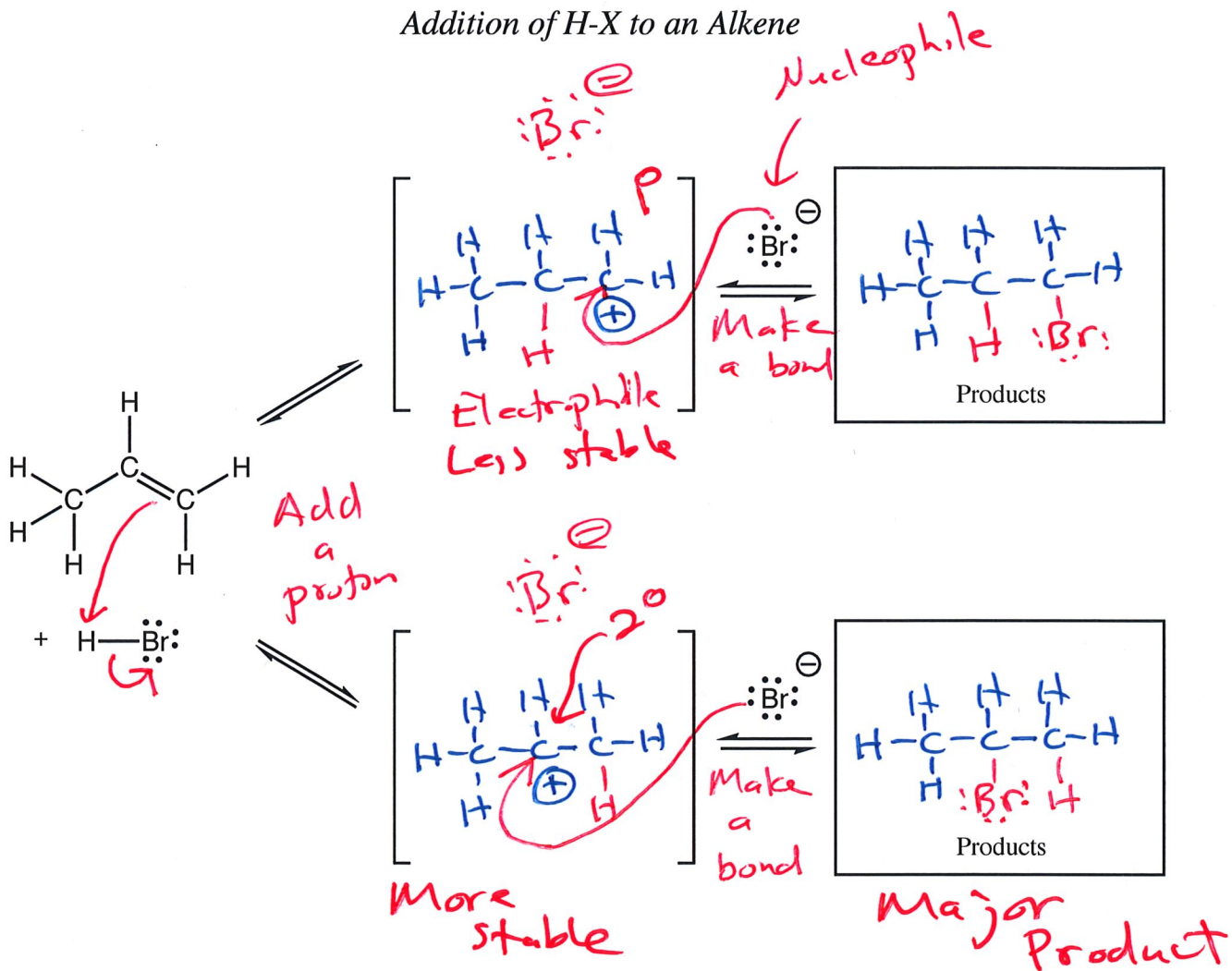


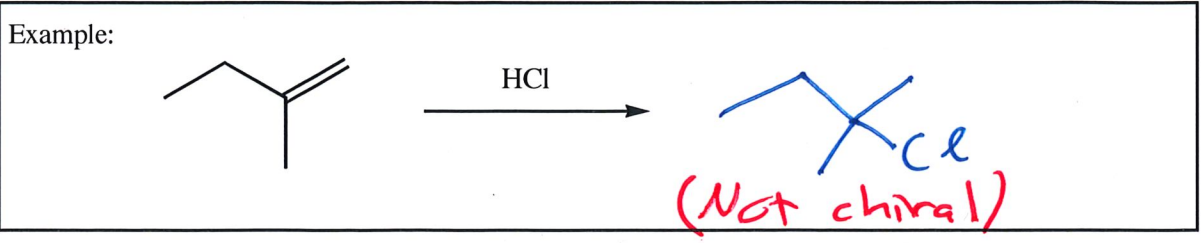
Addition of H-X to an Alkene



Summary: Alkenes react with H-X (X = Cl, Br, I) through addition a proton, creating a carbocation that reacts with X^- to make a bond

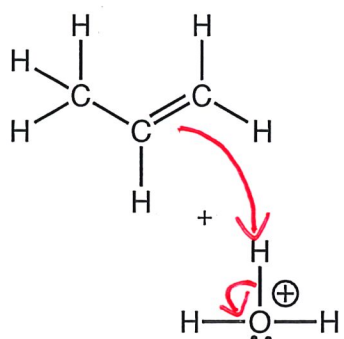
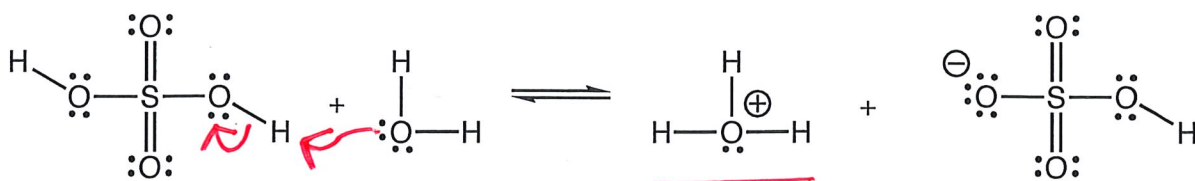
Regiochemistry: Markovnikov's Rule

Stereochemistry: Mixed \rightarrow both anti and syn

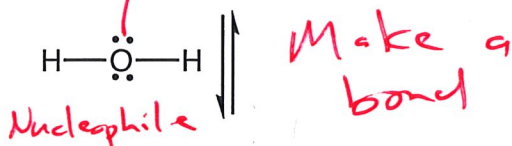
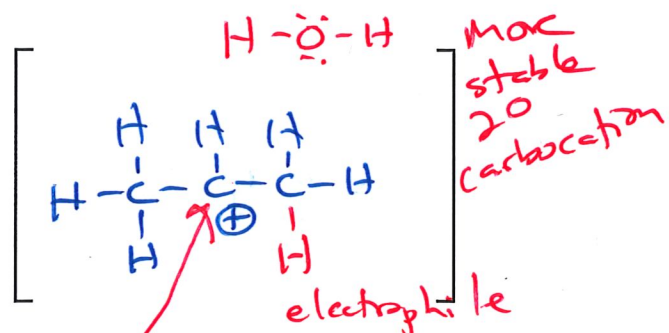


which carb. isomer? \rightarrow

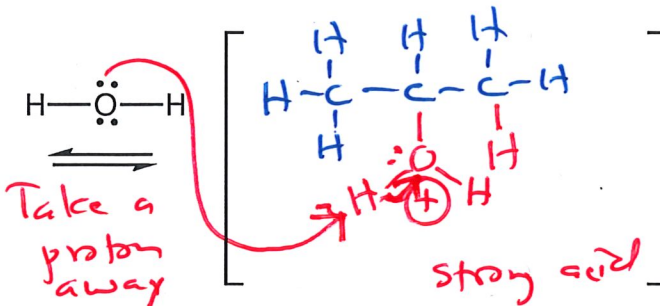
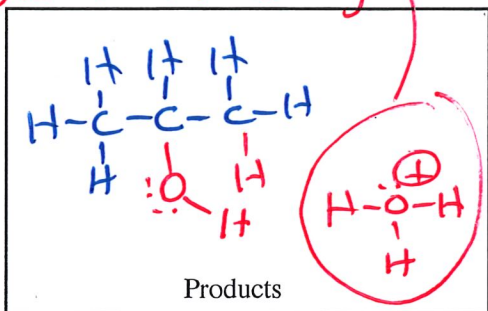
Acid-catalyzed Hydration of an Alkene



Add a proton



Catalytic in Acid \Rightarrow pH does not change

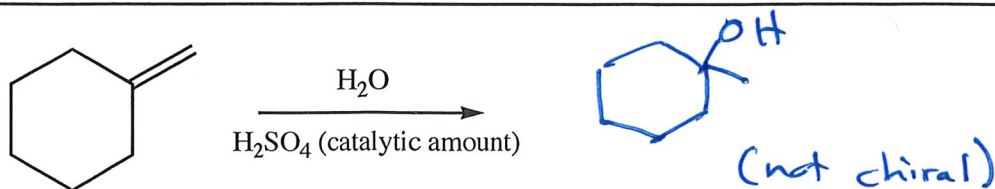


Summary: Add proton to give carbocation, make a bond with water, take a proton away to give alcohol

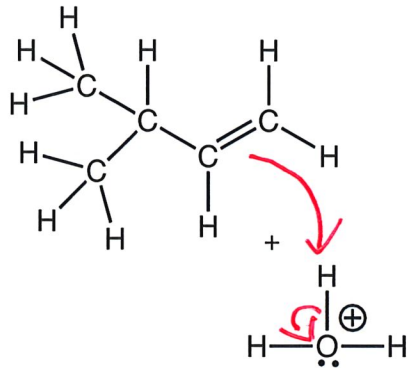
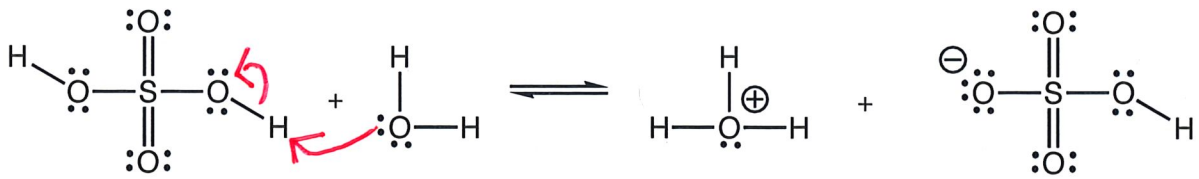
Regiochemistry: Markovnikov

Stereochemistry: Mixed \Rightarrow anti and syn

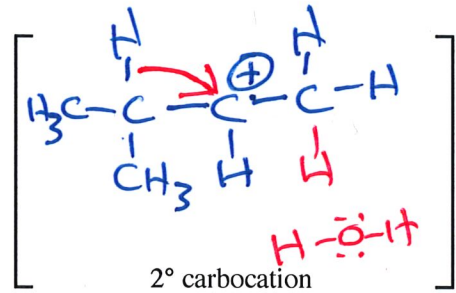
Example:



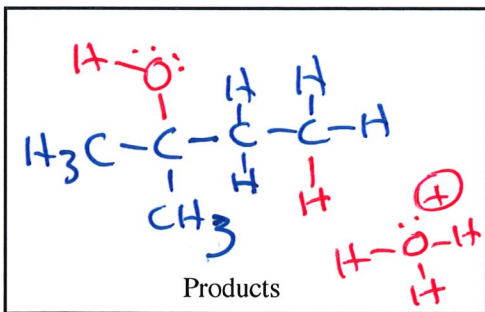
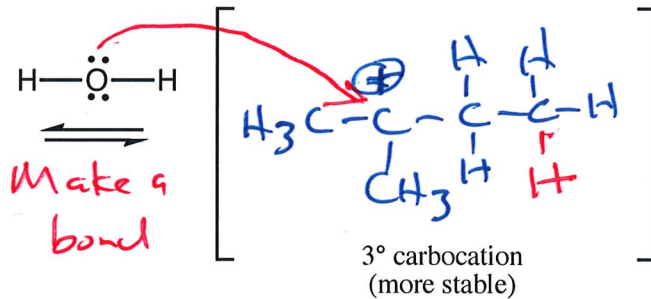
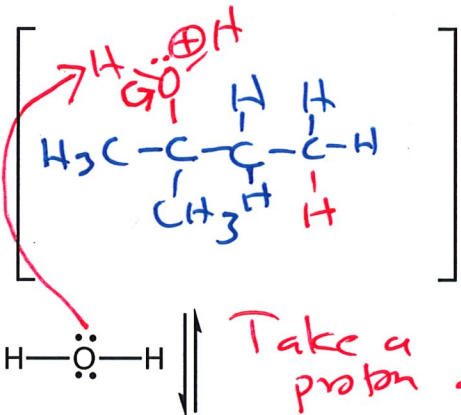
Cation Rearrangement





Add a proton

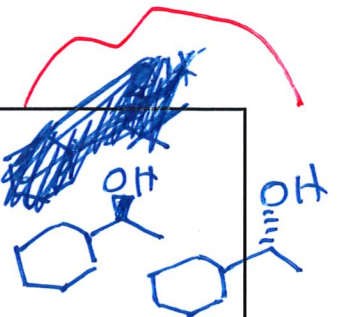
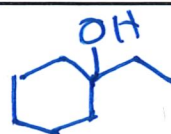
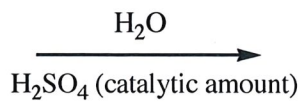
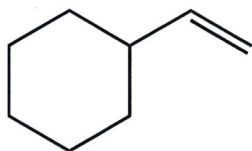


Rearrangement  1,2 hydride shift



Rearranged  Not rearranged 

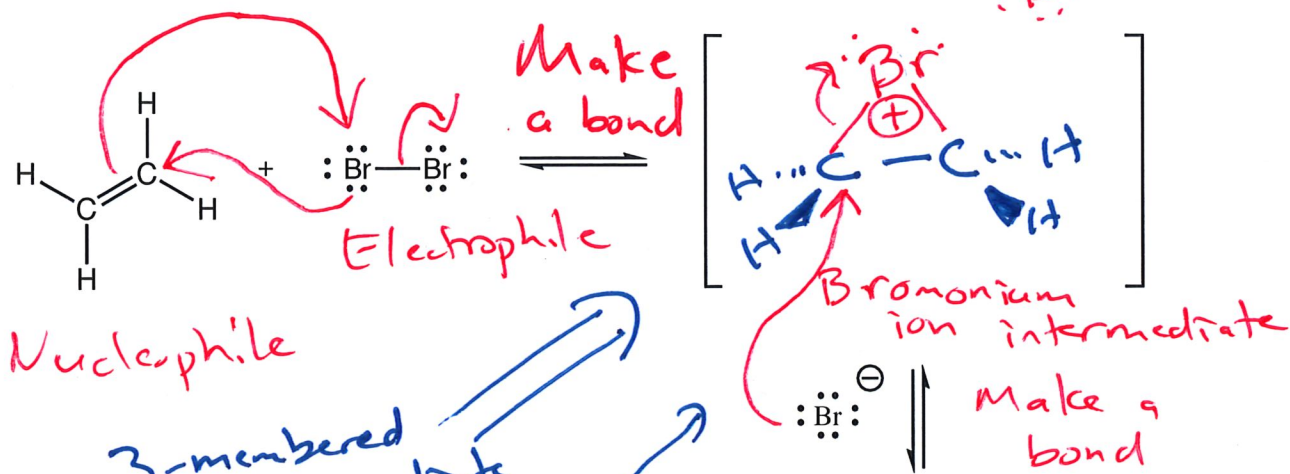
Example:



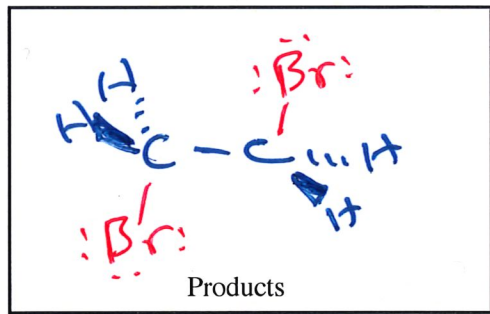
Racemized

Alkene add X_2 in solvent \rightarrow no water

Alkene Halogenation



3-membered ring intermediate (not carbocation)



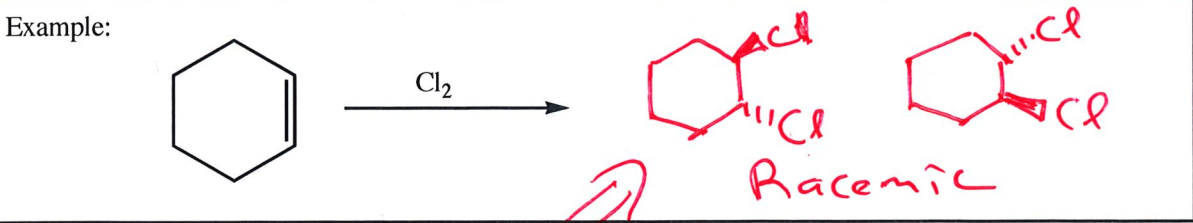
Br^- must attack from the side opposite the Br atom of 3-membered ring

\Rightarrow called "anti" addition geometry

Summary: Alkenes add X_2 to give a halonium ion (3-membered ring) that is attacked from the side opposite the X atom to make a bond

Regiochemistry: N/A

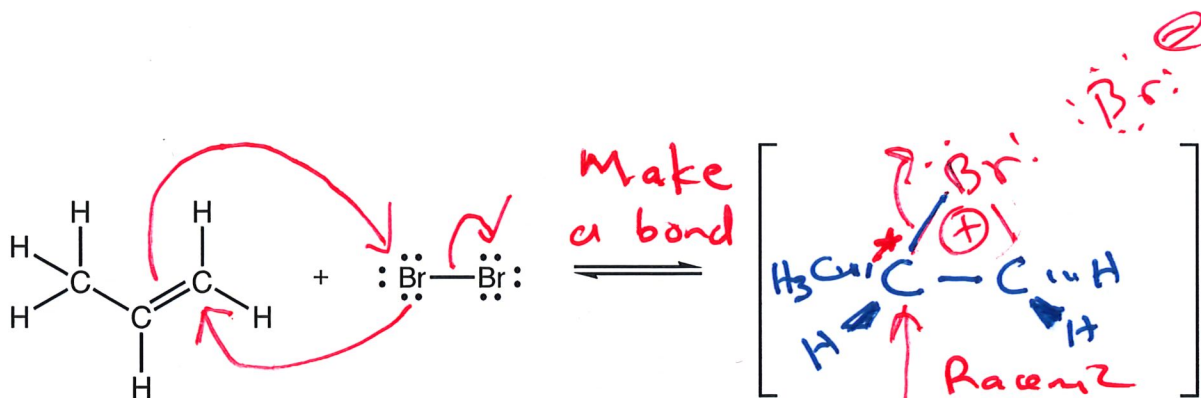
Stereochemistry: anti



anti addition means trans products only \Rightarrow No cis!!

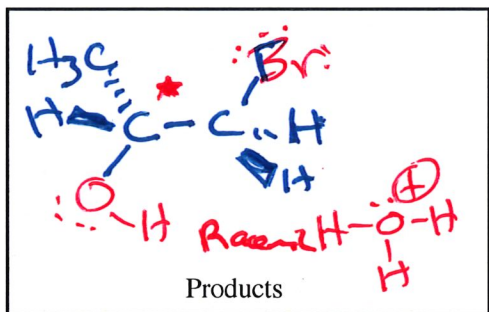
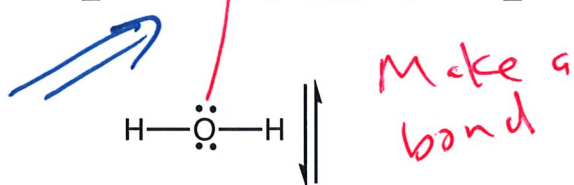
Add an alkene to a solution of water
then add the X_2

Alkene Hydrohalogenation

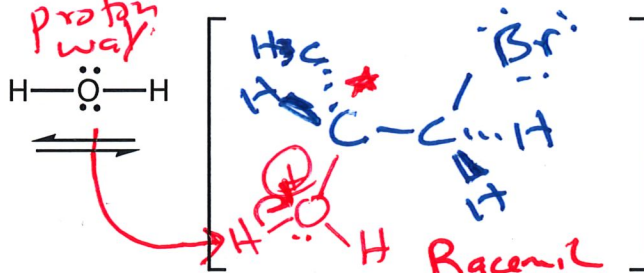


pH drops during reaction

This attack at the more substituted carbon



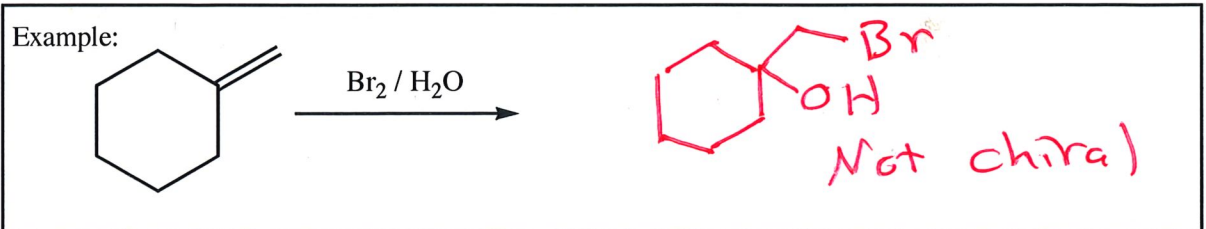
Take a proton away



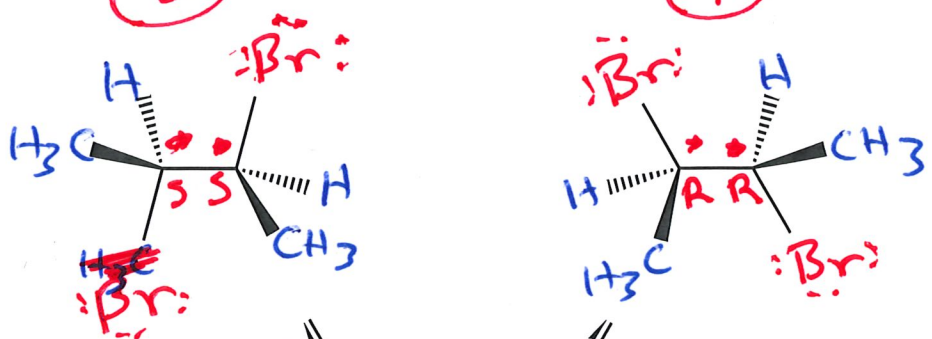
Summary: In H_2O , alkenes react with X_2 to give halonium ion intermediate that adds H_2O at more substituted carbon, take a proton away to give halohydrin

Regiochemistry: Markovnikov Rule

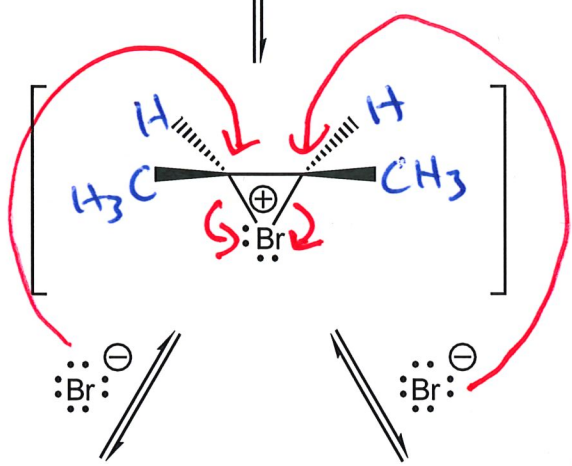
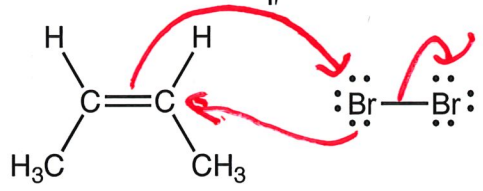
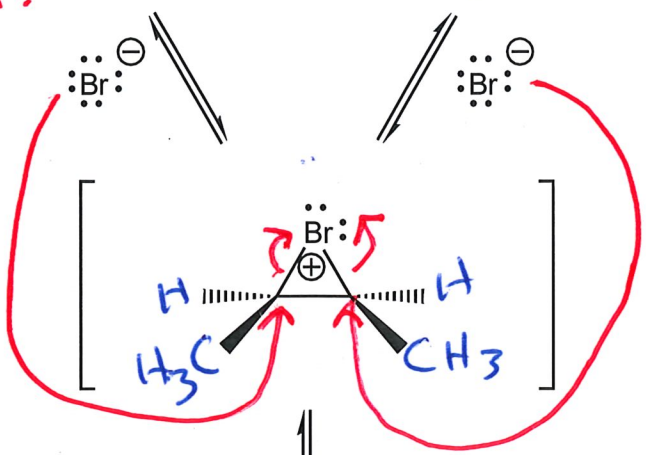
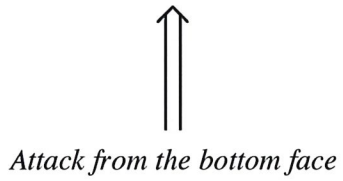
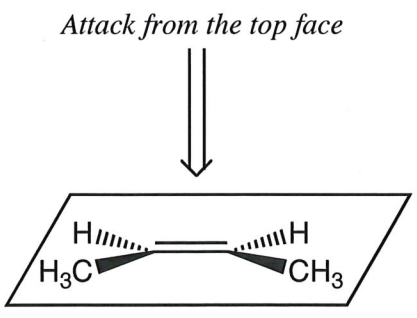
Stereochemistry: anti



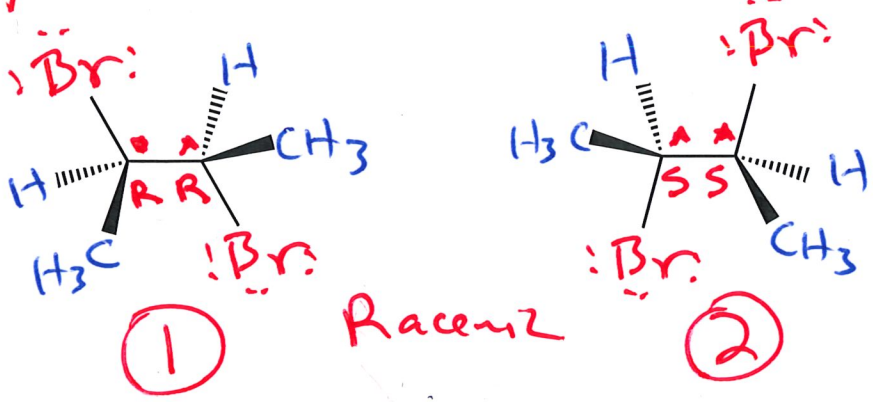
(2) Racemic (1)



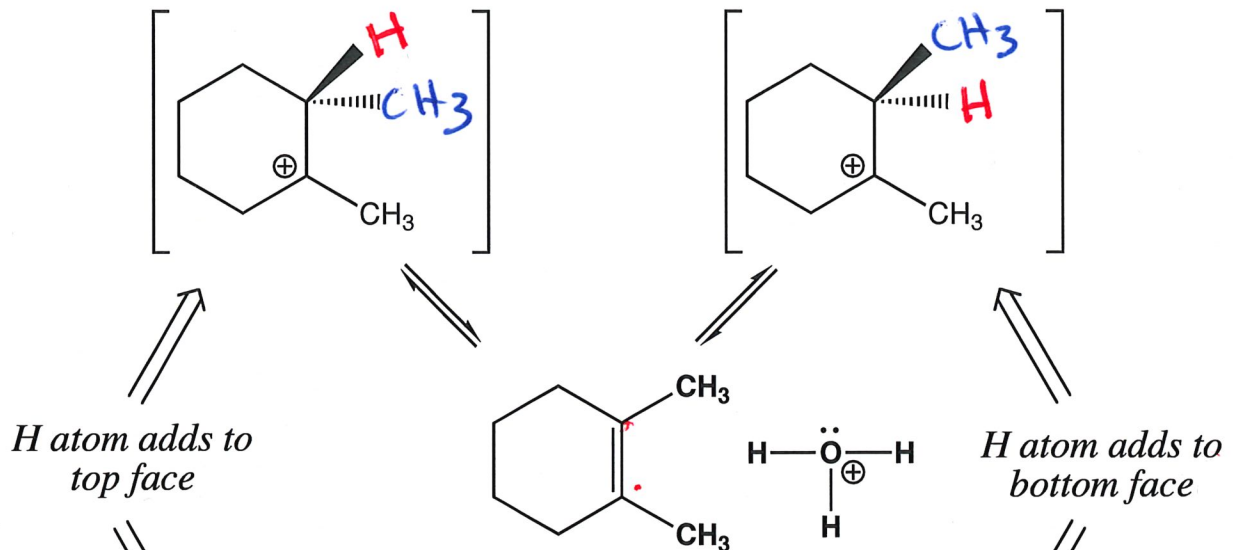
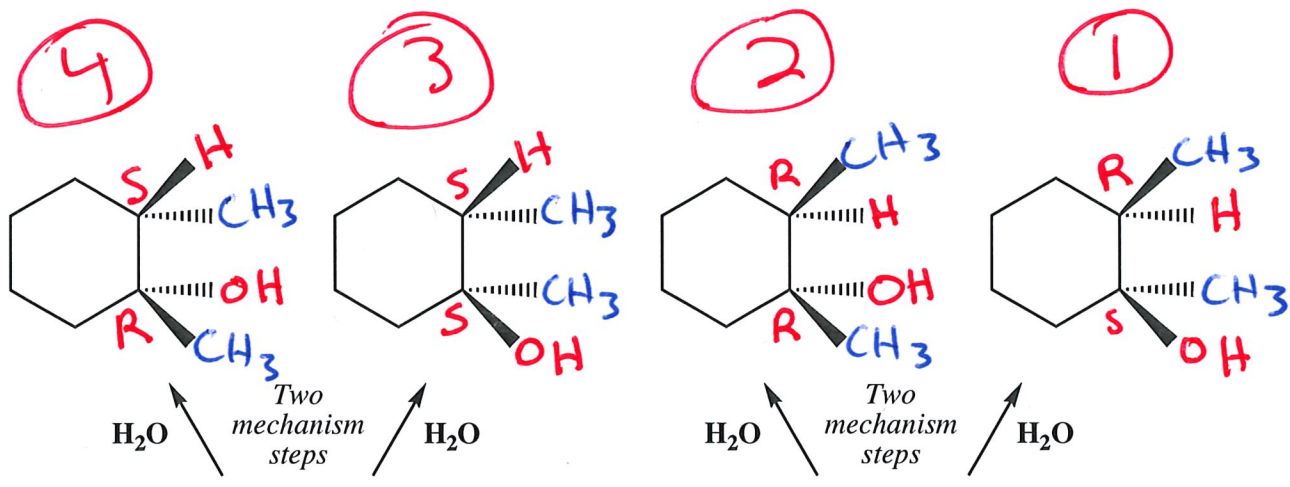
Anti addition only



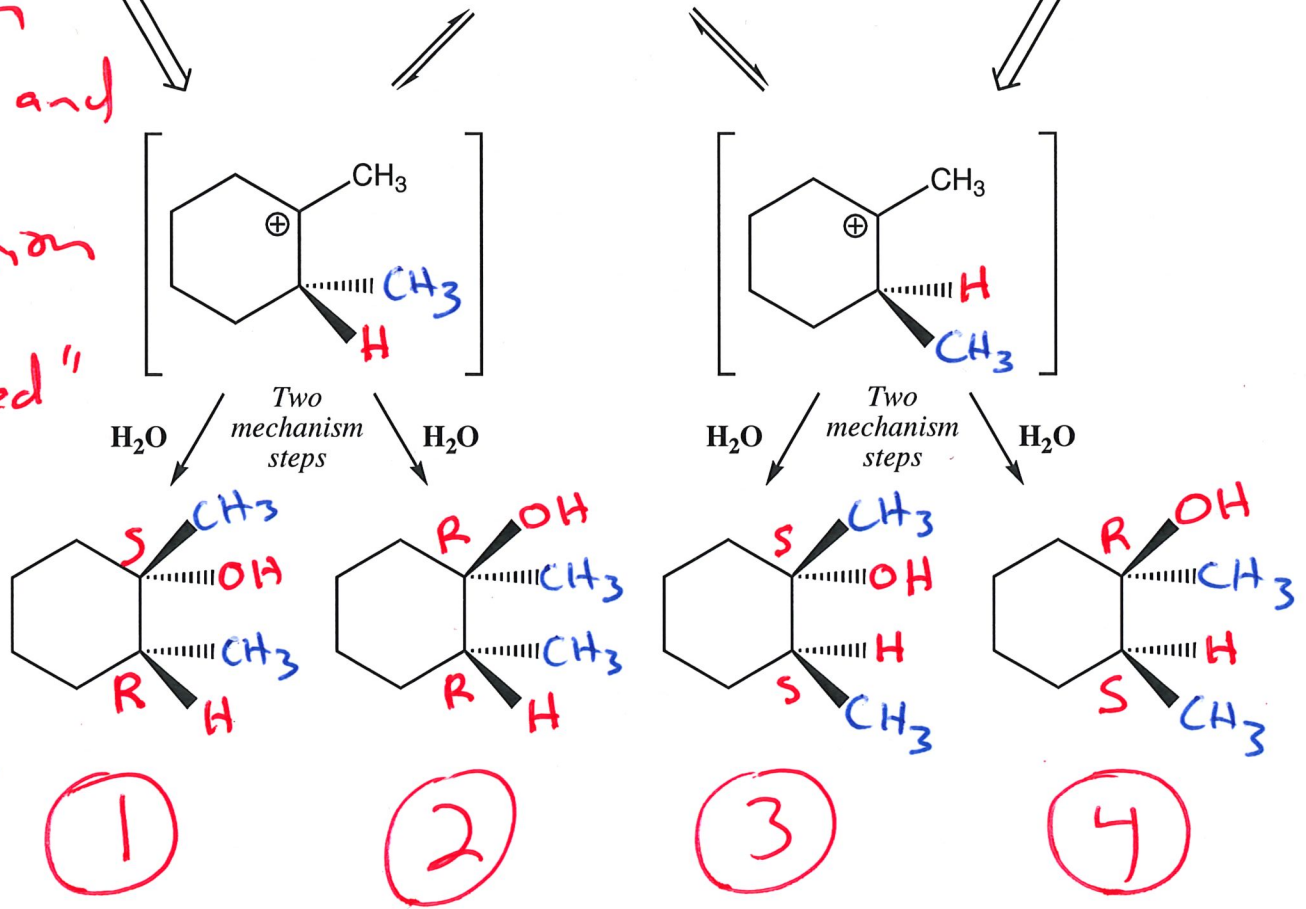
Anti addition only



Racemic



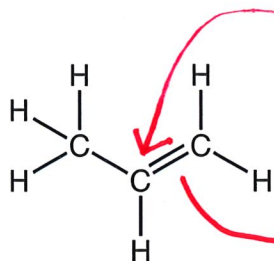
Both
syn and
anti
addition
⇒
"mixed"



Nucleophile

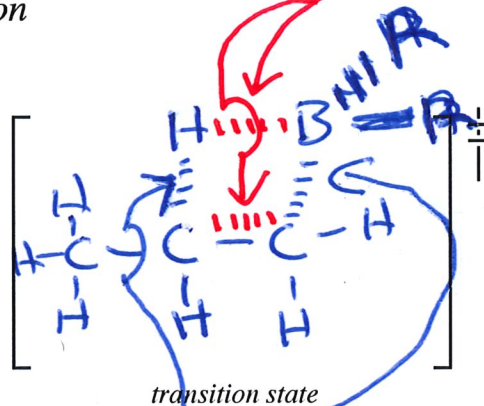
Hydroboration-Oxidation

Electrophilic B atom



(R = H or alkyl group depending on how far reaction has progressed)

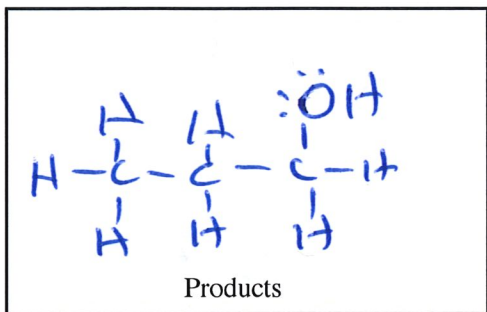
Bonds being broken



The B and H atoms add to the same face of the alkene

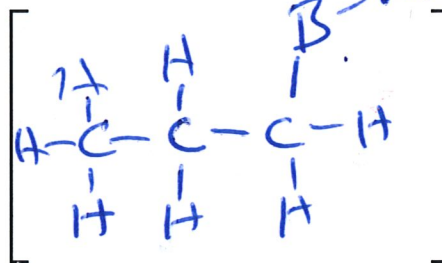
Bonds that are forming

⇓
Syn addition



2. H₂O₂ / HO[⊖]

(Chemist opens flask and adds new reagent)



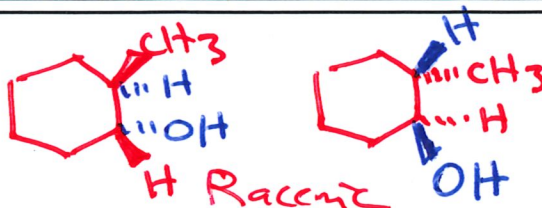
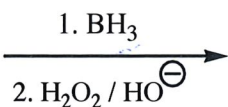
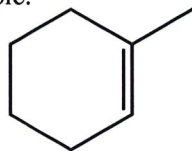
H ends up on more substituted C atom to minimize steric strain in transition state above

Summary: The pi bond of the alkene attacks the B atom while the H of BH₃ attaches to the more substituted C of the alkene.

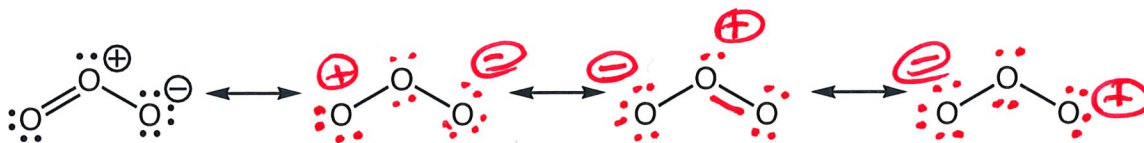
Regiochemistry: Non-Markovnikov

Stereochemistry: Syn

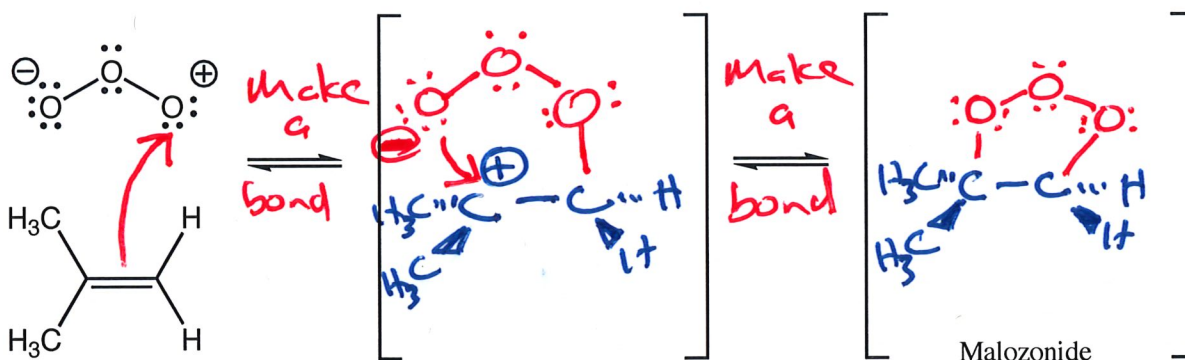
Example:



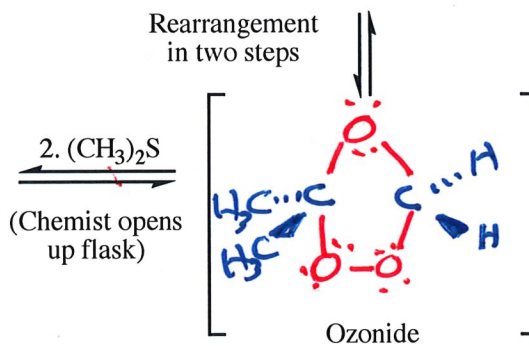
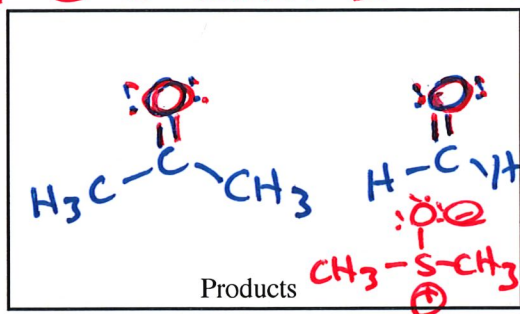
Ozonolysis Partial Mechanism



Ozone contributing structures



Replaced $C=C$ with 2 $C=O$

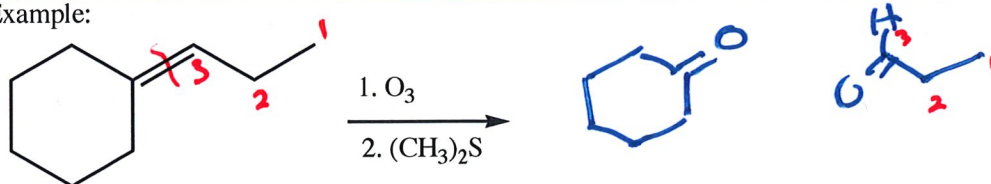


Summary: Reaction of an alkene with O_3 creates an ozonide that decomposes with $(CH_3)_2S$ to give aldehydes and ketones

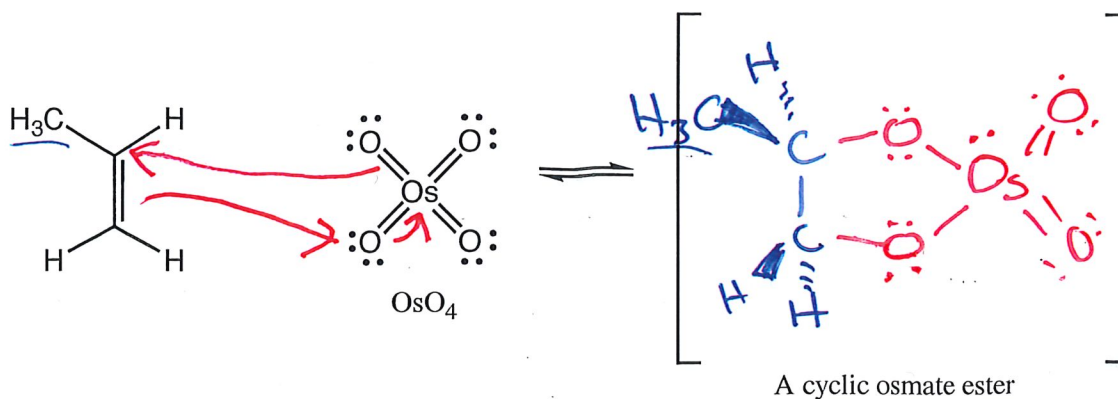
Regiochemistry: N/A

Stereochemistry: N/A

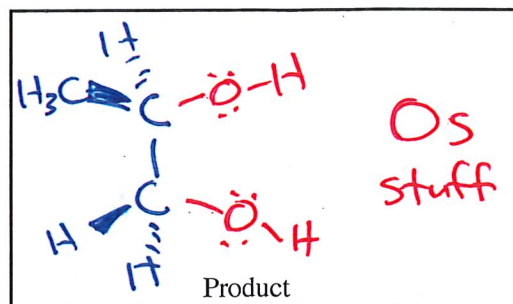
Example:



OsO_4 Partial Mechanism



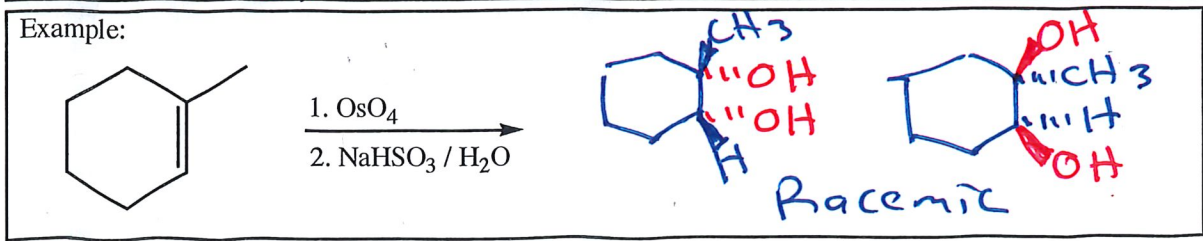
2. $NaHSO_3 / H_2O$
(Chemist opens up flask)



Summary: OsO_4 reacts with alkenes to give the cyclic osmate ester, $NaHSO_3/H_2O$ converts that to a 1,2 diol (glycol)

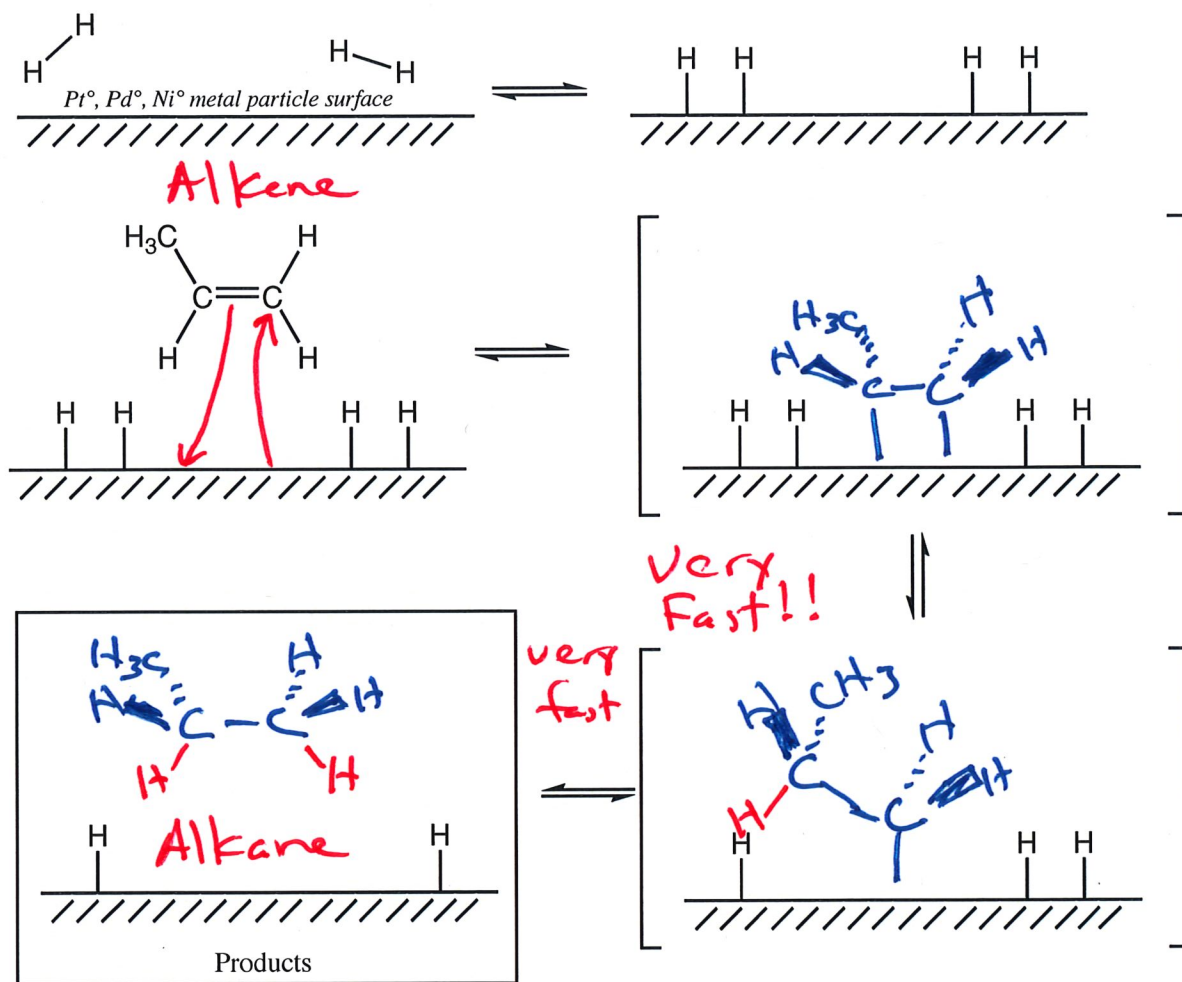
Regiochemistry: N/A

Stereochemistry: syn addition



Converts alkenes to alkanes

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



Summary:

H_2 adsorbs onto the metal surface
→ alkene adsorbs onto the metal surface
→ H atoms transfer to both C atoms on same face

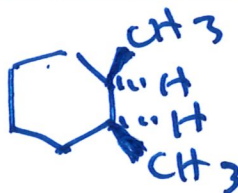
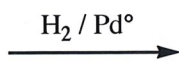
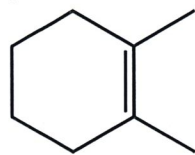
Regiochemistry:

N/A

Stereochemistry:

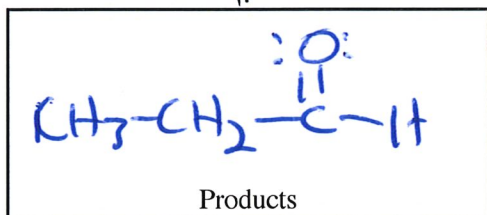
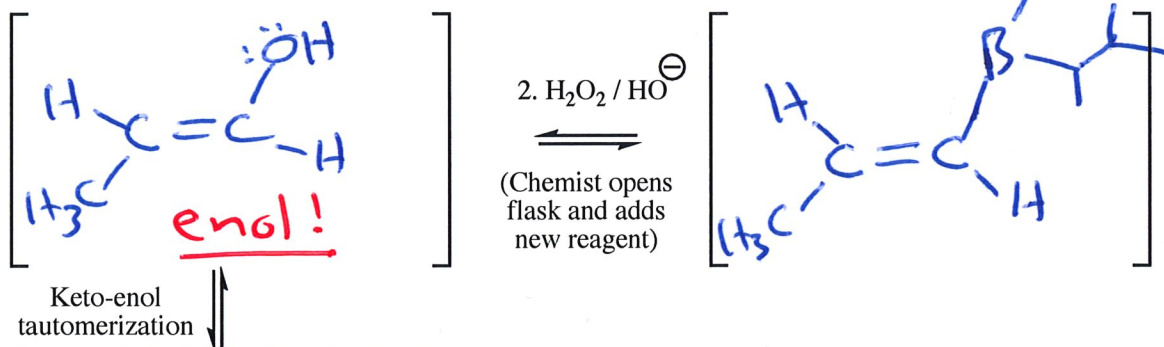
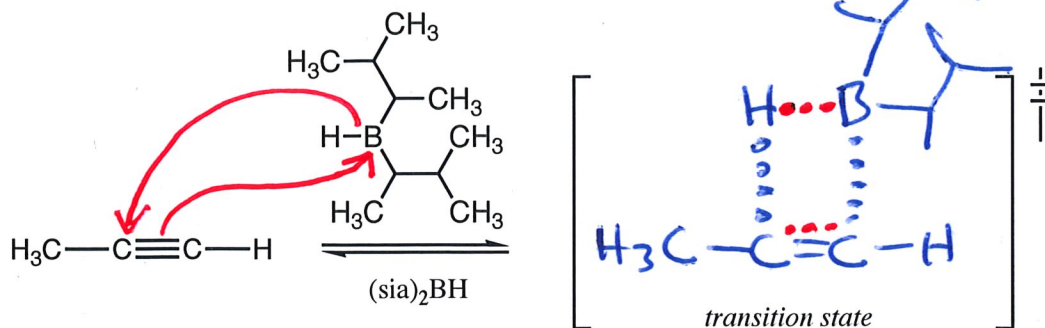
Syn addition

Example:



Not chiral

Terminal Alkyne Hydroboration

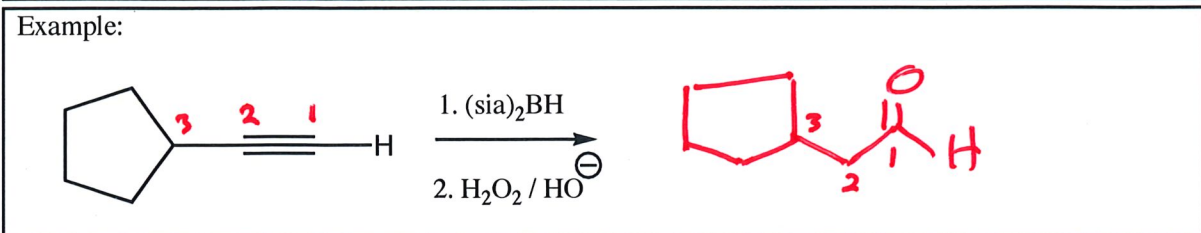


aldehyde

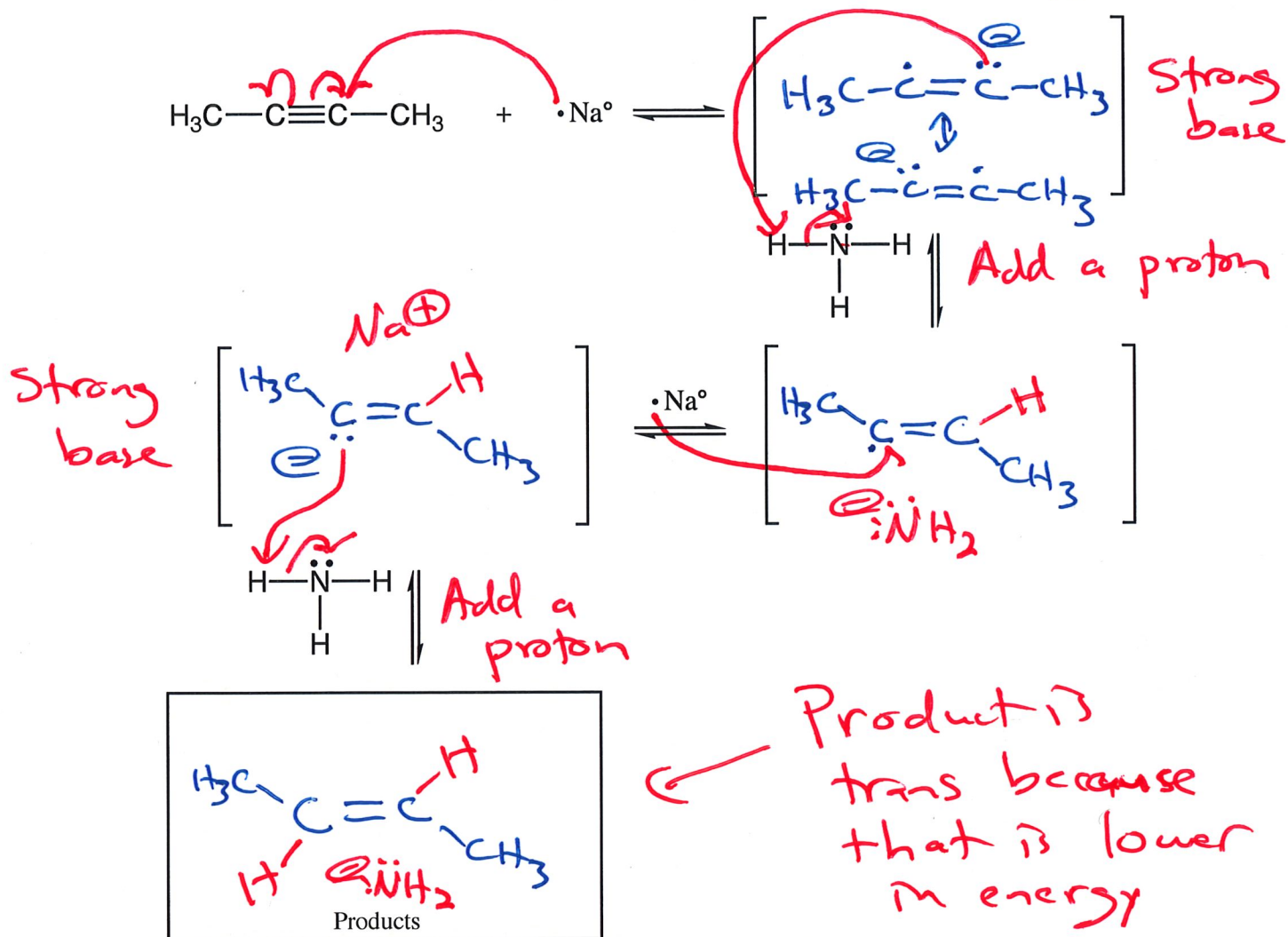
Summary: Hydroboration with $(\text{sia})_2\text{BH}$ places an OH group on the terminal carbon leading to an aldehyde

Regiochemistry: *Non-Markovnikov*

Stereochemistry: *N/A*



Reduction of Alkynes Using Sodium and Ammonia Na^{\oplus}



Summary:

2 $1e^{\ominus}$ reductions by Na^{\ominus}
and 2 protonations from NH_3

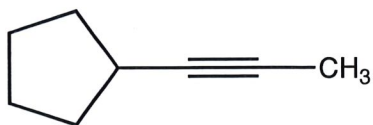
Regiochemistry:

N/A

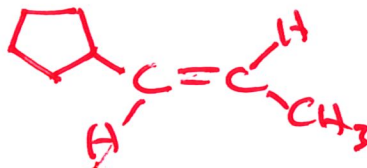
Stereochemistry:

Anti addition to give trans/E product

Example:

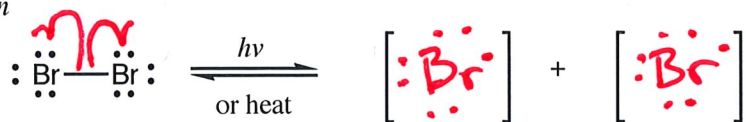


$\text{Na}^{\ominus} / \text{NH}_3$

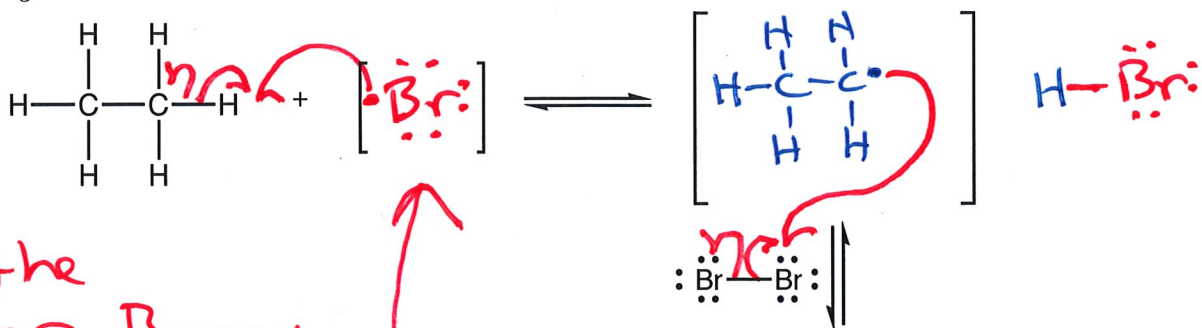


Alkane Free Radical Halogenation

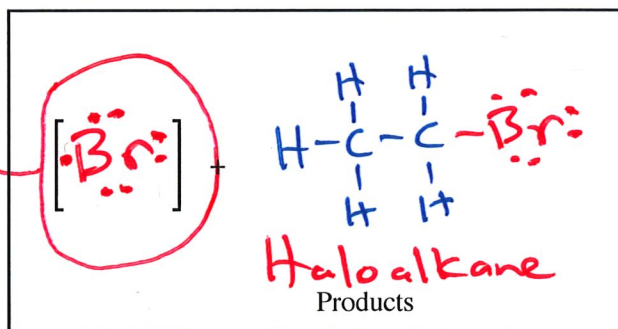
Initiation



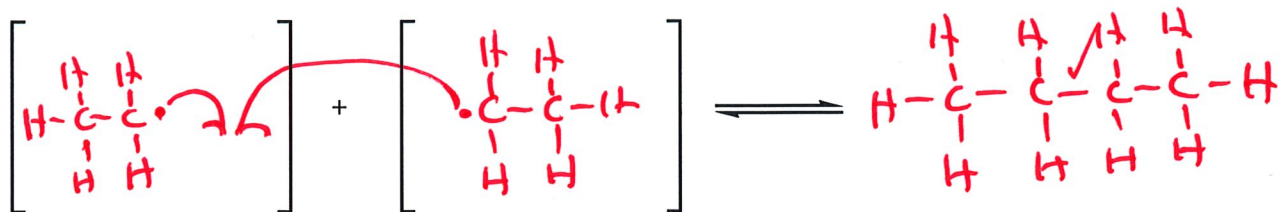
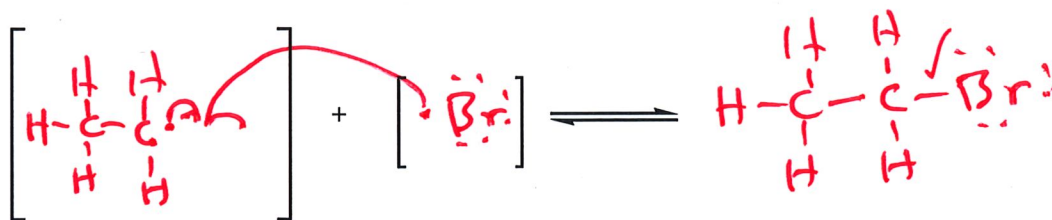
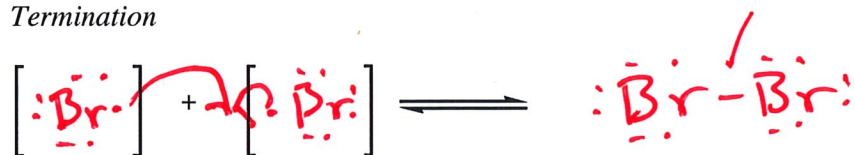
Propagation



Like the Energizer Bunny the radical chain process keeps going and going -

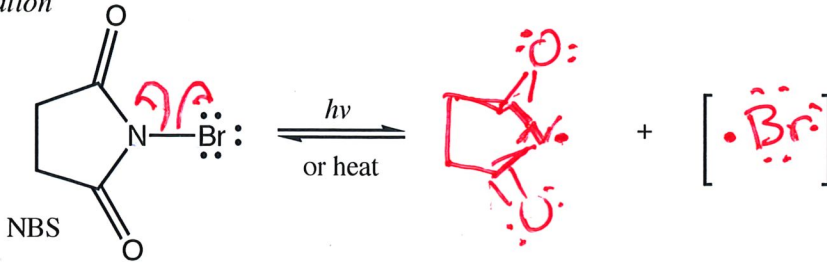


Termination

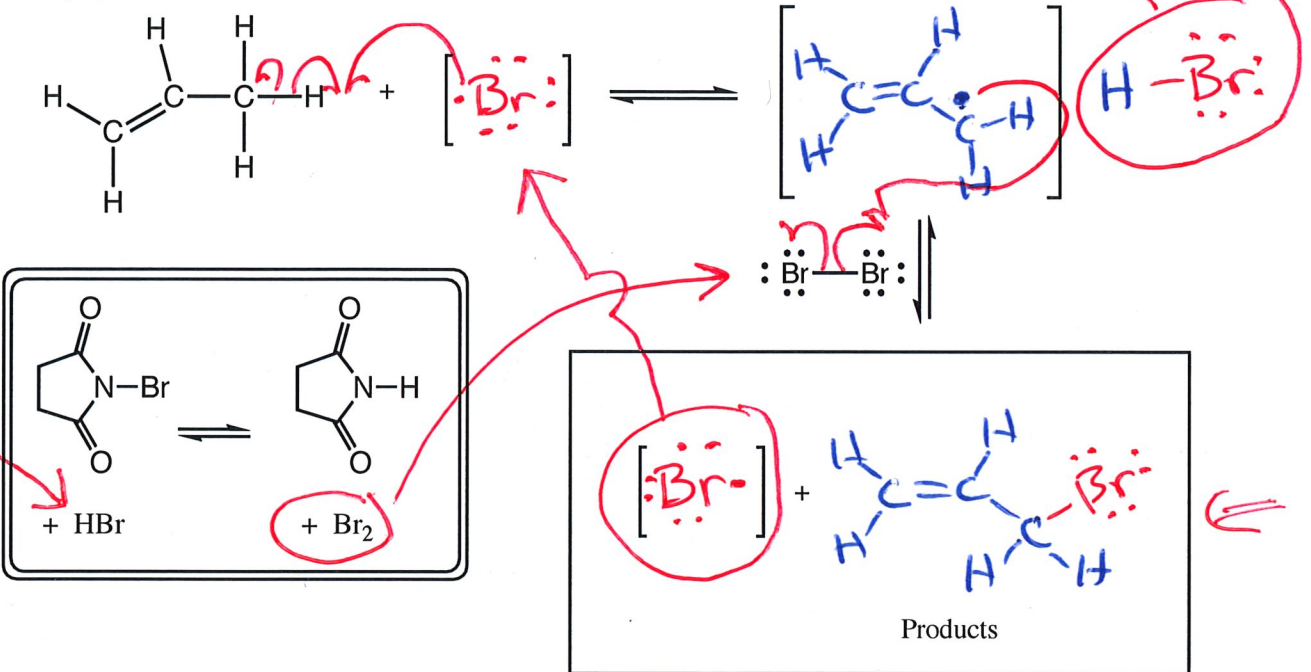


Allylic Halogenation

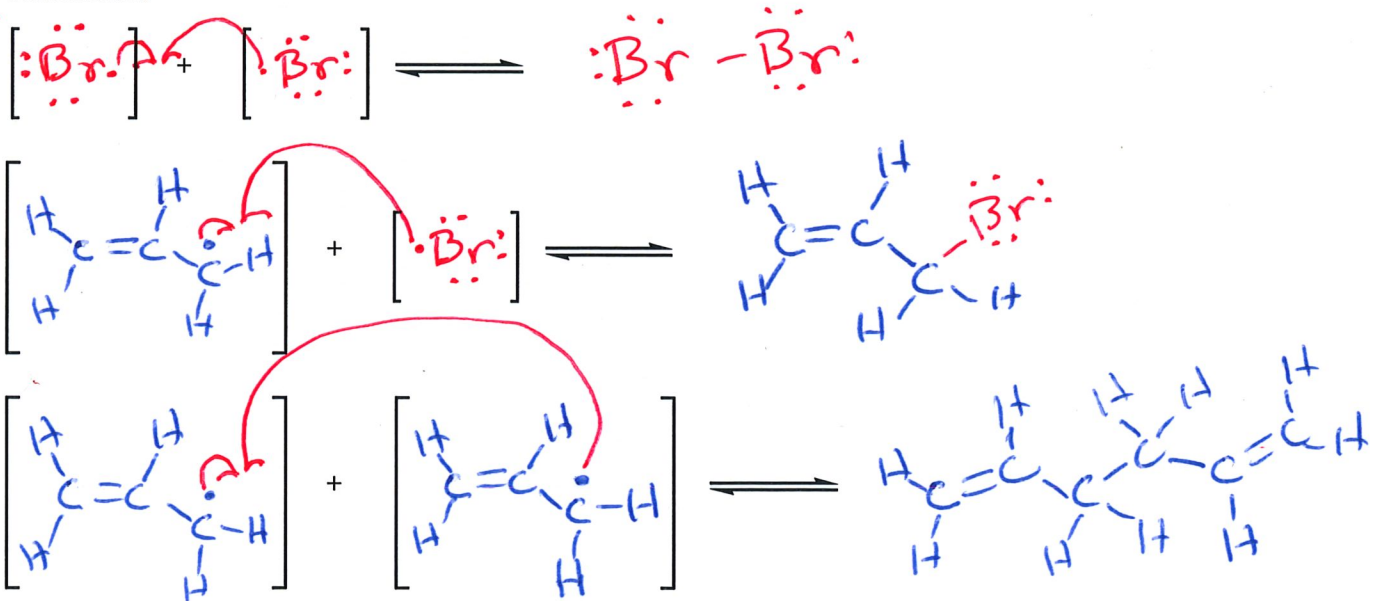
Initiation



Propagation



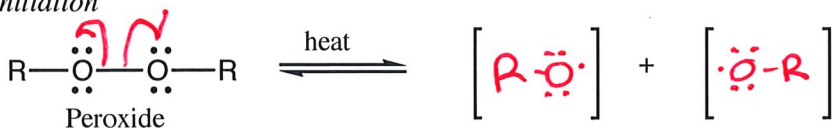
Termination



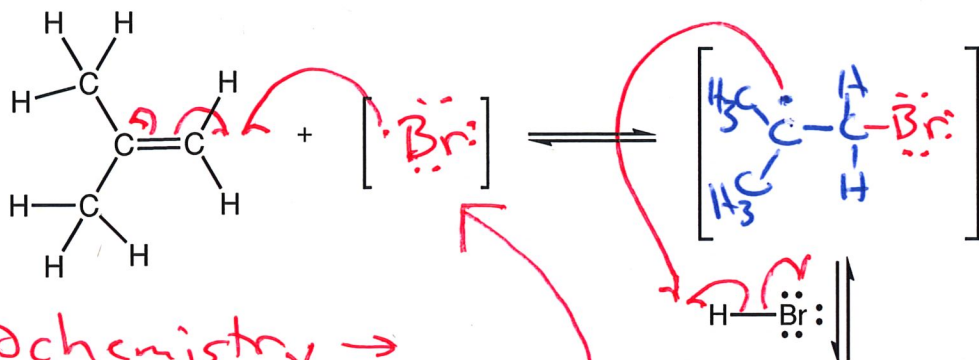
only small amounts of these are formed

Non-Markovnikov Addition of HBr to an Alkene

Initiation

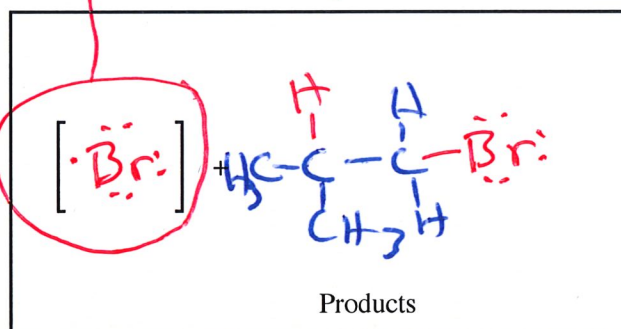


Propagation



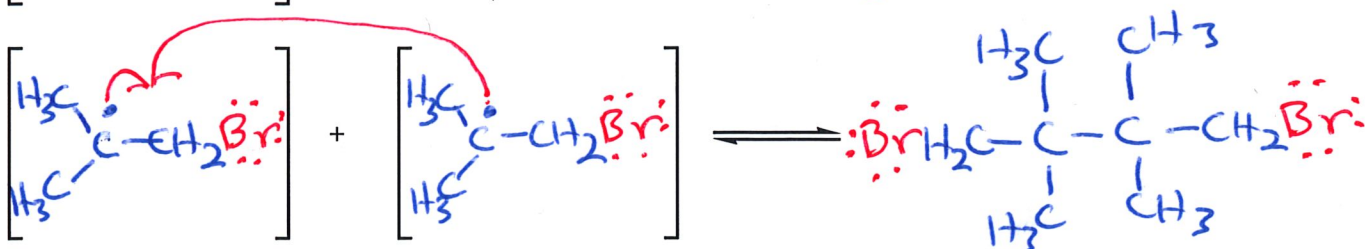
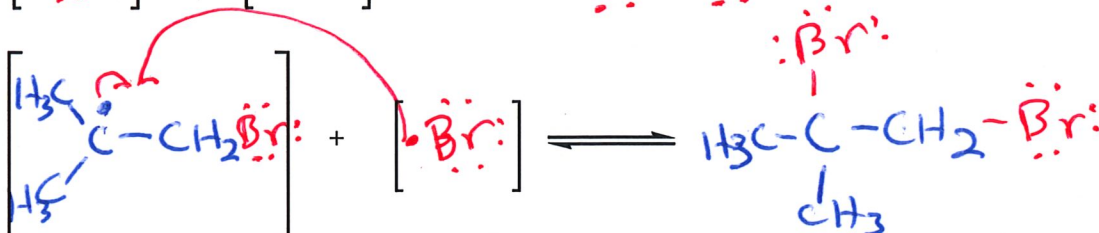
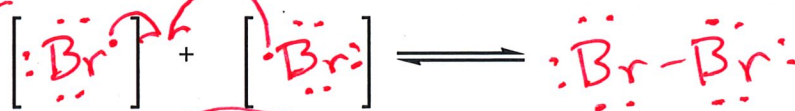
Make the more stable radical

Regiochemistry → non-Markovnikov!!!
Stereochemistry Mixed

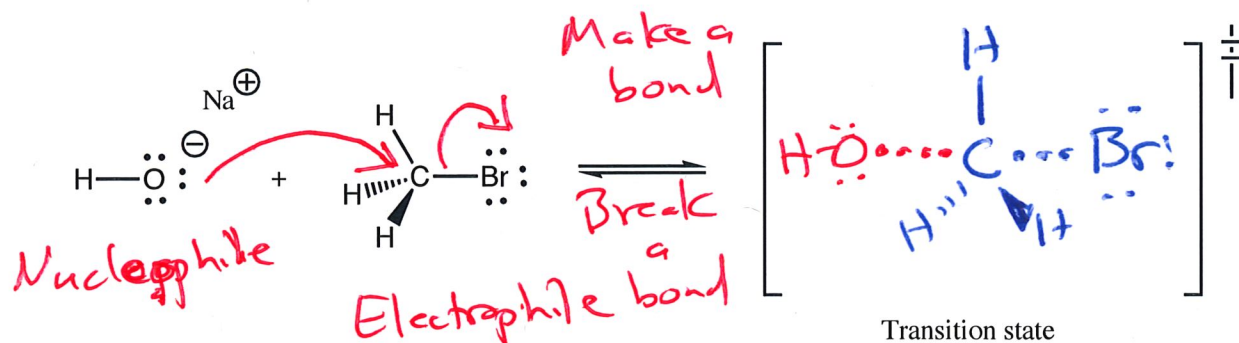


Termination

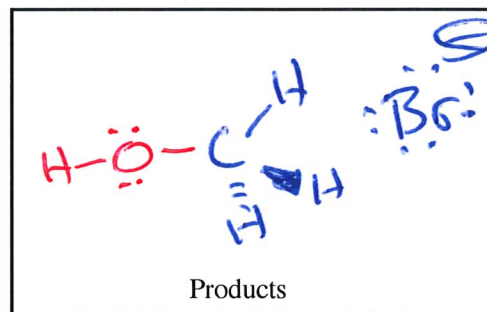
only small amounts of these are formed



The S_N2 Mechanism



Nucleophile is attracted to the back of the C-Br bond



Summary:

Nucleophile attacks the backside of C-Leaving group bond → as new bond is made the leaving group departs

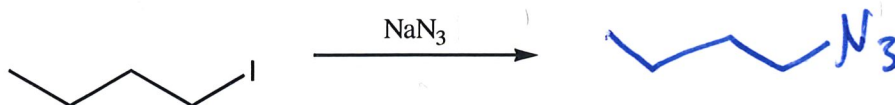
Regiochemistry:

N/A

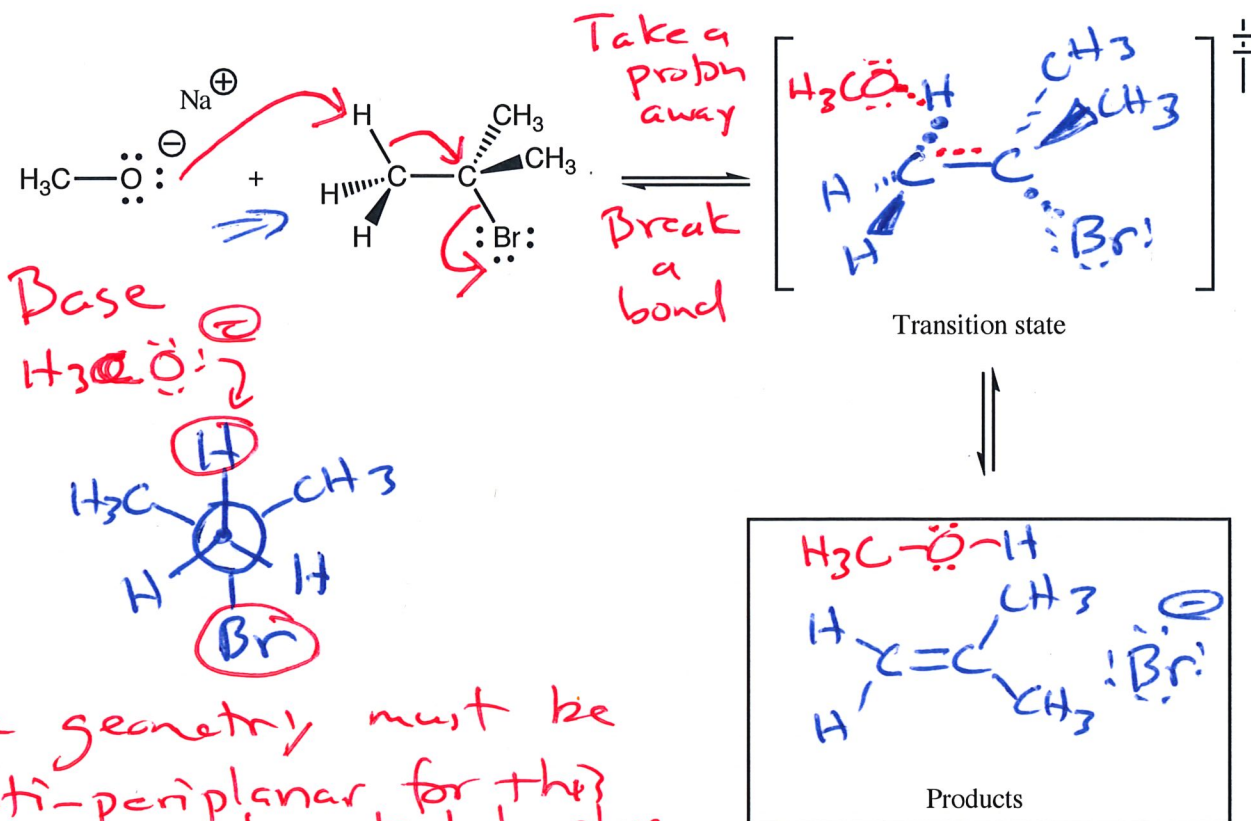
Stereochemistry:

INVERSION at site of reaction

Example:



The E2 Mechanism



Summary:

Base removes an H atom as a new pi bond is created when the leaving group departs

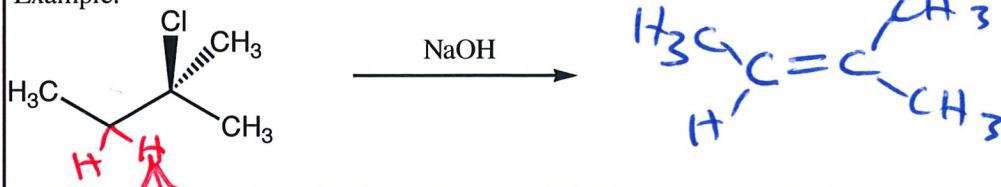
Regiochemistry:

Zaitsev's Rule \rightarrow make the most stable alkene

Stereochemistry:

Determined by anti-periplanar geometry

Example:

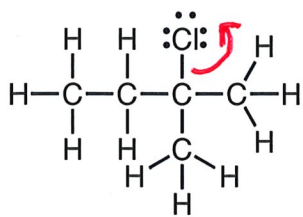


being removed

most substituted

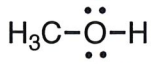
The S_N1 and $E1$ Mechanisms

only reagent involved in the key step

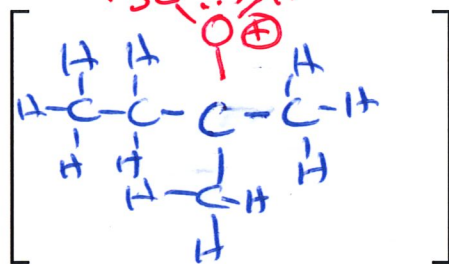


This stays close by

Break the bond



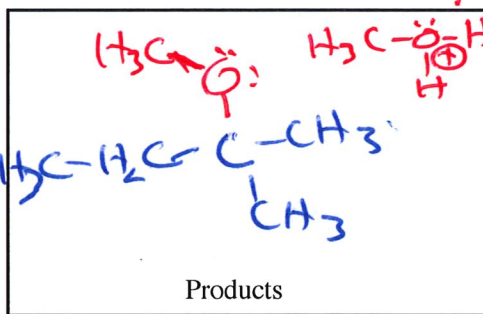
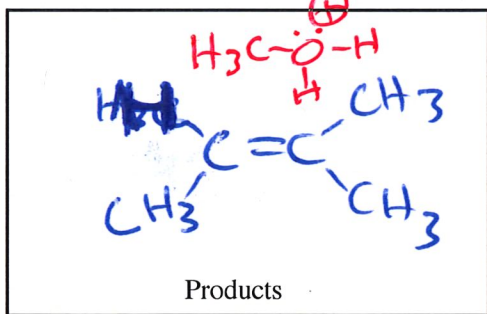
S_N1
Make a bond



carbocation!!
can rearrange

$E1$ H_3C-O-H Take a proton away

H_3C-O-H Take a proton away



Summary: The leaving group departs to give a carbocation, that loses a proton to give an alkene ($E1$) or adds a nucleophile (S_N1)

Regiochemistry: $E1 \rightarrow$ Zaitsev regiochemistry

Stereochemistry: $S_N1 \rightarrow$ Scrambled (not 1:1 necessarily)

Example:

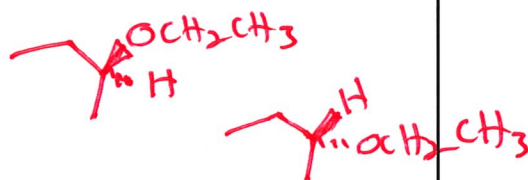
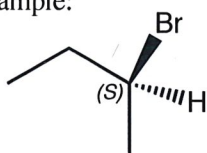


Table of Nucleophiles

Strong Nucleophiles Br^- , I^- , R-S^- , H-S^- , $\text{N}\equiv\text{C}^-$, N_3^-
$\text{R-C}\equiv\text{C}^-$, R-O^- , H-O^- Strong Bases
Medium Nucleophiles R-CO_2^- , R-S-H , R_2S , NH_3 , RNH_2 , R_2NH , NR_3
Weak Nucleophiles $\text{R-CO}_2\text{H}$, R-O-H , H_2O Very Weak Bases

Special Case

Tert-Butoxide (tBuO^-) is a strong base, but is not a nucleophile due to non-bonded interaction strain.

Substitution/Elimination Decision Map

Methyl Halide ⇒ **S_N2**

Primary Haloalkane ⇒ **tBuOK ?** ⇒ **Yes** ⇒ **E2**
 ↓
No ⇒ **S_N2**

Secondary Haloalkane
 or
Allylic/Benzylic Halides ⇒ **Very Weak Base ?** ⇒ **Yes** ⇒ **S_N1/E1** *
 ↓
Very Strong Base ? ⇒ **Yes** ⇒ **E2** **
 ↓
No ⇒ **S_N2**

Tertiary Haloalkane ⇒ **Very Weak Base ?** ⇒ **Yes** ⇒ **S_N1/E1**
 ↓
No ⇒ **E2**

For S_N2 Remember Chiral Center InVERSiON
For E2 Remember anti-periplanar and Zaitsev
For S_N1 Remember Chiral Center Scrambling
For E1 Remember Zaitsev

* Note: With Very Weak Bases, S_N2 can compete here, but for the purposes of this class, assume S_N1 / E1 predominate

** Note: If tBuOK is the very strong base, an appreciable amount of a non-Zaitsev product can be formed because the bulky tBuOK will tend to react with the most accessible H atom.