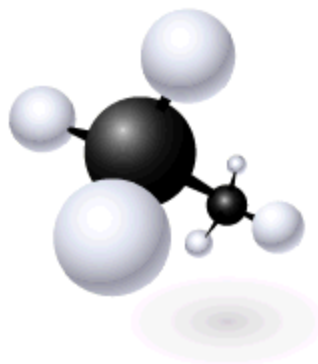
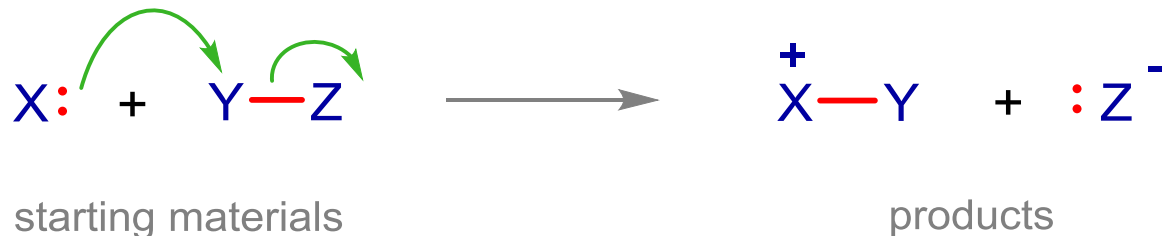


OCHEM 1 MECHANISM FLASHCARDS



Dr. Peter Norris, 2015

Mechanism Basics



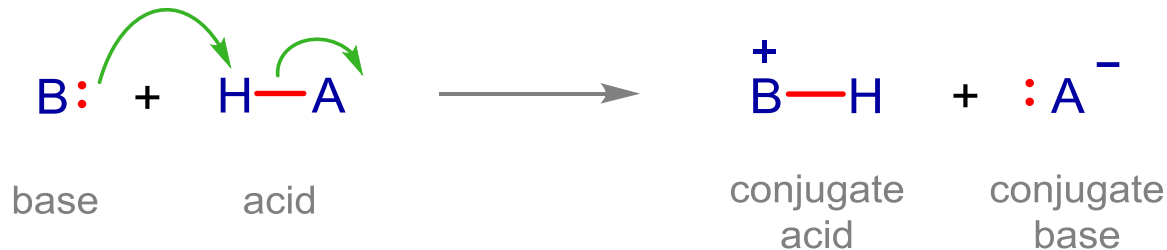
Chemical change involves bonds forming and breaking;
a mechanism describes those changes using curved arrows
to describe the electrons involved

There are two main types of curved arrow to describe either
2-electron or 1-electron processes

Above, the X-Y bond is forming and the Y-Z bond is breaking

There are ~100 mechanisms in OChem1 and OChem2

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



HI, HCl, HNO₃, H₃PO₄

H₃O⁺

RCO₂H

PhOH

H₂O, ROH

RCCH (alkynes)

RNH₂

RCH₃

pKa -10 to -5

pKa - 1.7

pKa ~ 5

pKa ~ 10

pKa ~ 16

pKa ~ 26

pKa ~ 36

pKa ~ 60

Super strong acids

acids

get

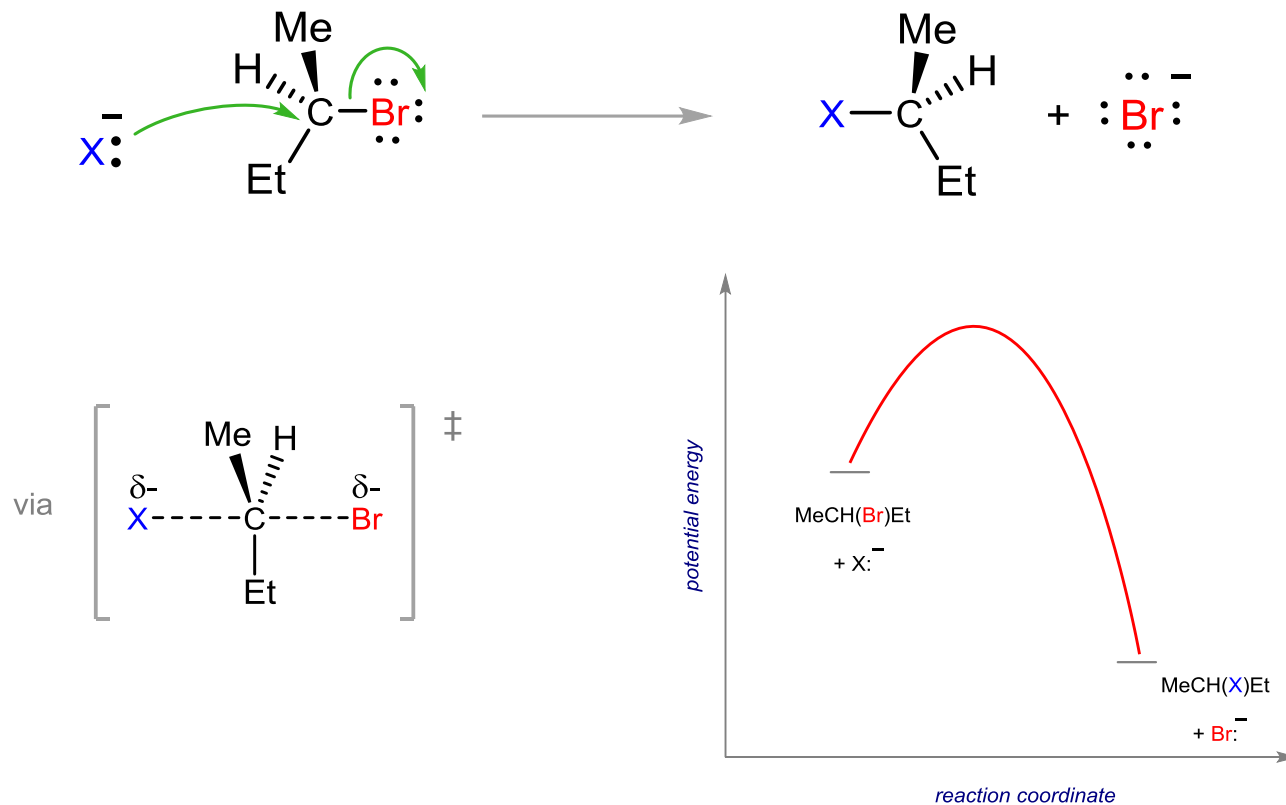
weaker

Extremely weak acid

Not acidic at all

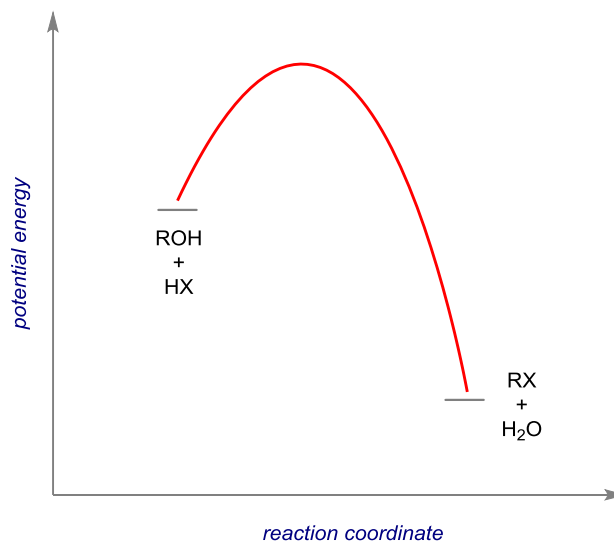
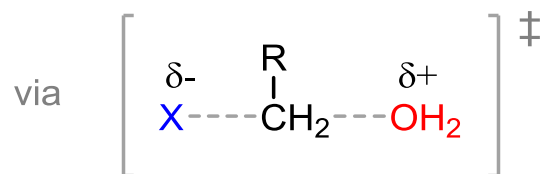
- Lone pair donor + Lone pair acceptor = Acid-Base reaction
- Rate-determining step is **bimolecular** (only one step involved)
- Acid-Base reactions are generally very fast (proton, H, is accessible)
- Acid-Base reactions appear as components of other mechanisms

Ch.7 Stereochemical Change in the S_N2 Reaction



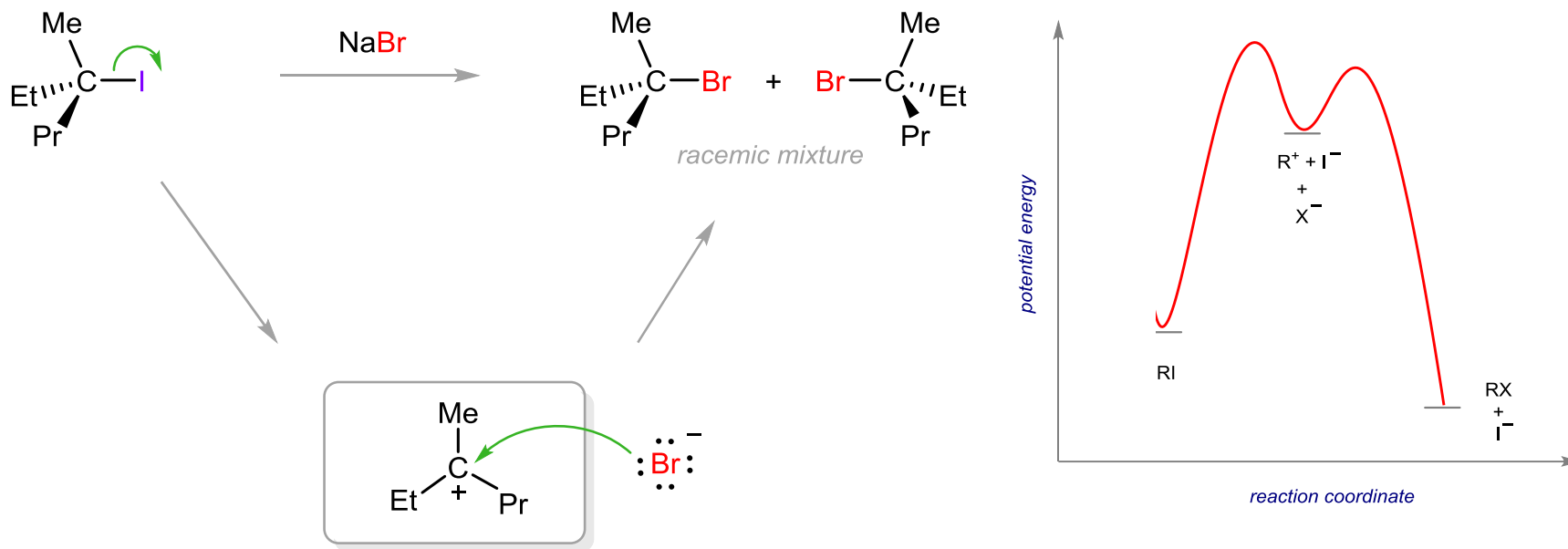
- Chiral 2° carbon with leaving group attached; strong nucleophile
- Rate-determining step is **bimolecular** (no carbocation formed)
- Proceeds with “*backside attack*” and “*stereochemical inversion*”
- Transition state is described as being *trigonal bipyramidal* shape

Ch.7 Primary Alcohols (& CH₃OH) with H-Cl/H-Br/H-I – S_N2



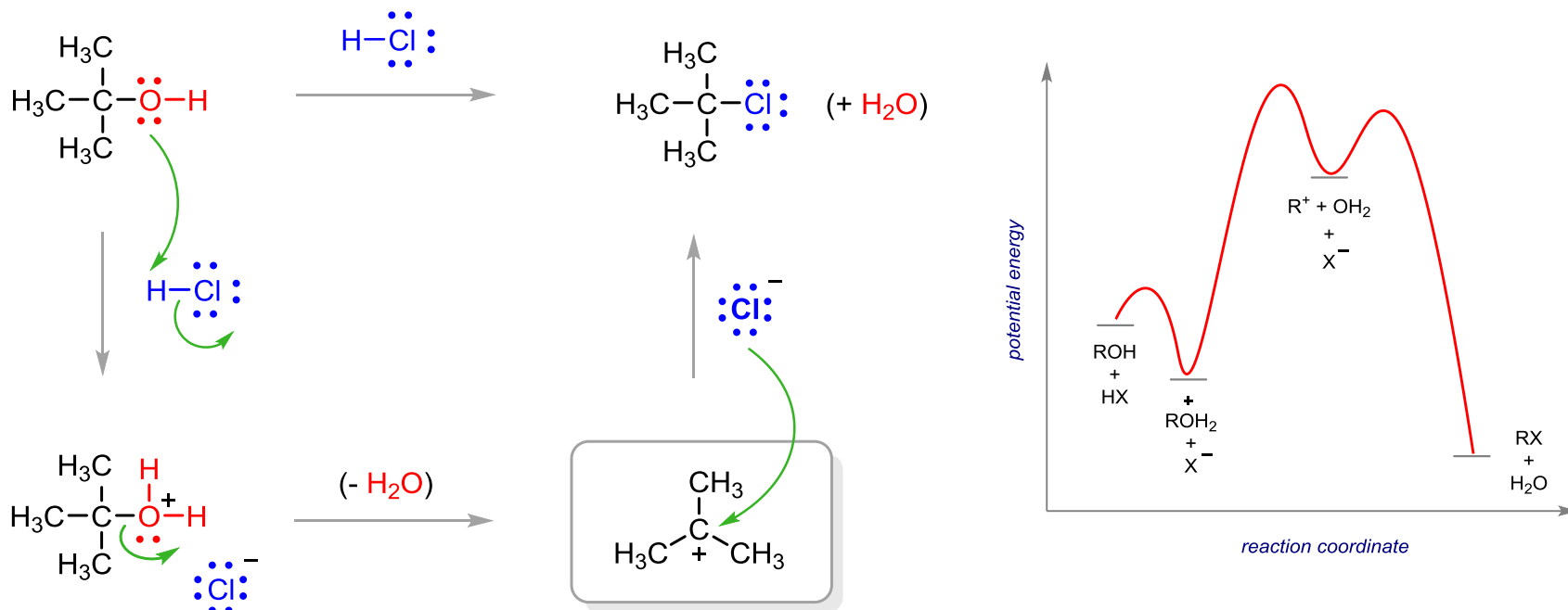
- 1° alcohol (or CH₃OH) + H-X → alkyl halide = S_N2 reaction
- Rate-determining step is **bimolecular** (no carbocation formed)
- Reaction slowed by **steric crowding** (CH₃ > 1° > 2° > 3°)
- Concerted process, no reactive intermediate involved

Ch.7 Stereochemical Change in the S_N1 Reaction



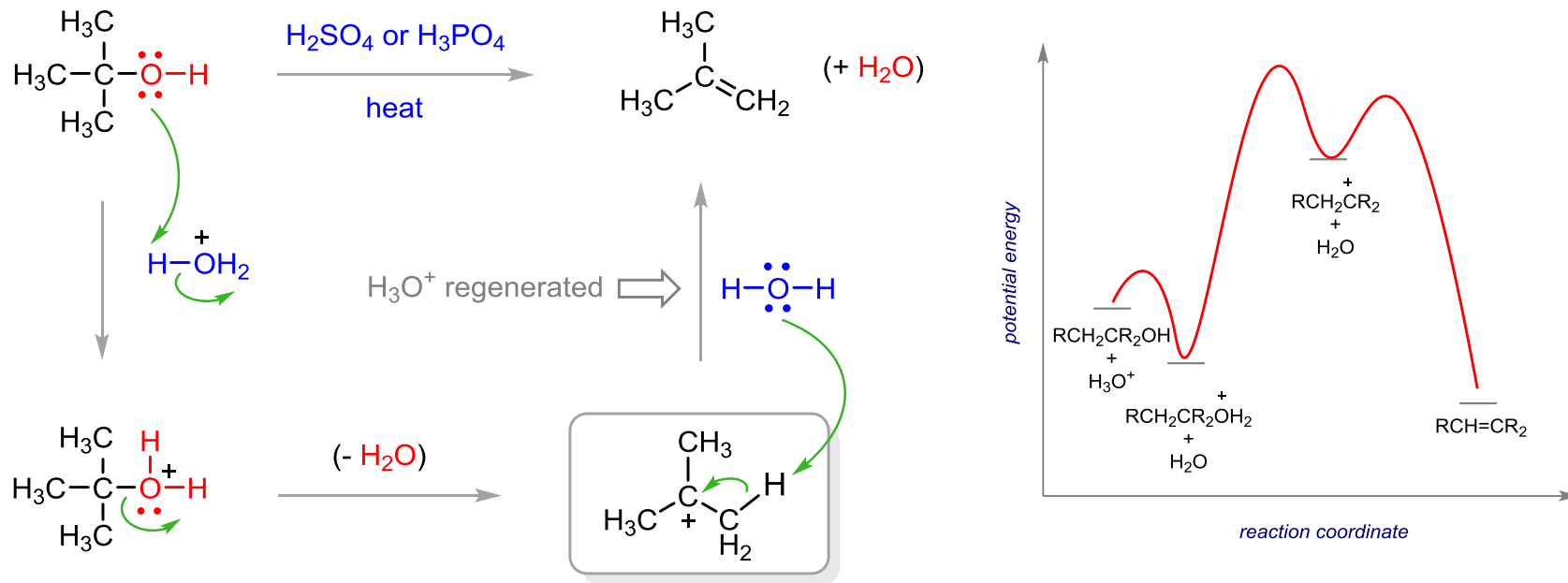
- 3° molecule (with leaving group) + nucleophile = S_N1 reaction
- Rate-determining step is **unimolecular** = CARBOCATION FORMED
- Carbocation is planar so is attacked from both sides to give 2 products
- Chiral starting material gives racemic mixture of enantiomeric products

Ch.7 Reaction of a Tertiary Alcohol with H-Cl/H-Br/H-I = S_N1



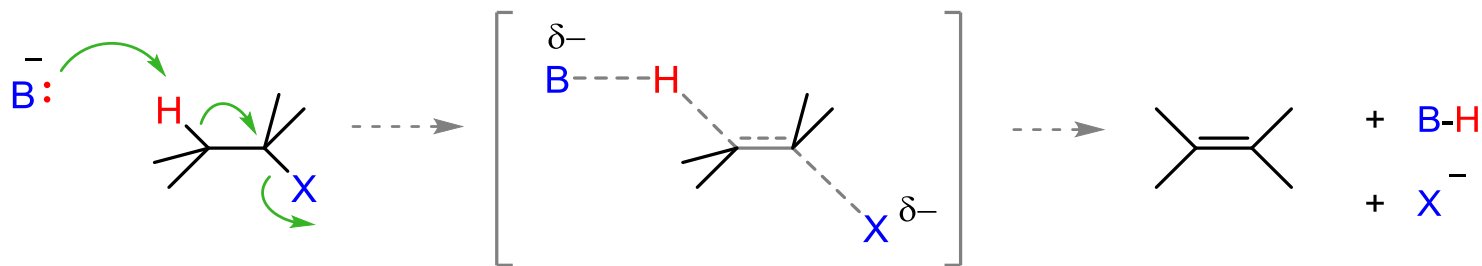
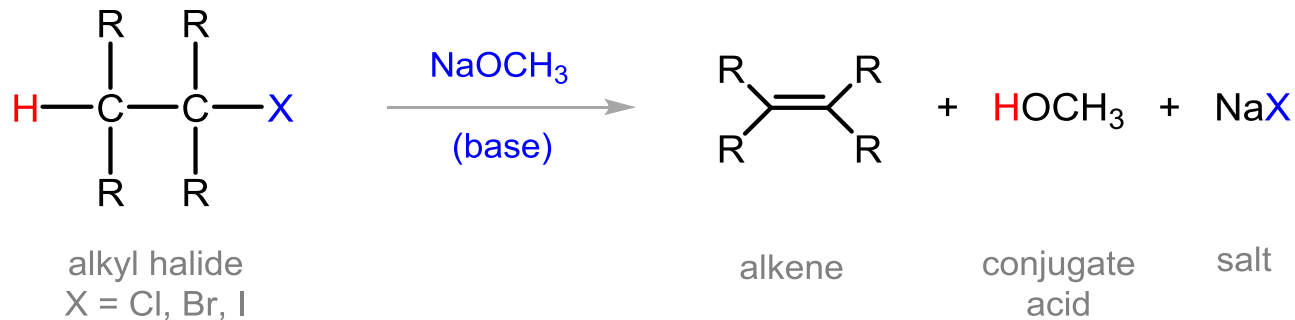
- 3° alcohol + H-X → alkyl halide = S_N1 reaction
- Rate-determining step is **unimolecular** = CARBOCATION FORMED
- Carbocation stabilized by **hyperconjugation** (3° > 2° > 1° > CH₃)
- Stepwise process, reactive intermediate (carbocation) involved

Ch.8 Reaction of 3°/2° Alcohol with H₂SO₄/H₃PO₄ – E1



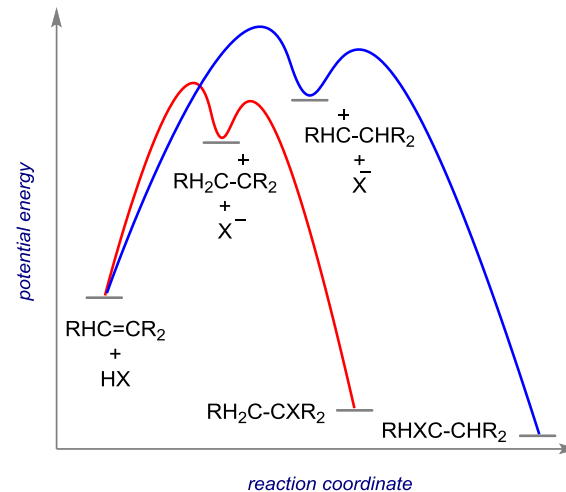
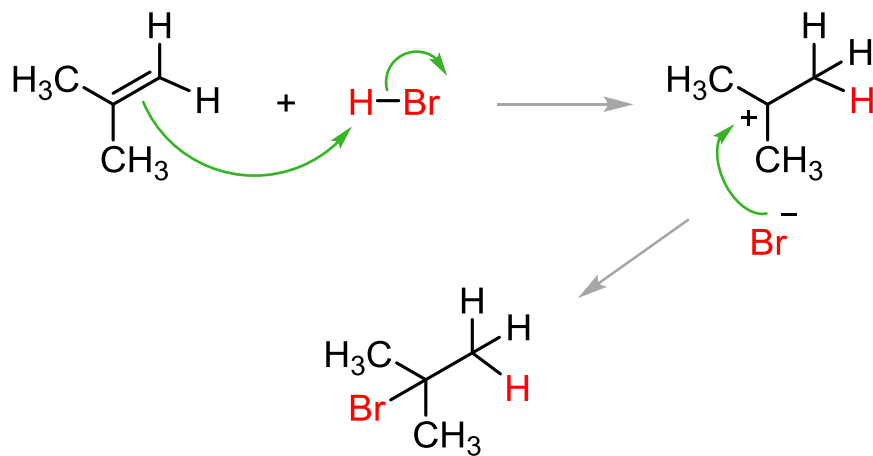
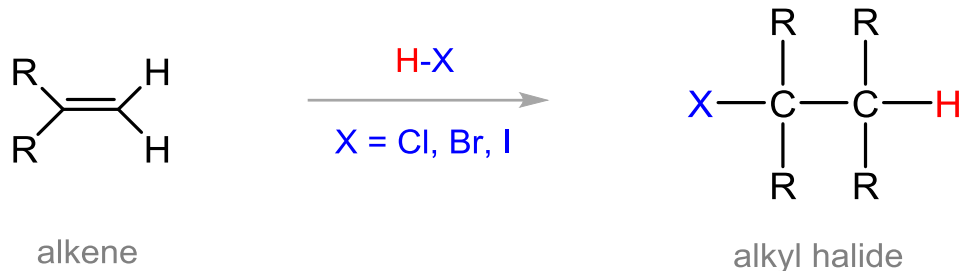
- 3° or 2° alcohol + H₂SO₄ or H₃PO₄ → alkene = E1 reaction
- Rate-determining step is **unimolecular** = CARBOCATION FORMED
- Carbocation stabilized by **hyperconjugation** (3° > 2° > 1° > CH₃)
- Product distribution is based on relative alkene stability (**Zaitsev** rule)

Ch.8 Reaction of 3°/2°/1° Alkyl Halide with Base – E2



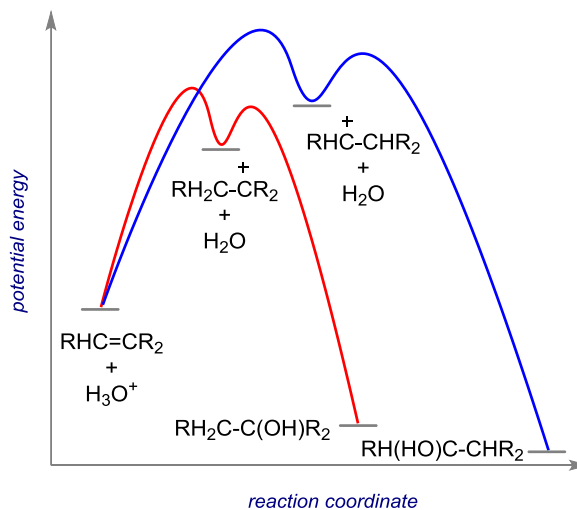
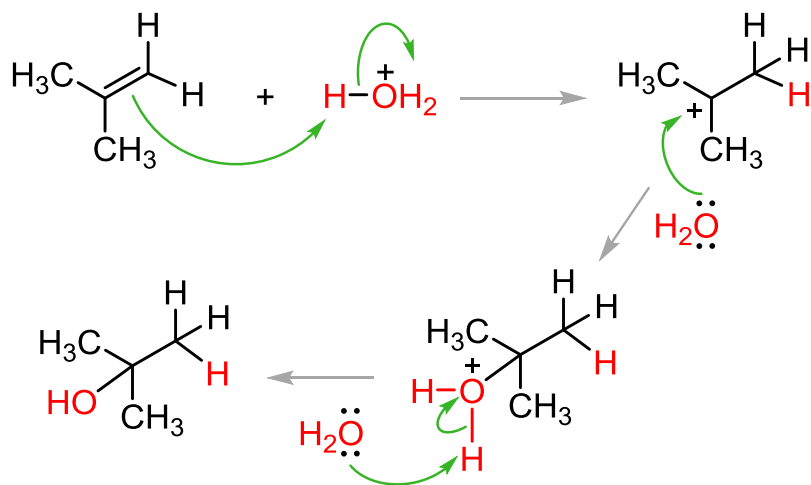
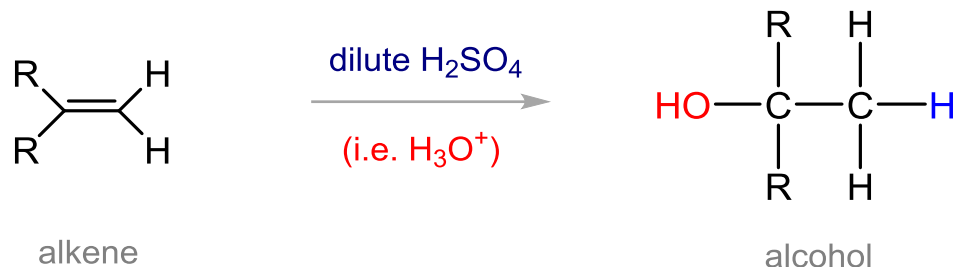
- 3°, 2°, or 1° alkyl halide + base → alkene = E2 reaction
- Rate-determining step is **bimolecular** = no intermediate formed
- **Zaitsev** outcome based on alkene stability (substitution pattern)
- Useful, predictable process since no intermediates are formed

Ch.9 Electrophilic Addition of H-X to Alkenes



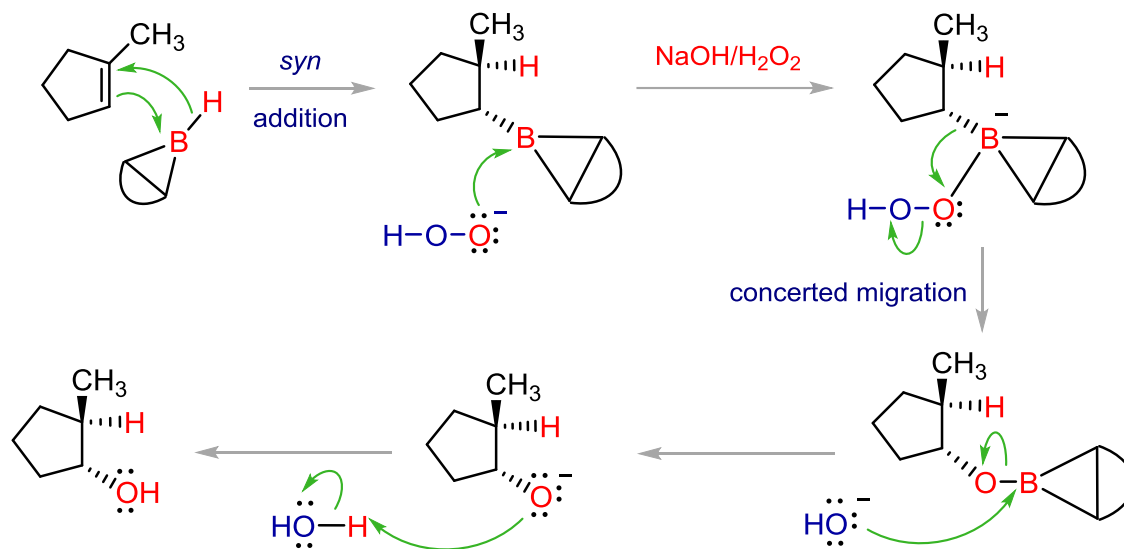
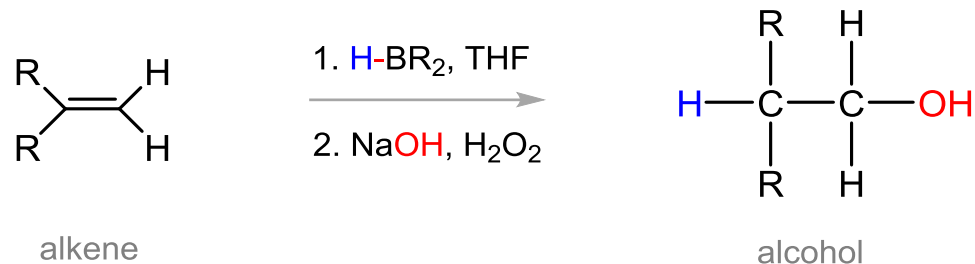
- Alkene + H-X (X = Cl, Br, I) gives alkyl halide addition product(s)
- Two-step process: slower step is carbocation formation
- Outcome based on carbocation stability (**Markovnikoff rule**)
- Carbocation formed so rearrangements are a possibility

Ch.9 Acid-catalyzed Hydration of Alkenes



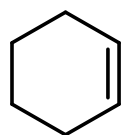
- Alkene + dilute H_2SO_4 (H_3O^+) gives alcohol addition product(s)
- Three-step process, the first being slow formation of carbocation
- Major product formed *via* more stabilized carbocation (**Markovnikoff**)
- Carbocation(s) generated so rearrangements will be possible

Ch.9 Addition-Oxidation Hydration of Alkenes

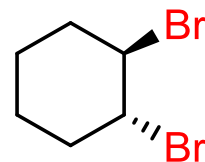
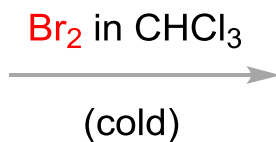


- Alkene + H-BR_2 gives addition based on sterics and electronics
- First step is concerted ***syn*** addition; no intermediate(s) formed
- Second (oxidation) step retains original C-BR_2 stereochemistry
- Overall outcome is opposite to that obtained using dilute H_2SO_4

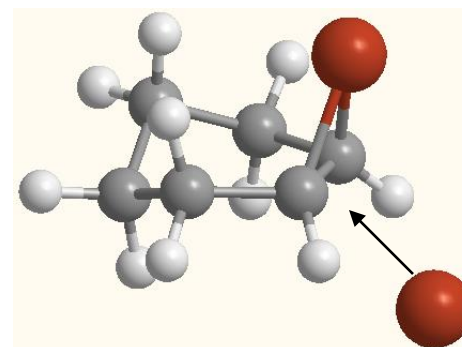
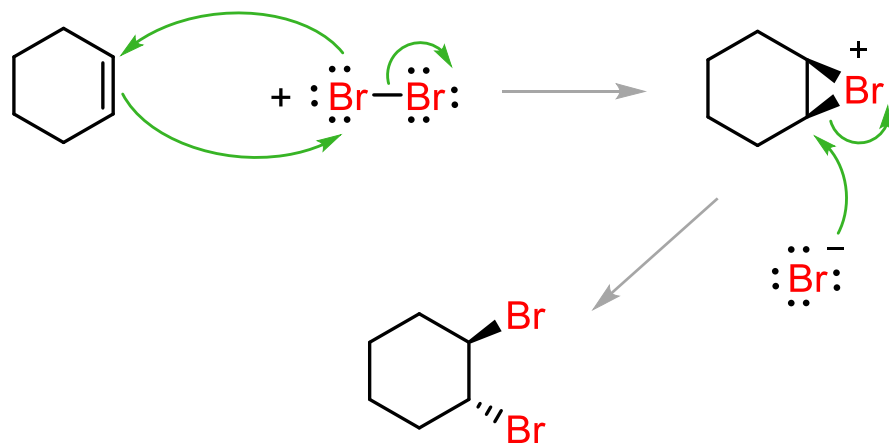
Ch.9 Addition of Halogens to Alkenes



alkene



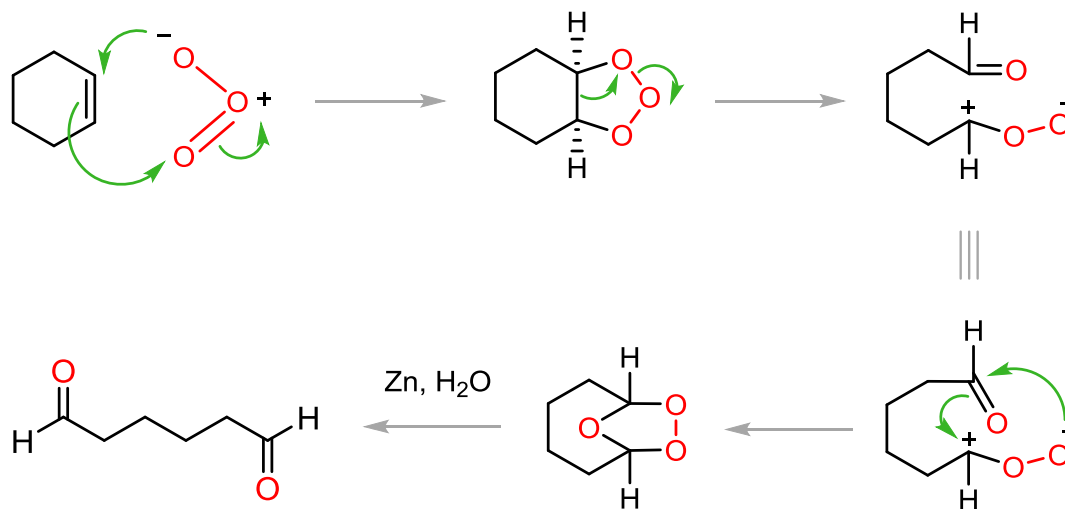
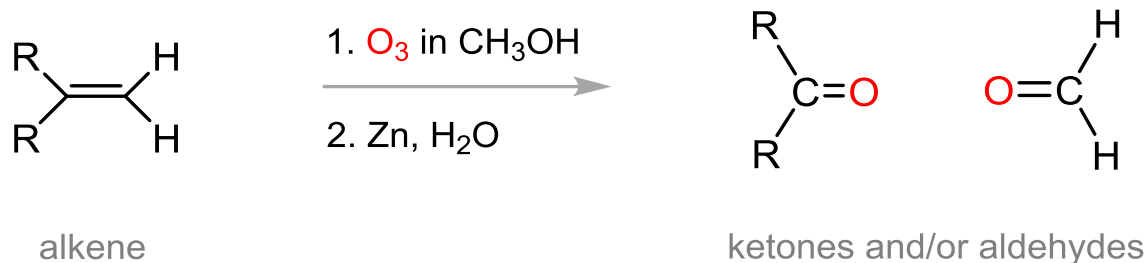
vicinal dibromide



Attack from opposite side preferred

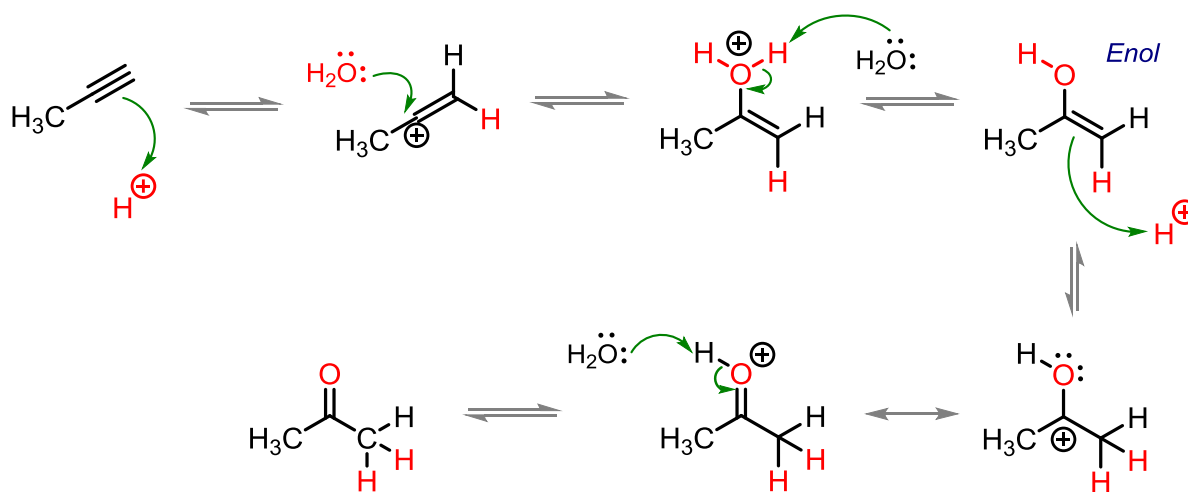
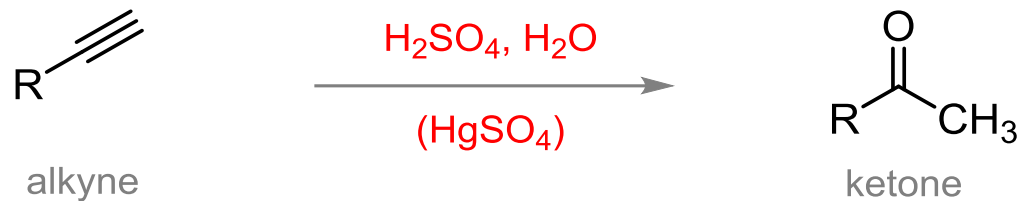
- Only **anti** product indicates that this is not a **syn** addition pathway
- One product only suggests a modified carbocation intermediate
- Formation of the **bromonium ion** explains stereochemical outcome
- Similar reaction with $\text{Br}_2/\text{H}_2\text{O}$ gives only **anti** addition of "BrOH"

Ch.9 Ozonolysis of Alkenes



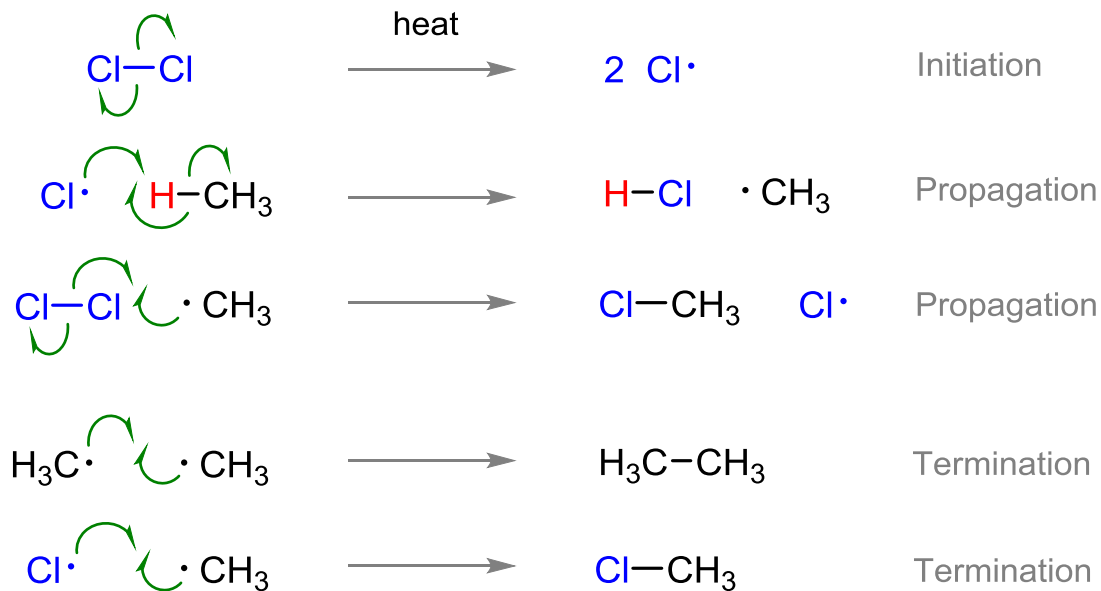
- Remarkable process that **breaks both the π and σ bonds** in the alkene
- First step is concerted ***syn*** addition; no intermediate(s) formed
- Subsequent steps involve breaking of weak O-O bonds and the C-C bond
- Malozonide product is then reduced to give the carbonyl products

Ch.10 Hydrolysis of Alkynes



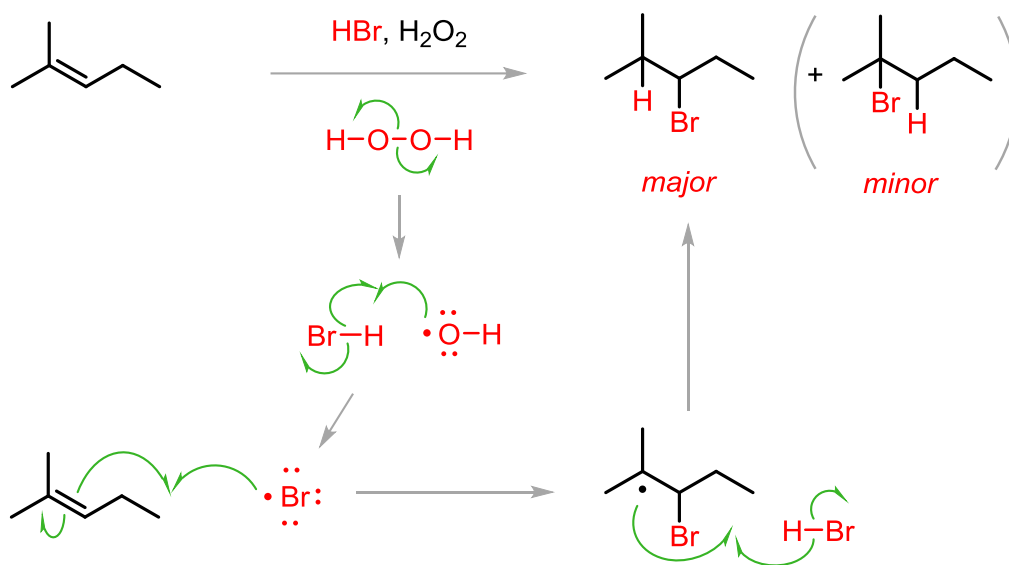
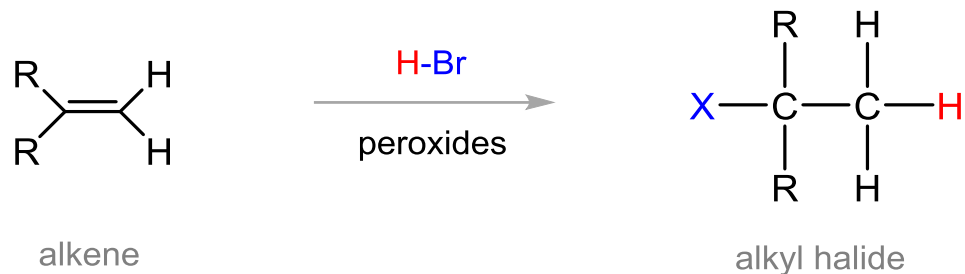
- Stepwise acid- and Lewis acid-catalyzed addition of water to an alkyne
- Formal product of the addition is the enol, which is often not isolated
- **Tautomerism** most often then leads to the more stable ketone product
- Process occurs through the more stable carbocation (**Markovnikoff**)

Ch.11 Cl/Br Substitution on Alkanes – Free Radicals



- Alkane + Cl₂/Br₂ 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.11 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