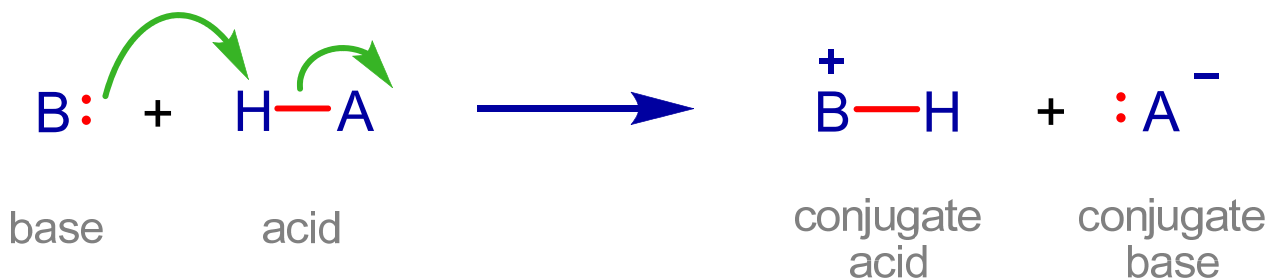


## 1.13 Acid-Base Reactions: Lone-Pair Donors & Acceptors



HI, HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>

*pKa* -10 to -5

Super strong acids

H<sub>3</sub>O<sup>+</sup>

*pKa* - 1.7

RCO<sub>2</sub>H

*pKa* ~ 5

acids

PhOH

*pKa* ~ 10

get

H<sub>2</sub>O, ROH

*pKa* ~ 16

weaker

RCCH (alkynes)

*pKa* ~ 26

RNH<sub>2</sub>

*pKa* ~ 36

Extremely weak acid

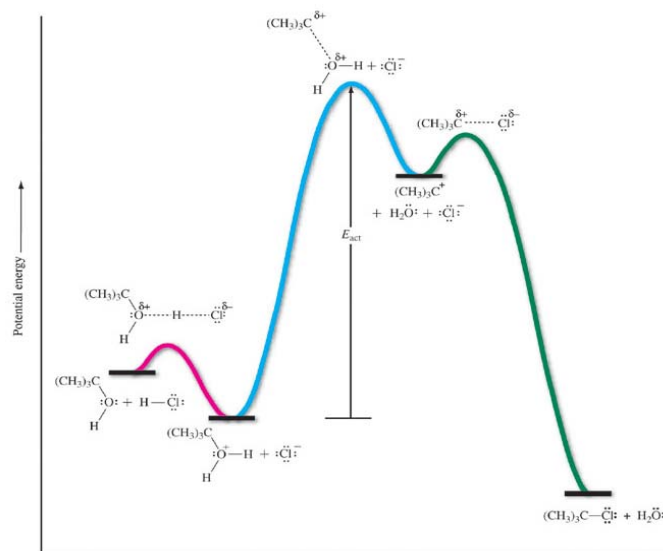
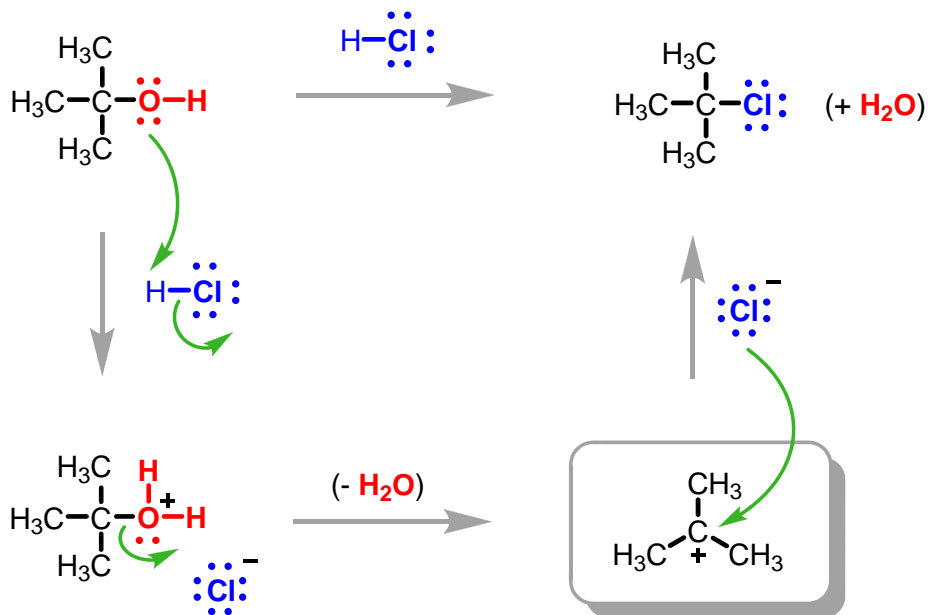
RCH<sub>3</sub>

*pKa* ~ 60

Not acidic at all

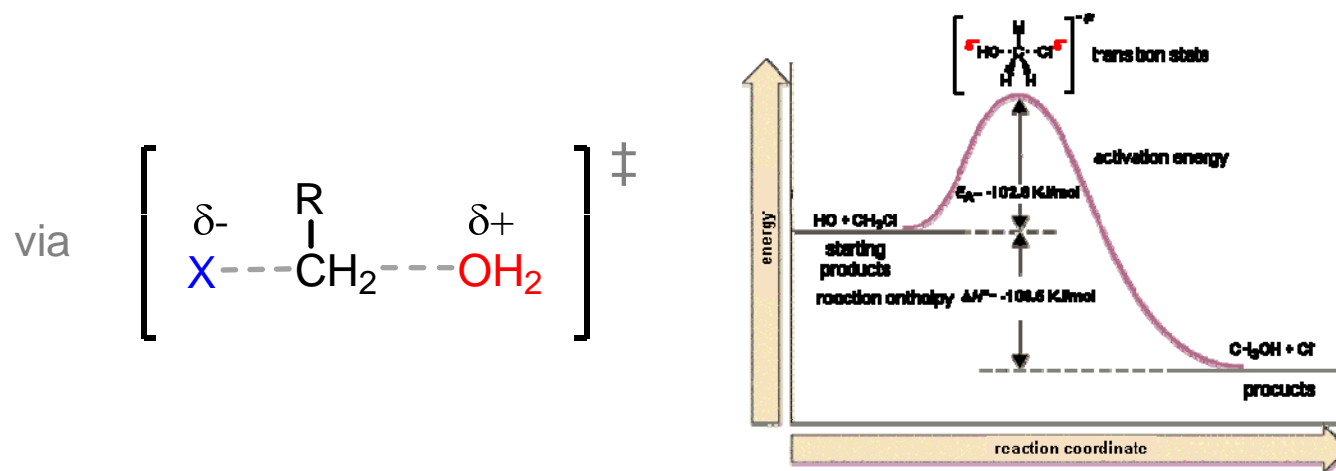
- Lone pair donor + Lone pair acceptor = Acid-Base reaction
- Rate-determining step is Bimolecular (only one step involved)
- Acid-Base reactions are generally very fast (proton, H, is accessible)
- Acid-Base reactions appear as components of other mechanisms

## 4.8 Reaction of a Tertiary Alcohol with H-Cl/H-Br/H-I = S<sub>N</sub>1



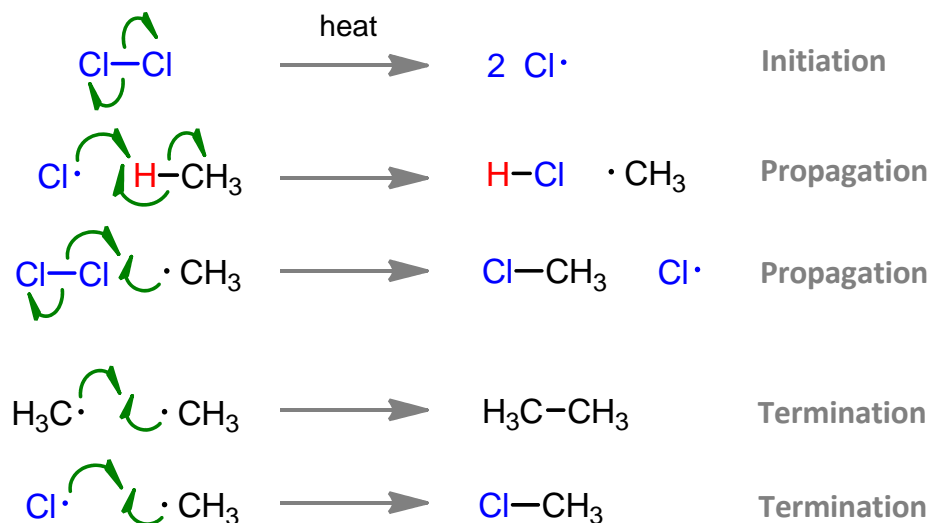
- 3° alcohol + H-X → alkyl halide = S<sub>N</sub>1 reaction
- Rate-determining step is Unimolecular = CARBOCATION FORMED
- Carbocation stabilized by Hyperconjugation (3° > 2° > 1° > CH<sub>3</sub>)
- Stepwise process, reactive intermediate (carbocation) involved

## 4.12 Primary Alcohols (& CH<sub>3</sub>OH) with H-Cl/H-Br/H-I – S<sub>N</sub>2



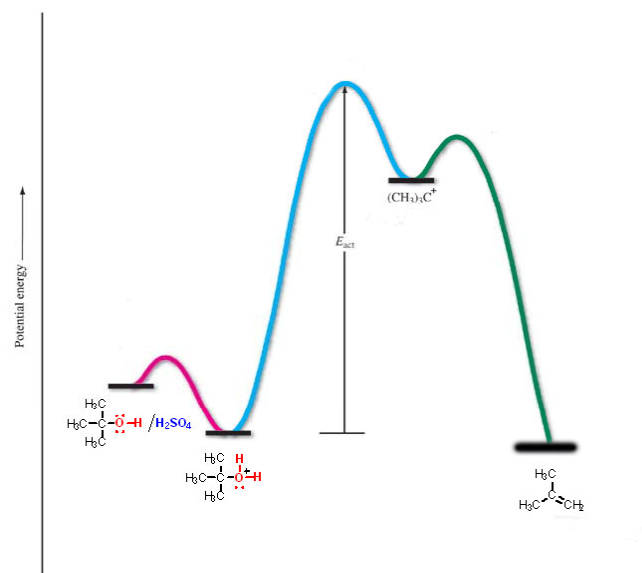
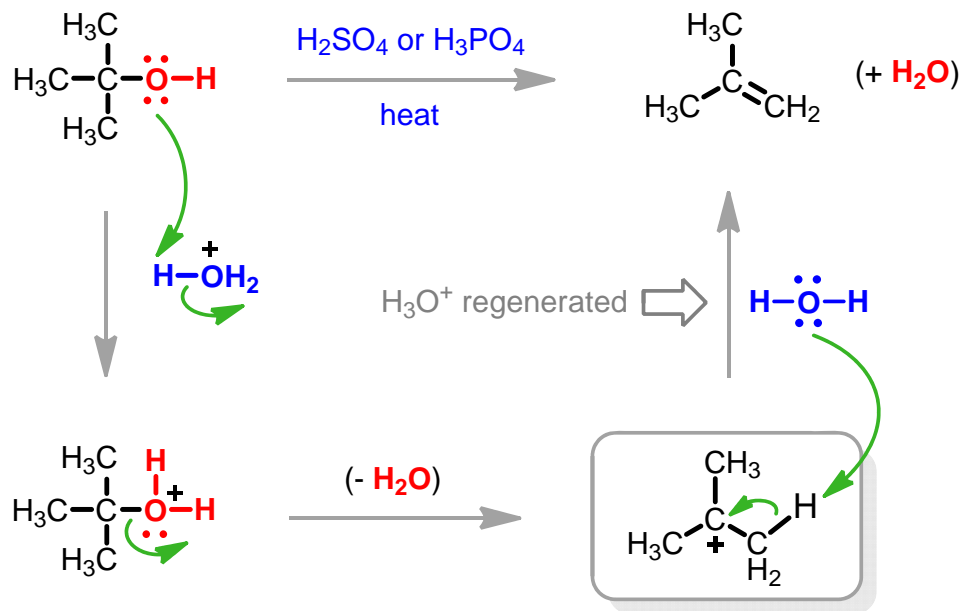
- 1° alcohol (or CH<sub>3</sub>OH) + H-X → alkyl halide = S<sub>N</sub>2 reaction
- Rate-determining step is Bimolecular (no carbocation formed)
- Reaction slowed by Steric Crowding (CH<sub>3</sub> > 1° > 2° > 3°)
- Concerted process, no reactive intermediate involved

## 4.15 Cl/Br Substitution on Alkanes – Free Radicals



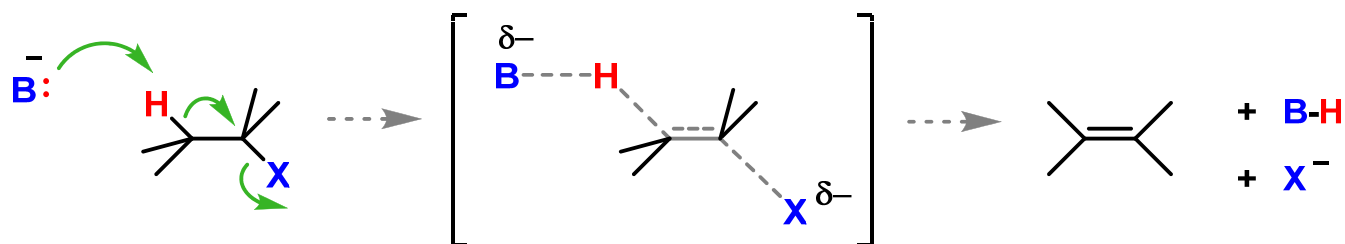
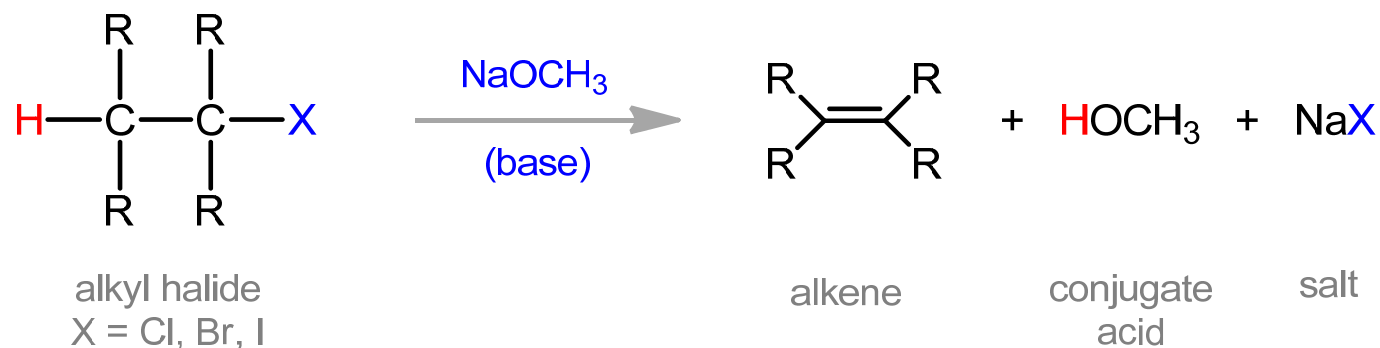
- Alkane +  $\text{Cl}_2/\text{Br}_2$  and heat/light = Radical halogenation reaction
- Non-polar mechanism with homolytic bond-breaking and forming
- Selectivity observed with abstraction of H ( $3^\circ > 2^\circ > 1^\circ$  C-H bond)
- Bromination more selective than chlorination (Br radical selective)

## 5.9 Reaction of 3°/2° Alcohol with H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> – E1



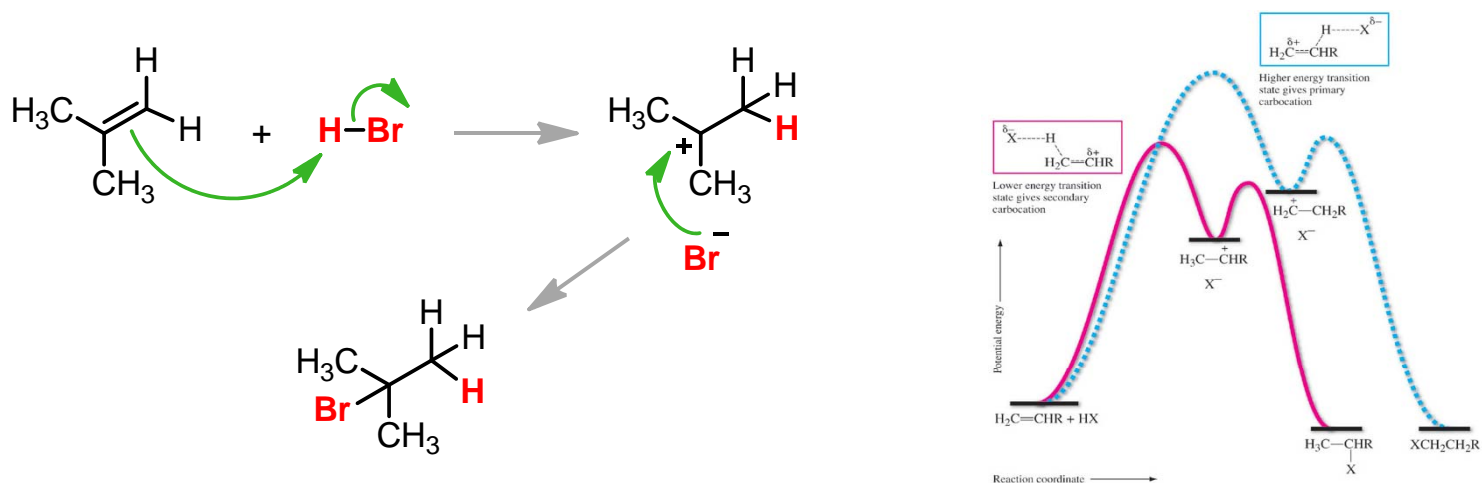
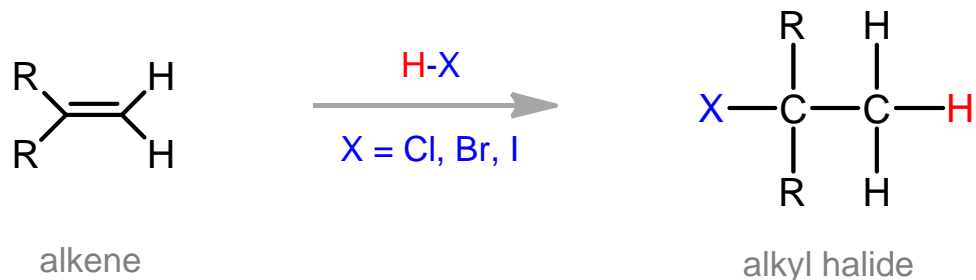
- 3° or 2° alcohol + H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> → alkene = E1 reaction
- Rate-determining step is Unimolecular = CARBOCATION FORMED
- Carbocation stabilized by Hyperconjugation (3° > 2° > 1° > CH<sub>3</sub>)
- Product distribution based on alkene stability (substitution pattern)

## 5.14 Reaction of 3°/2°/1° Alkyl Halide with Base – E2



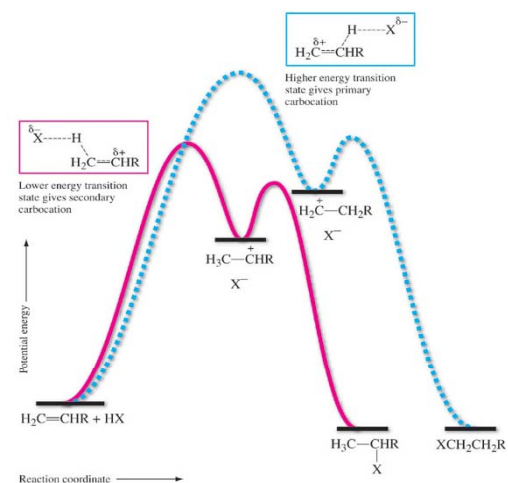
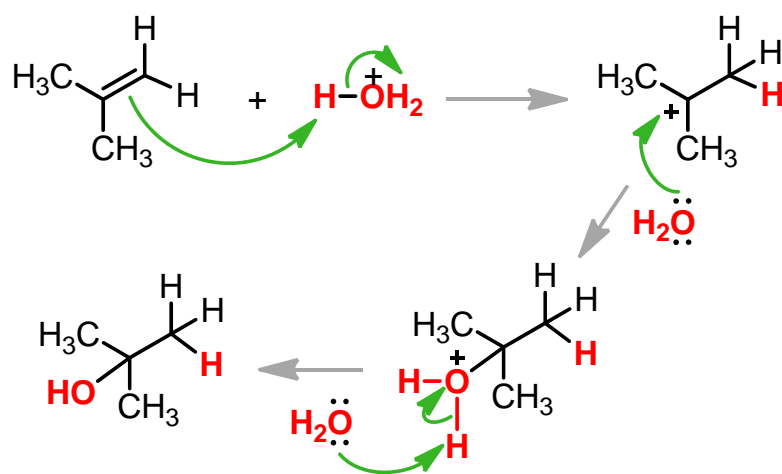
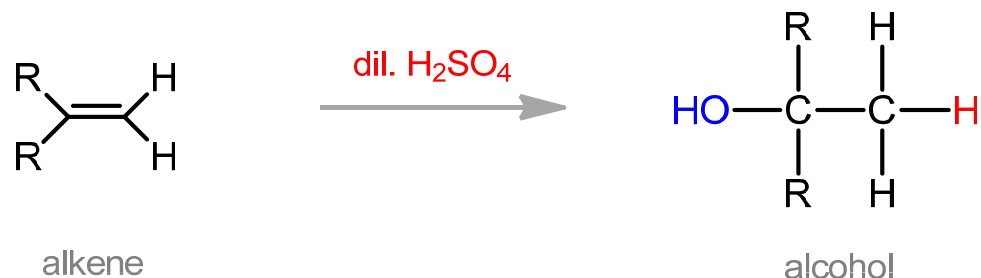
- 3°, 2°, or 1° alkyl halide + base → alkene = E2 reaction
- Rate-determining step is Bimolecular = no intermediate formed
- Zaitsev outcome based on alkene stability (substitution pattern)
- Useful, predictable process since no intermediates are formed

## 6.4 Electrophilic Addition of H-X to Alkenes



- Alkene + H-X (X = Cl, Br, I) gives alkyl halide addition product(s)
- Two-step process: slower step is carbocation formation
- Outcome based on carbocation stability (Markovnikoff rule)
- Carbocation formed so rearrangements are a possibility

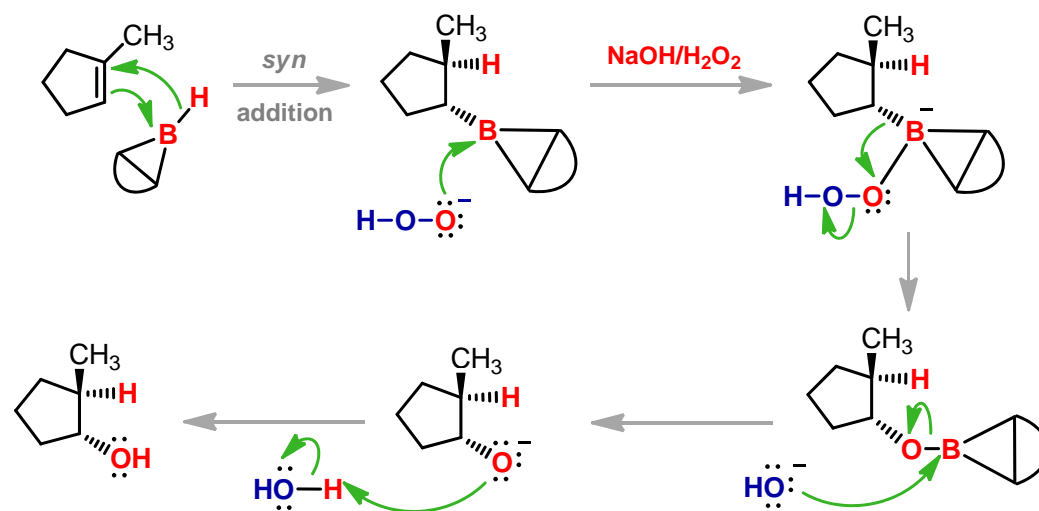
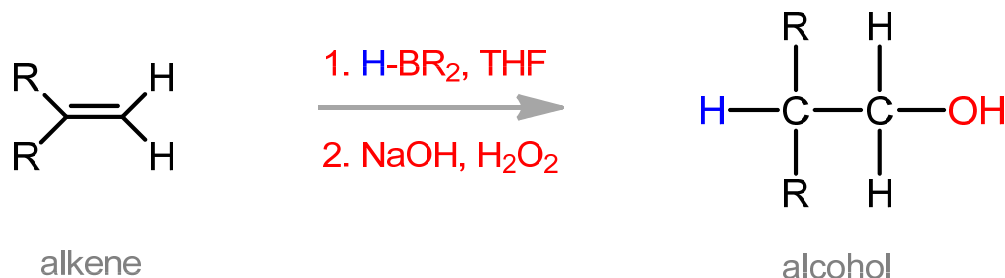
## 6.9 Acid-catalyzed Hydration of Alkenes



- Alkene + dilute  $\text{H}_2\text{SO}_4$  ( $\text{H}_3\text{O}^+$ ) gives alcohol addition product(s)
- Three-step process, the first being slow formation of carbocation
- Major product formed *via* more stabilized carbocation (Markovnikoff)
- Carbocation(s) generated so rearrangements will be possible

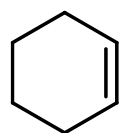


## 6.11 Addition-Oxidation Hydration of Alkenes

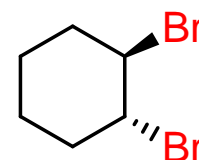
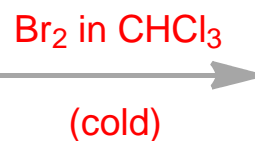


- Alkene +  $\text{H-BR}_2$  gives addition based on sterics and electronics
- First step is concerted *syn* addition; no intermediate(s) formed
- Second (oxidation) step retains original C- $\text{BR}_2$  stereochemistry
- Overall outcome is opposite to that obtained using dilute  $\text{H}_2\text{SO}_4$

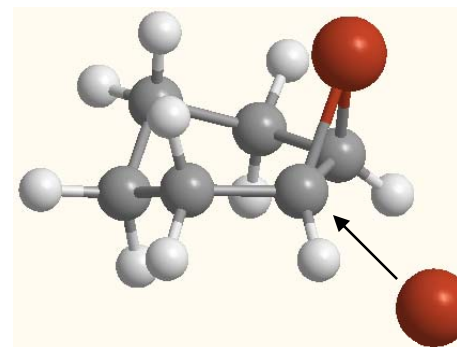
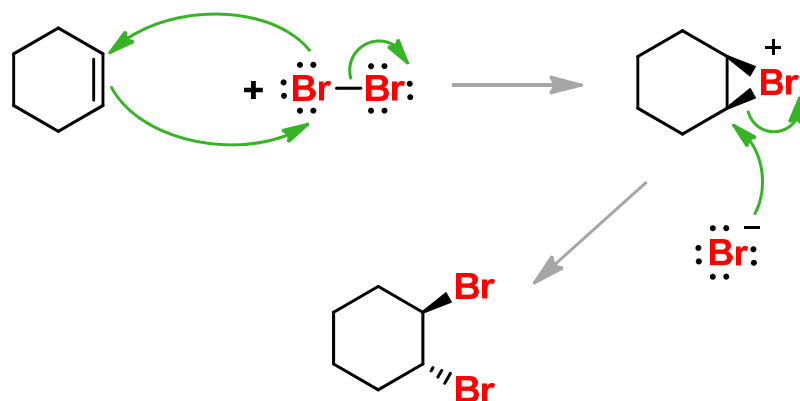
## 6.14 Addition of Halogens to Alkenes



alkene



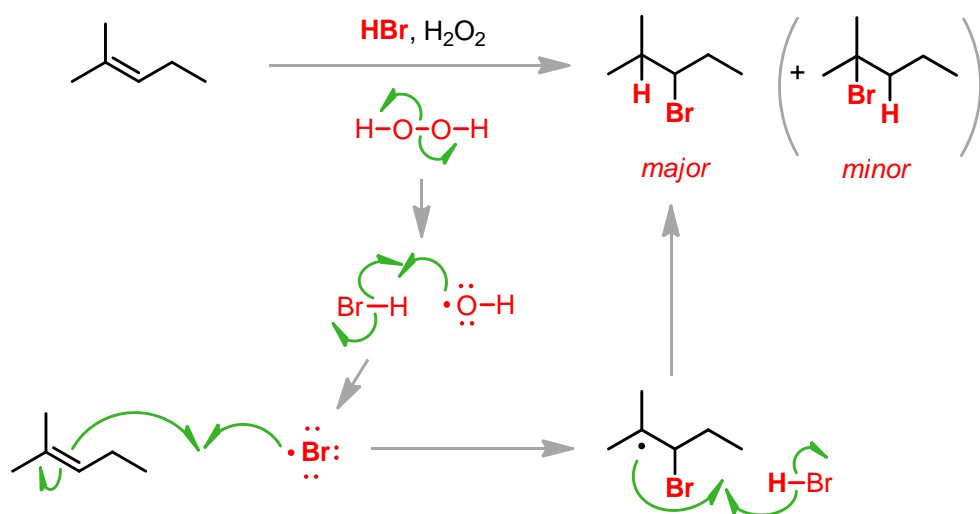
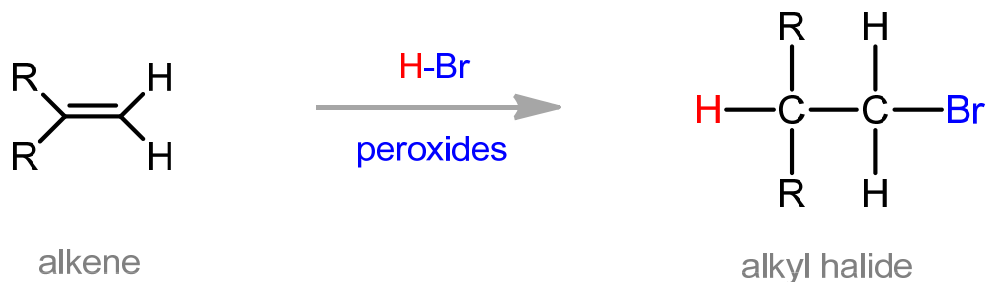
vicinal dibromide



Attack from opposite side preferred

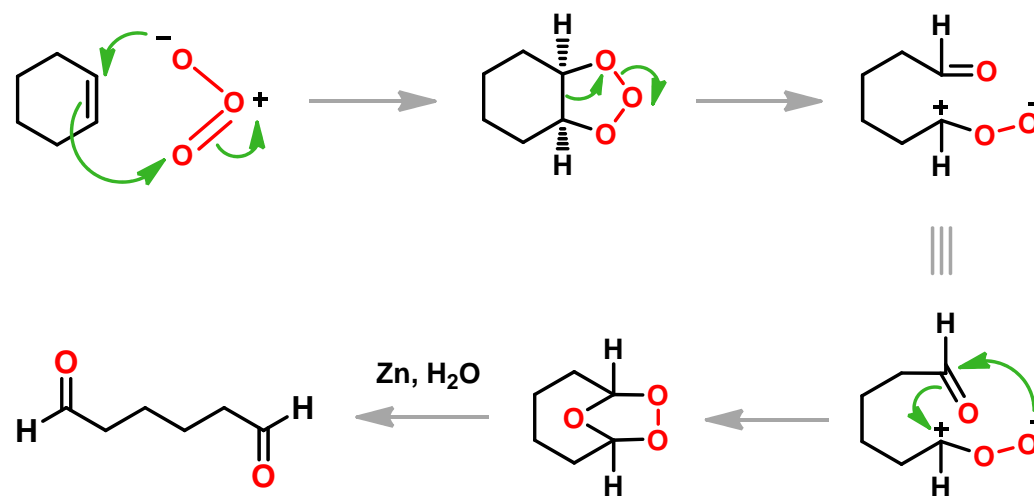
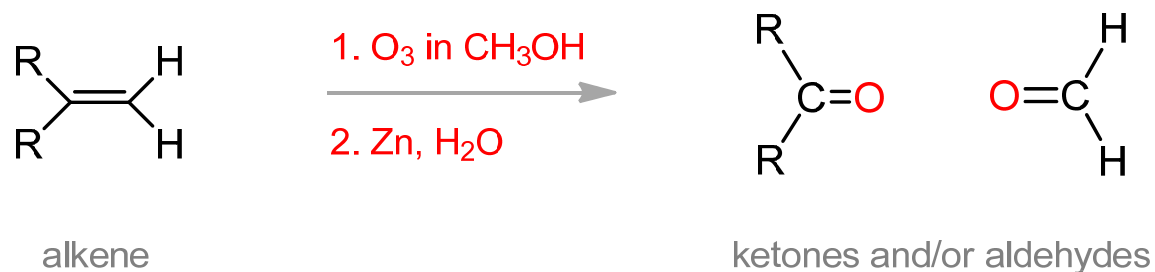
- Only *anti* product indicates that this is not a *syn* addition pathway
- One product only suggests a modified carbocation intermediate
- Formation of the *bromonium ion* explains stereochemical outcome
- Similar reaction with  $\text{Br}_2/\text{H}_2\text{O}$  gives only *anti* addition of “BrOH”

## 6.18 Radical Addition of H-Br to Alkenes



- Alkene + H-Br and peroxide gives alkyl halide addition product(s)
- Radical process with usual steps (initiation, propagation, termination)
- Outcome is based on relative radical stability (Markovnikoff process)
- No rearrangements observed with free radical intermediates here

## 6.20 Ozonolysis of Alkenes



- Remarkable process that **breaks both the  $\pi$  and  $\sigma$  bonds** in the alkene
- First step is concerted ***syn*** addition; no intermediate(s) formed
- Subsequent steps involve breaking of weak O-O bonds and the C-C bond
- Malozonide product is then reduced to give the carbonyl products