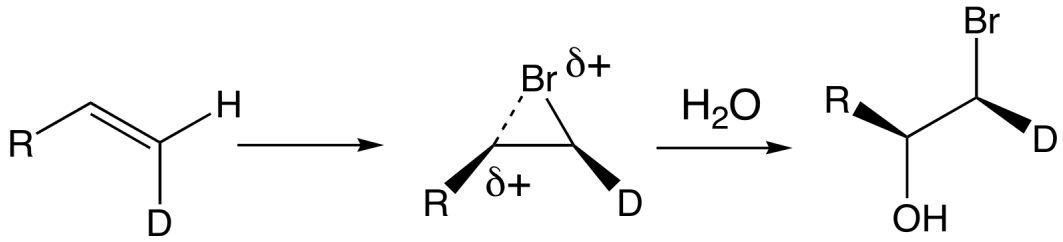
Regio- and Stereochemistry

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 will define both the regio- and stereochemistry for products formed



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

Boron is another potential electrophile

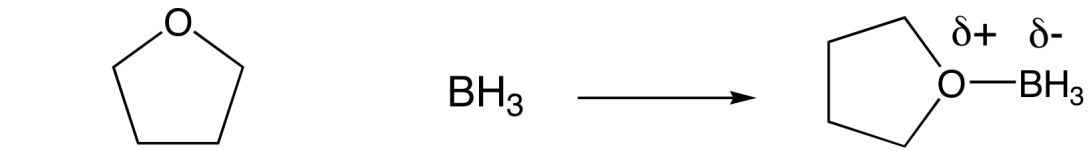
Boron is to the left of carbon in the periodic table

B C N O F

*therefore boron is electropositive compared to carbon

The neutral form of boron, BH_3, is unstable
(it only has 6 electrons in the outer shell)

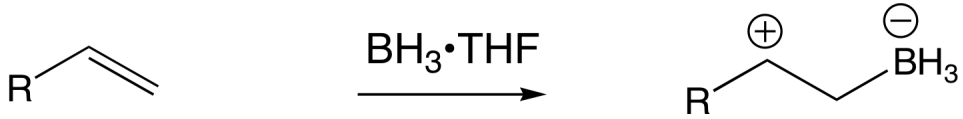
Boron often is complexed with an oxygen containing species to offer stability



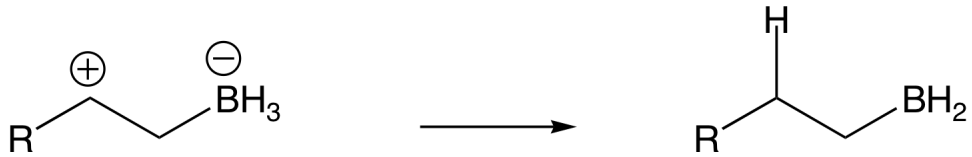
tetrahydrofuran (THF)

BH_3•THF

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



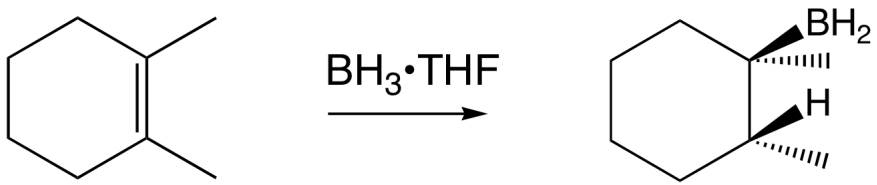
This complex will immediately shift a hydride
(if not concertedly) to form an alkyl borane



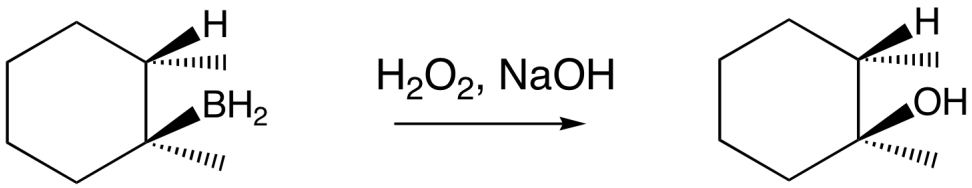
The borane therefore adds to the LEAST substituted carbon position
(anti-Markovnikov)

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)



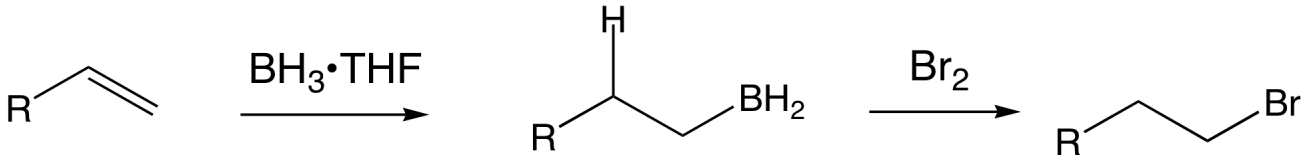
The borane can be removed in a subsequent step



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

The hydroxy group adds to the same face as the borane, thus an alcohol has been formed where both the hydrogen and hydroxy group have added in a SYN addition

The borane can also be replaced with bromine

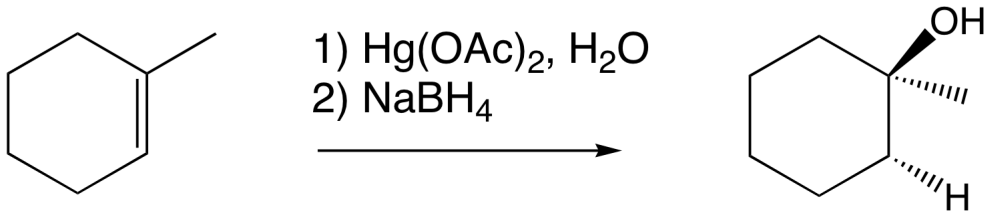


Both the alcohol and halogen reactions place the substituent
in the LEAST substituted position

Hydroboration thus yields anti-Markovnikov products

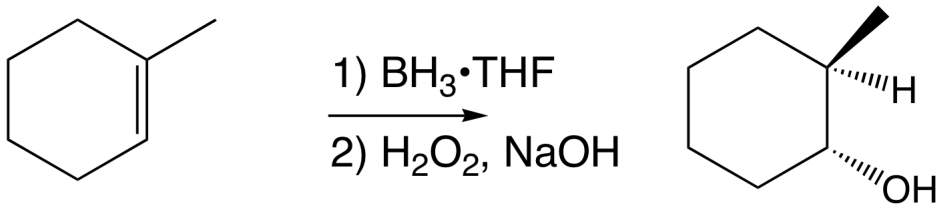
Compare two methods to generate alcohols from alkenes

Markovnikov addition



anti addition

anti-Markovnikov addition



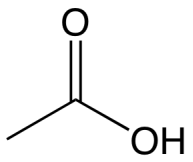
syn addition

These two methods yield different regio- and stereochemical products

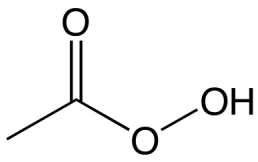
Adding Oxygen Directly as the Electrophile

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

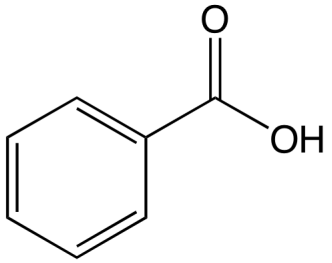


carboxylic acid

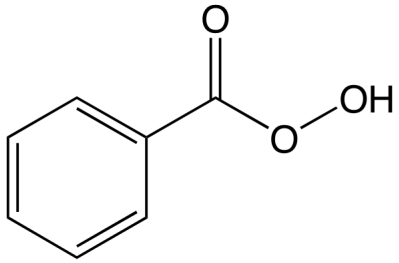


peroxy acid

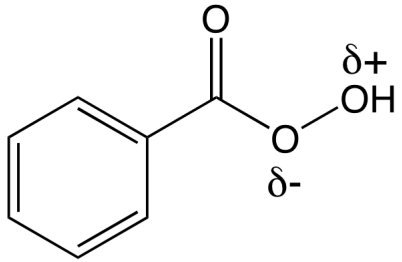
A peroxy acid is an oxidized form of a carboxylic acid



benzoic acid



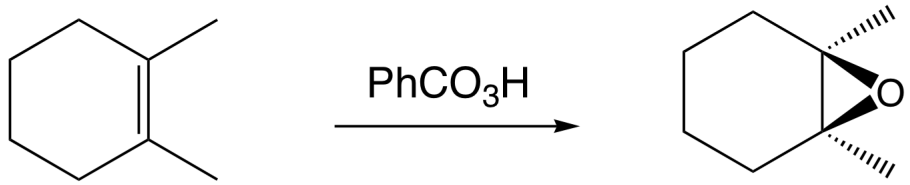
perbenzoic acid

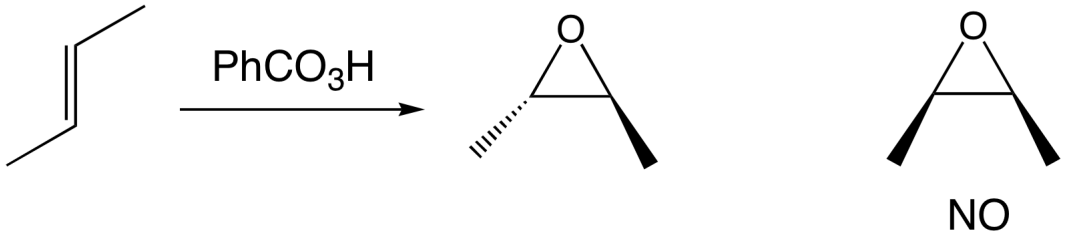


The terminal oxygen has a partial positive charge

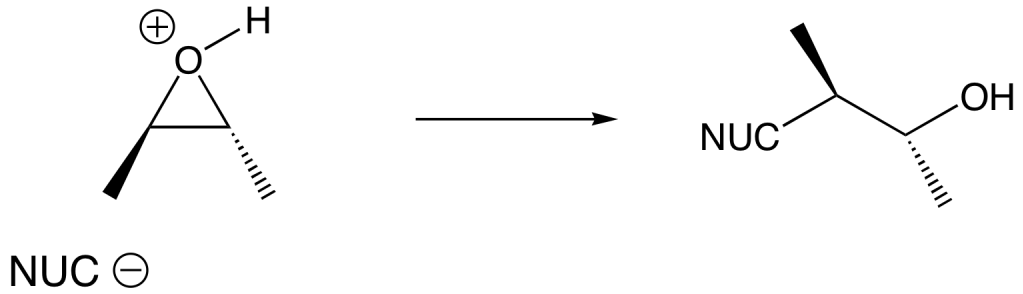
When reacted with an alkene a peracid forms an epoxide

Due to the cyclic nature of the transition state,
the epoxide is added in a SYN addition

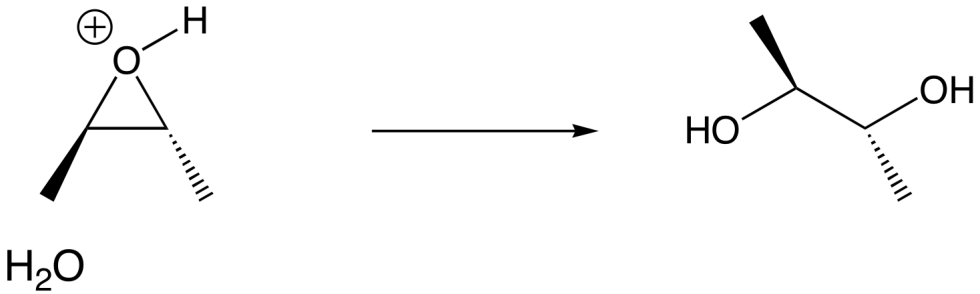




Nucleophiles can open epoxides
(especially in acidic media)



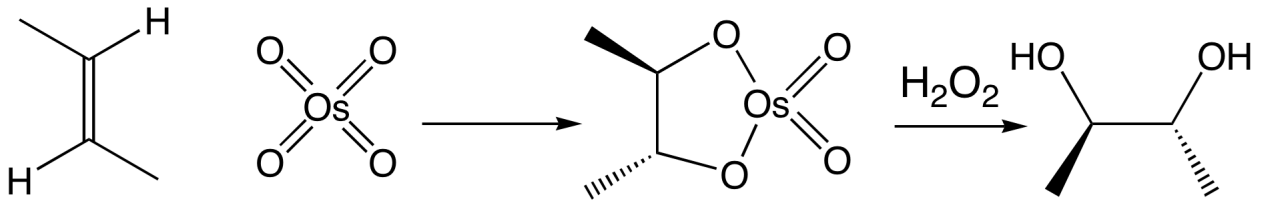
Therefore in acidic conditions a glycol (1,2-dihydroxy compound) is formed



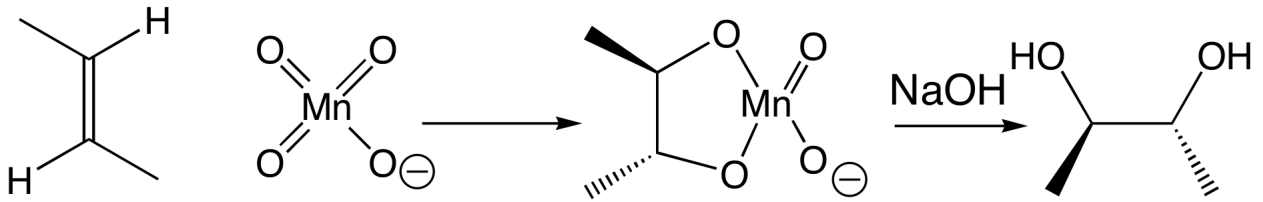
These conditions give an anti dihydroxy compound
SYN dihydroxylation requires both OH groups to be delivered from the same face

There are two common reagents for SYN dihydroxy addition to alkenes

Both involve transition metals that deliver both oxygens from the same face



+ OsO_4



+ MnO_2

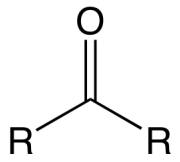
The transition metals thus are reduced (gain electrons) and the alkenes are oxidized

Carbonyl Nomenclature

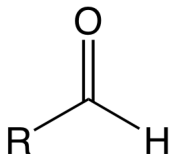
A carbon-oxygen double bond is a common, and useful, functional group in organic chemistry

Called a carbonyl group (the carbon is thus called the carbonyl carbon)

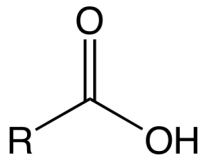
The type of carbonyl changes depending upon the substituents on the carbonyl carbon



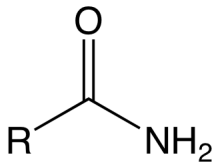
ketone



aldehyde

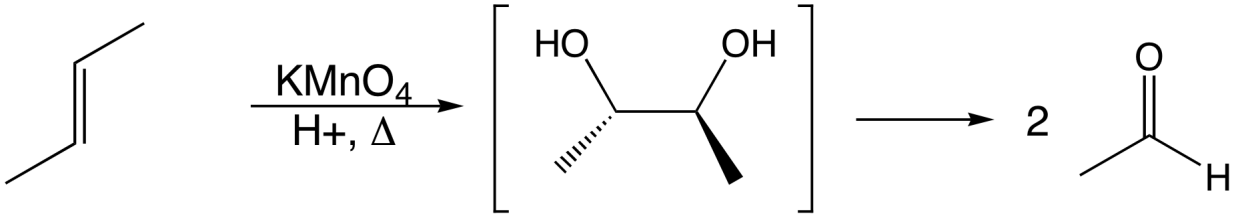


carboxylic acid



amide

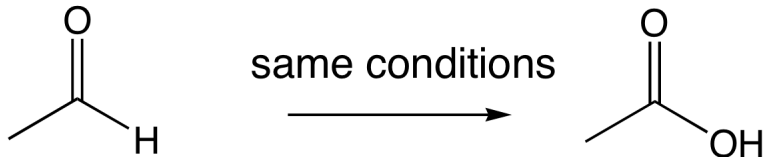
The dihydroxy compounds (glycols) can be cleaved to carbonyls



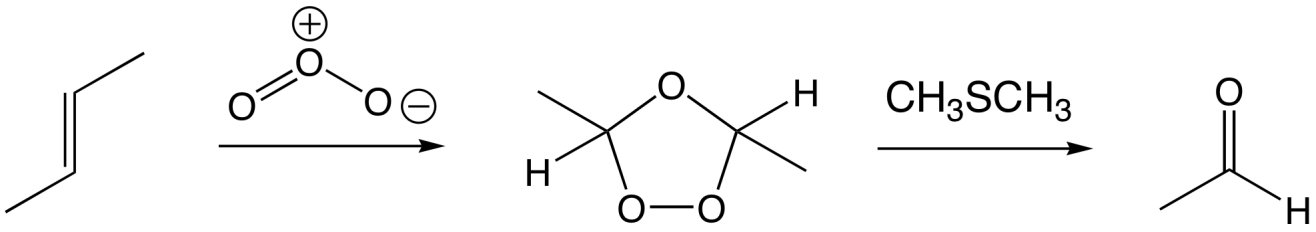
Under acidic potassium permanganate conditions the glycol
is cleaved to generate two carbonyl groups

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

But if the resulting carbonyl is an aldehyde,
it will be oxidized further to the carboxylic acid



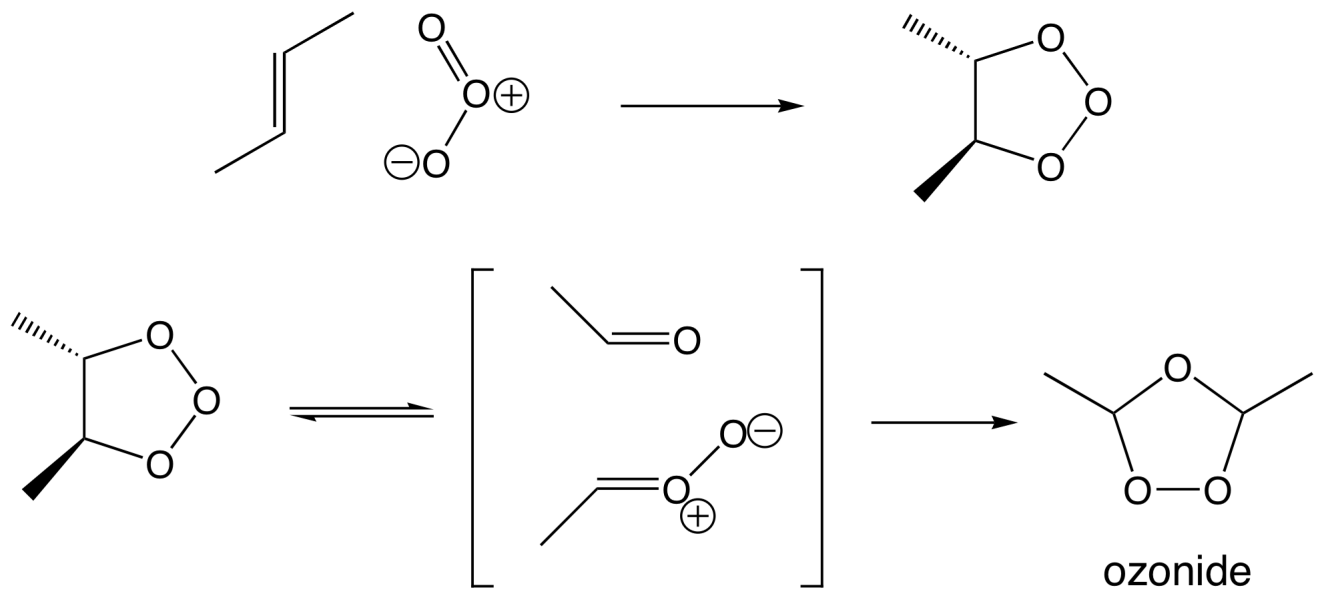
To prevent this “overoxidation” alkenes can be cleaved to carbonyls using ozone

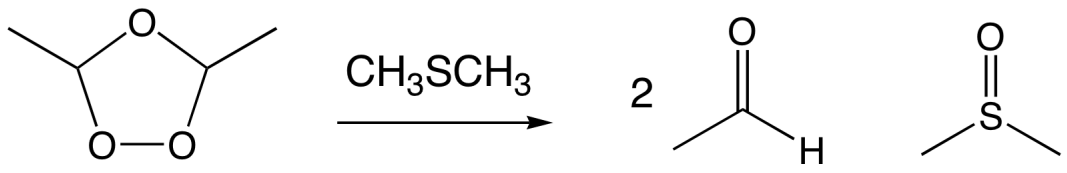


The aldehyde is stable under these conditions

In essence whatever is bonded at the carbon-carbon double bond of the alkene becomes a carbonyl under ozonolysis

Mechanism of Ozonolysis

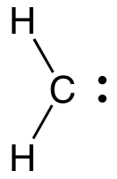




Other Reactions of Alkenes

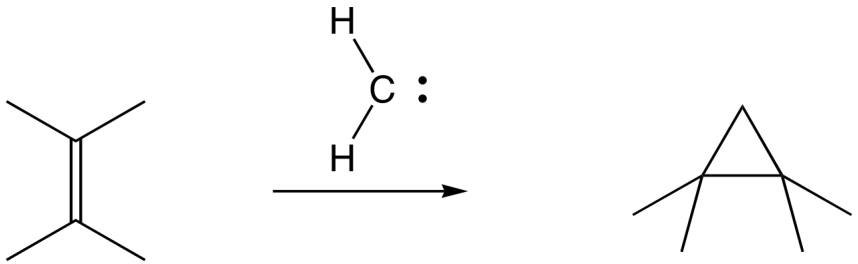
Carbenes

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



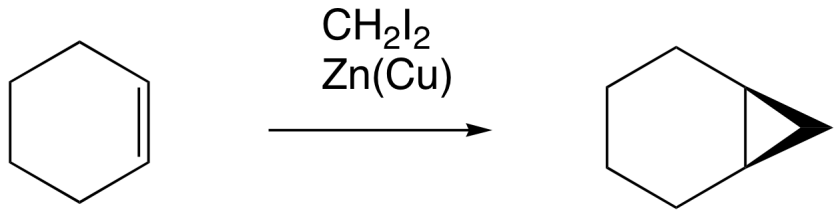
highly reactive

This compound will react quickly with alkenes to form a cyclopropane



Generation of Carbenes

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

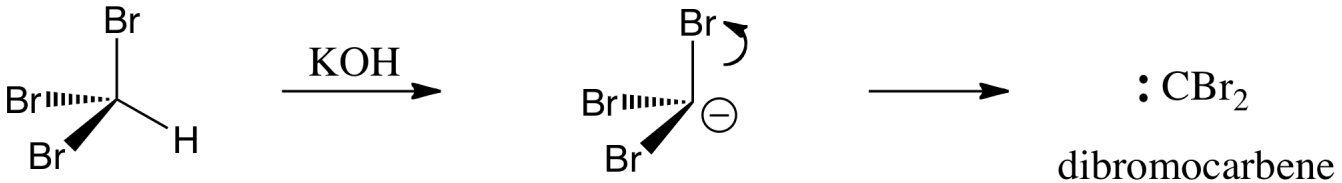


Reacts in a SYN fashion

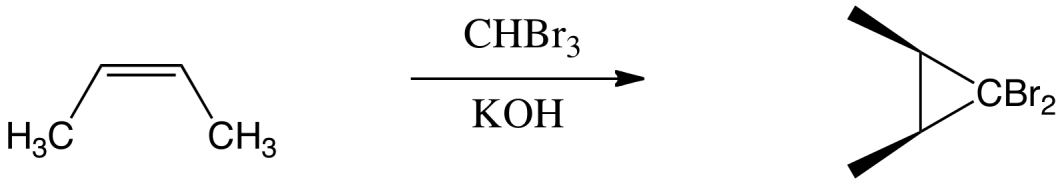
Carbenes Generated by Alpha Elimination

A second route to form carbenes that can be added to alkenes is to generate the carbene through an elimination

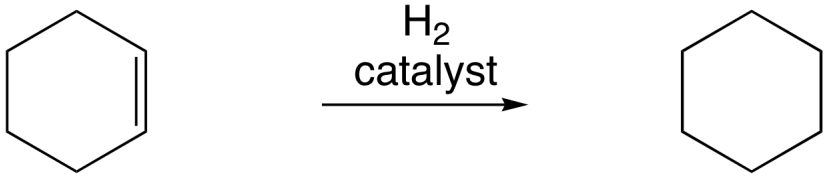
Typically use halogenated compounds that contain an acidic hydrogen



If carbene is generated *in situ* with an alkene, an addition will occur



An alkene can also be reduced to an alkane

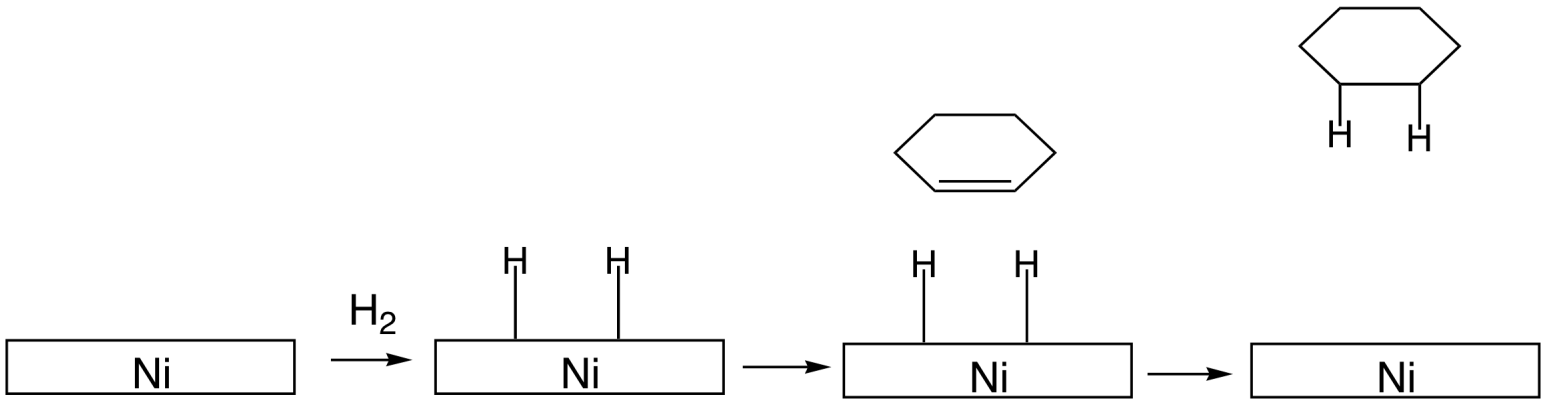


The catalyst is required for this process

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

The hydrogens add in a SYN addition

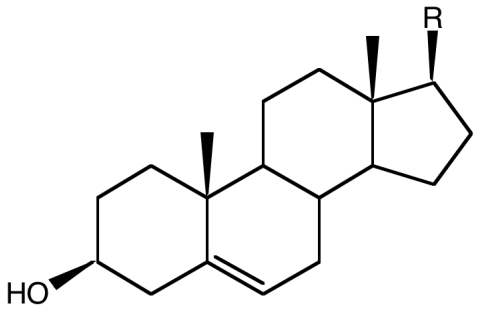
Both hydrogens are added to the same face of the alkene
as the alkene approaches the metal surface



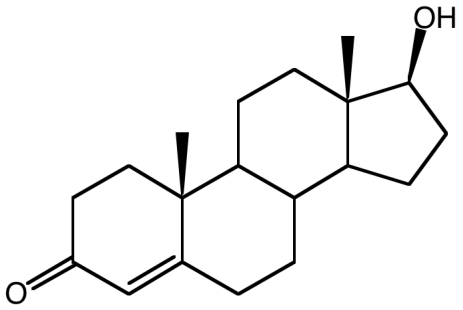
Alkene reactions are important biologically

The same reactions we have studied (and in not any more complexity)
are used in biosynthetic pathways

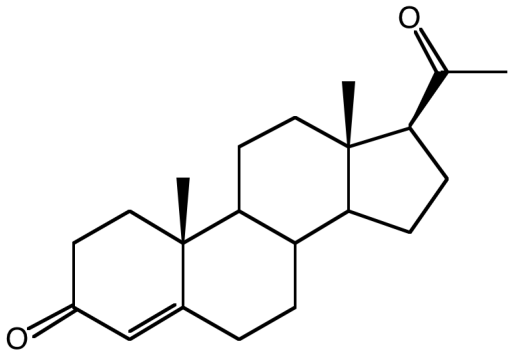
One example: used in synthesis of steroids



cholesterol



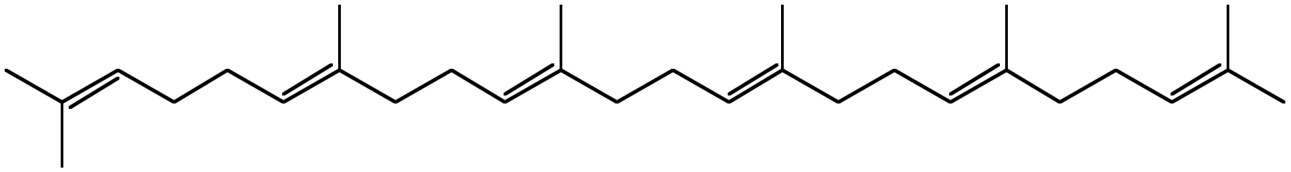
testosterone



progesterone

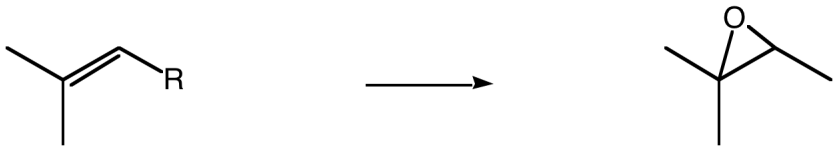
The body produces these 6-6-6-5 ring structures
through an exquisite alkene reaction pathway

The body first produces an alkene (squalene) with the same repeating units



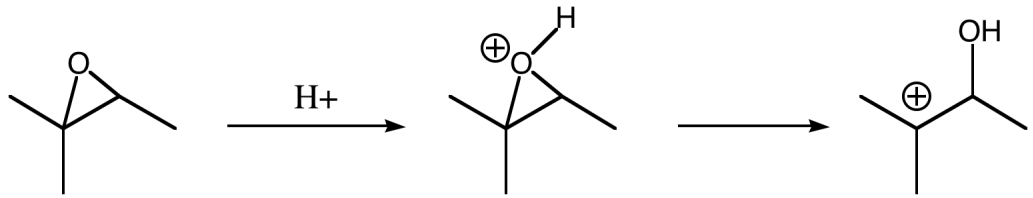
squalene

An enzyme then oxidizes a terminal alkene to an epoxide

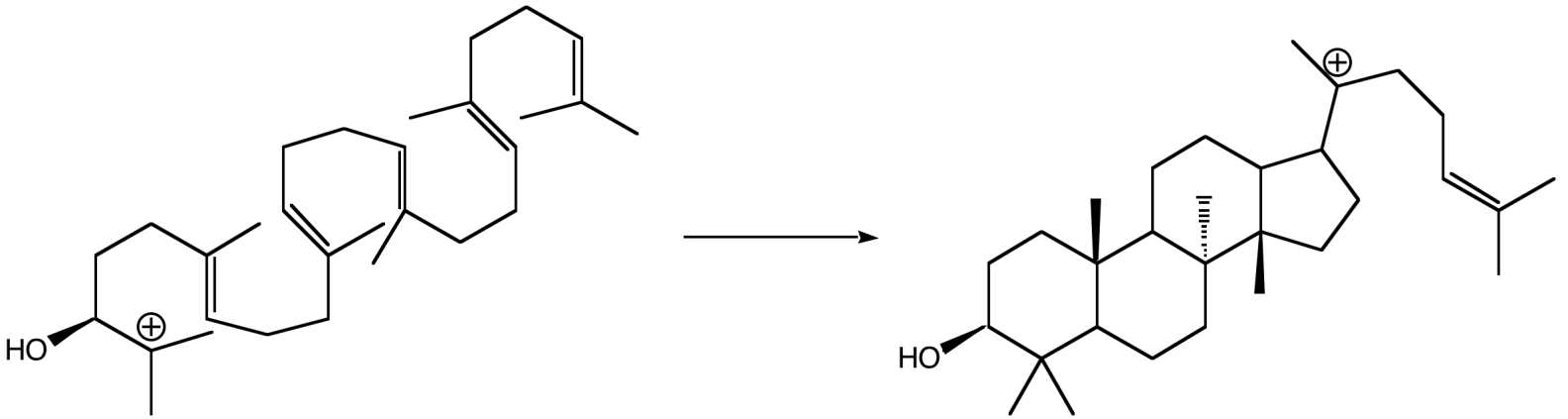


The enzyme now supplies a proton
(in a proton shuttle mechanism – to be seen in biochemistry class)

Important to realize that this proton will cause the protonated oxygen to generate a MORE stable carbocation



In the space of the enzyme then each double bond can form an intramolecular ring closure with the nucleophilic alkene reacting with the electrophilic carbocation

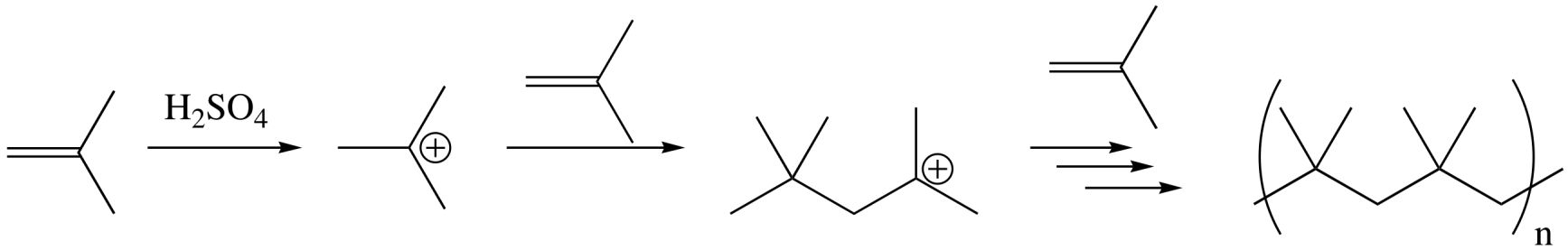


Polymerizations

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

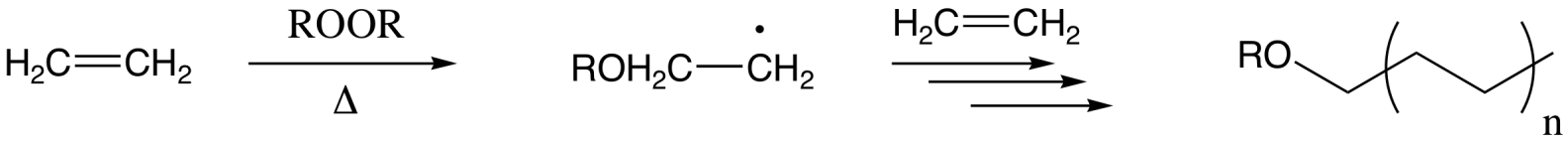
Routes:

Cationic polymerizations – carbocations are generated that react with other alkenes



polyisobutylene

Radical polymerization – radical sites are generated that react with other alkenes



polyethylene

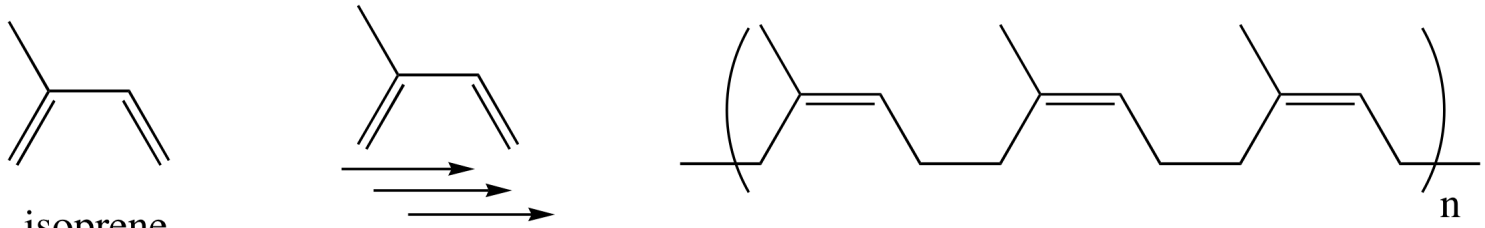
Can also do anionic polymerization – anions react with alkene sources

Natural Rubber

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

Originally named by Joseph Priestly 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 polymerization



isoprene

(2-methyl-1,3-butadiene)

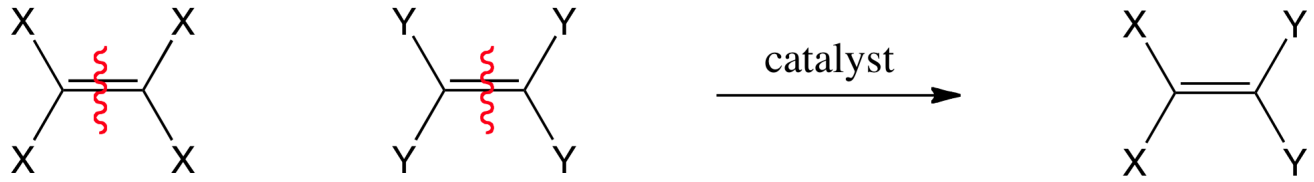
natural rubber - has Z alkenes

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

Olefin Metathesis

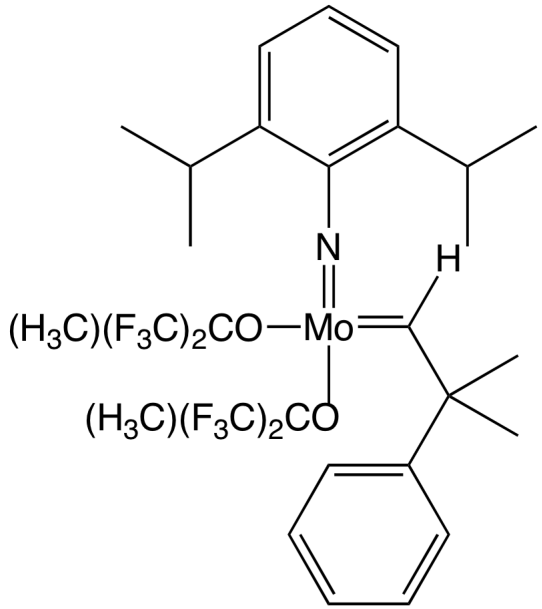
Catalysts have been developed that can take two different alkenes and reassemble the constituent parts



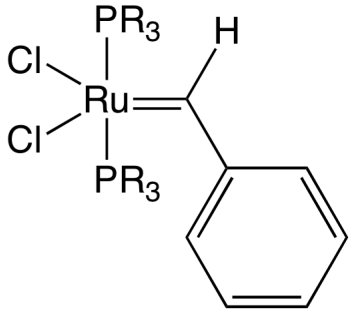
Consider each alkene as breaking into two alkylidene groups

Called olefin metathesis
Meta (change) thesis (position)

Catalysts Used



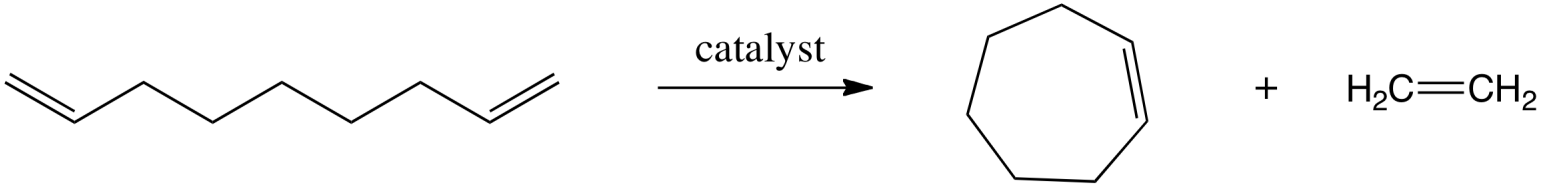
Schrock



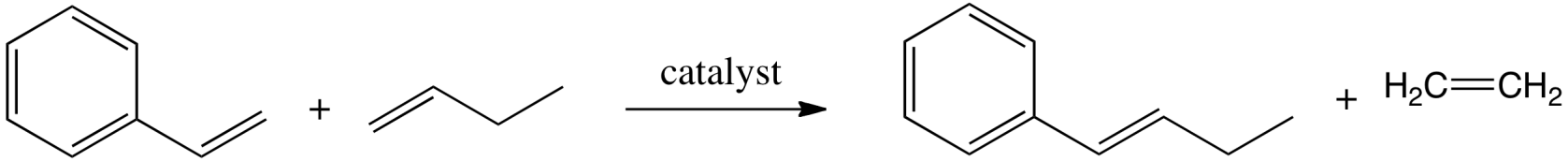
Grubbs

Both catalysts can be symbolized with [M]=CHR where [M] signifies the metal atom (either Mo for Schrock's catalyst or Ru for Grubbs' catalyst)

Some Examples of Reactions Using Olefin Metathesis



ring-closing metathesis



cross metathesis