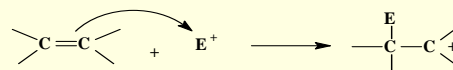


Reactivity of C=C

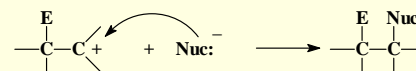
- Electrons in pi bond are loosely held.
- Electrophiles are attracted to the pi electrons.
- Carbocation intermediate forms.
- Nucleophile adds to the carbocation.
- Net result is addition to the double bond.

Electrophilic Addition

- Step 1: Pi electrons attack the electrophile.



- Step 2: Nucleophile attacks the carbocation.



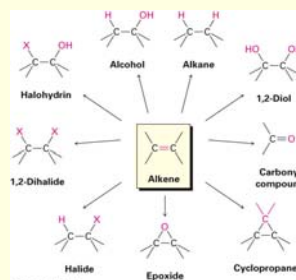
Types of Additions

Type of Addition [Elements Added]	Product
hydration [H ₂ O]	$\begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ \text{C}-\text{C} \\ \quad \end{array}$
hydrogenation [H ₂], a reduction	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C}-\text{C} \\ \quad \end{array}$
hydroxylation [HOOH], an oxidation	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}-\text{C} \\ \quad \end{array}$
oxidative cleavage [O ₃], an oxidation	$\begin{array}{c} \text{C}=\text{O} \quad \text{O}=\text{C} \\ \quad \end{array}$
epoxidation [O], an oxidation	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{C} \\ \quad \end{array}$
halogenation [X ₂], an oxidation	$\begin{array}{c} \text{X} \quad \text{X} \\ \quad \\ \text{C}-\text{C} \\ \quad \end{array}$
halohydrin formation [HOX], an oxidation	$\begin{array}{c} \text{X} \quad \text{OH} \\ \quad \\ \text{C}-\text{C} \\ \quad \end{array}$
HX addition [HX]	$\begin{array}{c} \text{H} \quad \text{X} \\ \quad \\ \text{C}-\text{C} \\ \quad \end{array}$
cyclopropanation [CH ₂]	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \\ \quad \end{array}$

*These are not the reagents used but simply the groups that appear in the product.

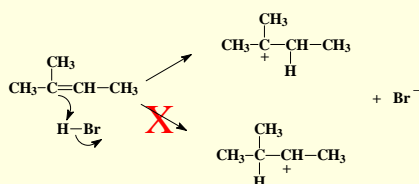
Diverse Reactions of Alkenes

- Alkenes react with many electrophiles to give useful products by addition (often through special reagents)

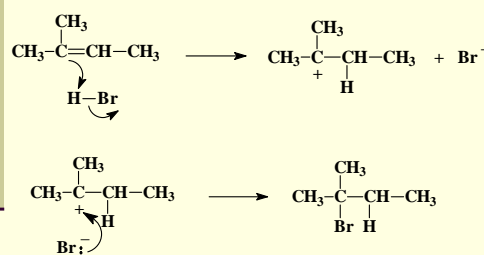


Addition of HX (1)

Protonation of double bond yields the most stable carbocation. Positive charge goes to the carbon that was not protonated.



Addition of HX (2)



Regiospecificity

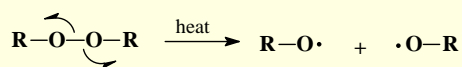
- Markovnikov's Rule: The proton of an acid adds to the carbon in the double bond that already has the most H's. "Rich get richer."
- More general Markovnikov's Rule: In an electrophilic addition to an alkene, the electrophile adds in such a way as to form the most stable intermediate.
- HCl, HBr, and HI add to alkenes to form Markovnikov products.

Free-Radical Addition of HBr

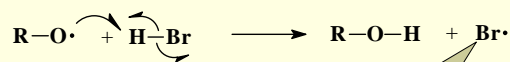
- In the presence of peroxides, HBr adds to an alkene to form the "anti-Markovnikov" product.
- Only HBr has the right bond energy.
- HCl bond is too strong.
- HI bond tends to break heterolytically to form ions.

Free Radical Initiation

- Peroxide O-O bond breaks easily to form free radicals.



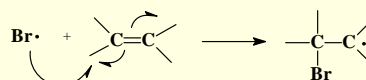
- Hydrogen is abstracted from HBr.



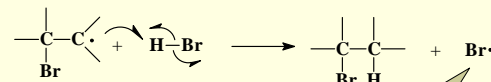
Electrophile

Propagation Steps

- Bromine adds to the double bond.

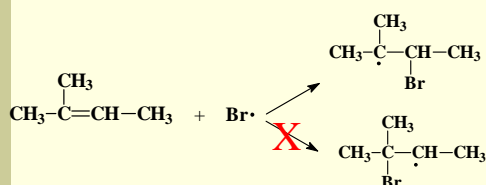


- Hydrogen is abstracted from HBr.



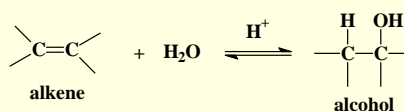
Electrophile =>

Anti-Markovnikov ??



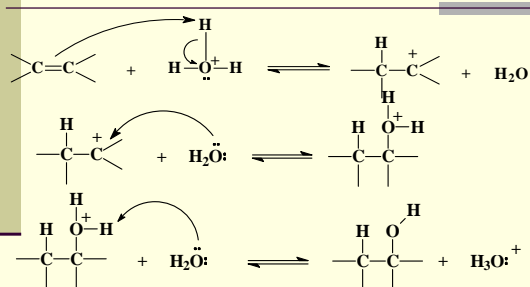
- Tertiary radical is more stable, so that intermediate forms faster.

Hydration of Alkenes



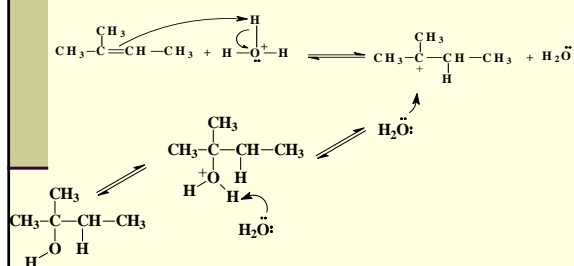
- Reverse of dehydration of alcohol
- Use very dilute solutions of H₂SO₄ or H₃PO₄ to drive equilibrium toward hydration.

Mechanism for Hydration



Orientation for Hydration

- Markovnikov product is formed.

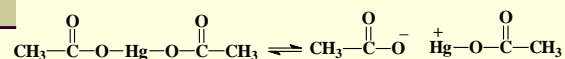


Indirect Hydration

- Oxymercuration-Demercuration
 - Markovnikov product formed
 - Anti addition of H-OH
 - No rearrangements
- Hydroboration
 - Anti-Markovnikov product formed
 - Syn addition of H-OH

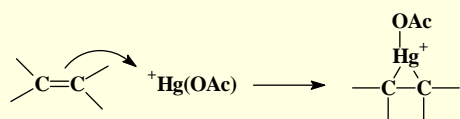
Oxymercuration (1)

- Reagent is mercury(II) acetate which dissociates slightly to form $^+\text{Hg}(\text{OAc})$.
- $^+\text{Hg}(\text{OAc})$ is the electrophile that attacks the pi bond.



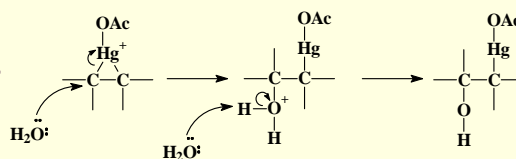
Oxymercuration (2)

The intermediate is a cyclic mercurinium ion, a three-membered ring with a positive charge.



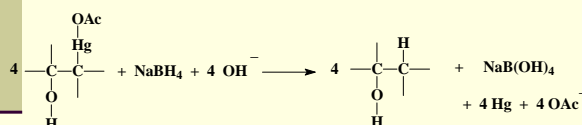
Oxymercuration (3)

- Water approaches the mercurinium ion from the side opposite the ring (anti addition).
- Water adds to the more substituted carbon to form the Markovnikov product.



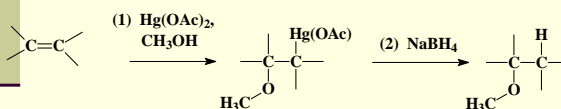
Demercuration

Sodium borohydride, a reducing agent, replaces the mercury with hydrogen.



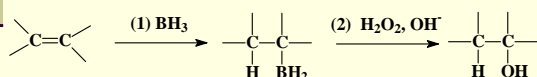
Alkoxymercuration - Demercuration

If the nucleophile is an alcohol, ROH, instead of water, HOH, the product is an ether.



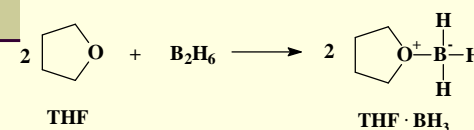
Hydroboration

- Borane, BH_3 , adds a hydrogen to the most substituted carbon in the double bond.
- The alkylborane is then oxidized to the alcohol which is the anti-Mark product.



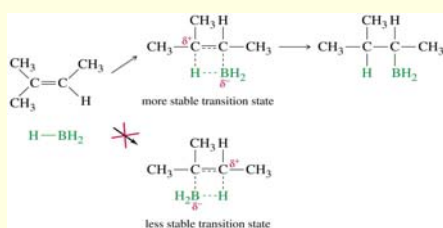
Borane Reagent

- Borane exists as a dimer, B_2H_6 , in equilibrium with its monomer.
- Borane is a toxic, flammable, explosive gas.
- Safe when complexed with tetrahydrofuran.



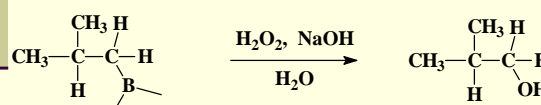
Mechanism

- The electron-deficient borane adds to the least-substituted carbon.
- The other carbon acquires a positive charge.
- H adds to adjacent C on same side (syn).



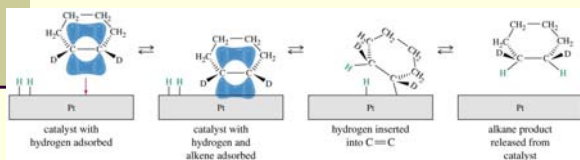
Oxidation to Alcohol

- Oxidation of the alkyl borane with basic hydrogen peroxide produces the alcohol.
- Orientation is anti-Markovnikov.



Hydrogenation

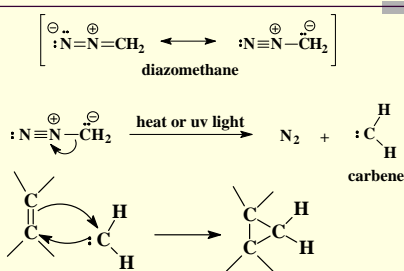
- Alkene + H₂ → Alkane
- Catalyst required, usually Pt, Pd, or Ni.
- Finely divided metal, heterogeneous
- Syn addition



Addition of Carbenes

- Insertion of -CH₂ group into a double bond produces a cyclopropane ring.
- Three methods:
 - Diazomethane
 - Simmons-Smith: methylene iodide and Zn(Cu)
 - Alpha elimination, haloform

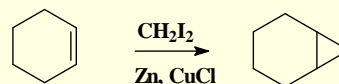
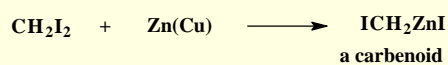
Diazomethane



Extremely toxic and explosive.

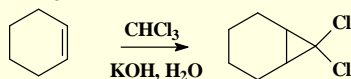
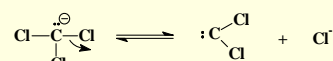
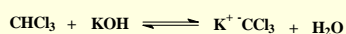
Simmons-Smith

Best method for preparing cyclopropanes.



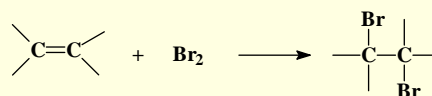
Alpha Elimination

- Haloform reacts with base.
- H and X taken from same carbon



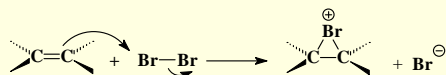
Addition of Halogens

- Cl₂, Br₂, and sometimes I₂ add to a double bond to form a vicinal dibromide.
- Anti addition, so reaction is stereospecific.



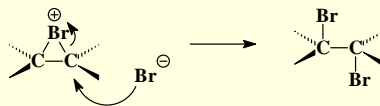
Mechanism for Halogenation

- Pi electrons attack the bromine molecule.
- A bromide ion splits off.
- Intermediate is a cyclic bromonium ion.

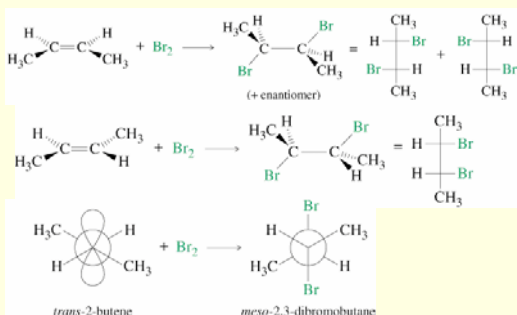


Mechanism (2)

Halide ion approaches from side opposite the three-membered ring.



Examples of Stereospecificity

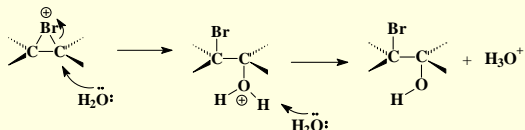


Test for Unsaturation

- Add Br_2 in CCl_4 (dark, red-brown color) to an alkene in the presence of light.
- The color quickly disappears as the bromine adds to the double bond.
- “Decolorizing bromine” is the chemical test for the presence of a double bond.

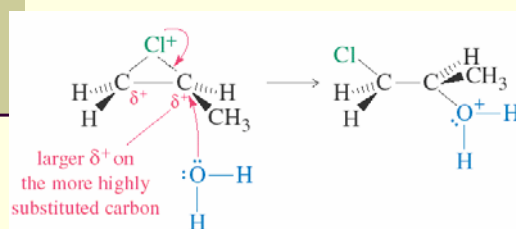
Formation of Halohydrin

- If a halogen is added in the presence of water, a halohydrin is formed.
- Water is the nucleophile, instead of halide.



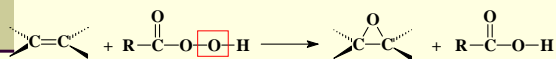
Regiospecificity

The most highly substituted carbon has the most positive charge, so nucleophile attacks there.



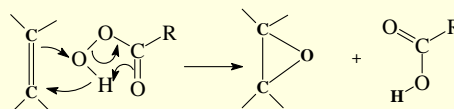
Epoxidation

- Alkene reacts with a peroxyacid to form an epoxide (also called oxirane).
- Usual reagent is peroxybenzoic acid.



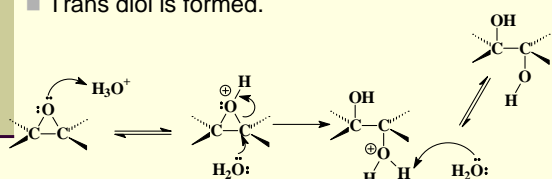
Mechanism

One-step concerted reaction. Several bonds break and form simultaneously.



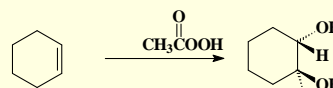
Opening the Epoxide Ring

- Acid catalyzed.
- Water attacks the protonated epoxide.
- Trans diol is formed.



One-Step Reaction

- To synthesize the glycol without isolating the epoxide, use aqueous peroxyacetic acid or peroxyformic acid.
- The reaction is stereospecific.

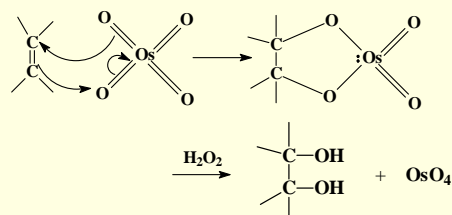


Syn Hydroxylation of Alkenes

- Alkene is converted to a *cis*-1,2-diol,
- Two reagents:
 - Osmium tetroxide (expensive!), followed by hydrogen peroxide *or*
 - Cold, dilute aqueous potassium permanganate, followed by hydrolysis with base

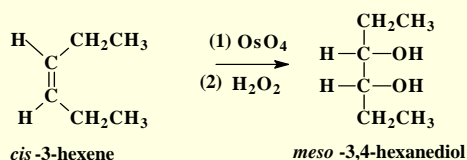
Mechanism with OsO₄

Concerted *syn* addition of two oxygens to form a cyclic ester.



Stereospecificity

If a chiral carbon is formed, only one stereoisomer will be produced (or a pair of enantiomers).



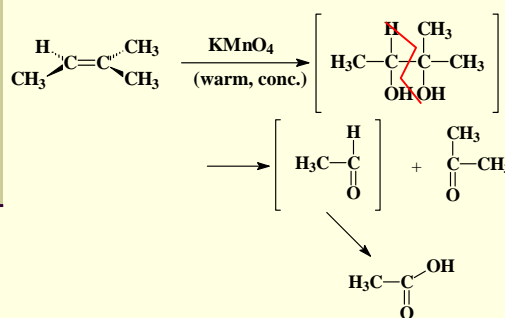
Oxidative Cleavage

- Both the pi and sigma bonds break.
- C=C becomes C=O.
- Two methods:
 - Warm or concentrated or acidic KMnO_4 .
 - Ozonolysis
- Used to determine the position of a double bond in an unknown.

Cleavage with MnO_4^-

- Permanganate is a strong oxidizing agent.
- Glycol initially formed is further oxidized.
- Disubstituted carbons become ketones.
- Monosubstituted carbons become carboxylic acids.
- Terminal $=\text{CH}_2$ becomes CO_2 .

Example

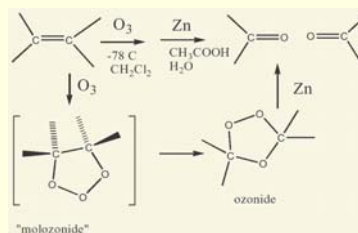


Ozonolysis

- Reaction with ozone forms an ozonide.
- Ozonides are not isolated, but are treated with a mild reducing agent like Zn or dimethyl sulfide.
- Milder oxidation than permanganate.
- Products formed are ketones or aldehydes.

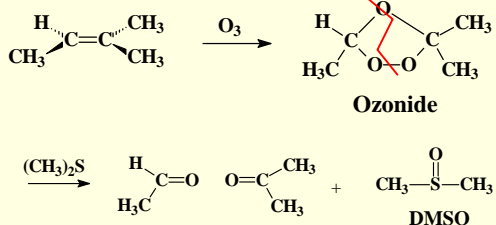
Alkene Cleavage: Ozone

- Ozone, O_3 , adds to alkenes to form molozonide
- Reduce molozonide to obtain ketones and/or aldehydes



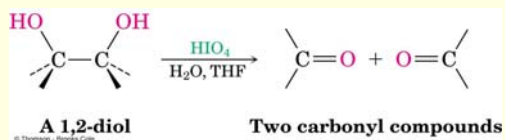
48

Ozonolysis Example



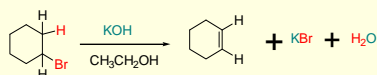
Cleavage of 1,2-diols

- Reaction of a 1,2-diol with periodic (*per-iodic*) acid, HIO_4 , cleaves the diol into two carbonyl compounds
- Sequence of diol formation with OsO_4 followed by diol cleavage is a good alternative to ozonolysis

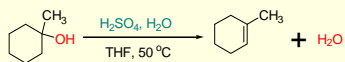


Synthesis of Alkenes

1) dehydrohalogenation

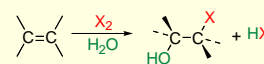


2) dehydration

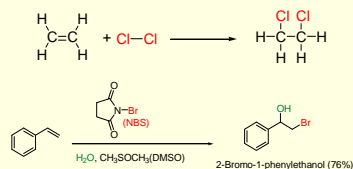


Reaction of Alkenes

1) Addition of Halogens to Alkenes

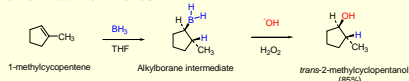


2) Halohydrin Formation

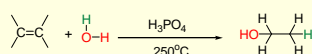


Reaction of Alkenes

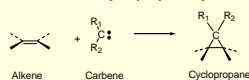
3) Addition of Water to Alkenes



4) Hydroboration-Oxidation Alcohol Formation

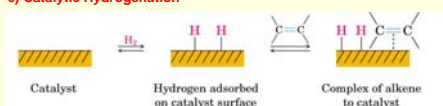


5) Carbene Formation – Cyclopropane synthesis

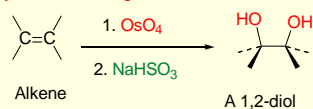


Reaction of Alkenes

6) Catalytic Hydrogenation

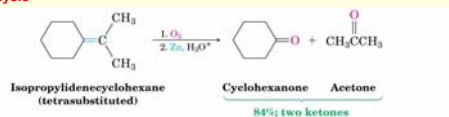


7) Hydroxylation and Cleavage

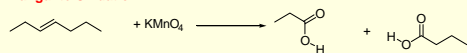


Breakdown of Alkenes

1) Ozonolysis



2) Permanganate Oxidation



3) Periodic Acid Oxidation, Cleavage of 1,2-diols

