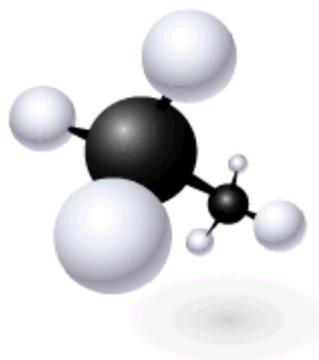


# OChem 1 Mechanism Flashcards

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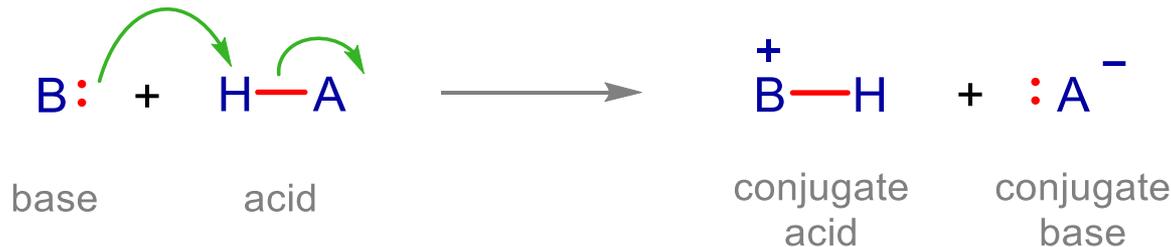


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*Dr. Peter Norris, 2018*



# Ch.3 Acid-Base Reactions: Lone-Pair Donors & Acceptors



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

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

RCO<sub>2</sub>H

PhOH

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

RCCH (alkynes)

RNH<sub>2</sub>

RCH<sub>3</sub>

*pKa* -10 to -5

*pKa* - 1.7

*pKa* ~ 5

*pKa* ~ 10

*pKa* ~ 16

*pKa* ~ 26

*pKa* ~ 36

*pKa* ~ 60

Super strong acids

acids

get

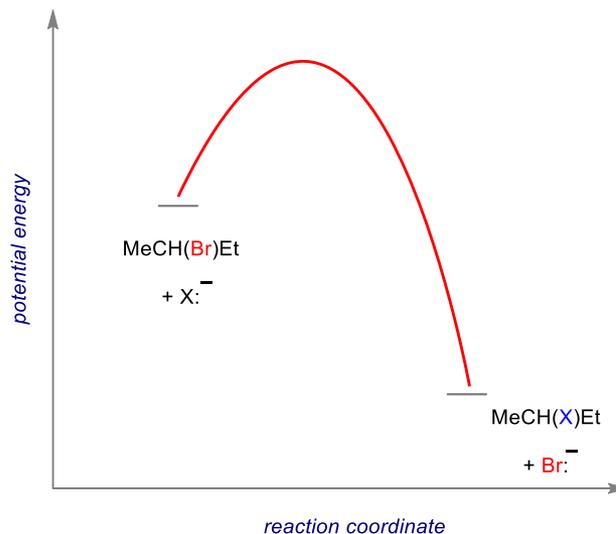
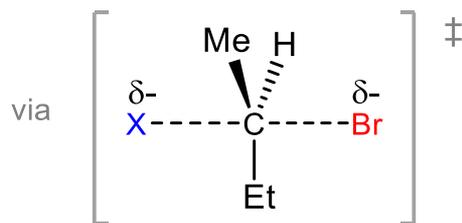
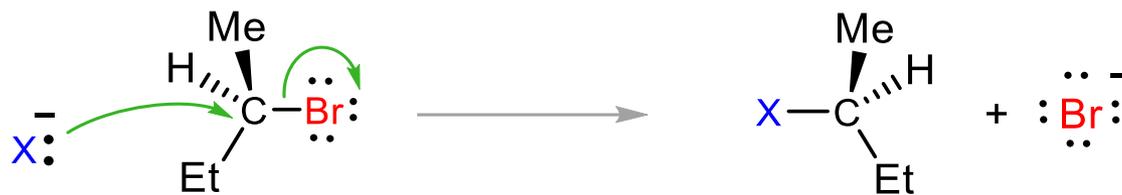
weaker

Extremely weak acid

Not acidic at all

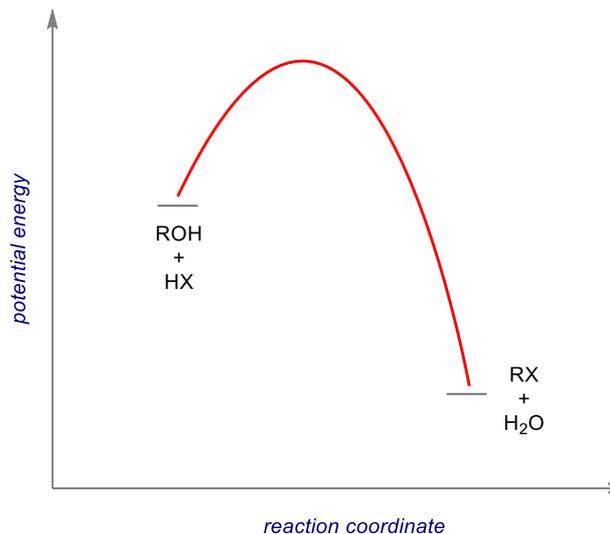
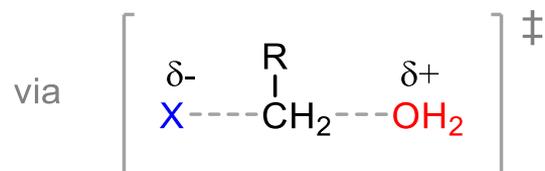
- Lone pair donor + Lone pair acceptor = Acid-Base reaction
- Rate-determining step is **bimolecular** (only one step involved)
- Acid-Base reactions are generally very fast (proton, H, is accessible)
- Acid-Base reactions appear as components of other mechanisms

# Ch.7 Stereochemical Change in the S<sub>N</sub>2 Reaction



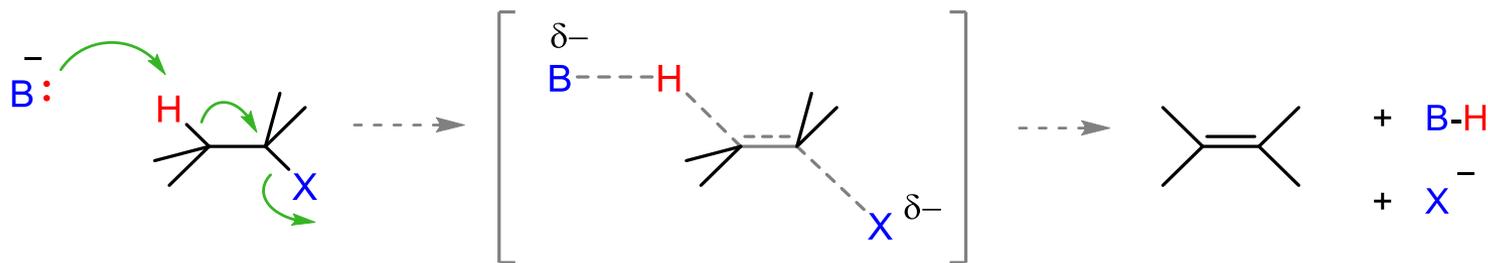
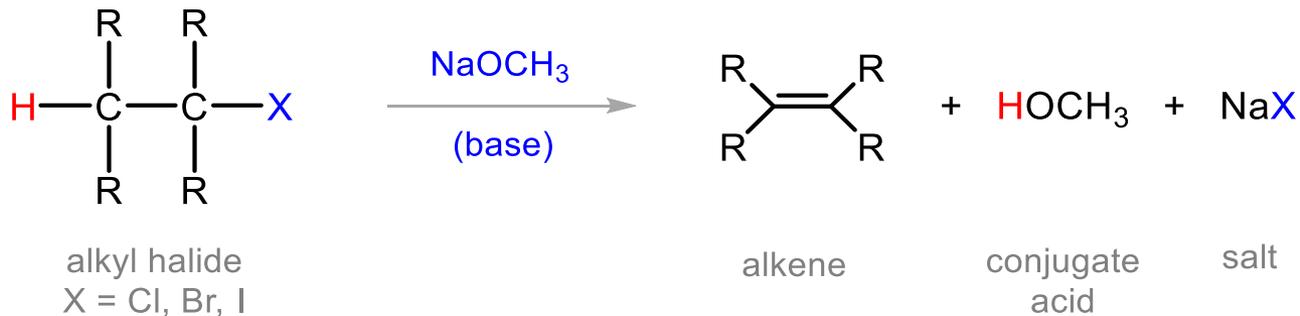
- Chiral 2° carbon with leaving group attached; strong nucleophile
- Rate-determining step is **bimolecular** (no carbocation formed)
- Proceeds with “*backside attack*” and “*stereochemical inversion*”
- Transition state is described as being *trigonal bipyramidal* shape

# Ch.7 Primary Alcohols (& CH<sub>3</sub>OH) with H-Cl/H-Br/H-I – S<sub>N</sub>2



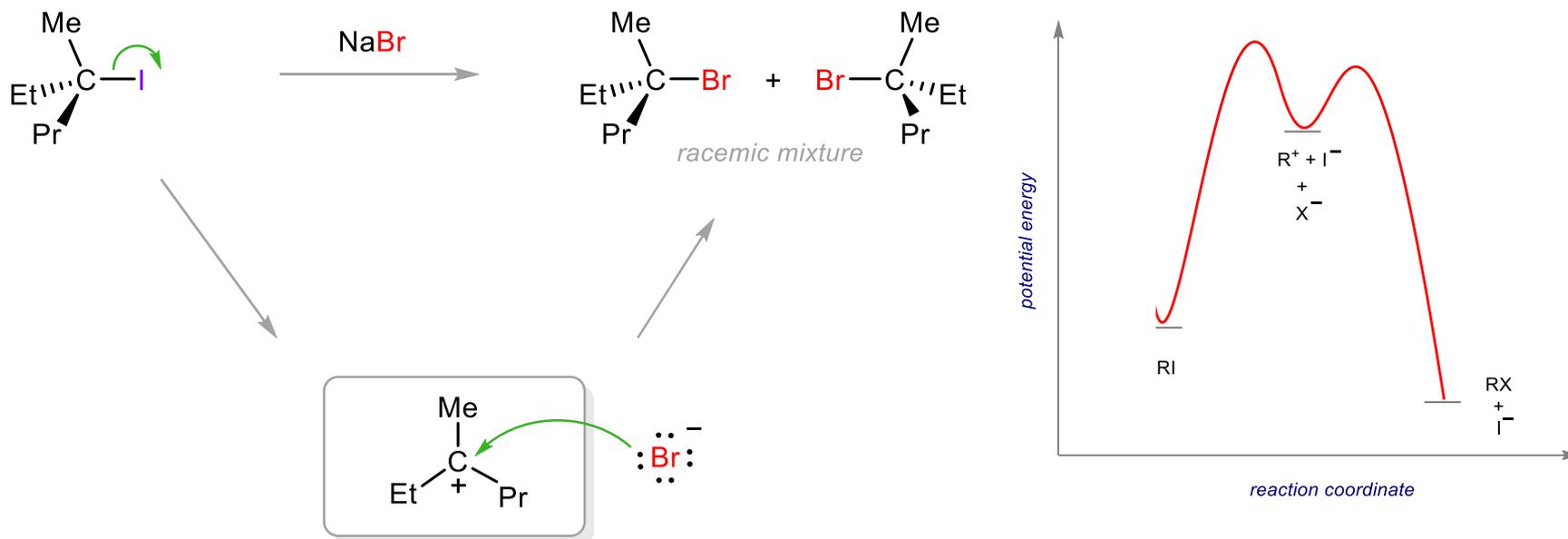
- 1° alcohol (or CH<sub>3</sub>OH) + H-X → alkyl halide = S<sub>N</sub>2 reaction
- Rate-determining step is **bimolecular** (no carbocation formed)
- Reaction slowed by **steric crowding** (CH<sub>3</sub> > 1° > 2° > 3°)
- Concerted process, no reactive intermediate involved

# Ch.7 Reaction of 3°/2°/1° Alkyl Halide with Base – E2



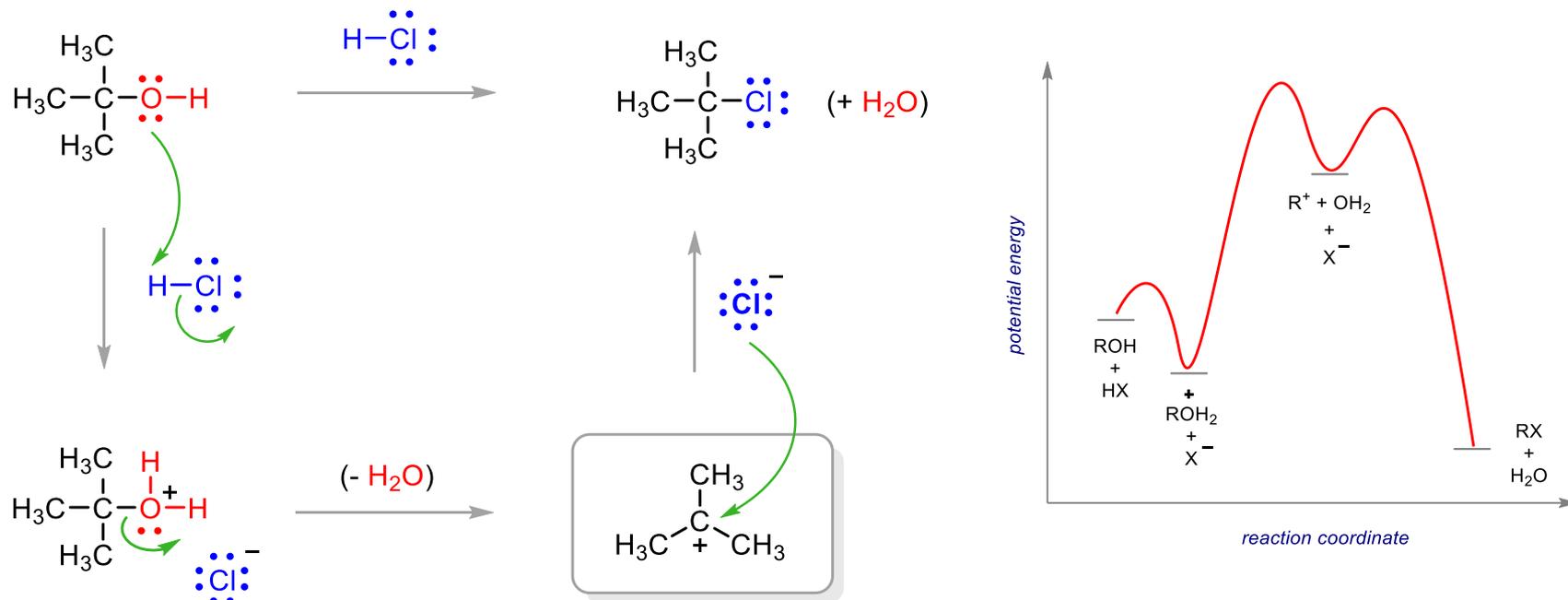
- 3°, 2°, or 1° alkyl halide + base → alkene = E2 reaction
- Rate-determining step is **bimolecular** = no intermediate formed
- **Zaitsev** outcome based on alkene stability (substitution pattern)
- Useful, predictable process since no intermediates are formed

# Ch.7 Stereochemical Change in the S<sub>N</sub>1 Reaction



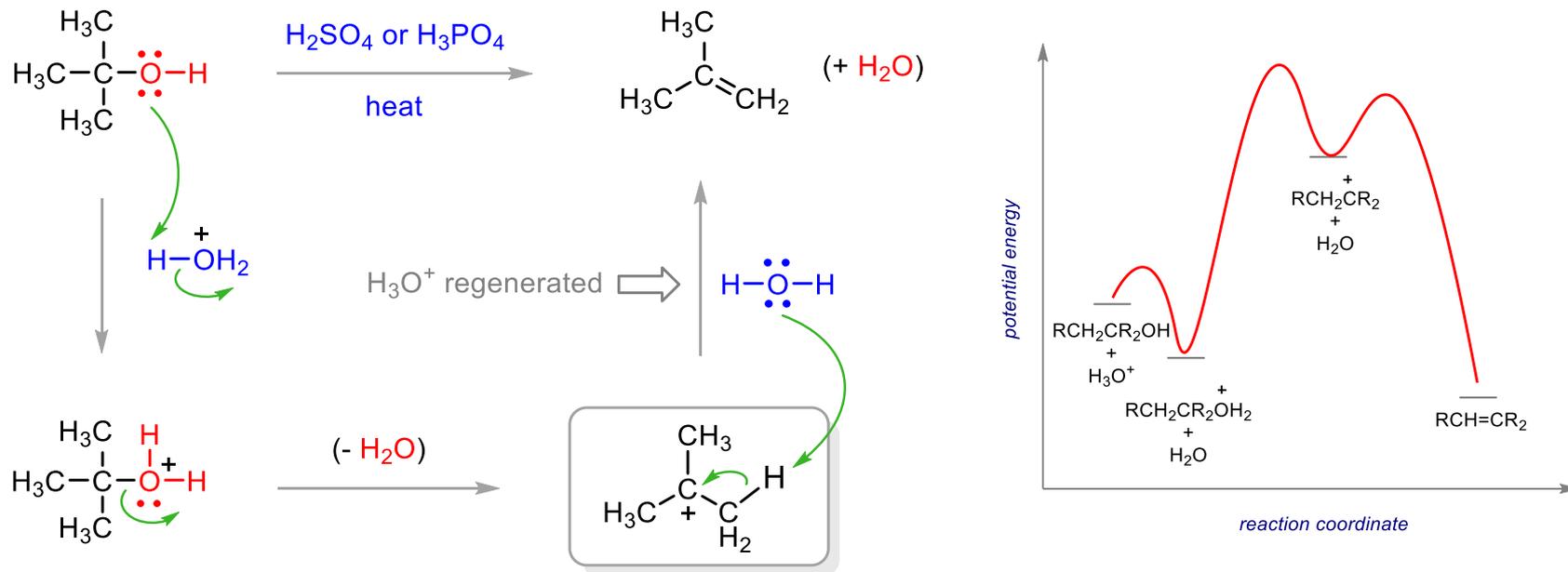
- 3° molecule (with leaving group) + nucleophile = S<sub>N</sub>1 reaction
- Rate-determining step is **unimolecular** = CARBOCATION FORMED
- Carbocation is planar so is attacked from both sides to give 2 products
- Chiral starting material gives racemic mixture of enantiomeric products

# Ch.7 Reaction of a Tertiary Alcohol with H-Cl/H-Br/H-I = S<sub>N</sub>1



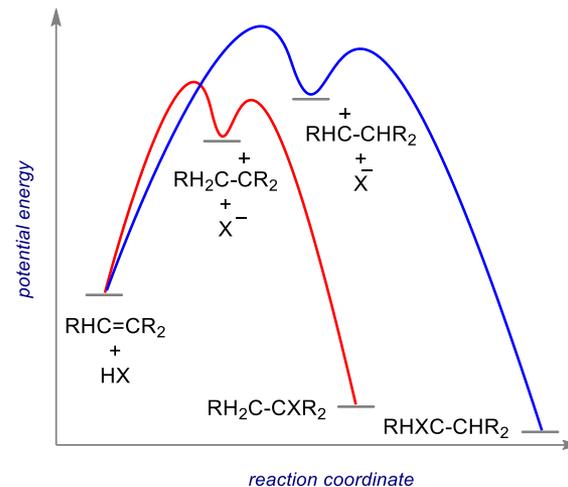
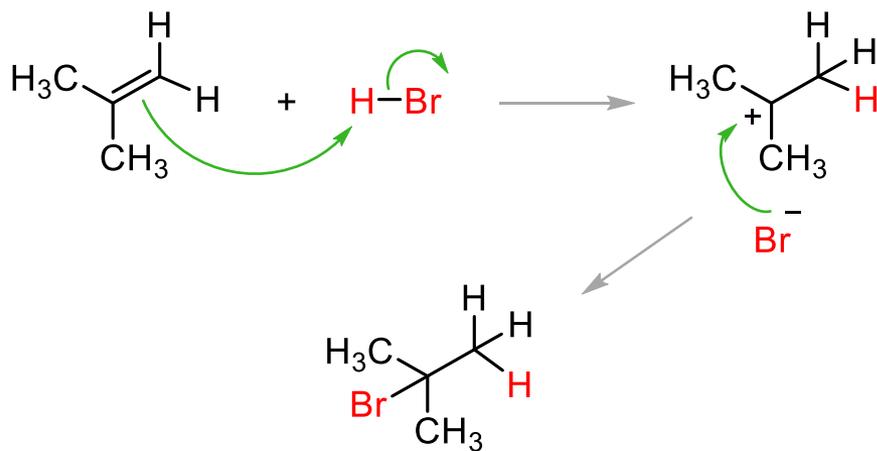
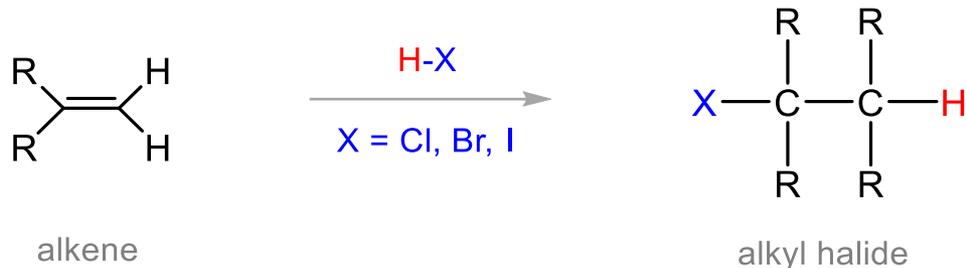
- 3° alcohol + H-X → alkyl halide = S<sub>N</sub>1 reaction
- Rate-determining step is **unimolecular** = CARBOCATION FORMED
- Carbocation stabilized by **hyperconjugation** (3° > 2° > 1° > CH<sub>3</sub>)
- Stepwise process, reactive intermediate (carbocation) involved

# Ch.7 Reaction of 3°/2° Alcohol with H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> – E1



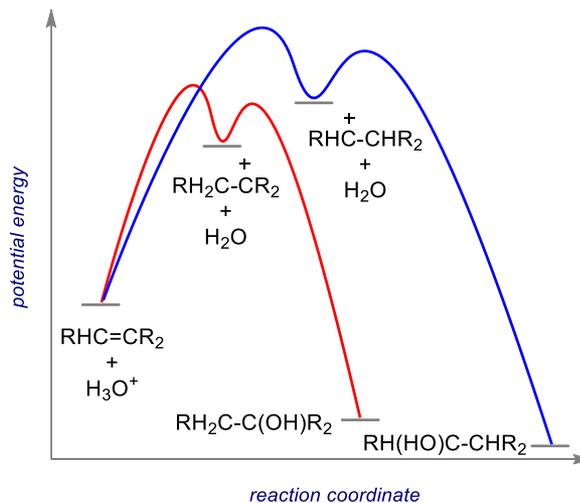
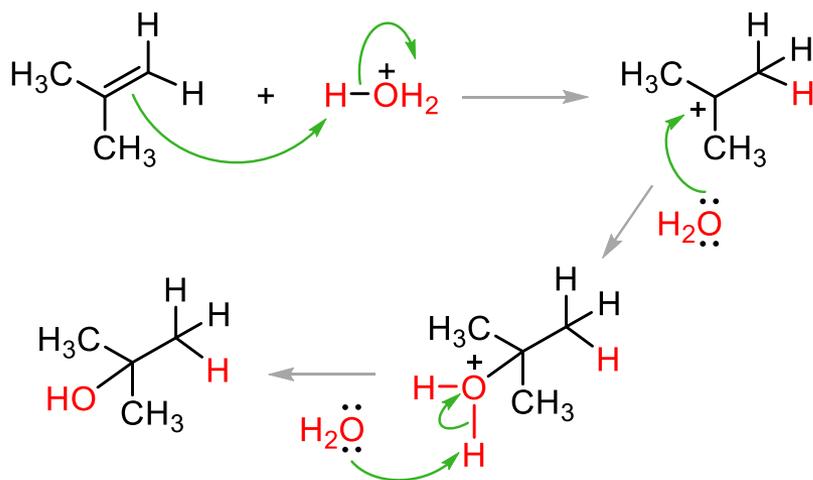
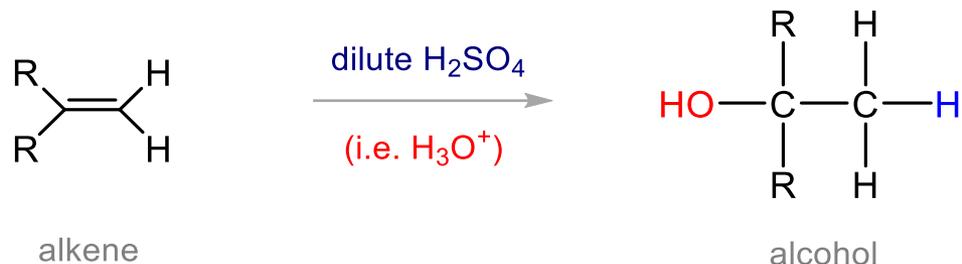
- 3° or 2° alcohol + H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> → alkene = E1 reaction
- Rate-determining step is **unimolecular** = CARBOCATION FORMED
- Carbocation stabilized by **hyperconjugation** (3° > 2° > 1° > CH<sub>3</sub>)
- Product distribution is based on relative alkene stability (**Zaitsev** rule)

# Ch.8 Electrophilic Addition of H-X to Alkenes



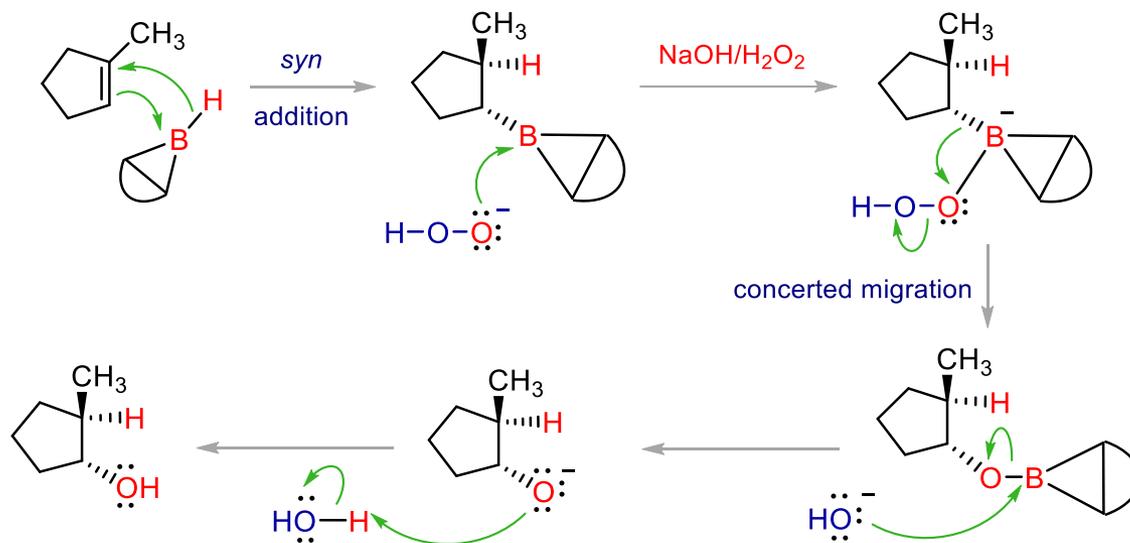
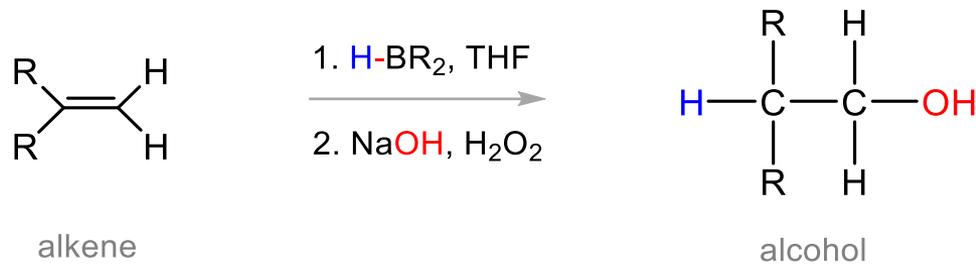
- Alkene + H-X (X = Cl, Br, I) gives alkyl halide addition product(s)
- Two-step process: slower step is carbocation formation
- Outcome based on carbocation stability (**Markovnikoff rule**)
- Carbocation formed so rearrangements are a possibility

# Ch.8 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 (**Markovnikov**)
- Carbocation(s) generated so rearrangements will be possible

# Ch.8 Addition-Oxidation Hydration of Alkenes

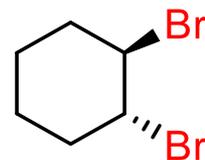
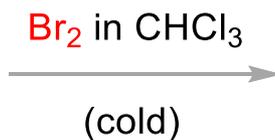


- Alkene +  $\text{H-BR}_2$  gives addition based on sterics and electronics
- First step is concerted **syn** addition; no intermediate(s) formed
- Second (oxidation) step retains original  $\text{C-BR}_2$  stereochemistry
- Overall outcome is opposite to that obtained using dilute  $\text{H}_2\text{SO}_4$

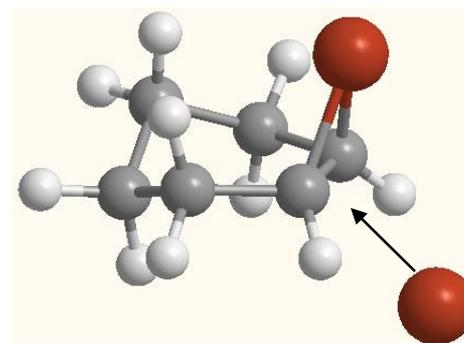
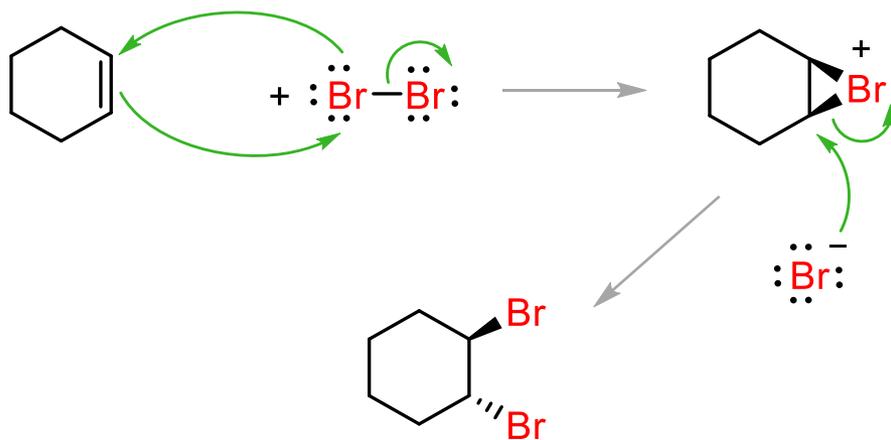
# Ch.8 Addition of Halogens to Alkenes



alkene



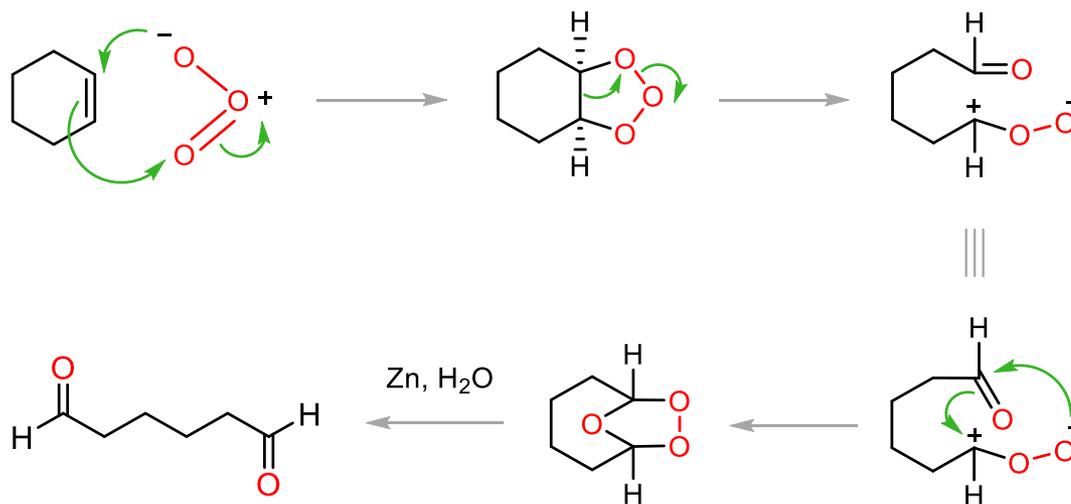
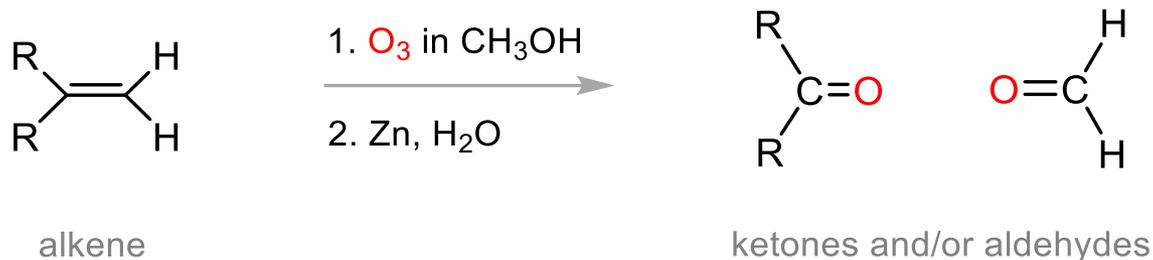
vicinal dibromide



Attack from opposite side preferred

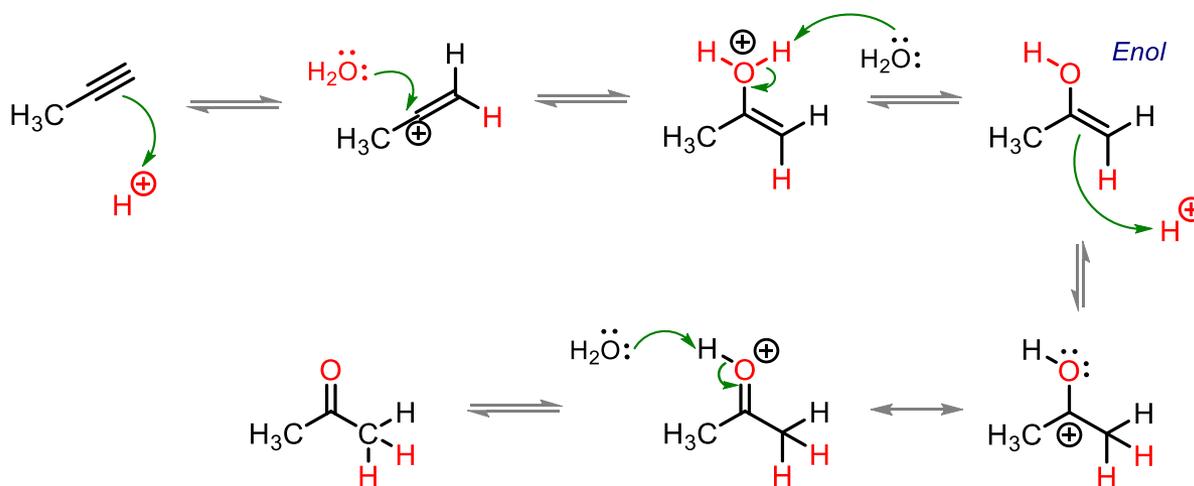
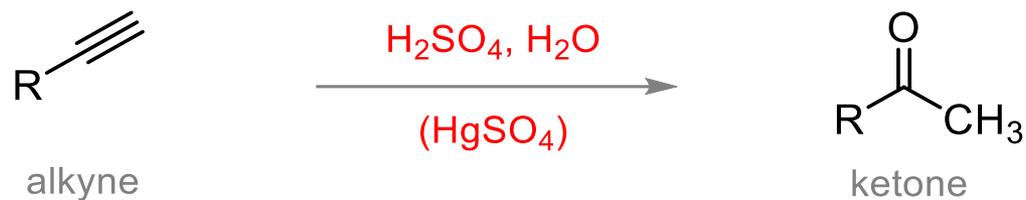
- Only **anti** product indicates that this is not a **syn** addition pathway
- One product only suggests a modified carbocation intermediate
- Formation of the **bromonium ion** explains stereochemical outcome
- Similar reaction with  $\text{Br}_2/\text{H}_2\text{O}$  gives only **anti** addition of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

# Ch.8 Ozonolysis of Alkenes



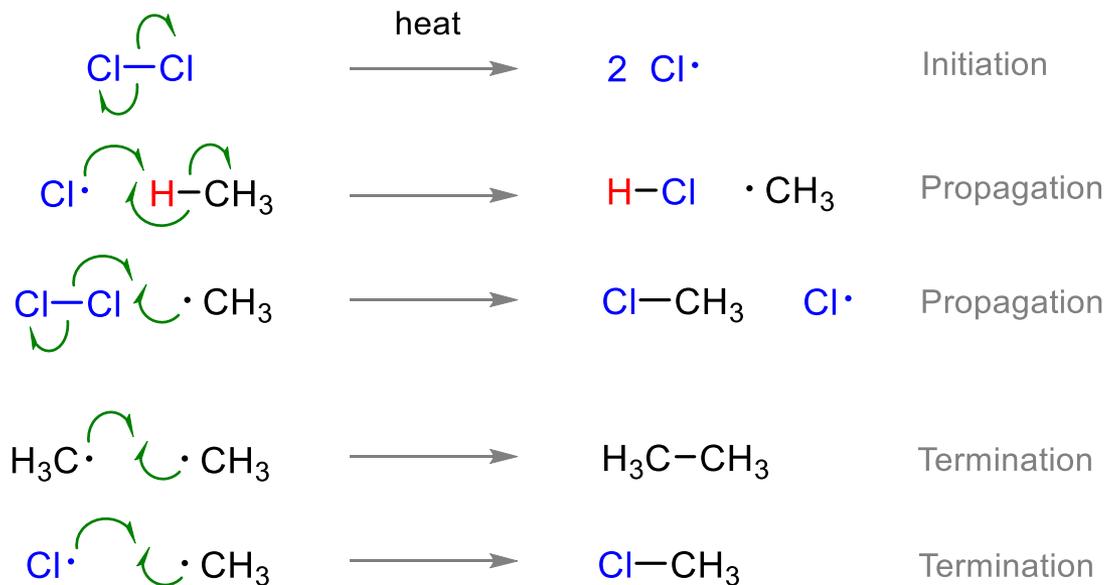
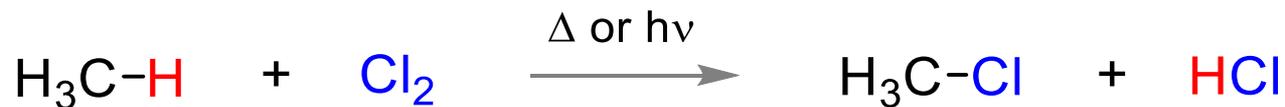
- Remarkable process that **breaks both the  $\pi$  and  $\sigma$  bonds** in the alkene
- First step is concerted ***syn*** addition; no intermediate(s) formed
- Subsequent steps involve breaking of weak O-O bonds and the C-C bond
- Malozonide product is then reduced to give the carbonyl products

# Ch.9 Hydrolysis of Alkynes



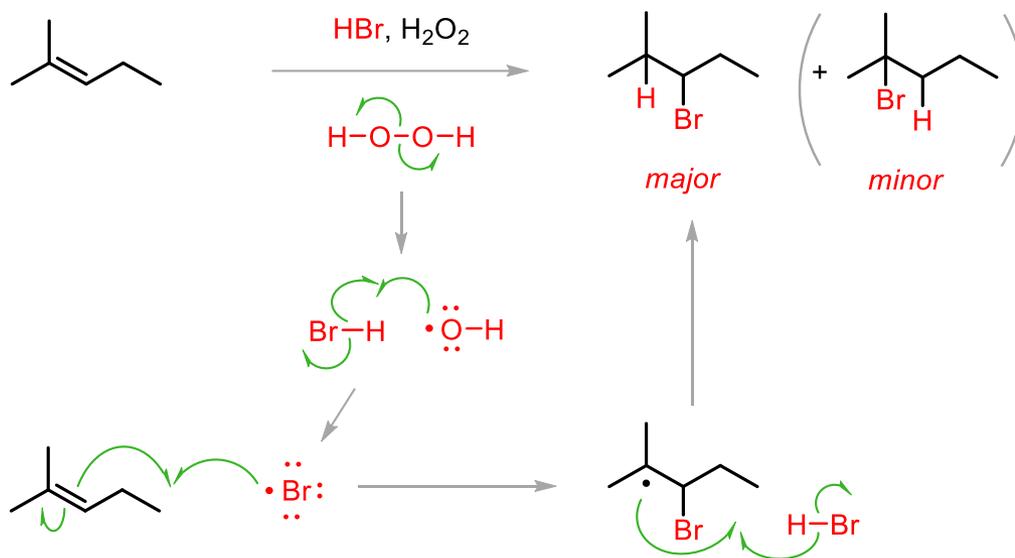
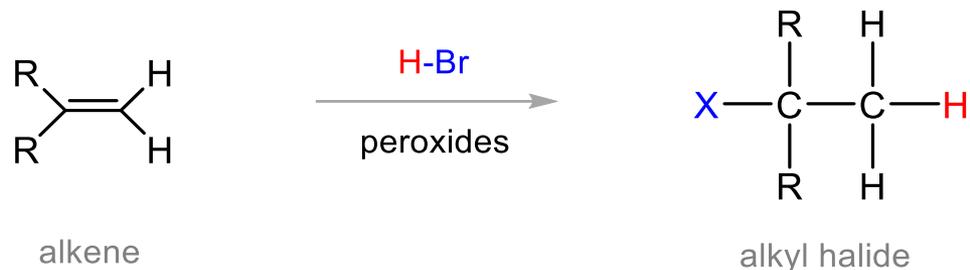
- Stepwise acid- and Lewis acid-catalyzed addition of water to an alkyne
- Formal product of the addition is the enol, which is often not isolated
- **Tautomerism** most often then leads to the more stable ketone product
- Process occurs through the more stable carbocation (**Markovnikoff**)

# Ch.10 Cl/Br Substitution on Alkanes – Free Radicals



- Alkane + Cl<sub>2</sub>/Br<sub>2</sub> and heat/light = Radical halogenation reaction
- Non-polar mechanism with **homolytic** bond-breaking and forming
- **Selectivity** observed with abstraction of H (3° > 2° > 1° C-H bond)
- Bromination more selective than chlorination (Br radical selective)

# Ch.10 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