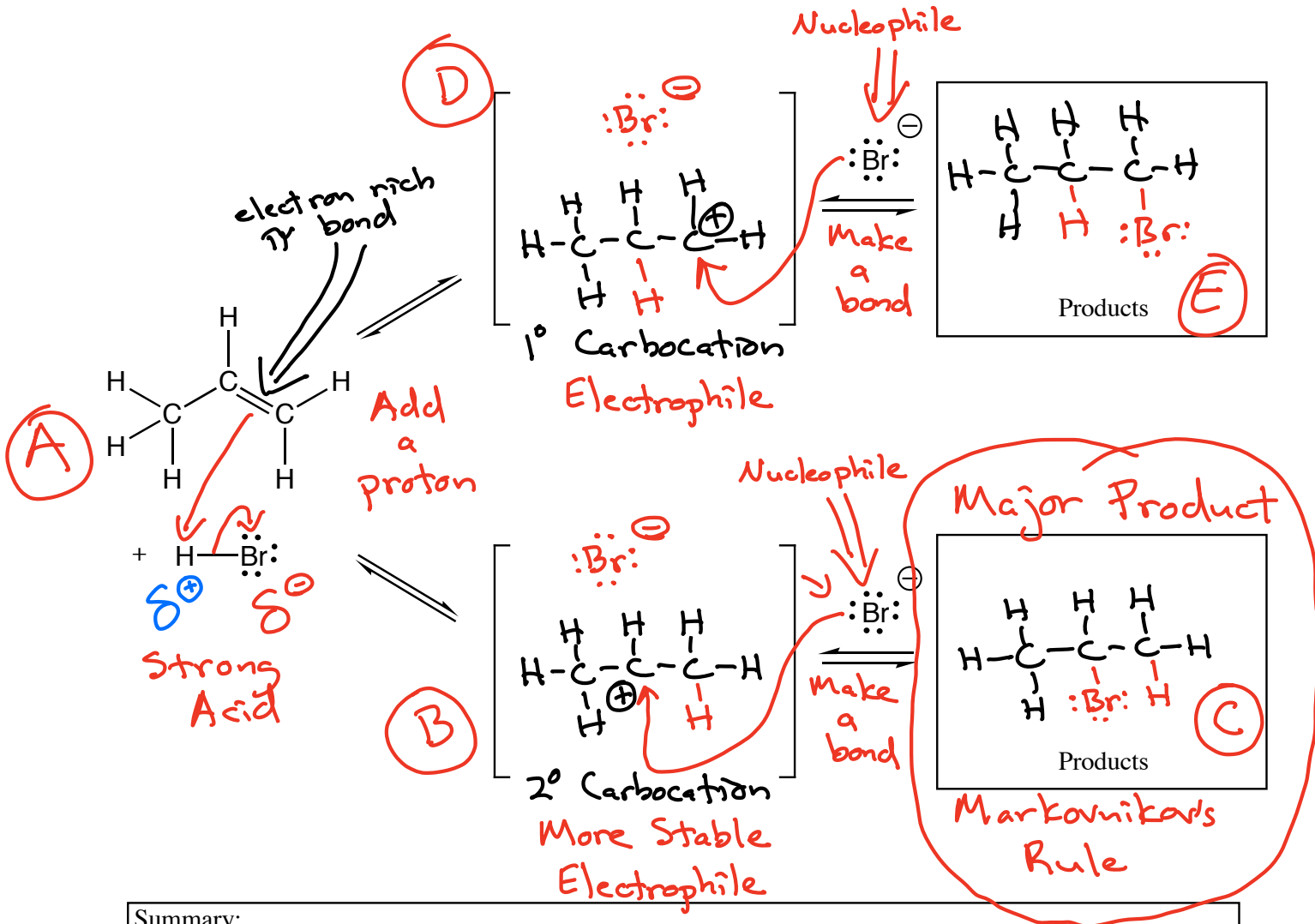


Addition of H-X to an Alkene

X = Cl, Br, I
but not F



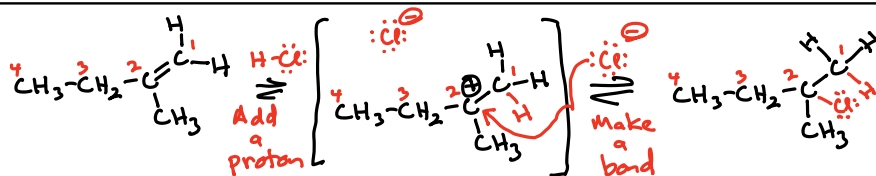
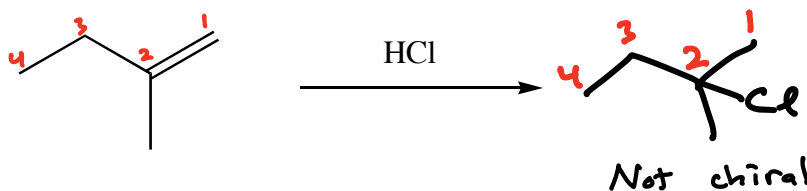
Summary:

The alkene pi bond reacts with H-X to add a proton to create a carbocation intermediate that makes a bond with X⁻ to give the product

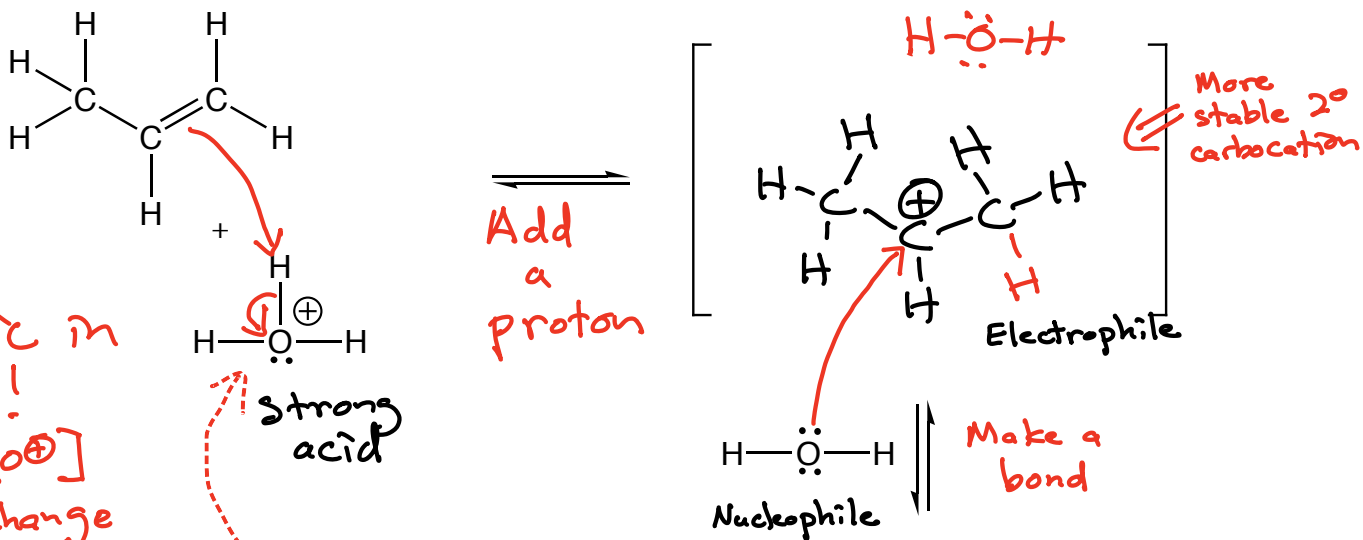
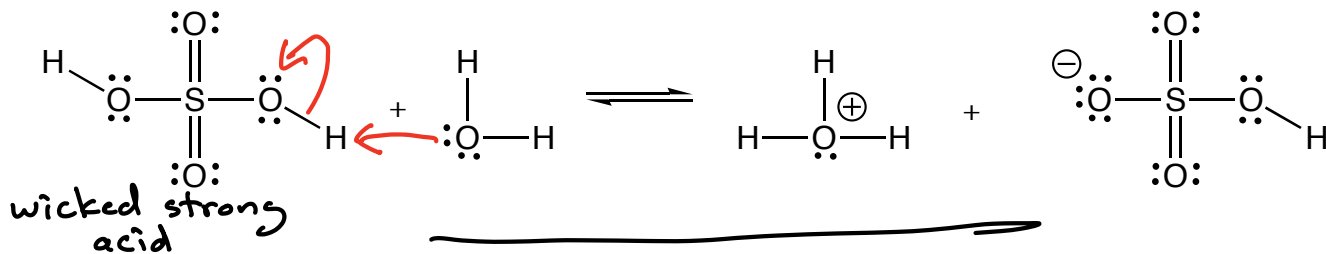
Regiochemistry: **Markovnikov's Rule**

Stereochemistry: **Mixed (time capsule) → Racemic Product**

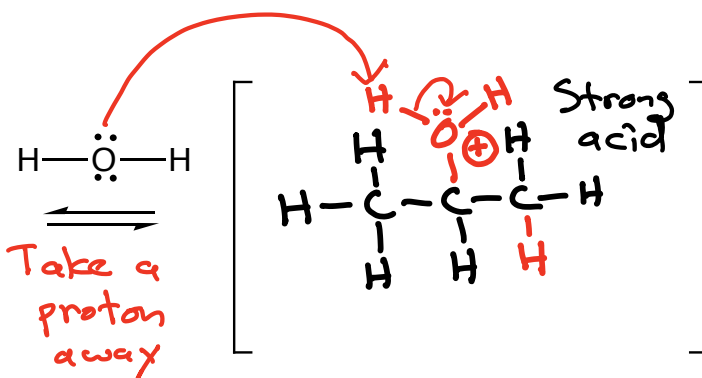
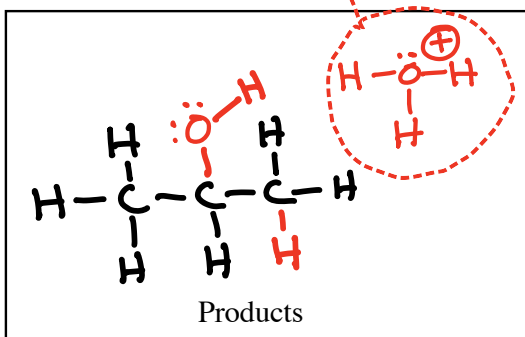
Example:



Acid-catalyzed Hydration of an Alkene



Catalytic in Acid!
 ⇒ The $[\text{H}_3\text{O}^+]$ does not change during the reaction

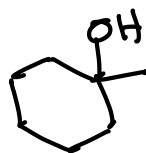
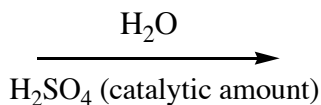
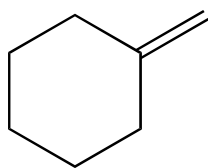


Summary: Proton adds to make a carbocation intermediate, water attacks to make a new bond, take a proton away to make the product alcohol. Catalytic in H_3O^+

Regiochemistry: **Markovnikov's Rule**

Stereochemistry: **Mixed (time capsule)**

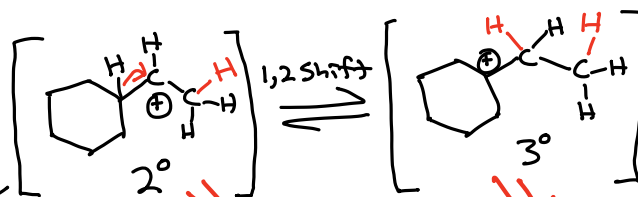
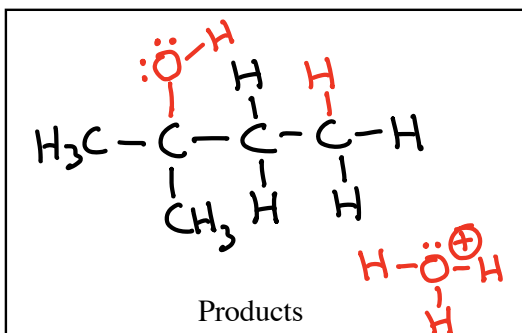
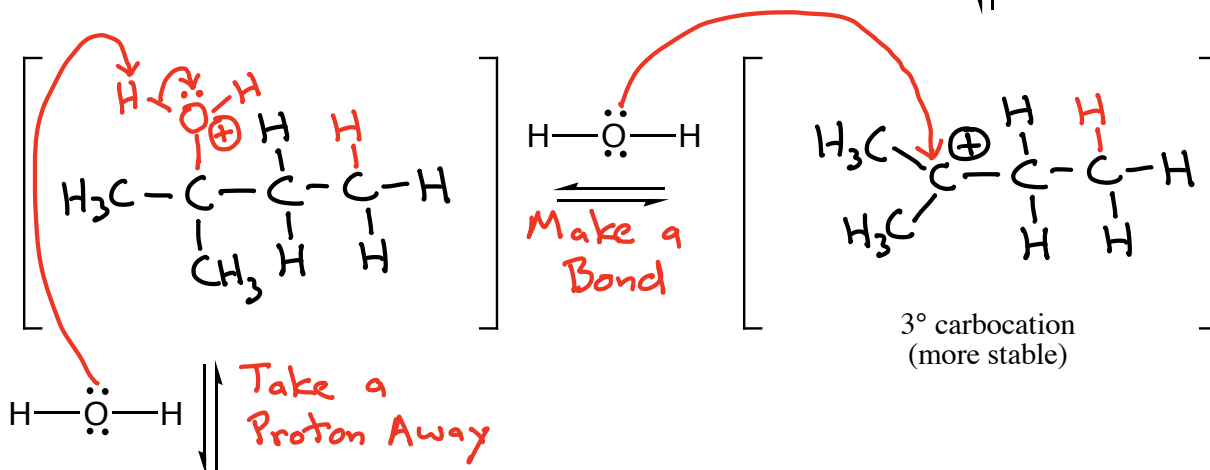
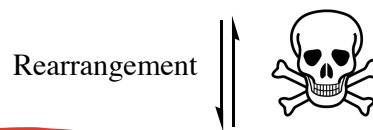
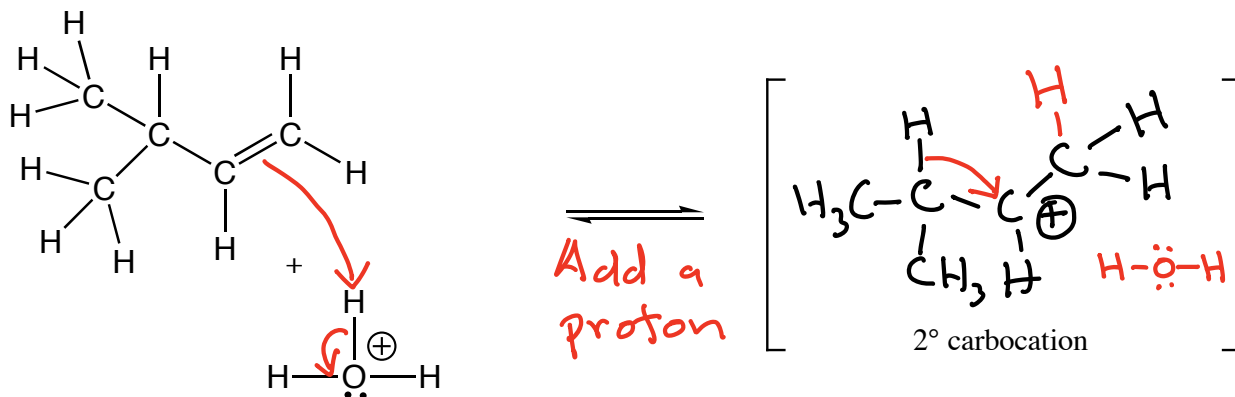
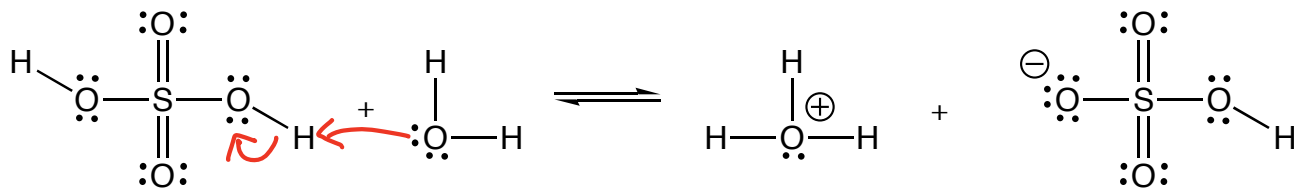
Example:



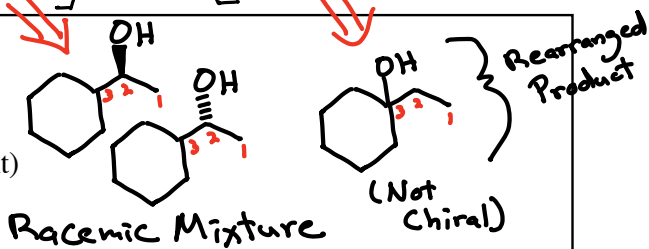
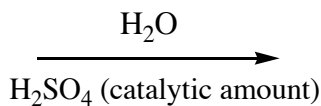
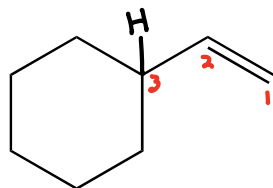
(Not chiral)

-OH on more substituted C atom ⇒ Markovnikov's Rule

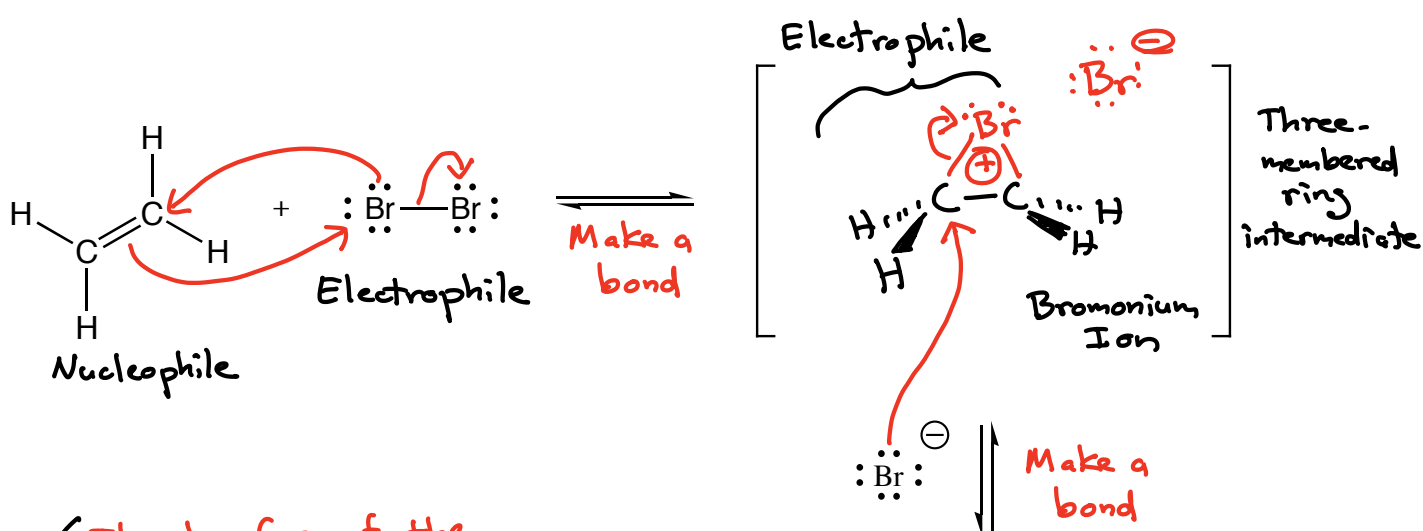
Cation Rearrangement



Example:



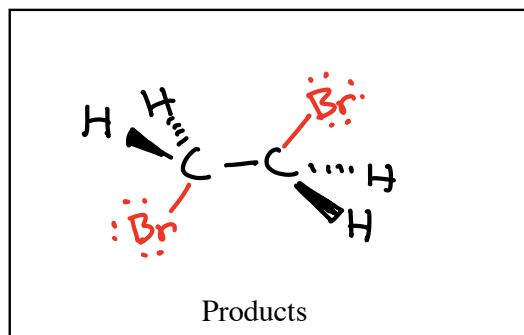
Alkene Halogenation



Called "anti" addition stereochemistry

The top face of the intermediate is "blocked" by the Br atom, so the Br^- nucleophile must react from the opposite face

⇓
Gives only a "trans" product - never "cis"

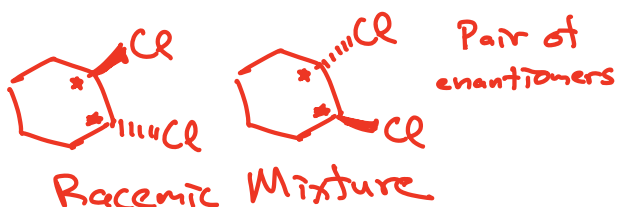
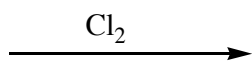
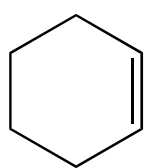


Summary: Alkenes react with X_2 to give a three-membered ring intermediate, then a new bond is made by X^- reacting from behind the C-X bond of the intermediate.

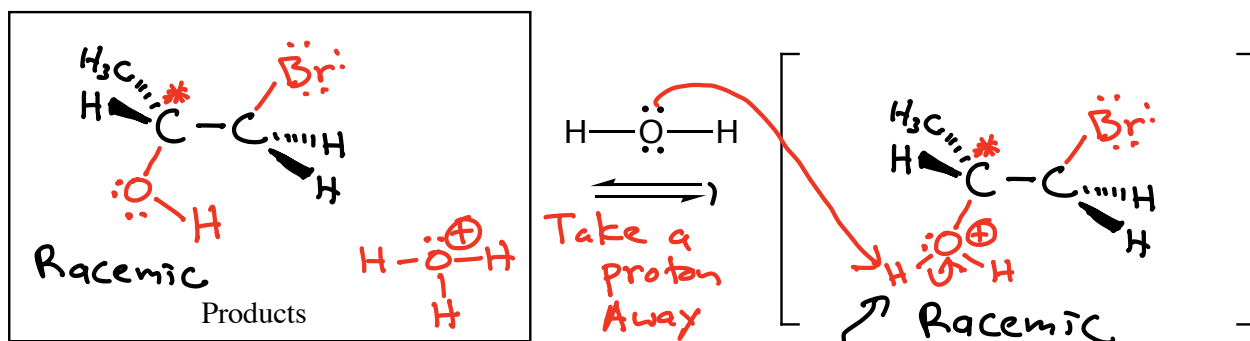
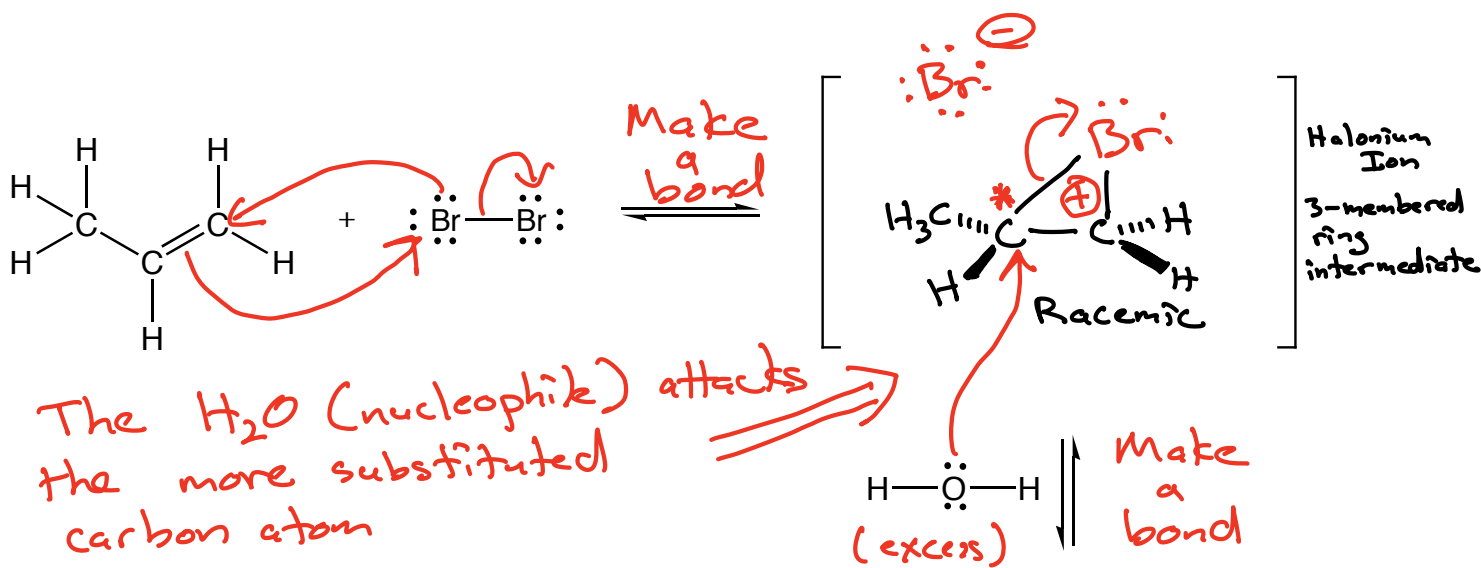
Regiochemistry: Not applicable \rightarrow Br is on both atoms

Stereochemistry: **Anti addition geometry** \rightarrow trans products

Example:



Alkene Hydrohalogenation



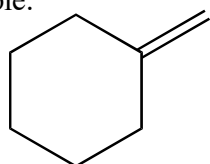
pH drops during the reaction!

Summary: Alkene reacts with X_2 to give a 3-membered ring intermediate (halonium ion) \rightarrow H_2O attacks the more substituted C atom and we take a proton away to give the halohydrin product.

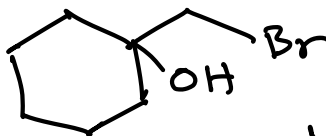
Regiochemistry: Markovnikov (OH on more substituted C atom)

Stereochemistry: Anti

Example:

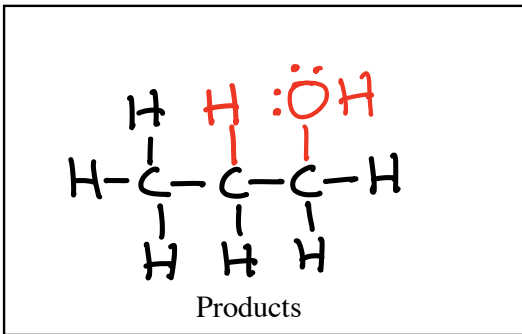
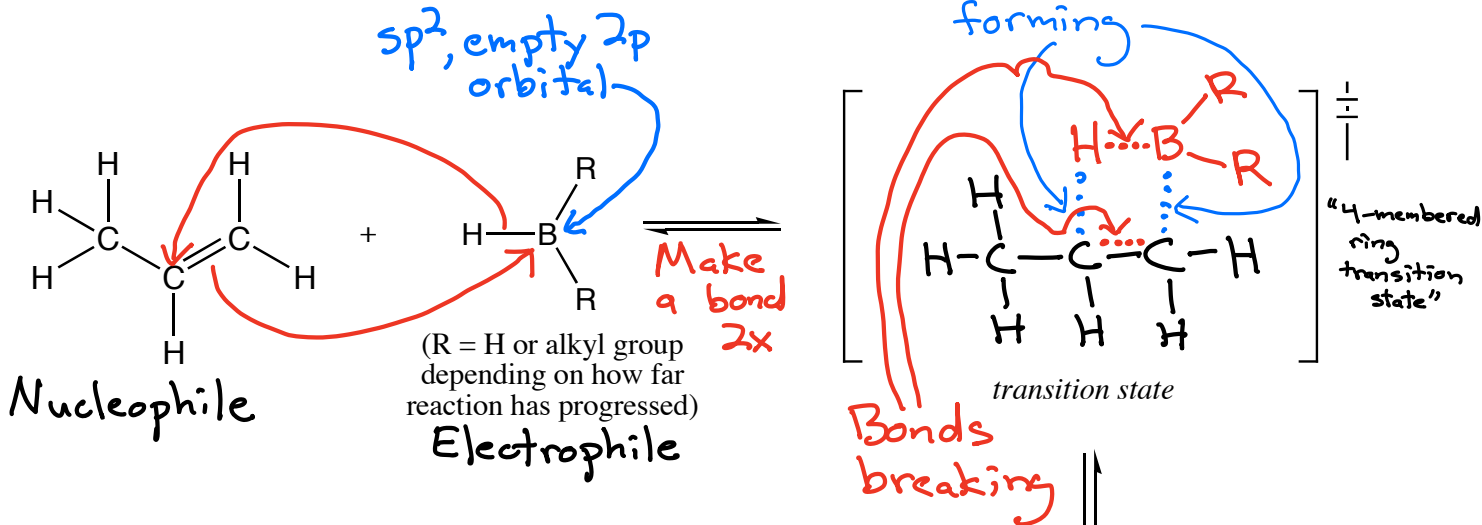


$\text{Br}_2 / \text{H}_2\text{O}$

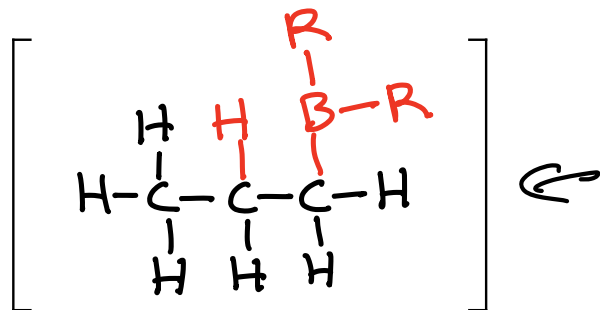


Not Chiral

Hydroboration-Oxidation



Not responsible for this mechanism
 2. $\text{H}_2\text{O}_2 / \text{HO}^-$
 (Chemist opens flask and adds new reagent)



H → More substituted C atom
OH → Less substituted C atom

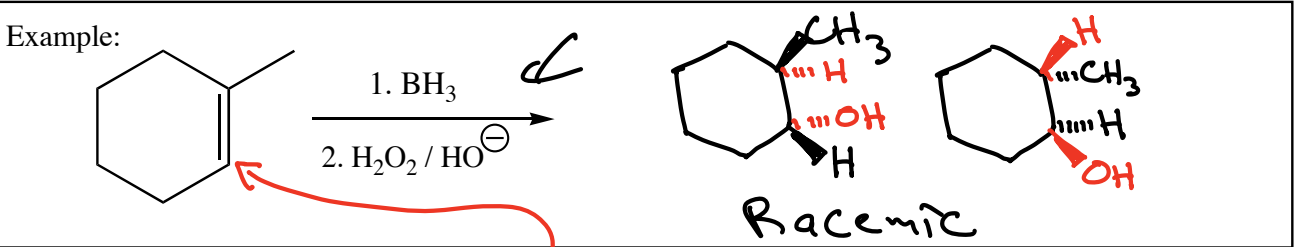
Steric strain in the first transition state

H and OH are syn

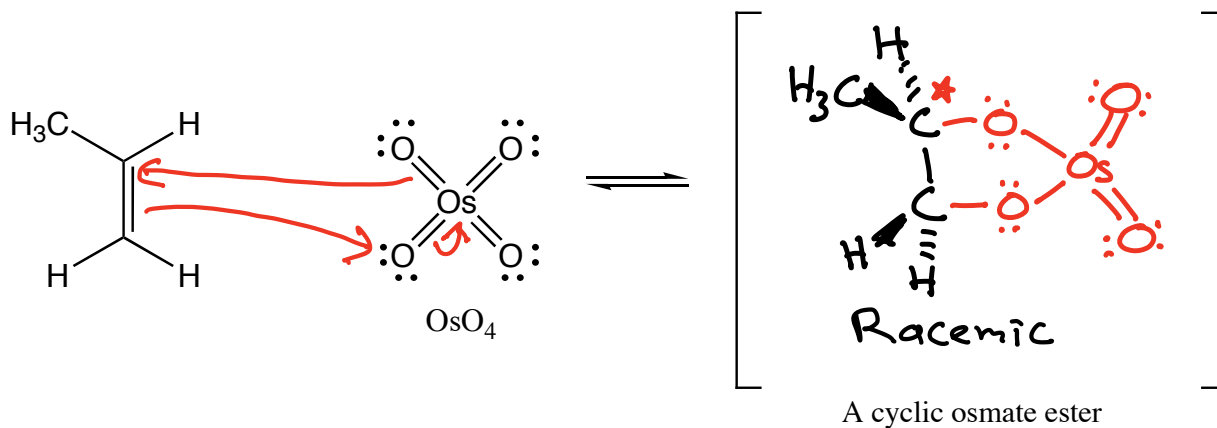
Summary: The pi bond of the alkene attacks the Lewis acid (electrophile) B atom at the same time a new bond forms between C and H. In 2nd step OH replaces $\text{B}(\text{R})_2$. "4-membered ring transition state"

Regiochemistry: *Non-Markovnikov*

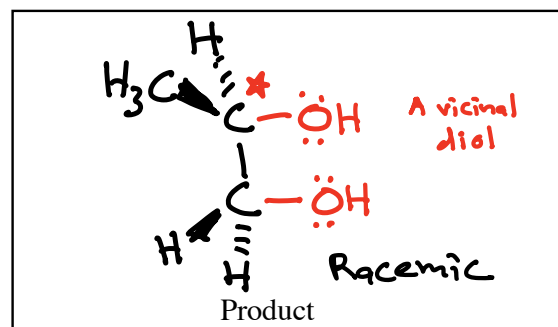
Stereochemistry: *Syn*



OsO_4 Partial Mechanism



2. $NaHSO_3 / H_2O$
(Chemist opens up flask) \Downarrow Not responsible for mechanism

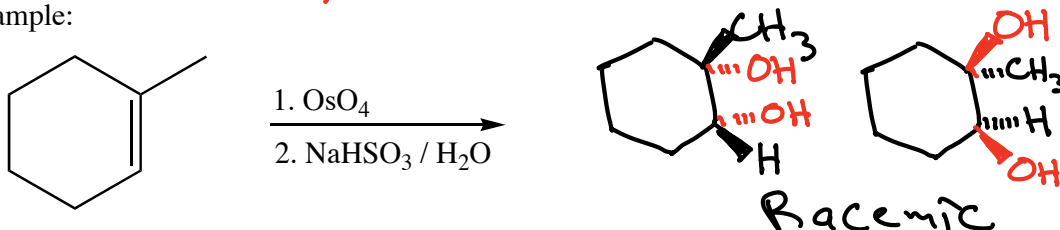


Summary: The mechanism involves a cyclic osmate ester, explaining the syn stereochemistry of addition.

Regiochemistry: N/A

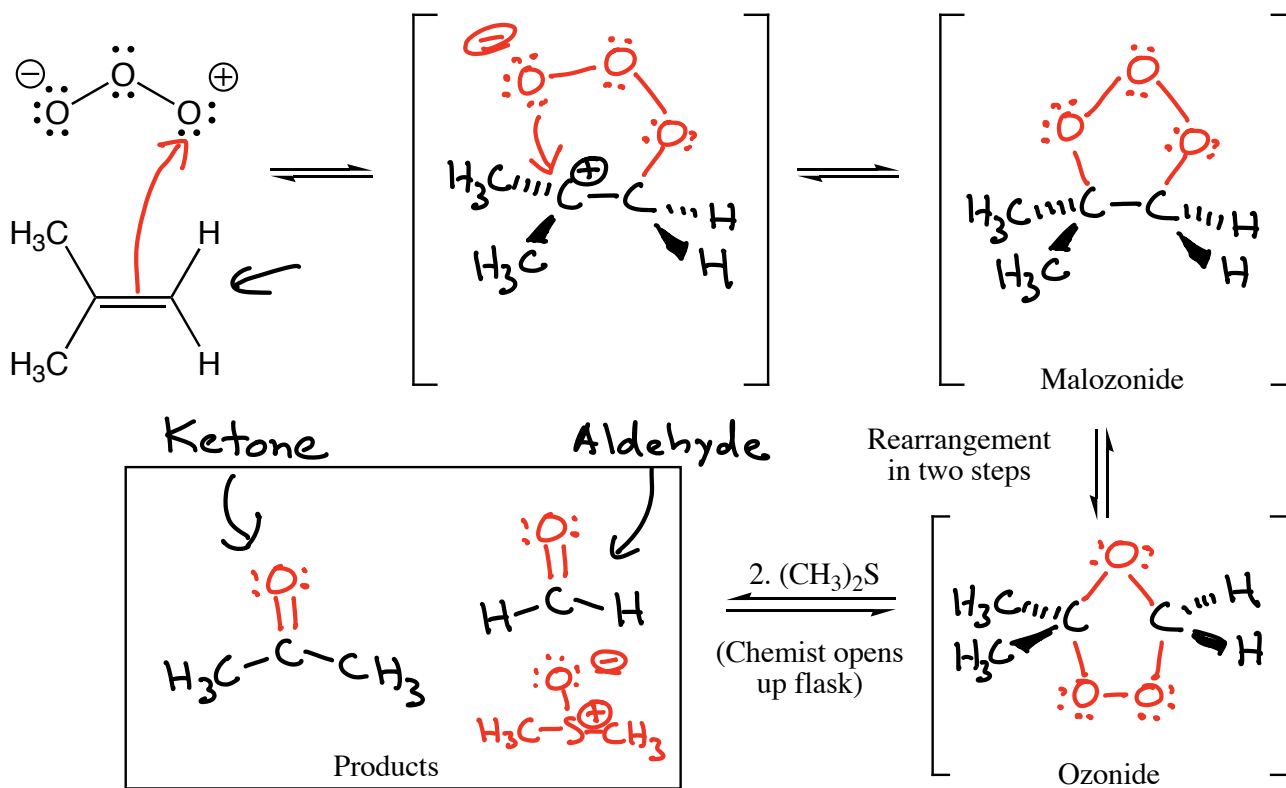
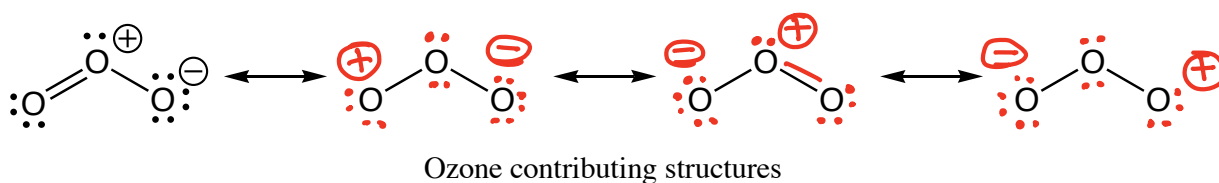
Stereochemistry: Syn

Example:



This breaks C=C bonds !!!

Ozonolysis Partial Mechanism

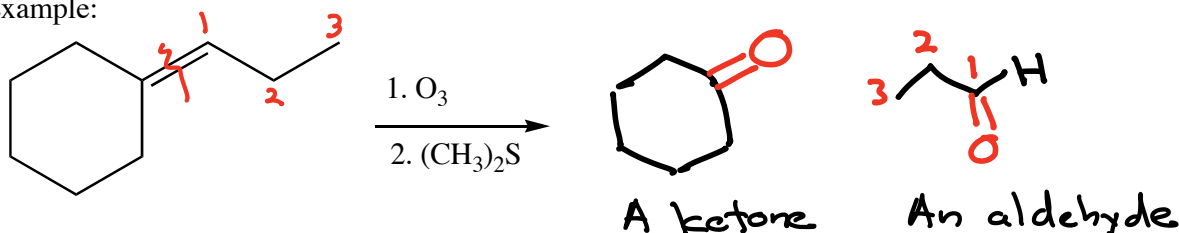


Summary: Reaction of an alkene with O_3 gives a malozonide than an ozonide intermediate (the C=C pi bond then C-C sigma bond is broken). Adding $(\text{CH}_3)_2\text{S}$ decomposes the ozonide into ketone and aldehyde products **Breaks C=C bond!**

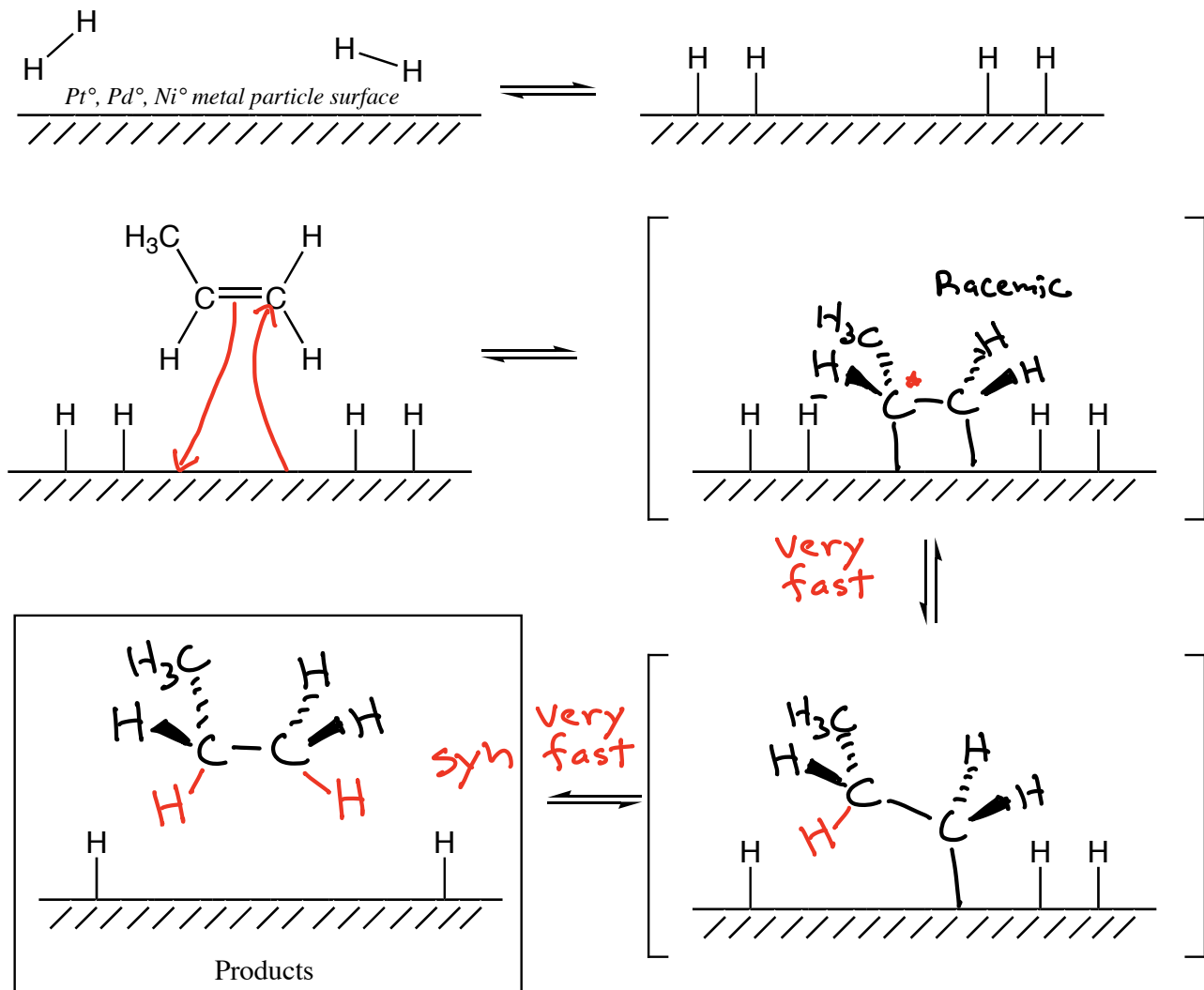
Regiochemistry: N/A

Stereochemistry: N/A

Example:



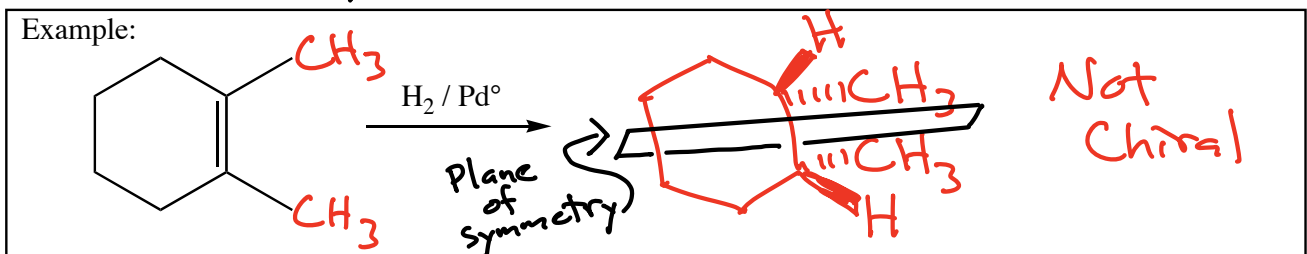
Hydrogenation: H_2 with Pt^0 , Pd^0 , Ni^0



Summary: H_2 adsorbs onto the metal surface. The alkene adsorbs onto the metal surface. H atoms transfer to both C atoms \rightarrow on the same face \rightarrow before the $C-C$ bond rotates

Regiochemistry: N/A

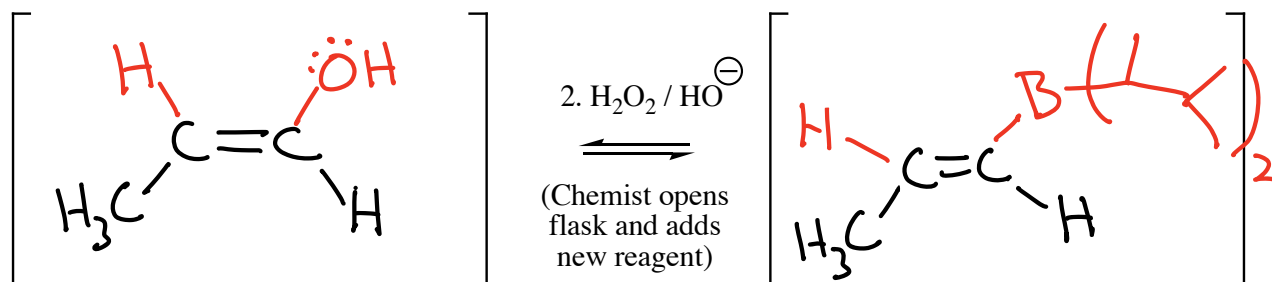
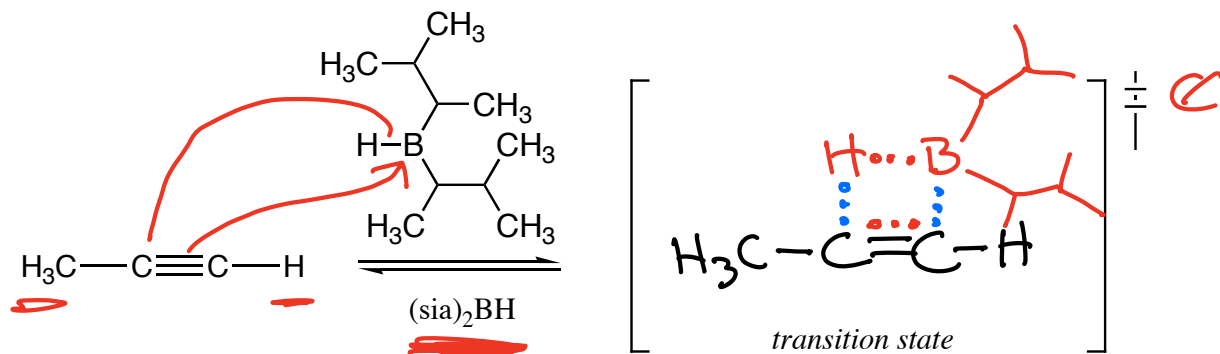
Stereochemistry: Syn



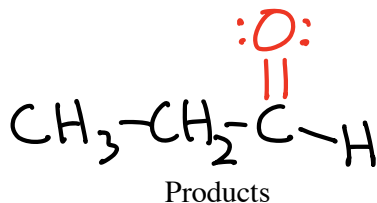
Alkene

Alkane

Terminal Alkyne Hydroboration



Keto-enol
tautomerization



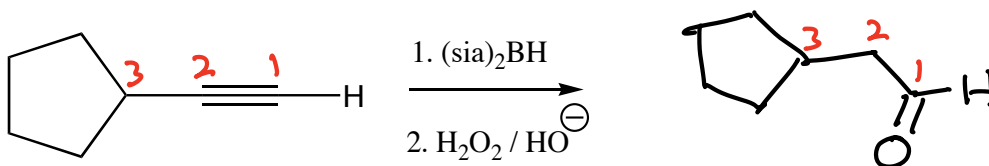
⇐ The C=O is on the C on the end → "non-Markovnikov"

Summary: The $(\text{sia})_2\text{BH}$ reacts so the B atom attaches to the C atom on the end. The four-membered ring transition state makes both bonds simultaneously. $2. \text{H}_2\text{O}_2 / \text{HO}^- \rightarrow \text{enol} \rightarrow \text{keto}$

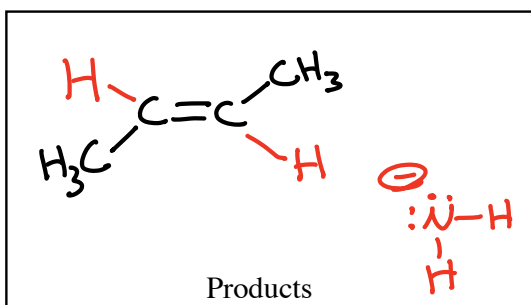
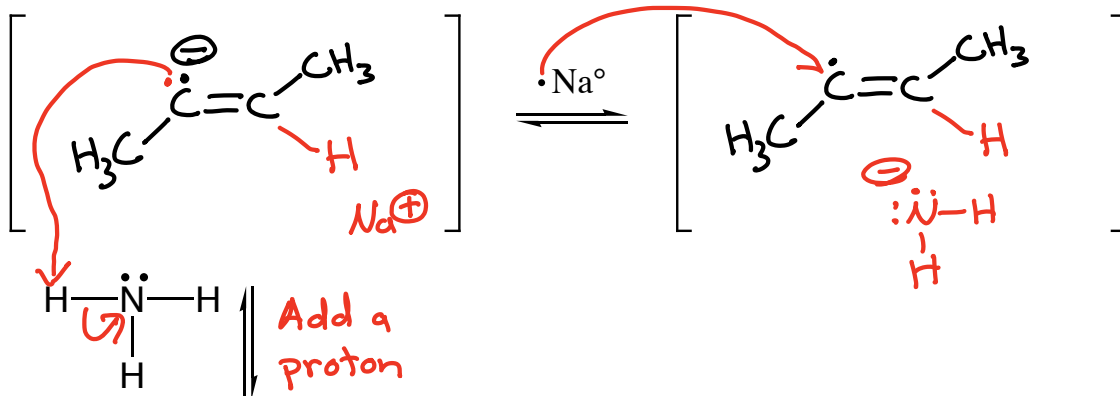
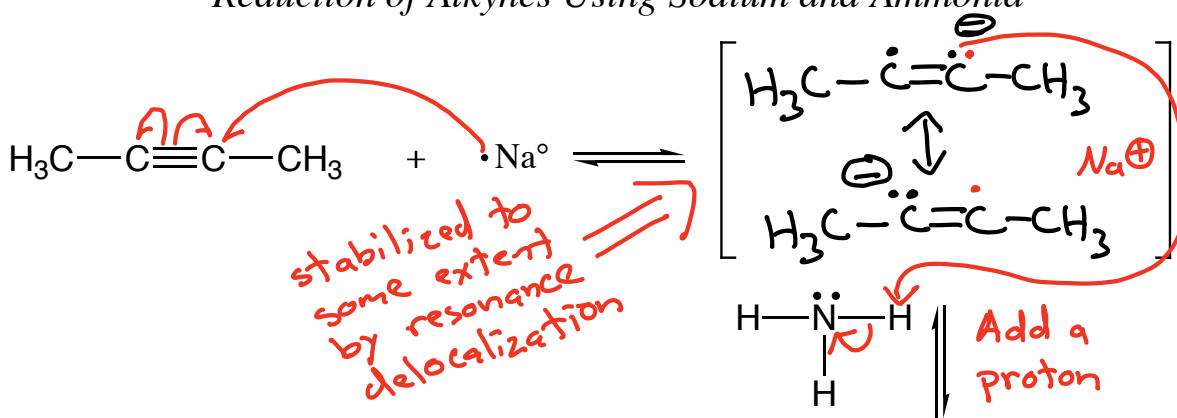
Regiochemistry: non-Markovnikov

Stereochemistry: N/A

Example:



Reduction of Alkynes Using Sodium and Ammonia



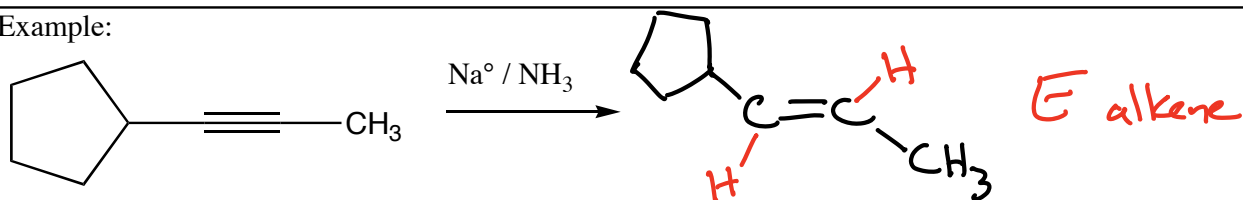
This reaction makes the more stable E alkene

Summary: Alkynes are reduced to E alkenes by Na^\ominus in NH_3 via two one-electron reductions by Na^\ominus , each of which is followed by adding a proton from the NH_3 solvent

Regiochemistry: N/A

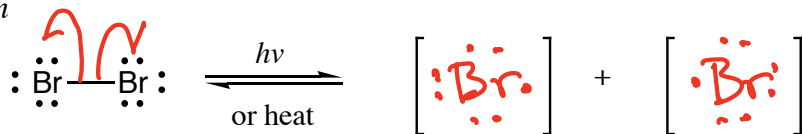
Stereochemistry: Anti \rightarrow E products

Example:

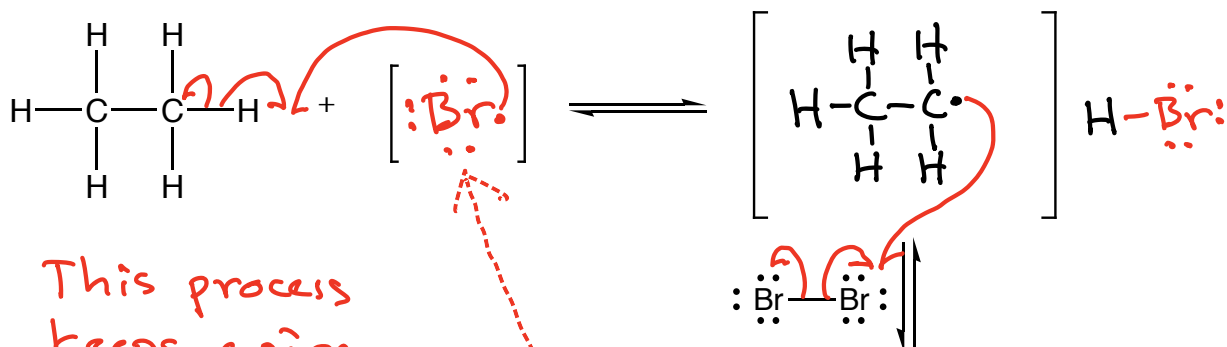


Alkane Free Radical Halogenation

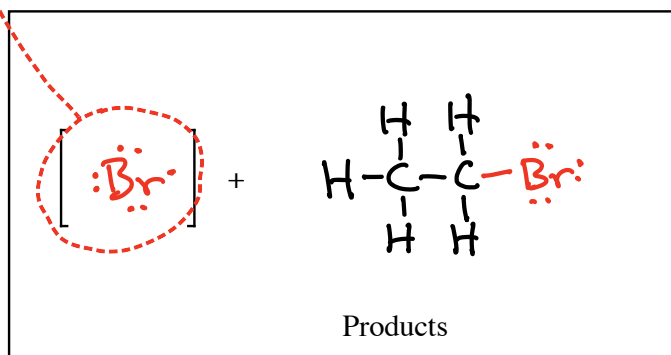
Initiation



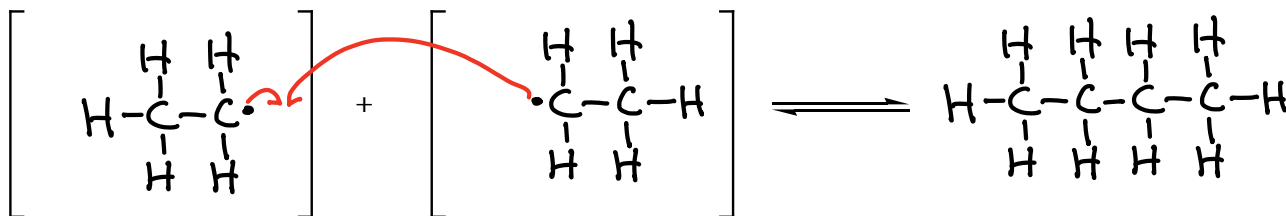
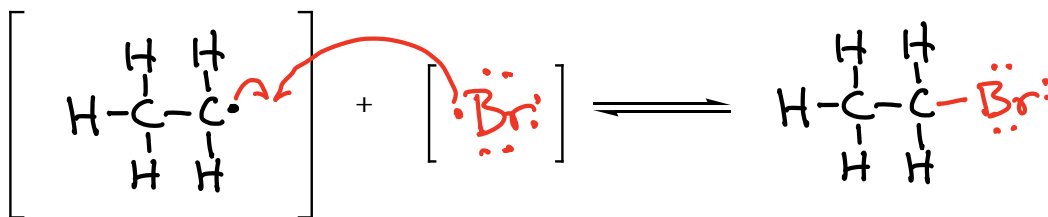
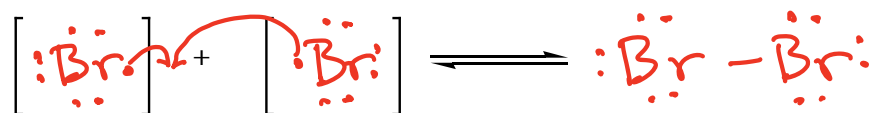
Propagation



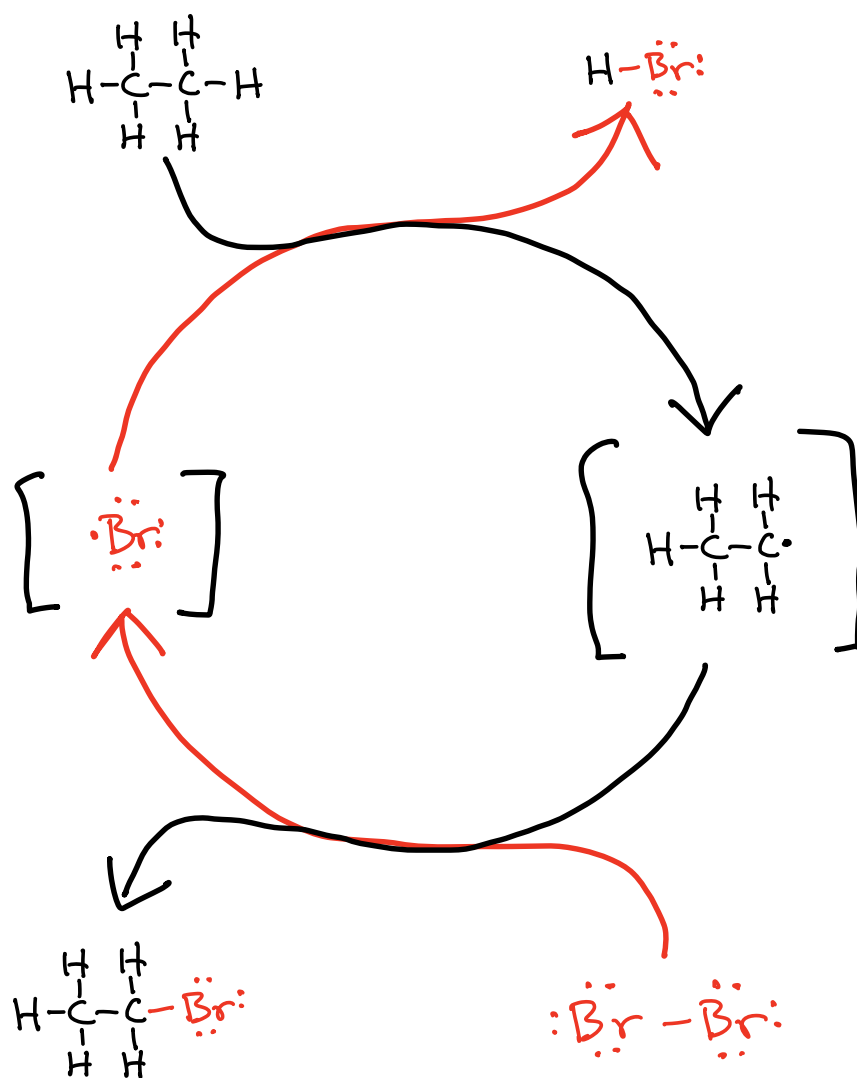
This process keeps going and going and going....



Termination

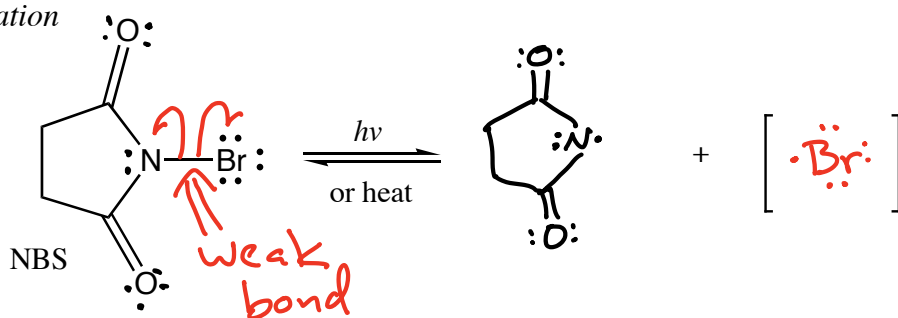


Propagation Process Diagram

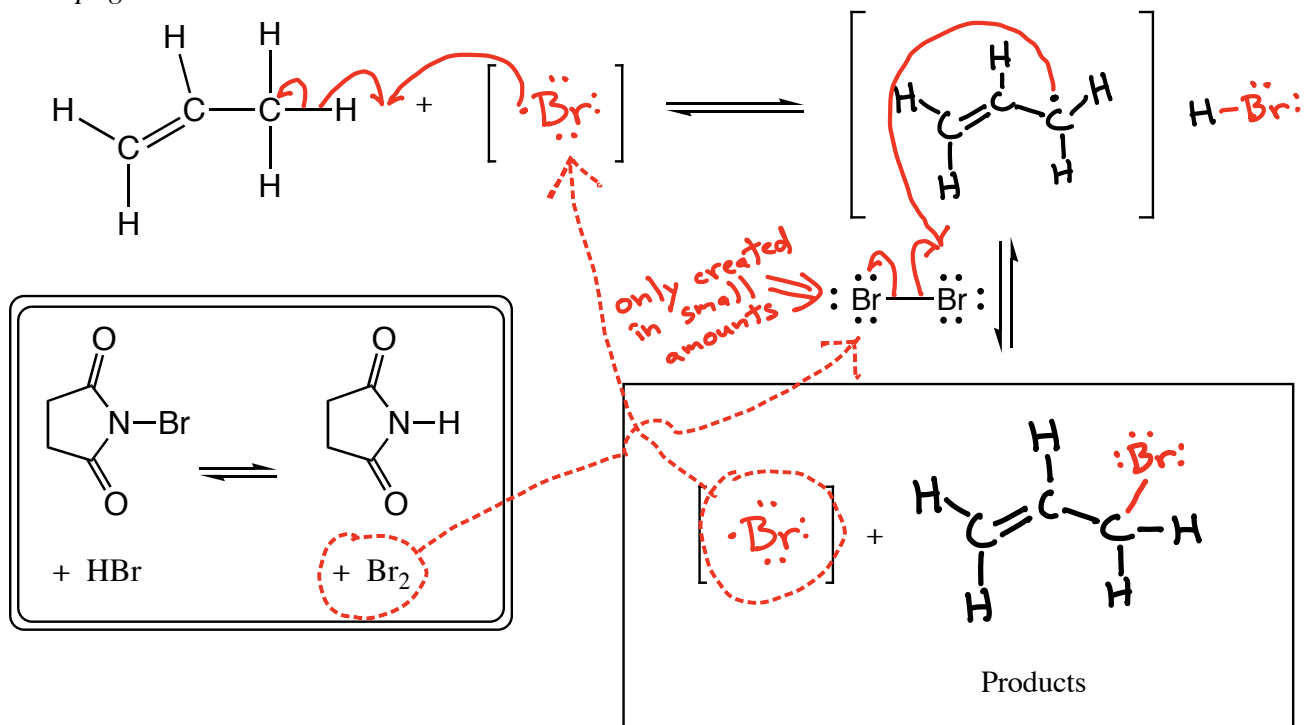


Allylic Halogenation

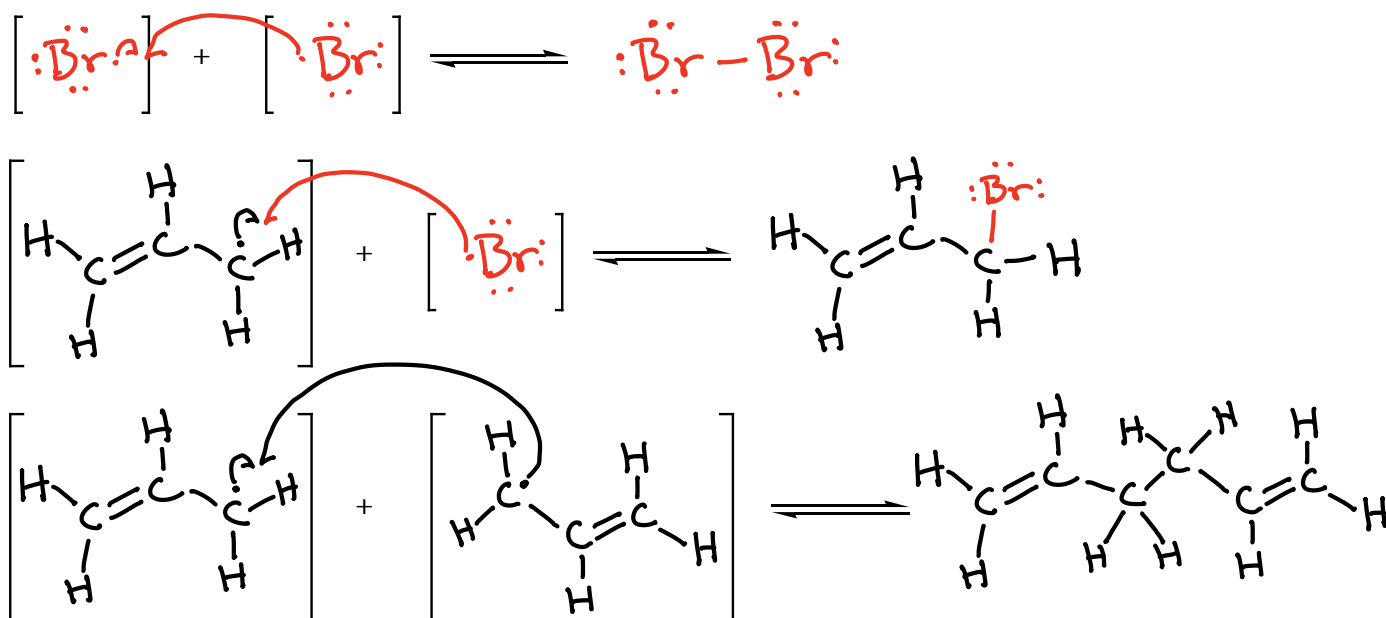
Initiation



Propagation

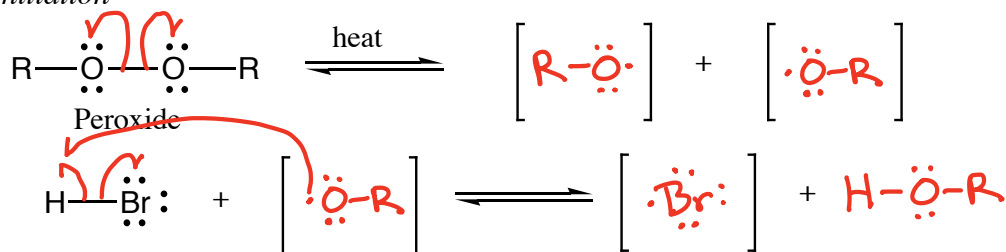


Termination

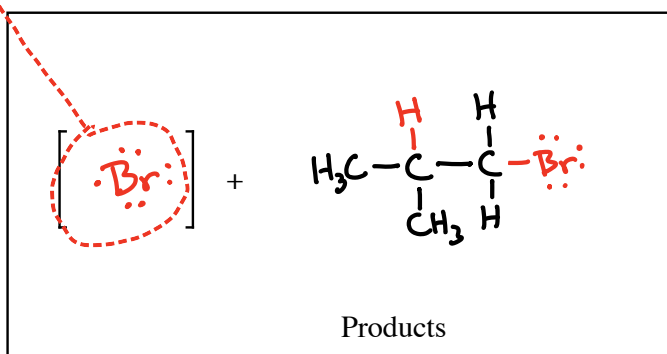
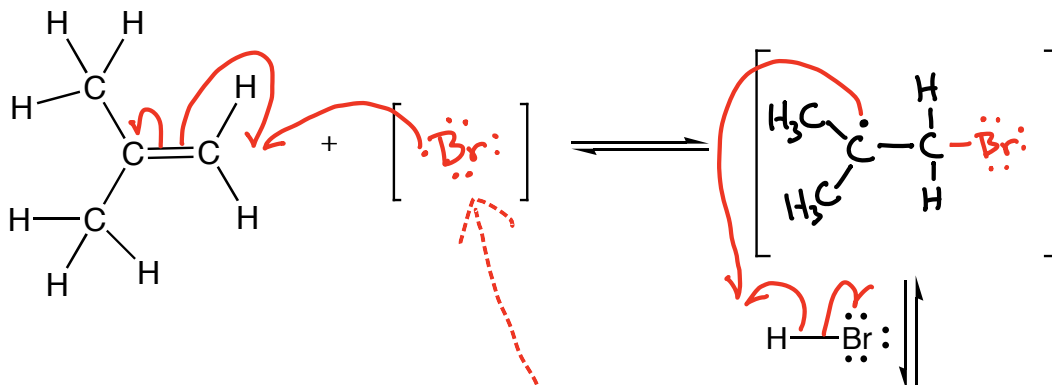


Non-Markovnikov Addition of HBr to an Alkene

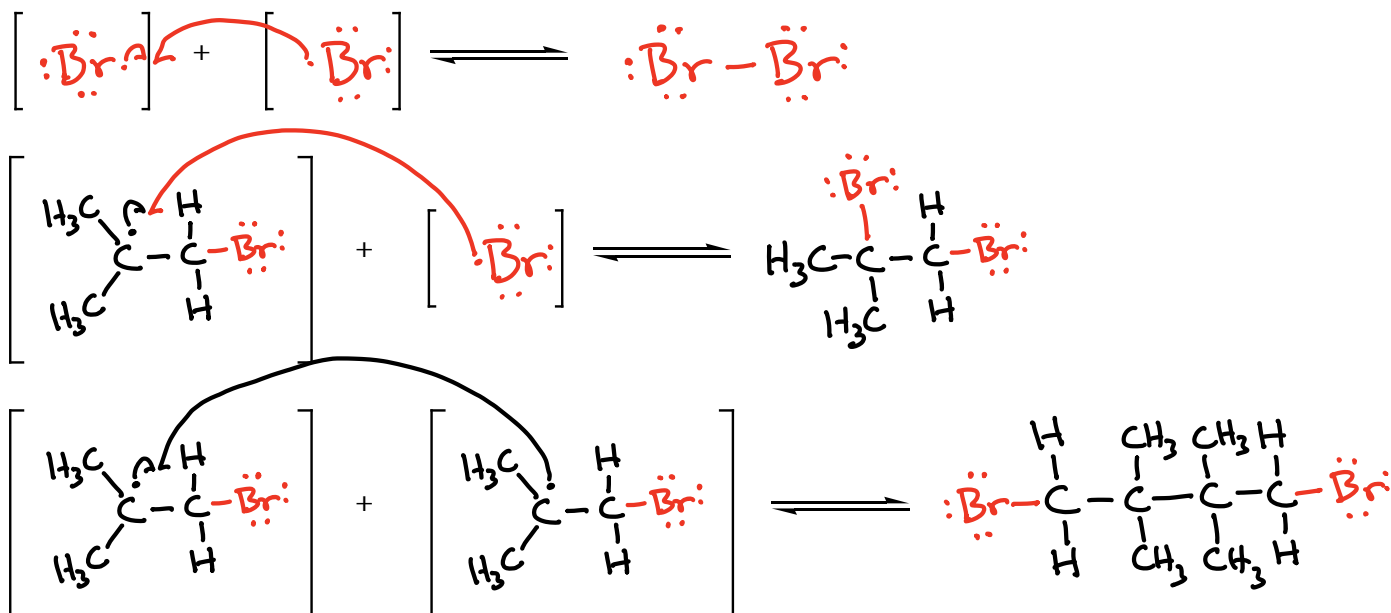
Initiation



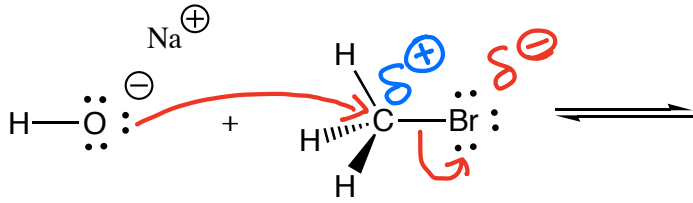
Propagation



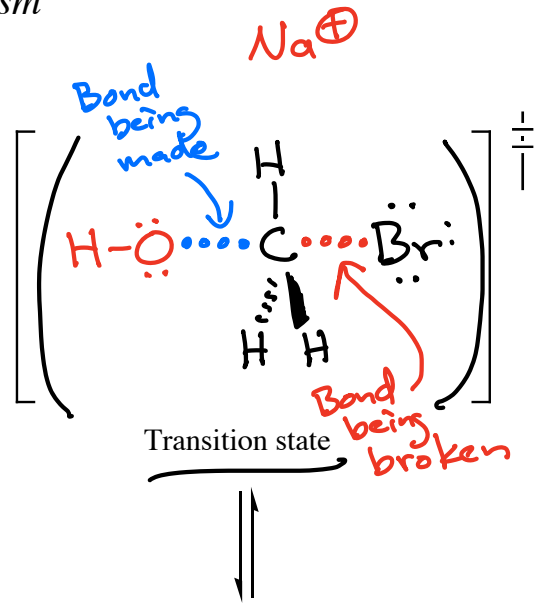
Termination



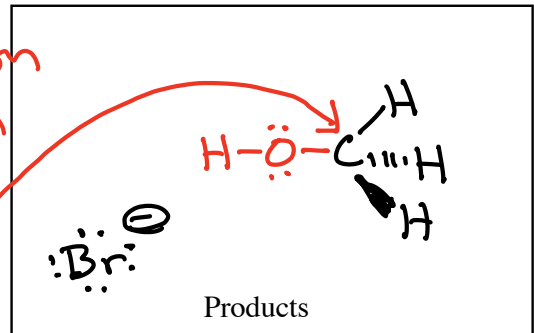
The S_N2 Mechanism



Nucleophile → must attack at the back of the C-Br bond. ⇒ This angle and direction of attack helps break the C-Br bond



The configuration at this carbon atom is inverted

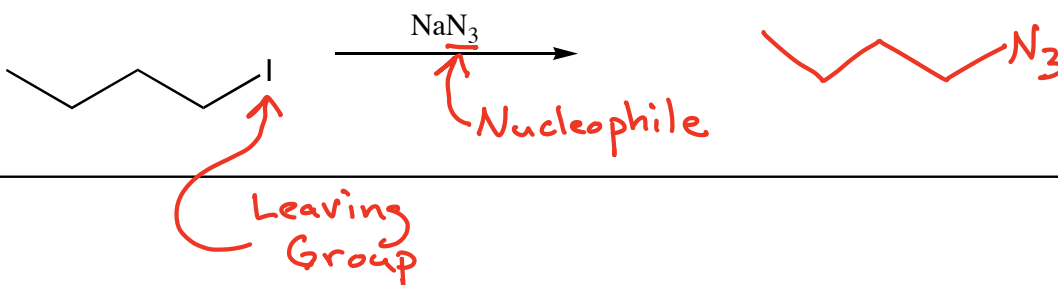


Summary: The nucleophile attacks by making a new bond to C from the back of the C-X bond just as X leaves

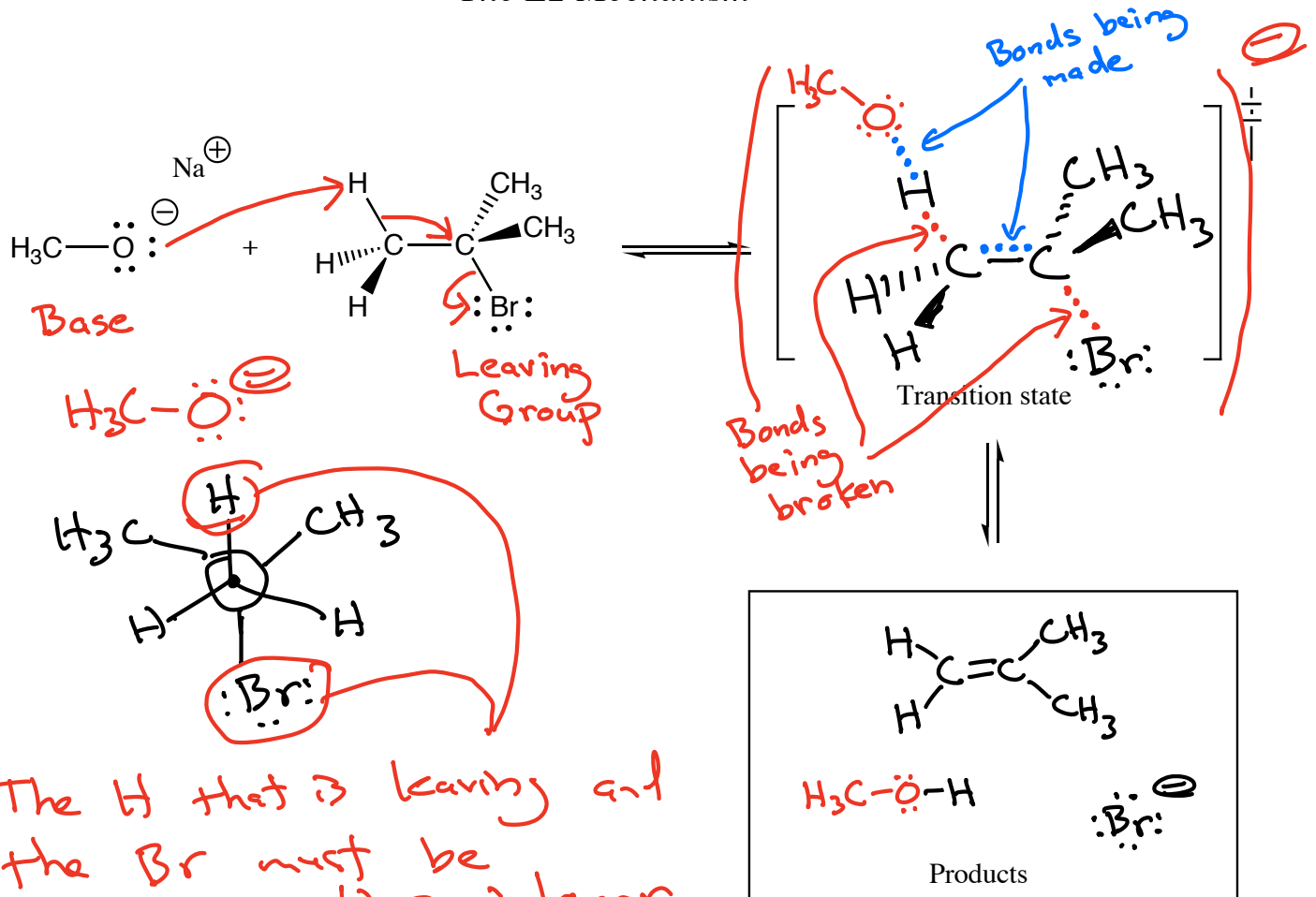
Regiochemistry: N/A

Stereochemistry: **INVERSION** at the site of reaction

Example:



The E2 Mechanism

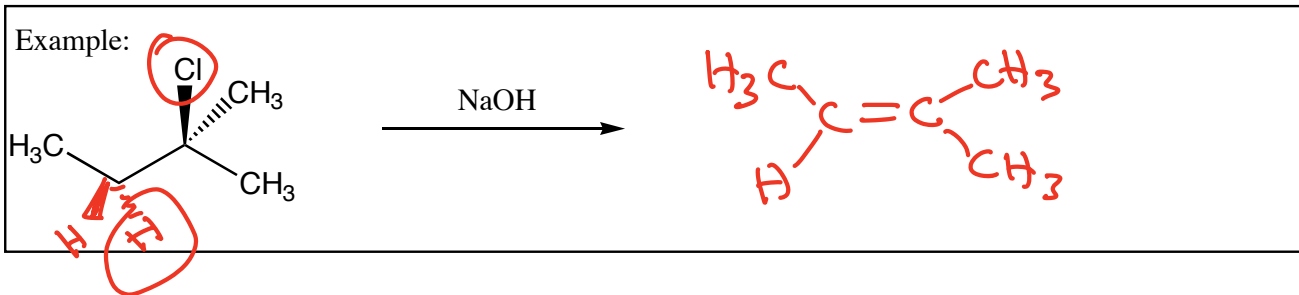


The H that is leaving and the Br must be anti-periplanar

Summary: Base removes an H atom as a pi bond forms and the Br atom leaves
 → The H and Br must be anti-periplanar

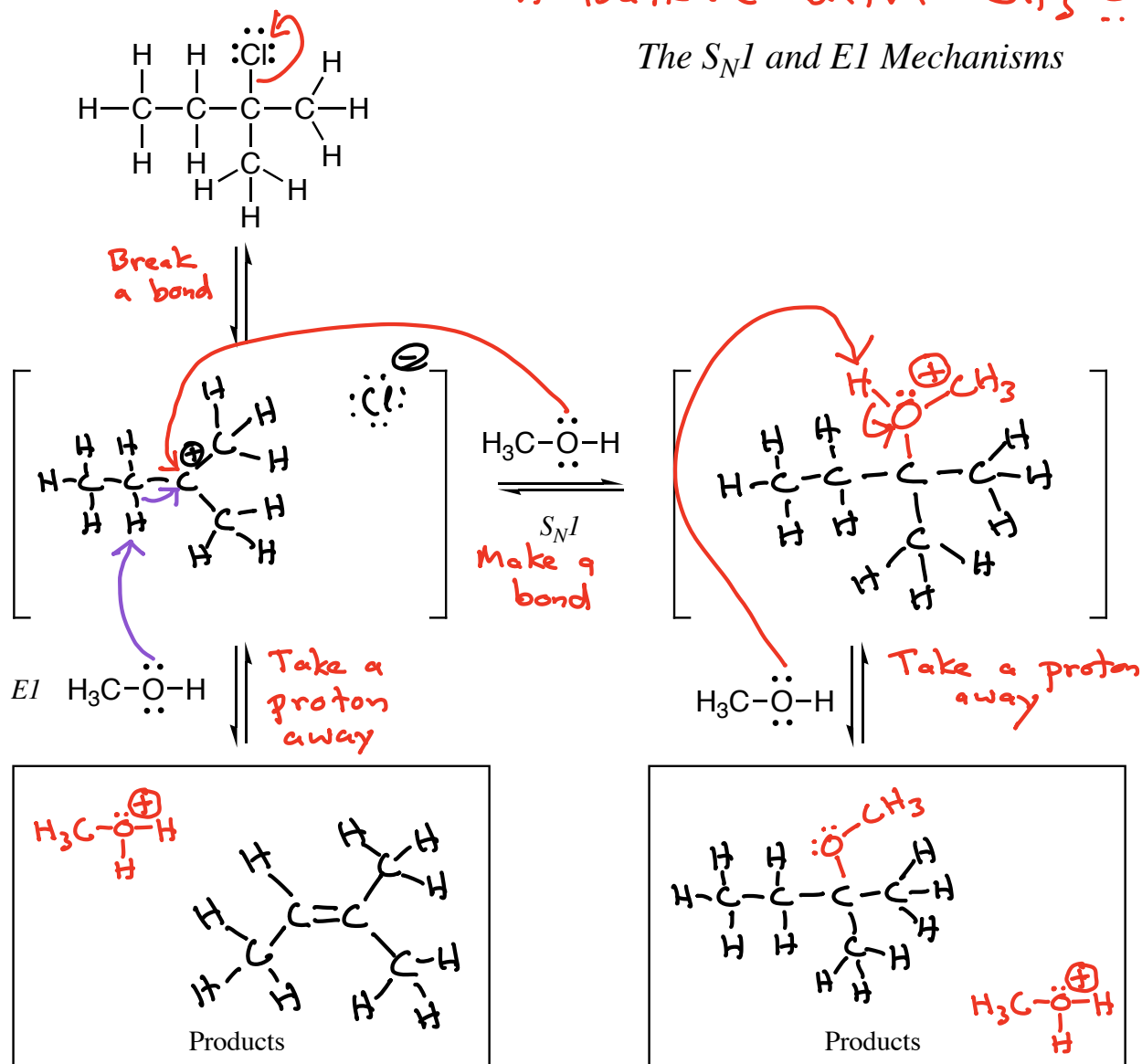
Regiochemistry: Zaitsev's Rule → most stable alkene product

Stereochemistry: Determined by anti-periplanar transition state



Haloalkane with $\text{CH}_3\text{-}\ddot{\text{O}}\text{-H}$

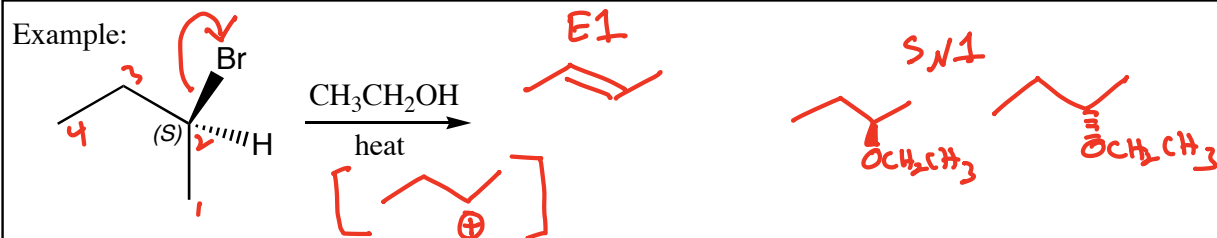
The $\text{S}_{\text{N}}1$ and $\text{E}1$ Mechanisms



Summary: For sterically hindered haloalkanes, the C-X bond breaks to give a carbocation intermediate that either reacts as an electrophile ($\text{S}_{\text{N}}1$) or has a proton taken away ($\text{E}1$)

Regiochemistry: $\text{E}1 \rightarrow$ Zaitsev's Rule

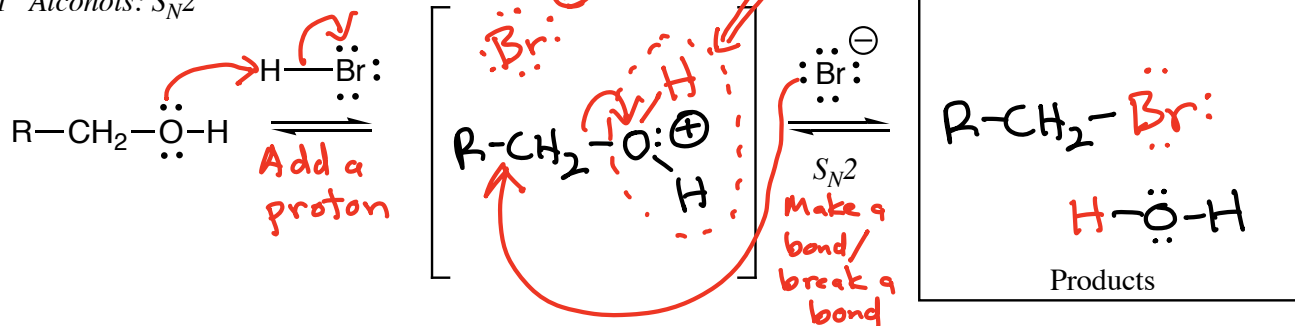
Stereochemistry: $\text{S}_{\text{N}}1 \rightarrow$ Scrambled \rightarrow not quite 1:1 exactly



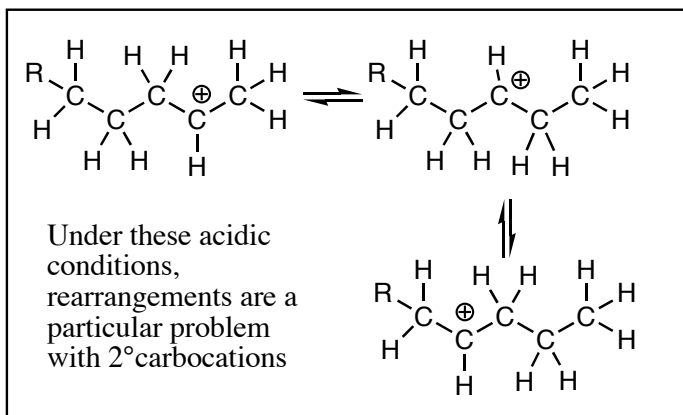
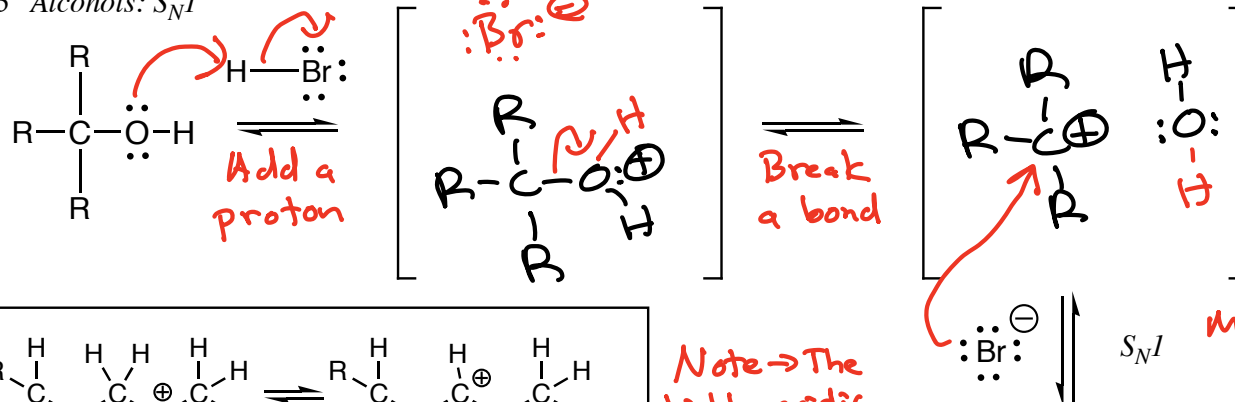


Alcohols + H-X Good leaving group

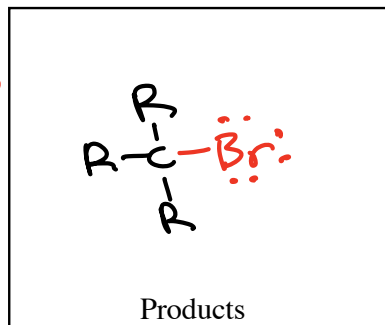
1° Alcohols: S_N2



2°/3° Alcohols: S_N1



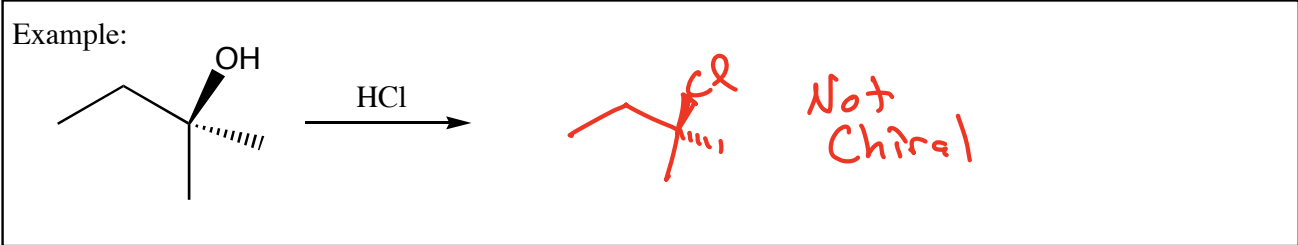
Note → The highly acidic nature of this reaction prevents any $E1$ before the S_N1 is finished



Summary: Reaction of primary alcohols → S_N2
 Reaction of secondary/tertiary alcohols → S_N1
 The -OH group is converted to a good leaving group by being protonated, followed by S_N2 or S_N1 substitution

Regiochemistry: N/A

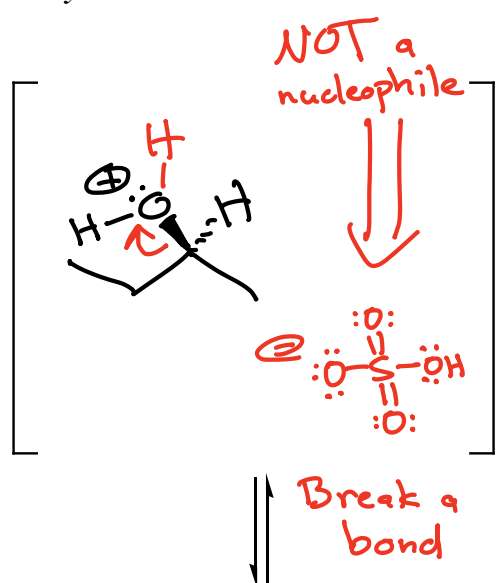
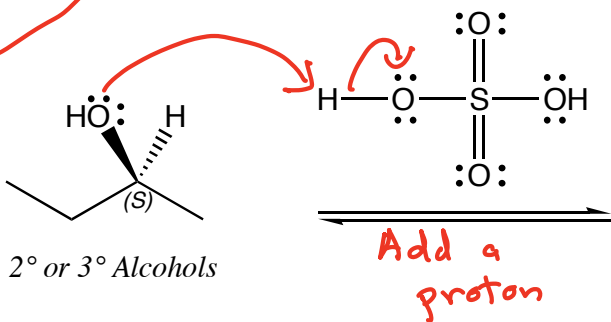
Stereochemistry: Chiral tertiary alcohols give scrambled products ← S_N1



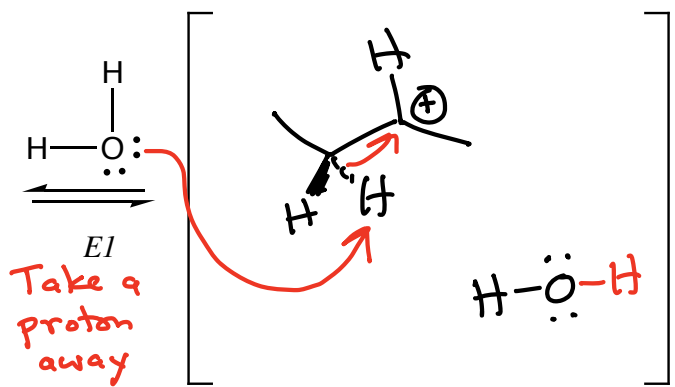
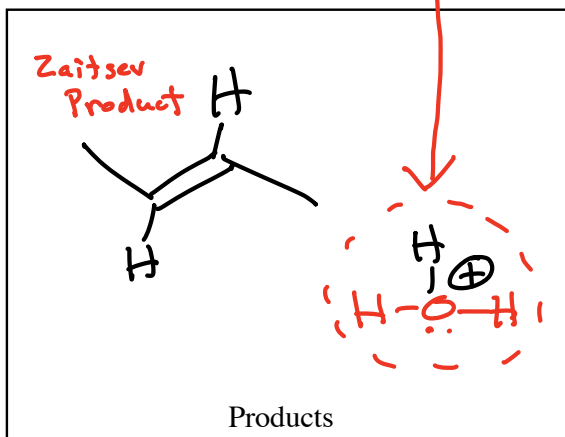
1° alcohols react via E2

2° or 3° Alcohol Dehydration

E1



Catalytic in acid



Summary: The OH group is protonated in strong acid to make a good leaving group, water, which breaks a bond to give a carbocation that has a proton taken away to give the product alkene

Regiochemistry: Zaitsev's Rule

Stereochemistry: N/A

Example:

