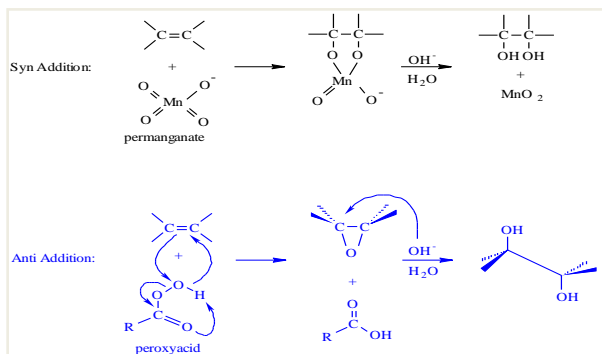


## Addition Reactions

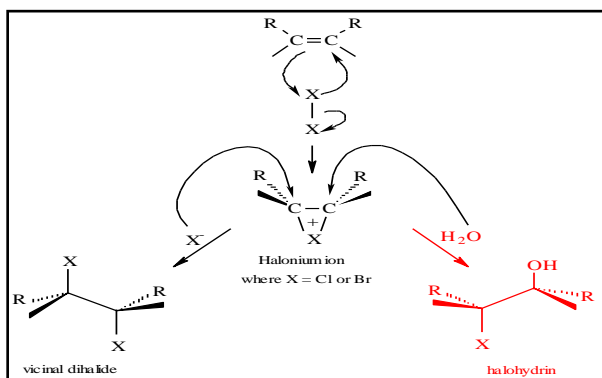
- A) Syn addition : *Hydrogenation; Hydroxylation; Hydroboration*  
 B) Anti addition : *Hydroxylation; Halogenation ; Halohydrin formation*

### Hydroxylation: Syn addition and Anti addition

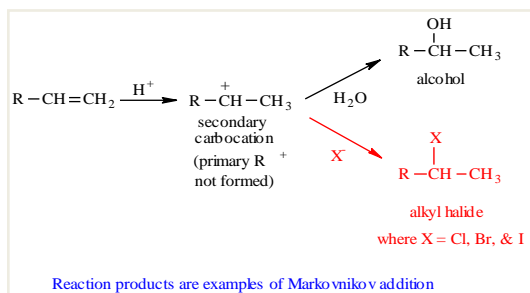
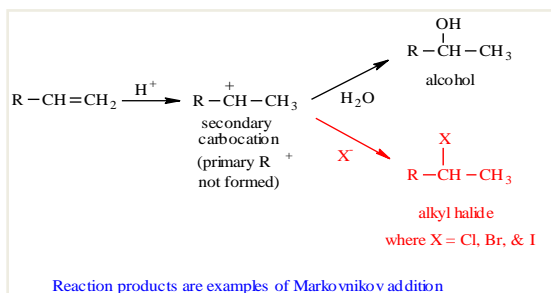


### Alkene Addition Reactions via Halonium Ions

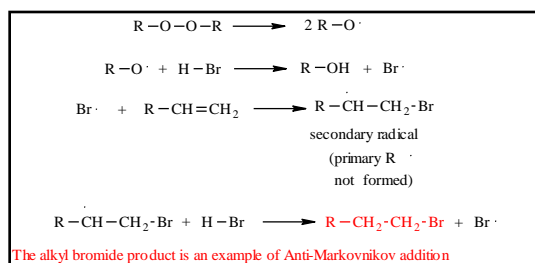
#### Halogenation and Halohydrin formation



### C) Carbocation Formation: Alkene Addition Reactions via Carbocation Intermediates Hydration (Alcohol formation) and Hydrogen halide addition (Alkyl halide formation)

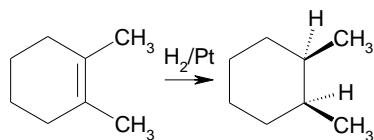


- D) Radical formation: *Radical Addition, HBr Addition/ROOR present, Anti-Markovnikov regiochemistry, Peroxide-mediated HBr Addition to Alkenes*

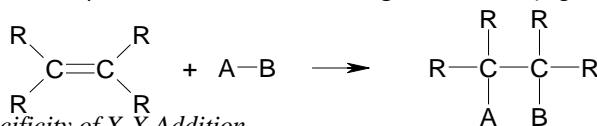


### Hydrogenation (Alkene Reduction)

- Platinum or Palladium catalysts allow conversion of alkenes or alkynes to alkanes.
- The catalyst has a large surface area. Under high pressure the H<sub>2</sub> will dissociate to atomic hydrogen adsorbed to catalyst surface.



- The H will add to the same face of the alkene (*syn* addition).
- Alkenes are substrates for reactions in which groups add across the double bond.
- An example is the addition of a halogen molecule (e.g. Br<sub>2</sub>) to form a vicinal dibromide.

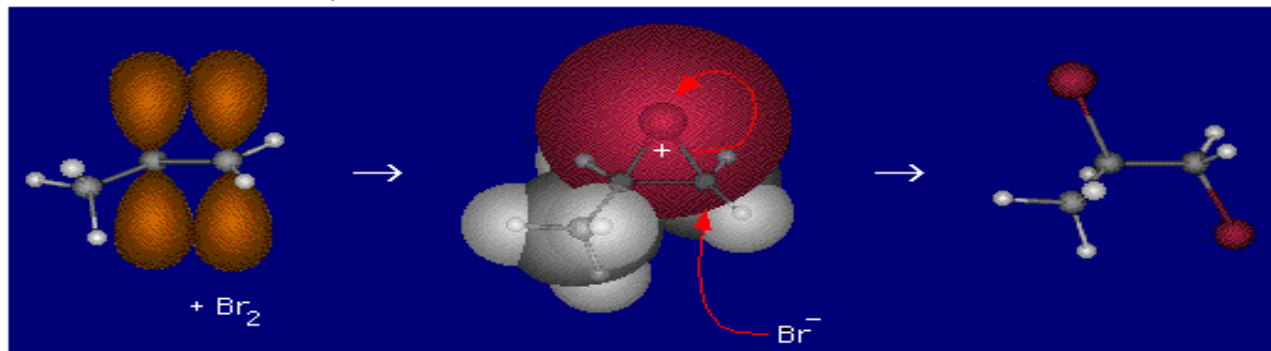


### Stereospecificity of X-X Addition

\*\* pdf1 p8

The large size of a bromine atom necessitates back side attack on the cyclic bromonium intermediate by the bromide ion

- This results in **anti** addition of the two bromine atom



### Problem

- What stereoisomers will be produced by the addition of Br<sub>2</sub> to *E*-2-butene? When water is used as a solvent for halogen addition, a halohydrin, rather than a dihalide is produced. Why?

*Mechanism for H-Z Addition Hydroboration, addition of  $BH_3$ • The electrophilic atom in this case is **boron**, not hydrogen• Boron also has an empty orbital, thus the hydrogen does not need to be displaced when the pi bond reacts with the boron atom*

*four-center transition state*

\*\*\*P12

*Problem*

• Given the mechanism on the previous slide. What regiochemical outcome do you expect for the hydroboration of 1-methylcyclopentene? What stereochemical outcome do you expect for the hydroboration of 1,2-dimethylcyclobutene?

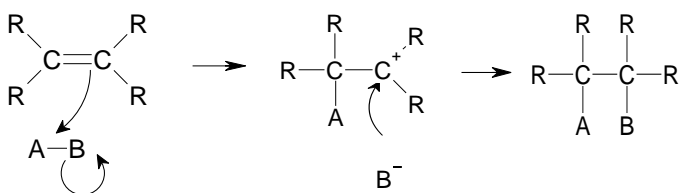
### Reactivity of Alkenes

- The  $\pi$  bond of an alkene is weaker than typical  $\sigma$  bonds. Replacing a  $\pi$  bond with a  $\sigma$  bond usually results in a lower energy state.
- The  $\pi$  orbitals of a double bond are exposed to attack. Steric hindrance is minimal.
- The  $\pi$  orbitals contain relatively loosely associated electrons, and are subject to **electrophilic** attack.

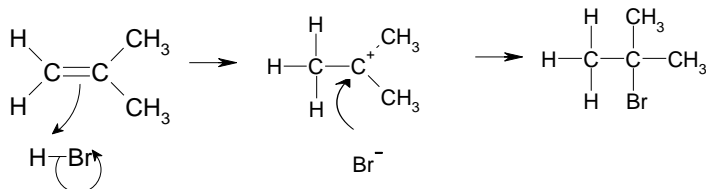
Electrophile = “electron-loving”

### General Mechanism

- An alkene can act as a Lewis base.
- Carbocations are Lewis acids.

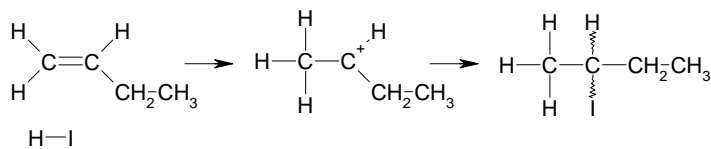


### Hydrogen Halide Addition



- **Markovnikov's rule** – the hydrogen adds to the carbon that has more hydrogens.
- Markovnikov's rule – the addition occurs to yield the more stable carbocation intermediate.
- This is an example of **regioselectivity** – the predictable preference of one product over others.

### Hydrogen Halide Addition



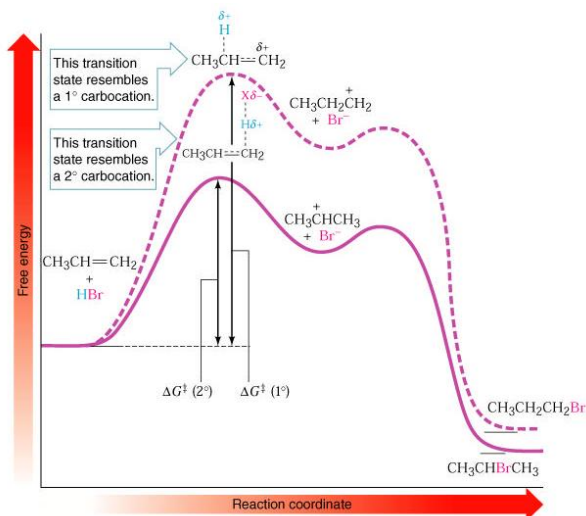
Hydrogen halide addition may result in the creation of a stereocenter.

- The products form as a racemic mixture.

### Addition Reaction Regioselectivity

For addition reactions that can give multiple constitutional isomers, the major product is determined based on the rate at which the intermediate carbocations are generated – Example: Addition of HBr to propene gives 2-bromopropane as the major product rather than 1-bromopropane

### Addition Free Energy Changes



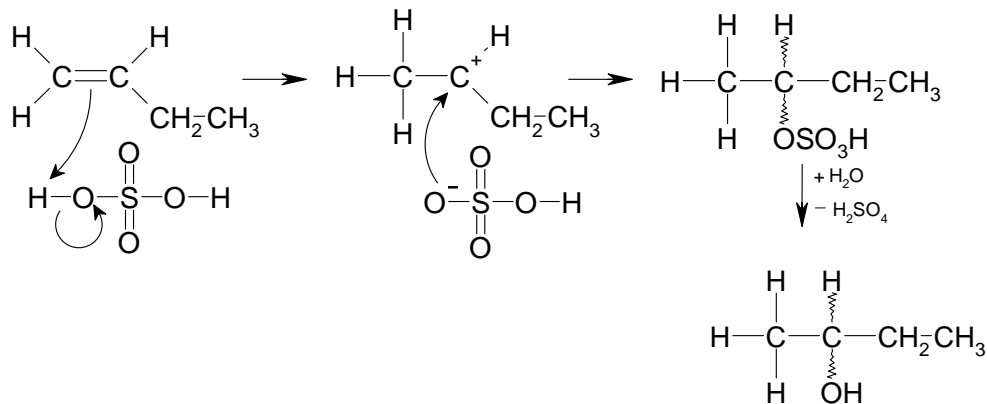
### Problem

- What stereoisomers (and relative amounts) will be produced by the addition of HCl to 2-butene?

What do you think will happen if propyne is mixed with HBr? If a reaction occurs, what product or products can form?

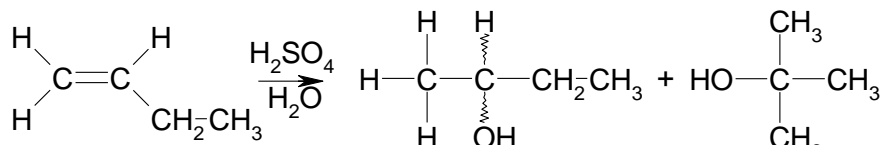
### Sulfuric Acid Addition

- Although hydrogen sulfate ion is a poor nucleophile, in the absence of other nucleophiles, it will attack carbocations.



## Alcohol Synthesis

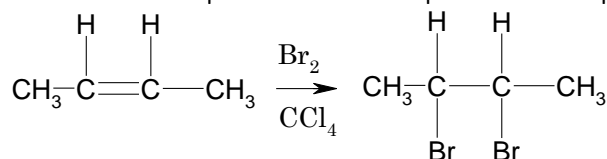
- Alcohols may be synthesized directly.
- The reaction is the reverse of the dehydration reaction.
- Rearrangement is a problem, whenever a more stable carbocation can be formed.



- Because the reaction is reversible, it is difficult to get the reaction to go to completion; dilute acid is used.
- The dehydration reaction is more useful, because the product can be removed by distillation during the reaction.
- The conjugate base of the acid must be a poor nucleophile (e.g. sulfate or phosphate) to prevent  $\text{S}_{\text{N}}1$  and other reactions.

## Alkenes and Halogens

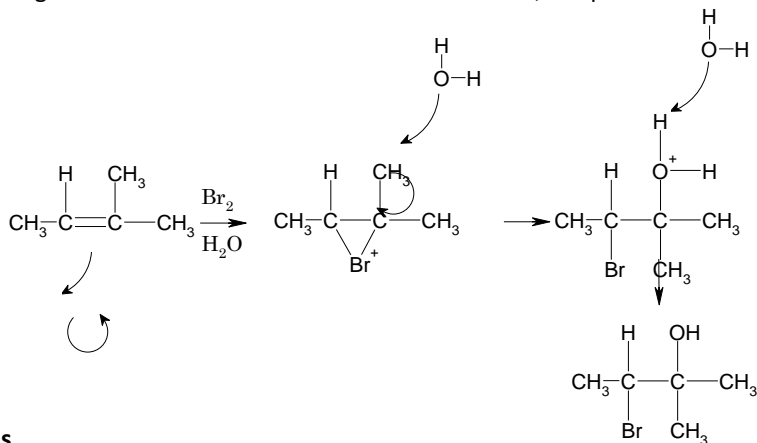
- Alkenes react readily with halogen molecules.
- The reaction must be performed in a non-polar solvent to prevent other nucleophilic reactions.



- Alkenes react readily with halogen molecules.
- The reaction must be performed in a non-polar solvent to prevent other nucleophilic reactions.

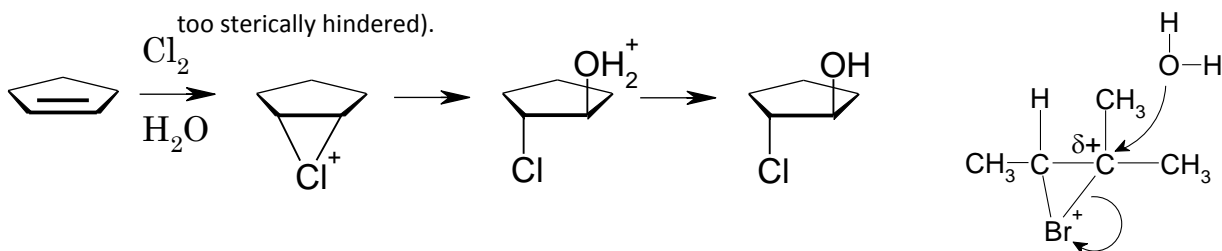
## Halohydrin Formation

- If a halogen molecule reaction with an alkene in water, the product is a halohydrin.



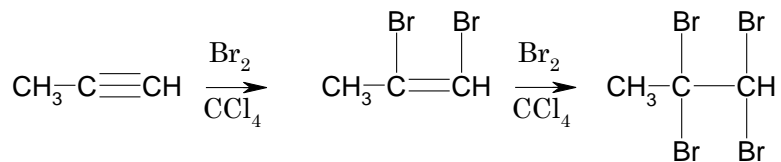
## Halonium Ions

- The properties of the cyclic halonium ion have two consequences:
  - The second attack occurs *anti* to the first.
  - The second attack occurs at the **more substituted** carbon (unless the more substituted carbon is too sterically hindered).



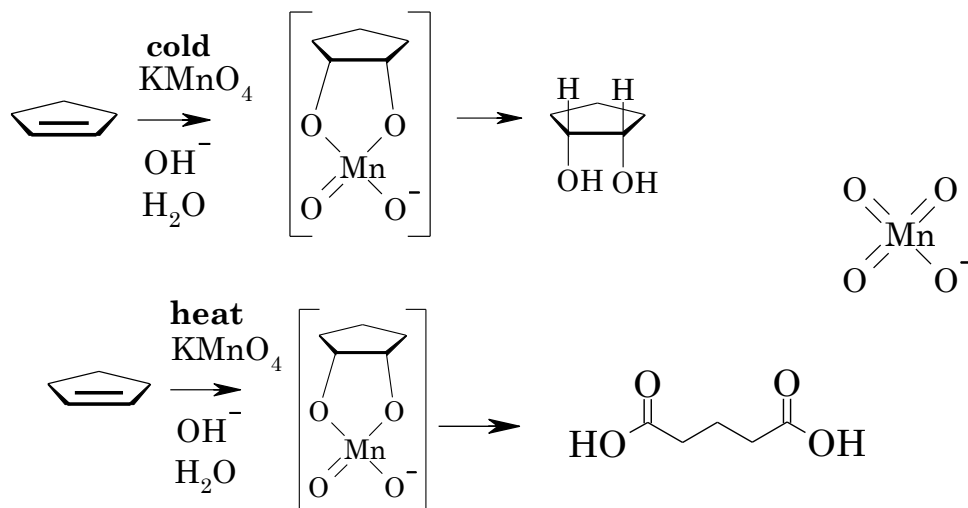
### Alkyne Addition

- Halogens add across triple bonds in the same way as across double bonds.



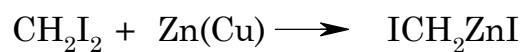
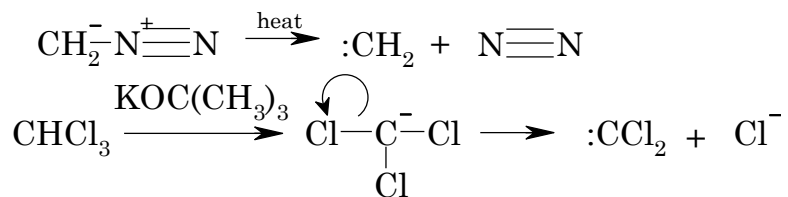
- Hydrohalogen addition across triple bonds is also similar to addition across double bonds. Addition follows Markovnikov's rule.

### Alkene Oxidation

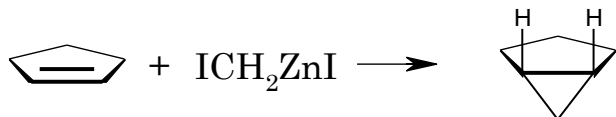


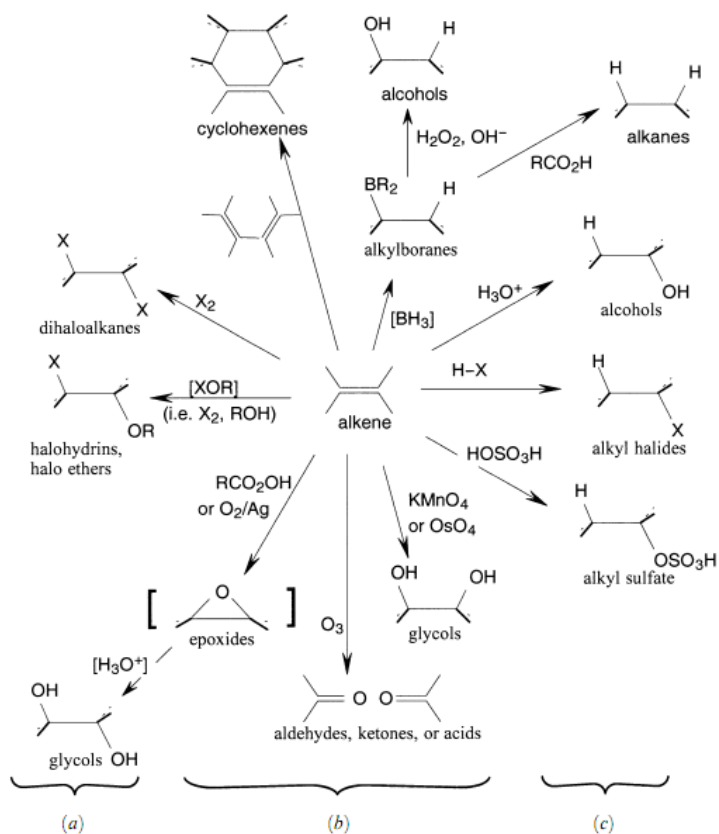
### Carbenes

- A carbene is a *highly unstable* compound containing a carbon with **two bonds**.

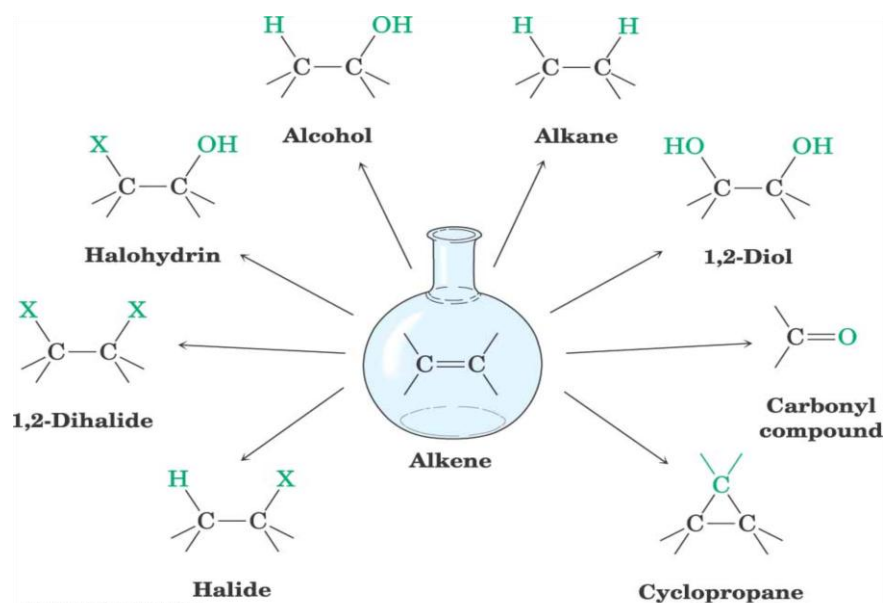


- Carbenes react readily with double bonds, by forming a three membered ring.





**Figure 6.1.** Summary of the most common electrophilic addition reactions of olefins. In each case, the olefin reacts as a Lewis base. All reactions are regioselective. The overall stereochemistry is (a) stereospecific anti; (b) stereospecific syn; (c) not stereospecific, in general.



## Polar Reaction Mechanisms Additions

### Addition Mechanisms

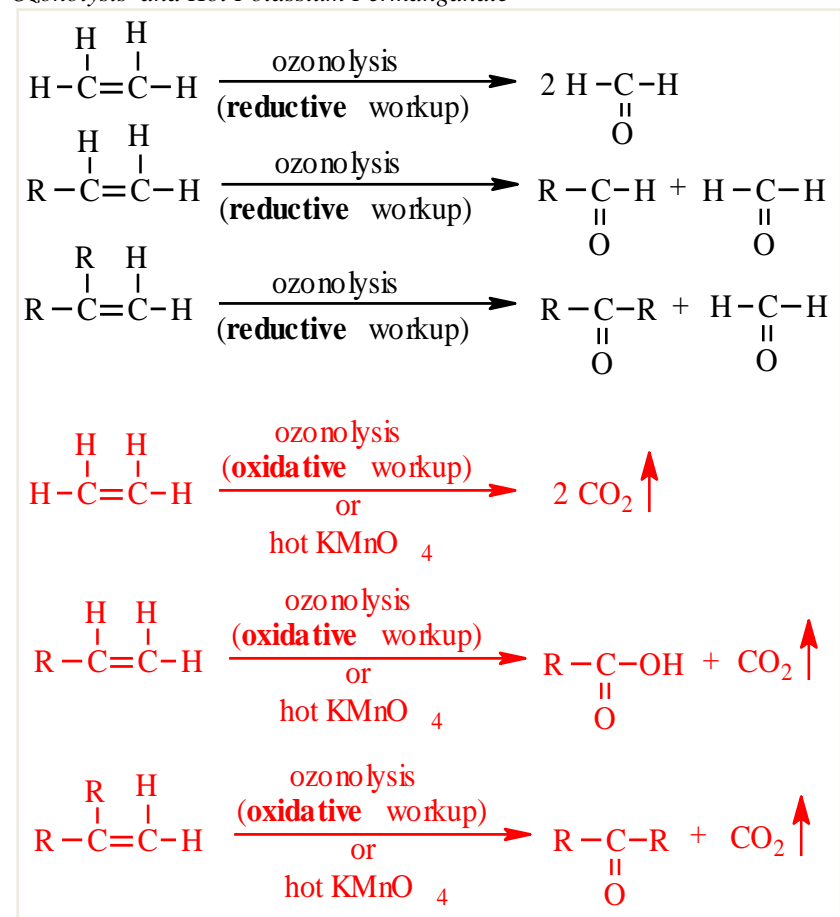
- Some deviation in addition mechanisms occurs due to differences in the electrophile
- Electrophile categories
  - H-X (Hydrogen attached to electronegative atom)
- Strong acids – no catalyst needed
- Weak acids – acid catalyst needed
  - X-X (Polarizable non-polar molecule – halogens)
  - H-Z (Hydrogen attached to electropositive atom)

When H-X is a strong acid:

.....

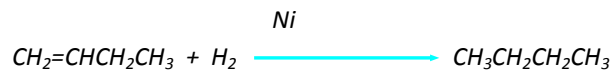
### Cleavage Reactions of Alkenes

#### Ozonolysis and Hot Potassium Permanganate





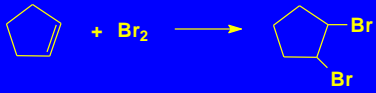
What is the product of adding  $H_2$  (Ni catalyst) to 1-butene?



Write the product of the following addition reactions:



Write the product of the following addition reactions:

$$CH_3CH=CHCH_3 + H_2 \longrightarrow CH_3CH_2CH_2CH_3$$


LecturePLUS Timberlake 15

### Unsaturated Fatty Acids

- Fatty acids in vegetable oils are omega-6 acids (the first double bond occurs at carbon 6 counting from the methyl group)
- A common omega-6 acid is linoleic acid



↑  
6

**linoleic acid, a fatty acid**

### Trans Fats

- In vegetable oils, the unsaturated fats usually contain *cis* double bonds.
- During hydrogenation, some *cis* double bonds are converted to *trans* double bonds (more stable) causing a change in the fatty acid structure
- If a label states “partially” or “fully hydrogenated”, the fats contain *trans* fatty acids.
- In the US, it is estimated that 2-4% of our total Calories is in the form of *trans* fatty acid.
- *trans* fatty acids behave like saturated fatty acids in the body.
- Several studies reported that *trans* fatty acids raise LDL-cholesterol. Some studies also report that *trans* fatty acid lower HDL-cholesterol
- The *trans* fatty acids controversy will continue to be debated.

### Fats and Atherosclerosis

- Inuit people of Alaska have a high fat diet and high blood cholesterol levels, but a very low occurrence of atherosclerosis and heart attacks.
- Fat in the Inuit diet was primarily from fish such as salmon, tuna and herring rather than from land animals (as in the American diet).

### Omega-3 Fatty Acids

- Fatty acids in the fish oils are mostly the omega-3 type (first double bond occurs at the third carbon counting from the methyl group).
- linolenic acid 18 carbon atoms
- $CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$

↑

- eicosapentaenoic acid (EPA) 20 carbon atoms  $\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_5(\text{CH}_2)_2\text{COOH}$

Atherosclerosis

- Plaques of cholesterol adhere to the walls of the blood vessels
- Blood pressure rises as blood squeezes through smaller blood vessels
- Blood clots may form
- Omega-3 fatty acids decrease the “sticking” of blood platelets (fewer blood clots)
- Omega-3 fatty acids can increase bleeding time

1) True or (2) False

- A. T There are more unsaturated fats in vegetable oils.
- B. F Vegetable oils have more omega-3 oils than found in fish.
- C. T Hydrogenation of oils converts some *cis*-double bonds to *trans*- double bonds.
- D. T Animal fats have more saturated fats.