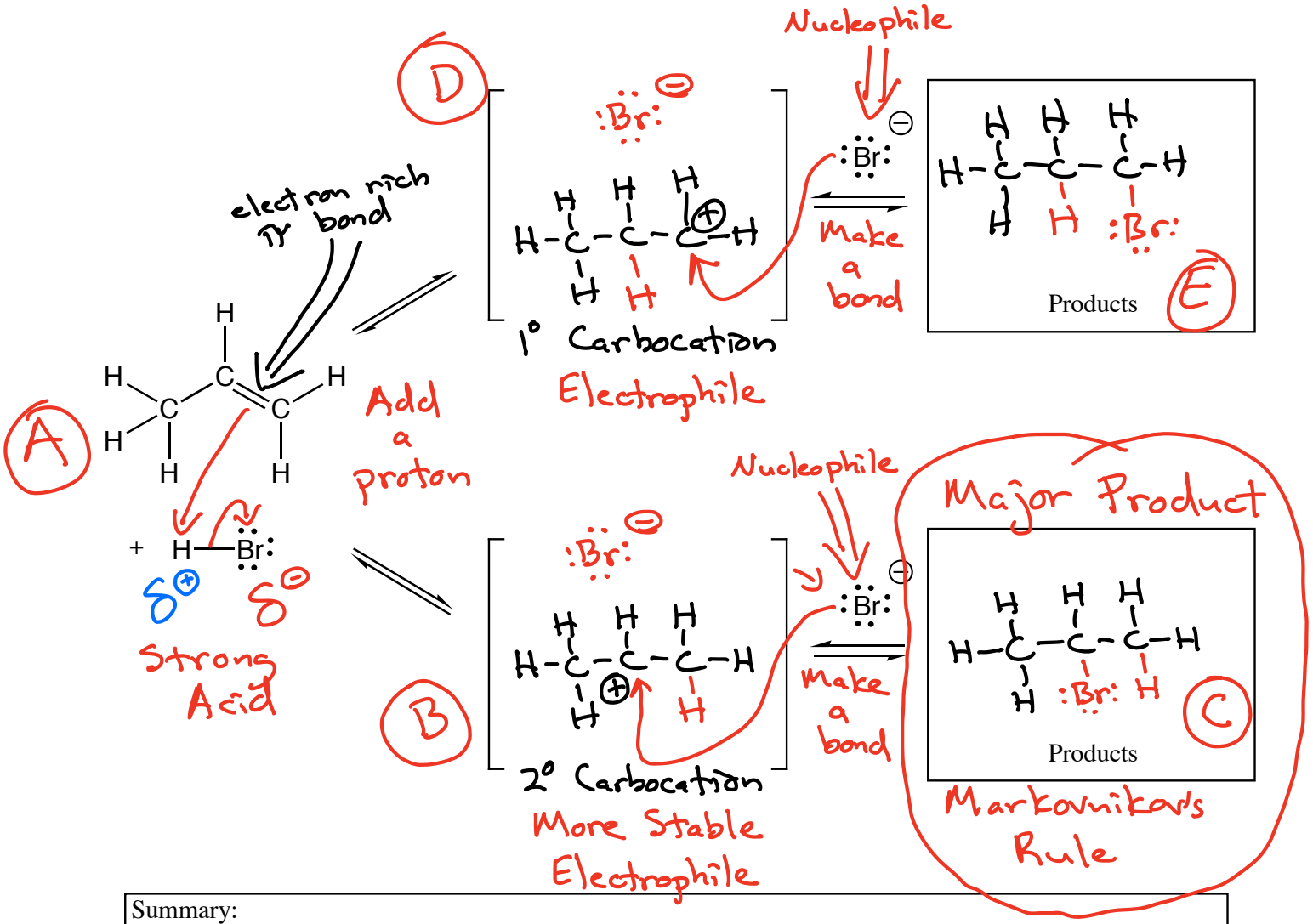
Addition of H-X to an Alkene

X = Cl, Br, I but not F



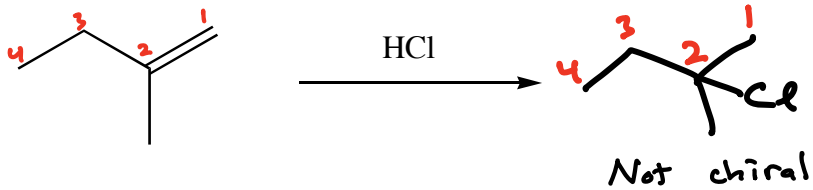
Summary:

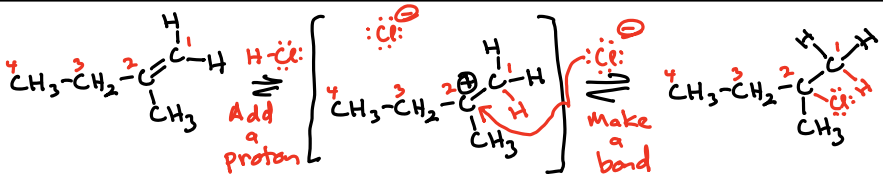
The alkene pi bond reacts with H-X to add a proton to create a carbocation intermediate that makes a bond with $X^{\ominus}$ to give the product

Regiochemistry: Markovnikov's Rule

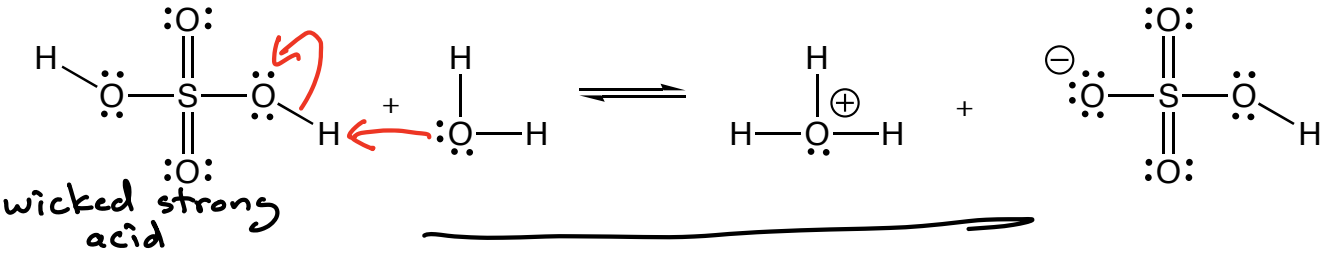
Stereochemistry: Mixed (time capsule) → Racemic Product

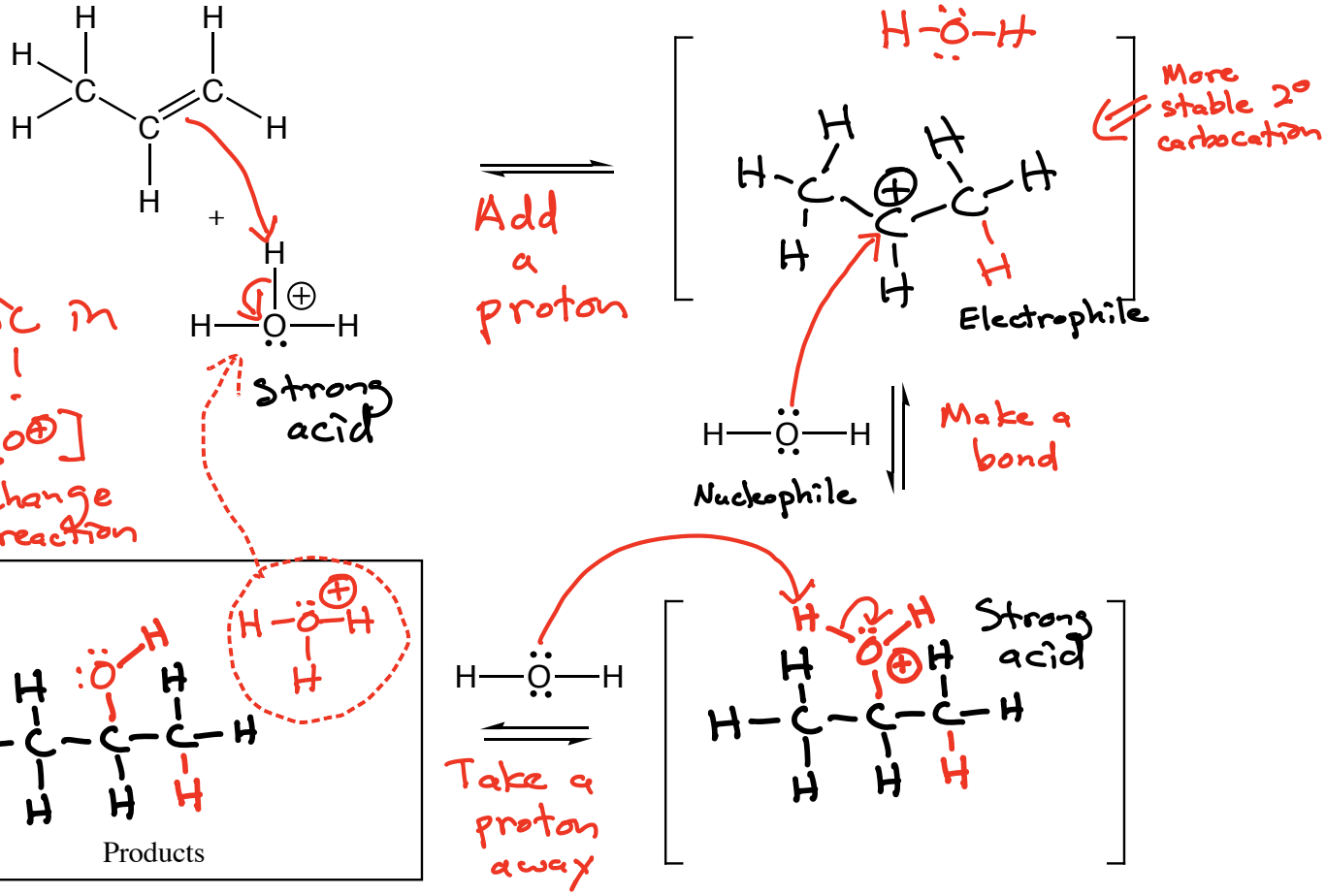
Example:





Acid-catalyzed Hydration of an Alkene

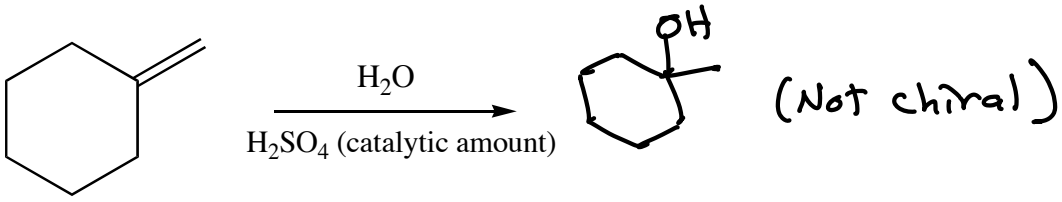




Catalytic in Acid!
⇒ The $[H_3O^{\oplus}]$ does not change during the reaction

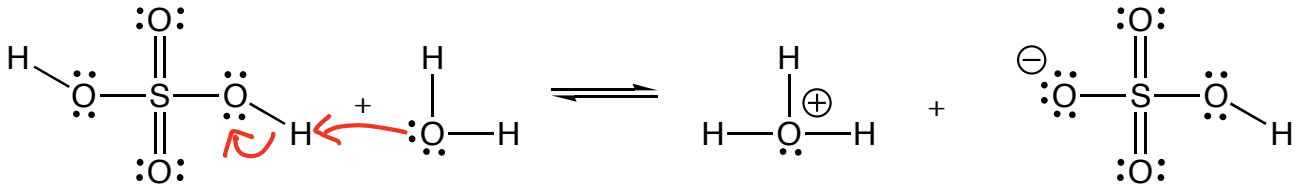
Summary:	Proton adds to make a carbocation intermediate, water attacks to make a new bond, take a proton away to make the product alcohol. Catalytic in $H_3O^{\oplus}$
Regiochemistry:	Markovnikov's Rule
Stereochemistry:	Mixed (time capsule)

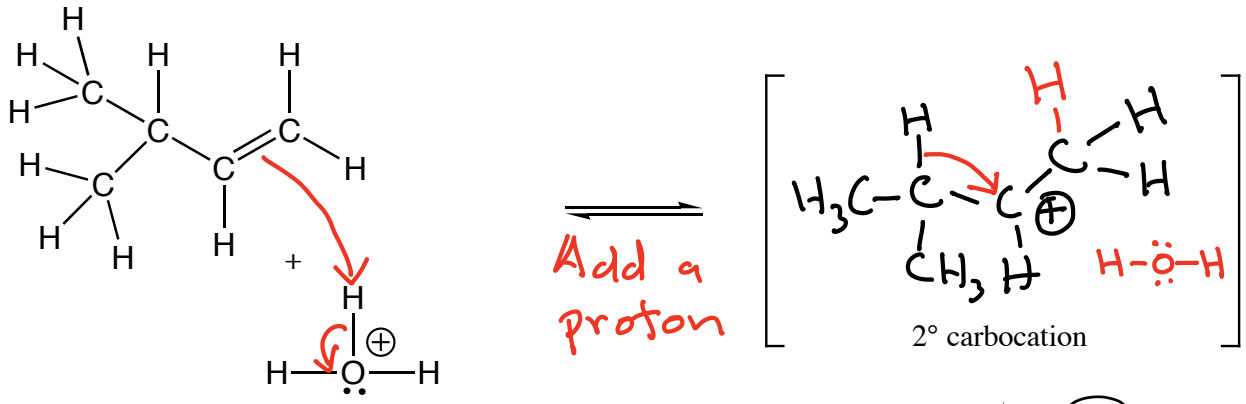
Example:



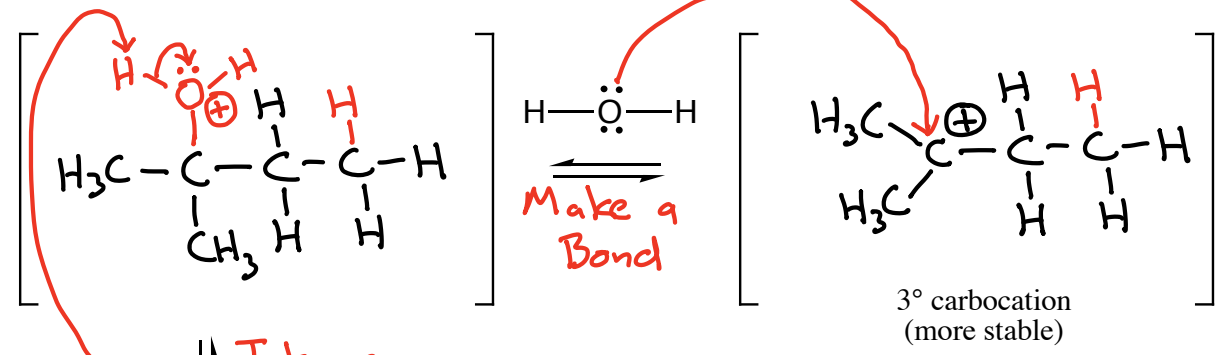
-OH on more substituted C atom ⇒ Markovnikov's Rule

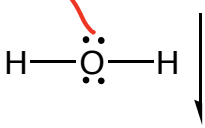
Cation Rearrangement

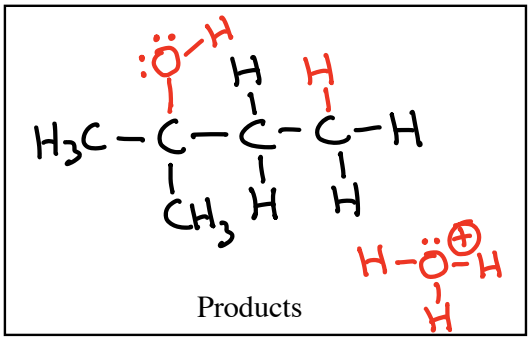


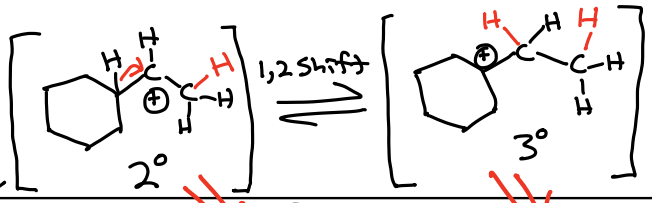


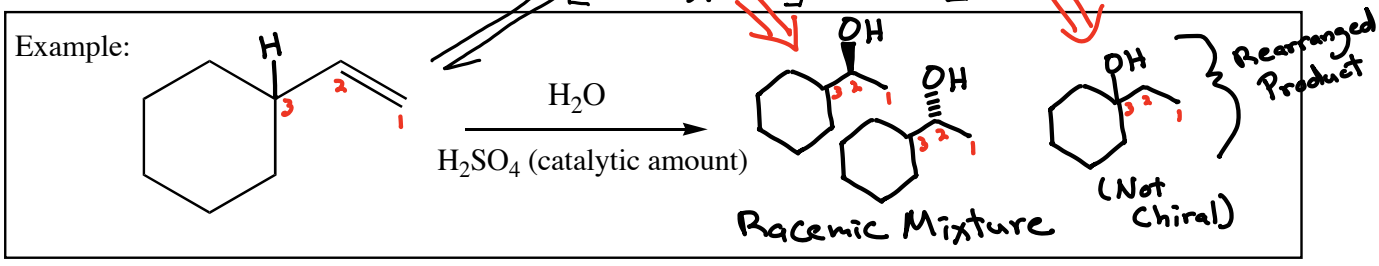
Rearrangement



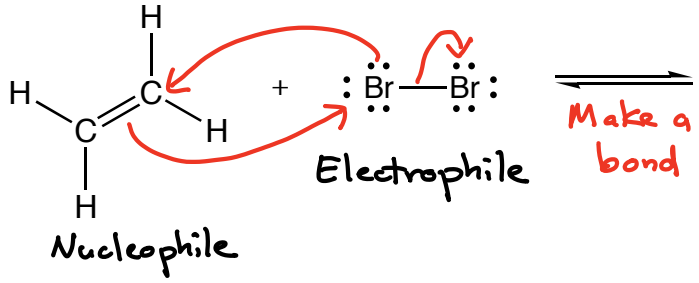


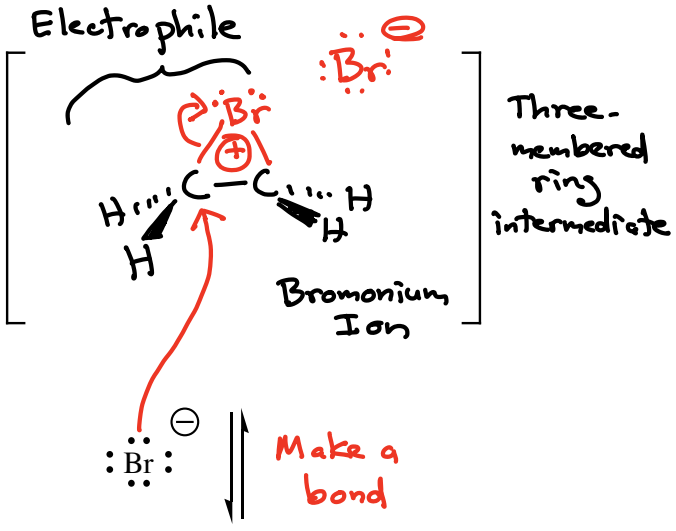






Alkene Halogenation

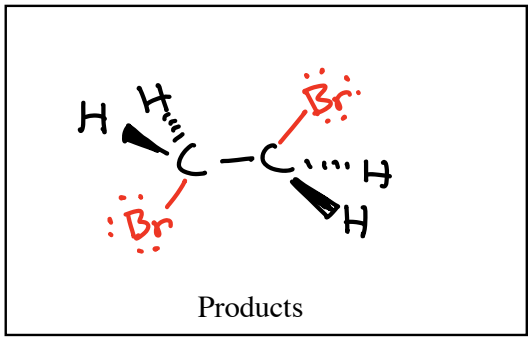




Called "anti" addition stereochemistry

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"

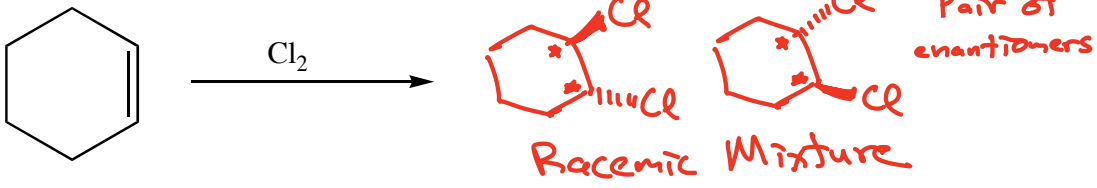


Summary: Alkenes react with X_2 to give a three-membered ring intermediate, then a new bond is made by $X^{\ominus}$ reacting from behind the C–X bond of the intermediate.

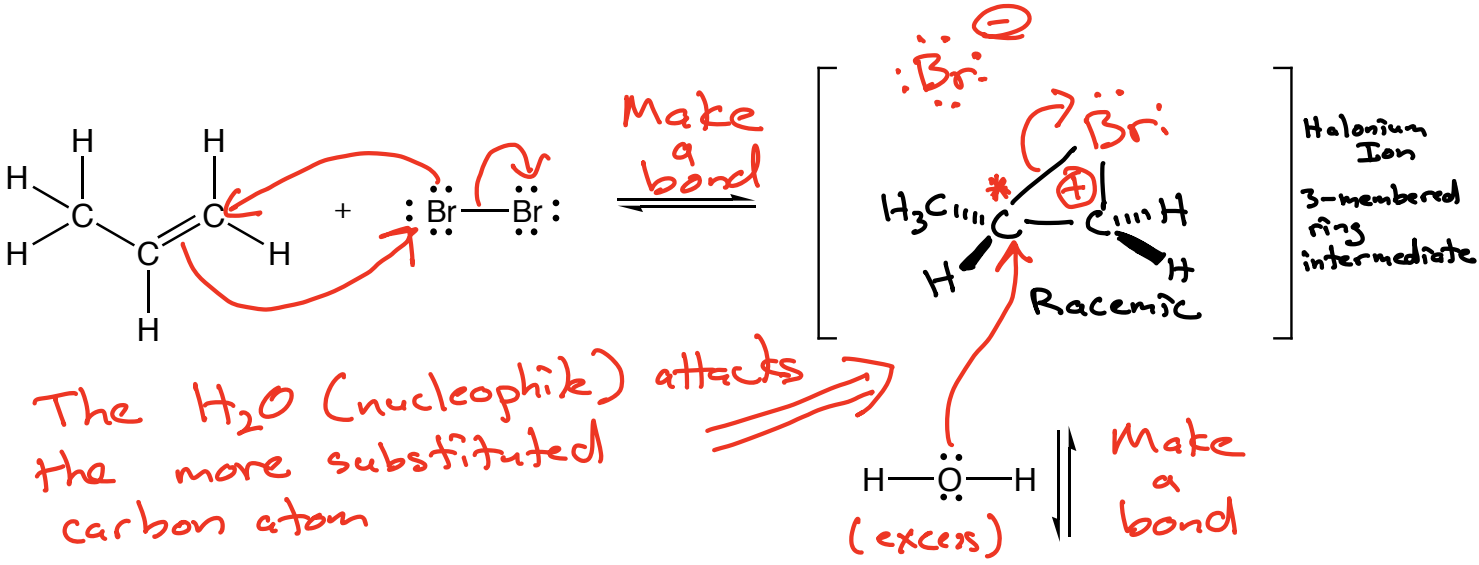
Regiochemistry: Not applicable → Br is on both atoms

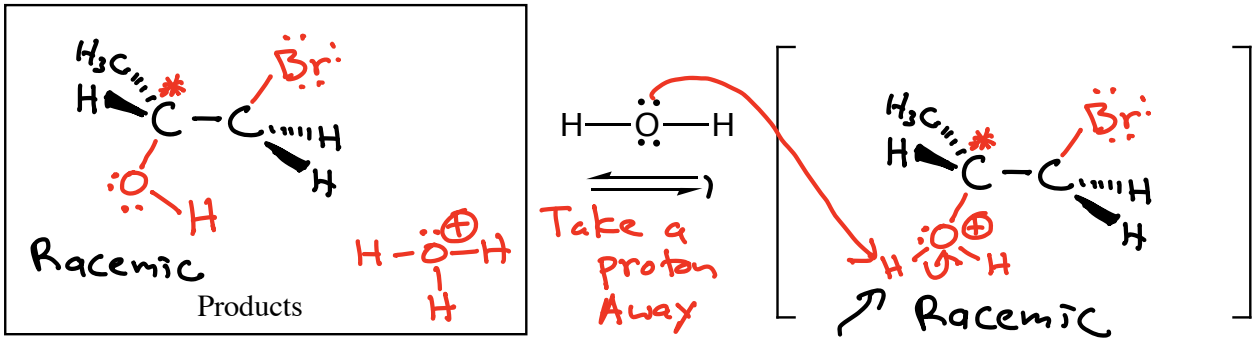
Stereochemistry: Anti addition geometry → trans products

Example:



Alkene Hydrohalogenation





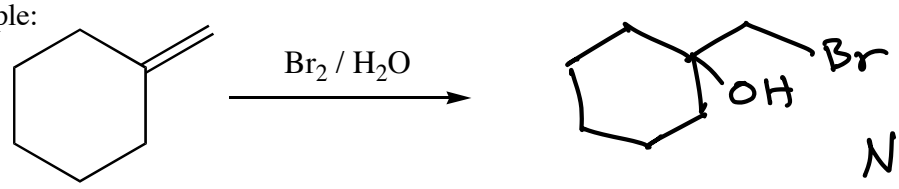
pH drops during the reaction!

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

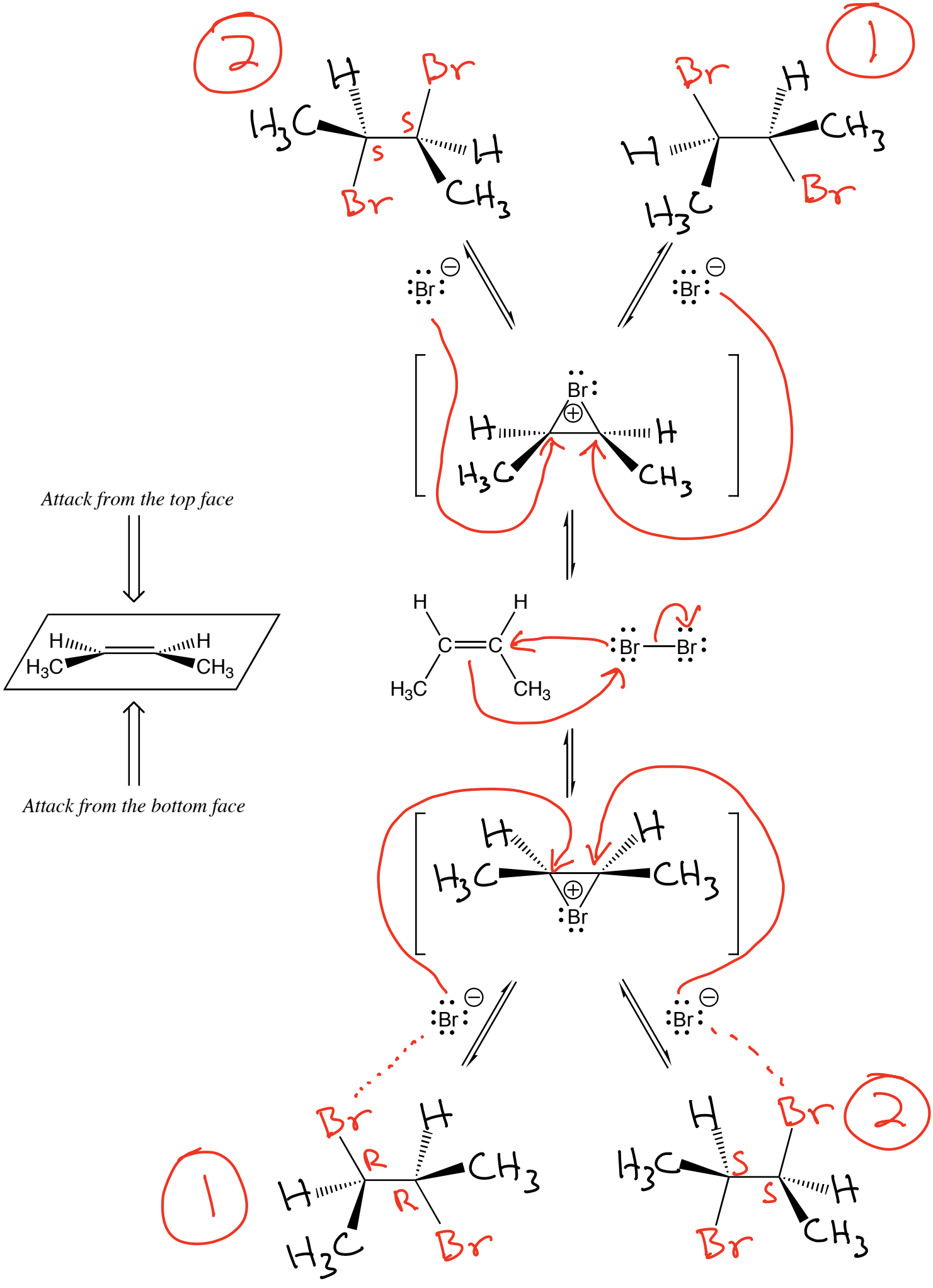
Regiochemistry: Markovnikov (OH on more substituted C atom)

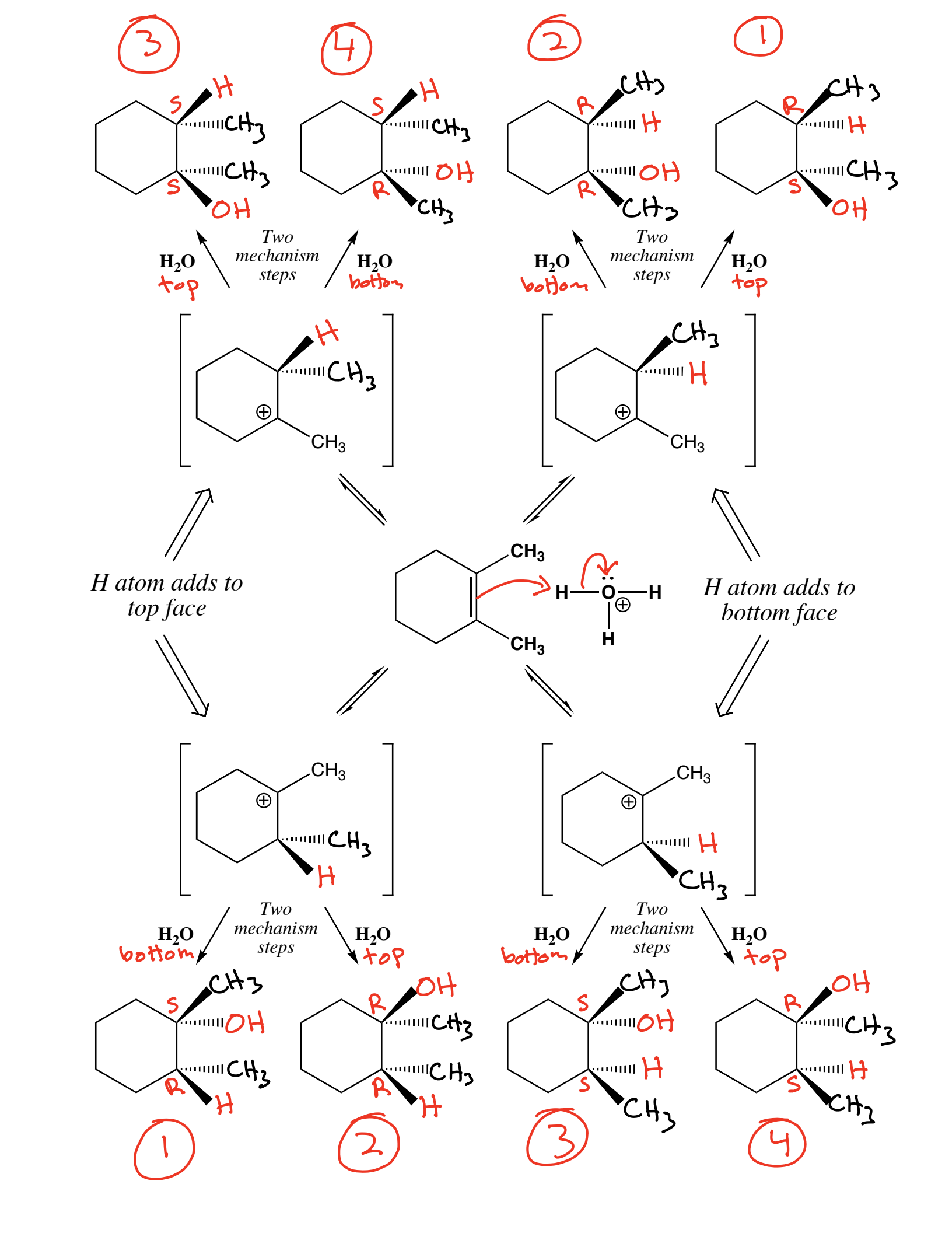
Stereochemistry: Anti

Example:

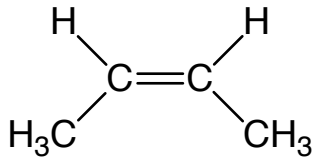


Not Chiral

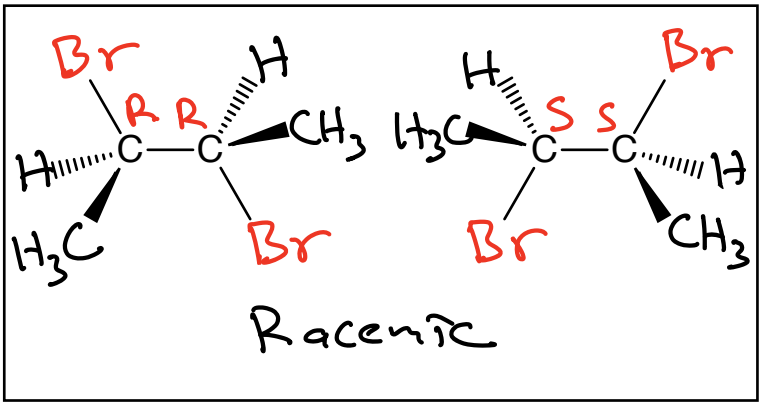

2
1
Attack from the top face
Attack from the bottom face
1
2


3
4
2
1
S
H
CH3
OH
R
Two mechanism steps
H2O top
H2O bottom
H2O bottom
H2O top
H atom adds to top face
H atom adds to bottom face
CH3
H
O
Two mechanism steps
H2O bottom
H2O top
H2O bottom
H2O top
1
2
3
4

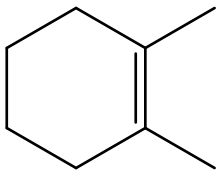
Examples

1) 

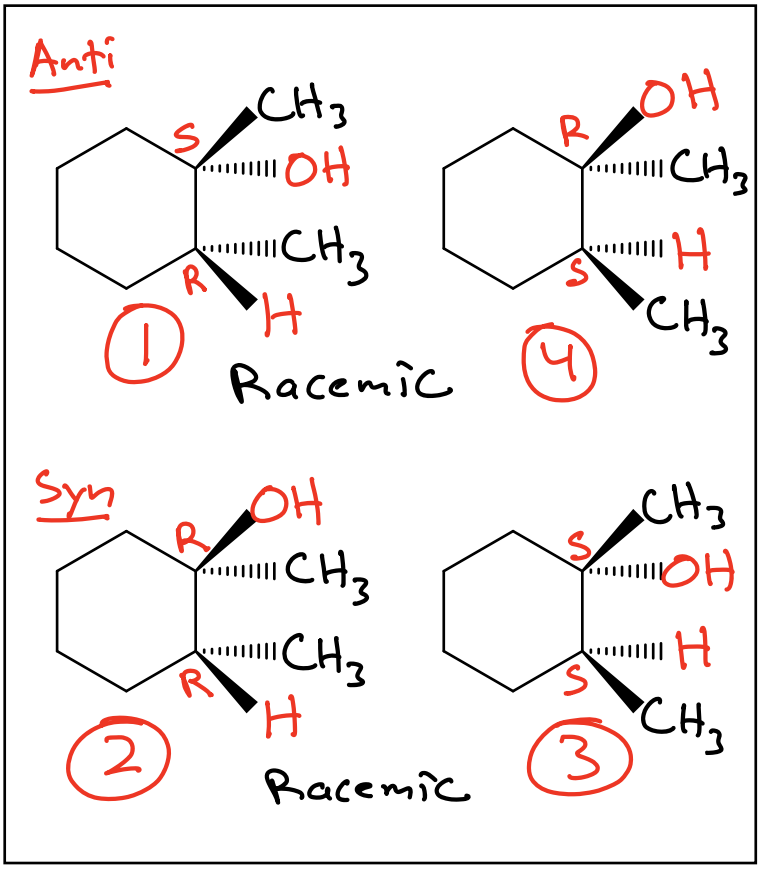
$\xrightarrow{Br_2}$



⇒ Anti

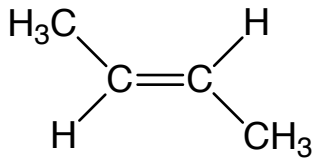
2) 

$\xrightarrow[H_2SO_4\ (catalytic)]{H_2O}$

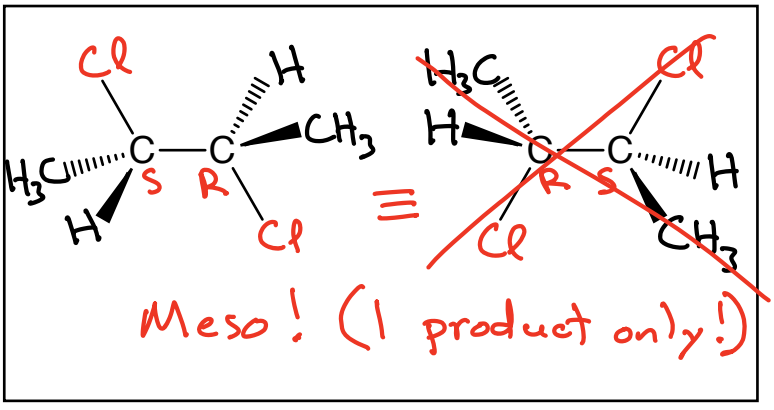


⇒ Mixed → Anti and Syn

⇒ Markovnikov

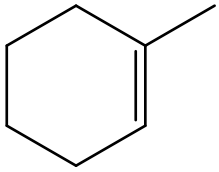
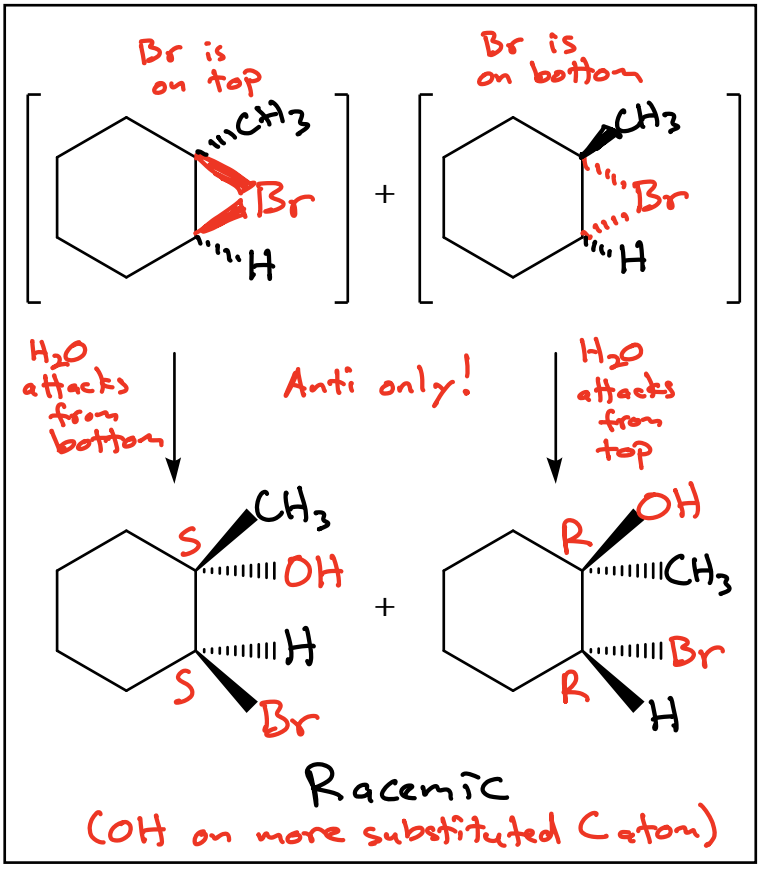
3) 

$\xrightarrow{Cl_2}$



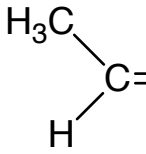
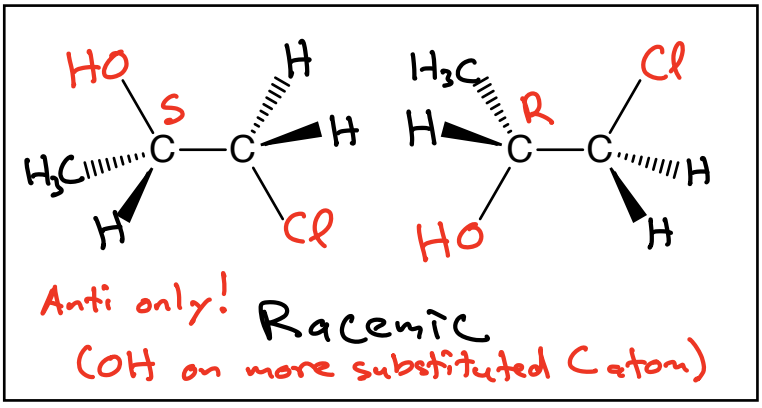
⇒ Anti

More Examples

4)  $\xrightarrow[H_2O]{Br_2}$ 

⇒ Anti

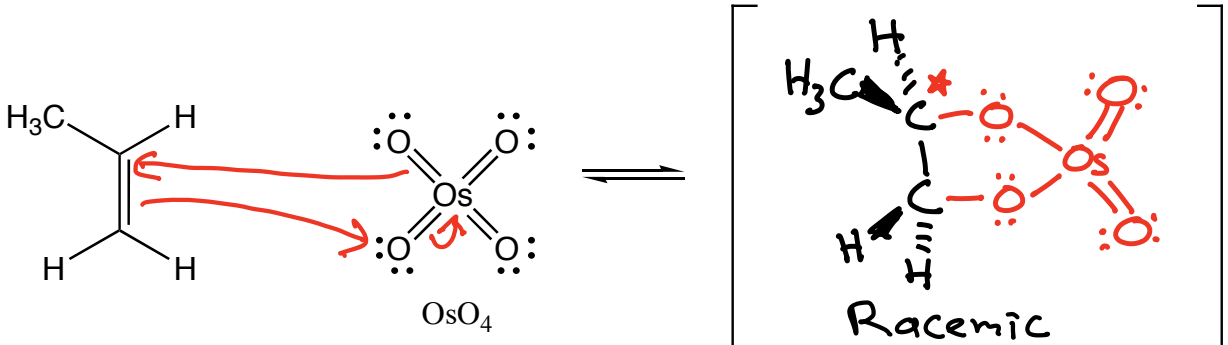
⇒ Markounikou

5)  $\xrightarrow[H_2O]{Cl_2}$ 

⇒ Anti

⇒ Markounikou

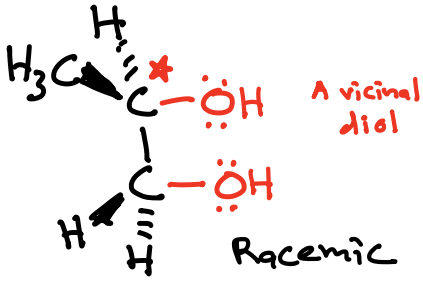
OsO_4 *Partial Mechanism*



A cyclic osmate ester

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

Not responsible for mechanism



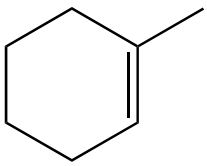
Product

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

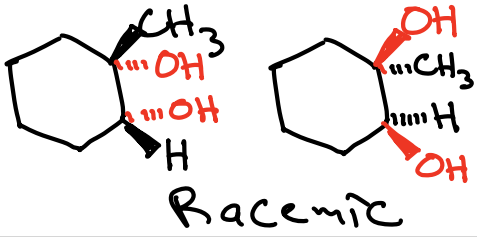
Regiochemistry: N/A

Stereochemistry: Syn

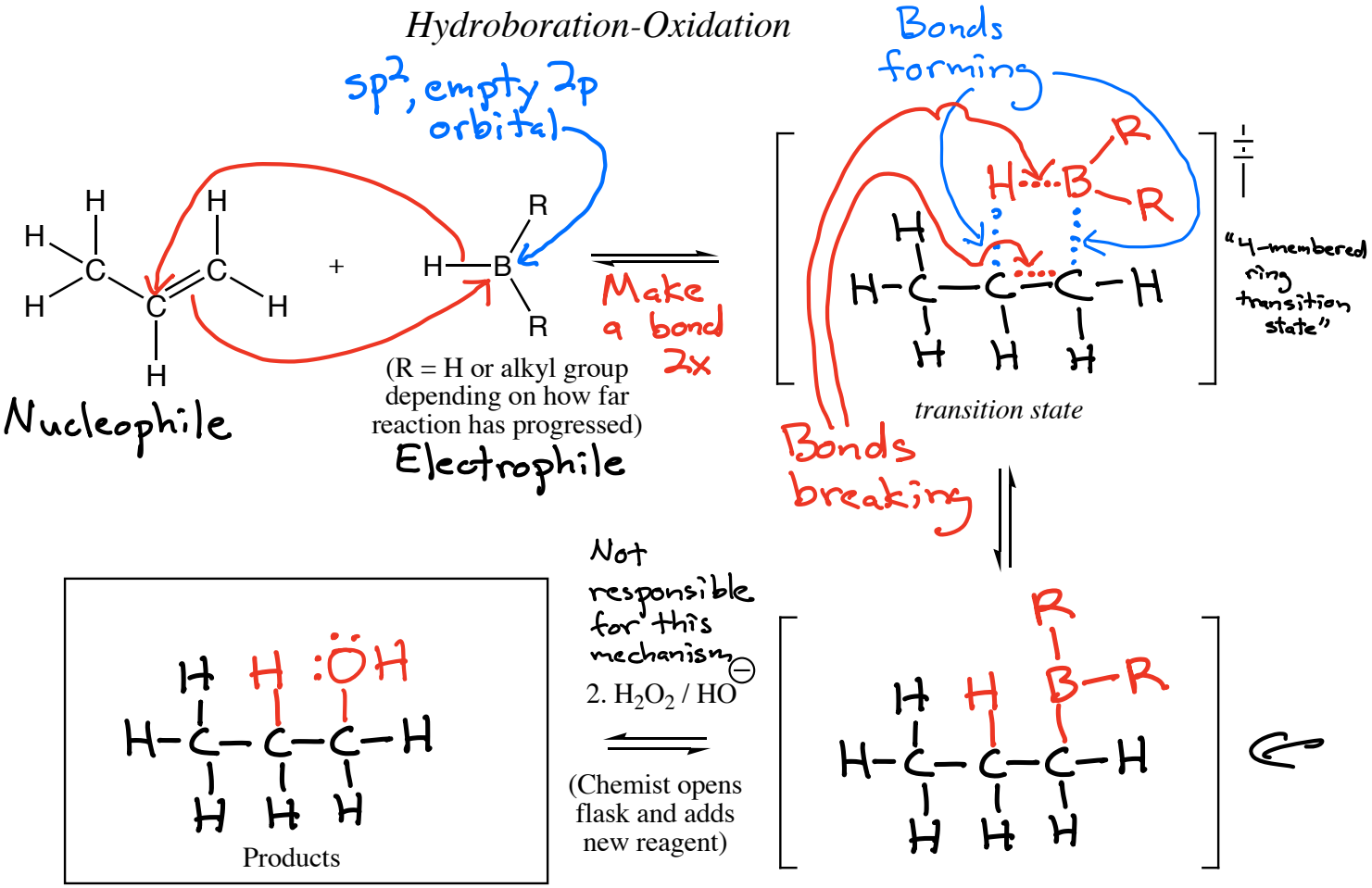
Example:



1. OsO_4
2. $NaHSO_3$ / H_2O



Hydroboration-Oxidation



H → More substituted C atom
OH → Less substituted C atom
} Steric strain in the first transition state

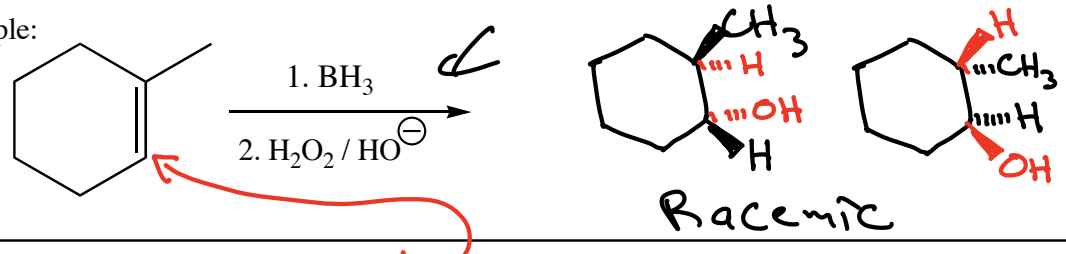
H and OH are syn

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 B(R)2. "4-membered ring transition state"

Regiochemistry: Non-Markovnikov

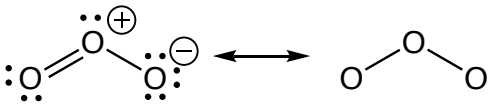
Stereochemistry: Syn

Example:

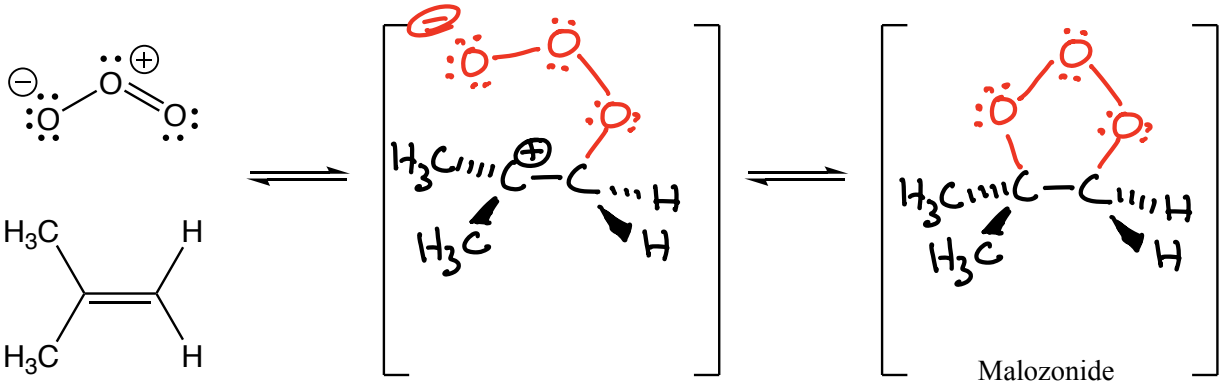


This reaction breaks a C=C bond!

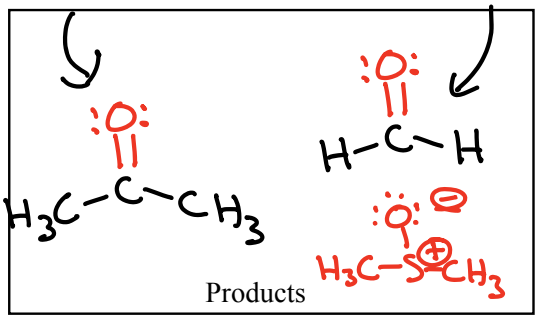
Ozonolysis Partial Mechanism



Ozone contributing structures



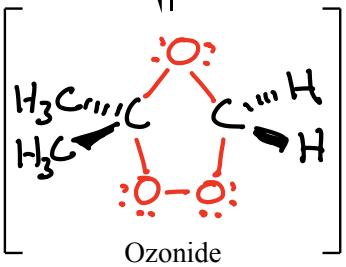
Ketone Aldehyde



Rearrangement in two steps

2. $(CH_3)_2S$

(Chemist opens up flask)

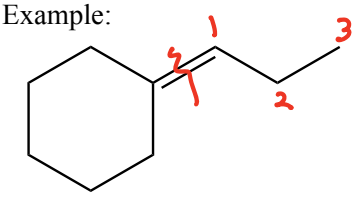


Summary: Reaction of an alkene with O_3 gives a malozonide than an ozonide intermediate (the C=C pi bond then C–C sigma bond is broken). Adding $(CH_3)_2S$ decomposes the ozonide into ketone and aldehyde products. Breaks C=C bond!

Regiochemistry: N/A

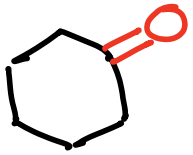
Stereochemistry: N/A

Example:

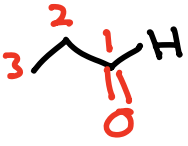


1. O_3

2. $(CH_3)_2S$

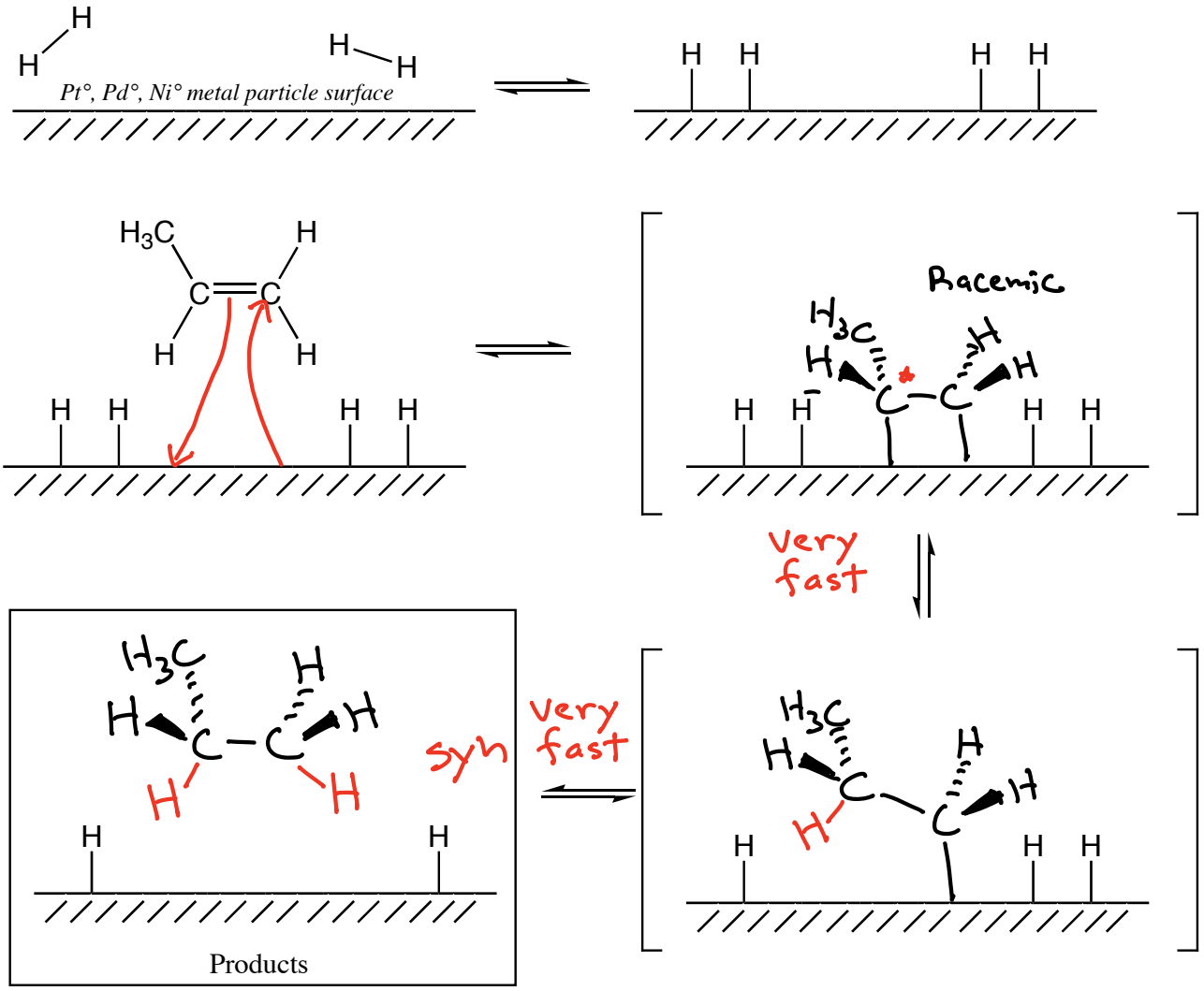


A ketone



An aldehyde

Hydrogenation: H_2 with Pt°, Pd°, Ni°

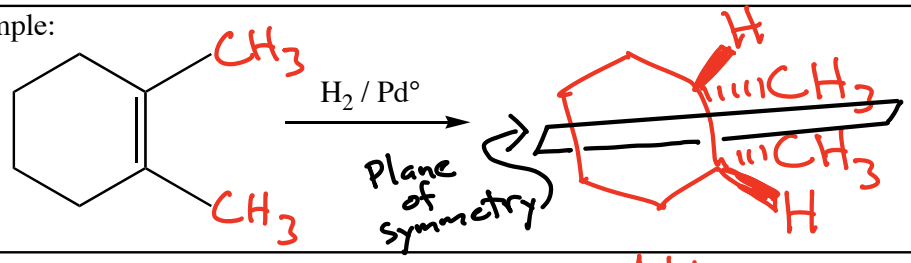


Summary: H_2 adsorbs onto the metal surface. The alkene adsorbs onto the metal surface. H atoms transfer to both C atoms → on the same face → before the C-C bond rotates

Regiochemistry: N/A

Stereochemistry: Syn

Example:



Alkene Alkane

Who do you call when you need help?

When studying OChem → Call a NIRRS

Learn each of these things for every reaction → then you will be able to predict mechanisms and therefore products

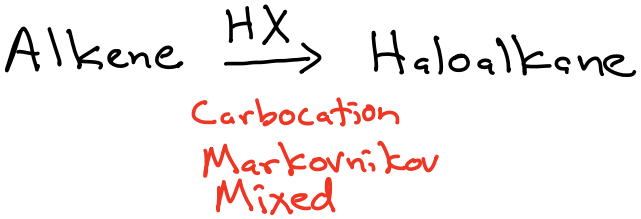
Nature of the reaction; what is the starting material/product? (i.e. alkene converted to an alcohol)

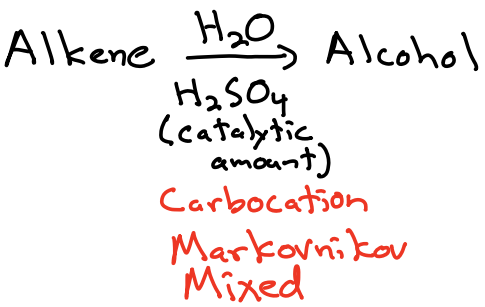
Intermediate (or "**I**mportant transition state" if applicable) of the reaction, the key to the mechanism (carbocation, halonium ion, etc.)

Reagents Learn the exact way to designate the reagents for each reaction

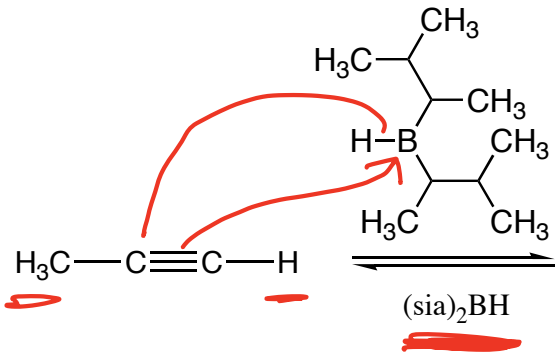
Regiochemistry What is the regiochemistry of addition? (Markovnikov, non-Markovinikov, etc.)

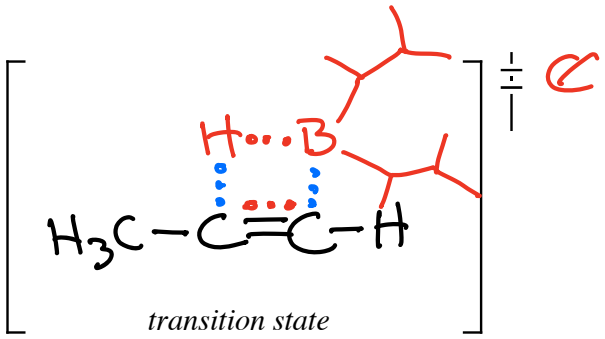
Stereochemistry of addition (anti, syn or mixed)

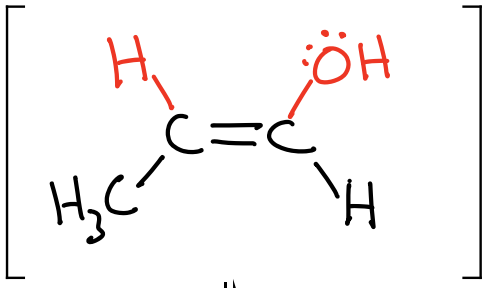




Terminal Alkyne Hydroboration

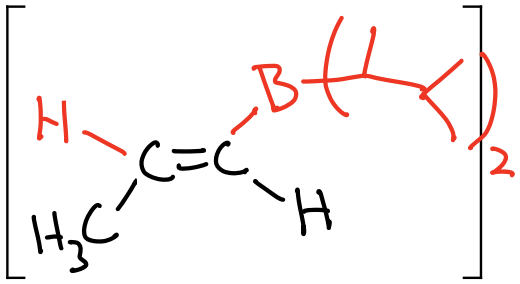




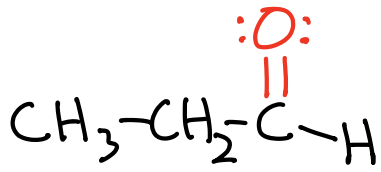


2. H_2O_2 / $HO^{\ominus}$

(Chemist opens flask and adds new reagent)



Keto-enol tautomerization



Products

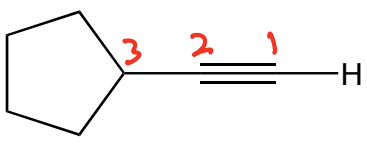
⇐ The C=O is on the C on the end → "non-Markovnikov"

Summary: The $(sia)_2BH$ reacts so the B atom attaches to the C atom on the end. The four-membered ring transition state makes both bonds simultaneously. 2. $H_2O_2/HO^{\ominus}$ → enol → keto

Regiochemistry: non-Markovnikov

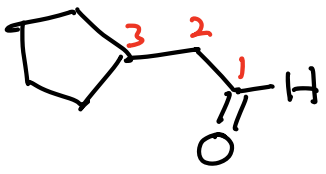
Stereochemistry: N/A

Example:

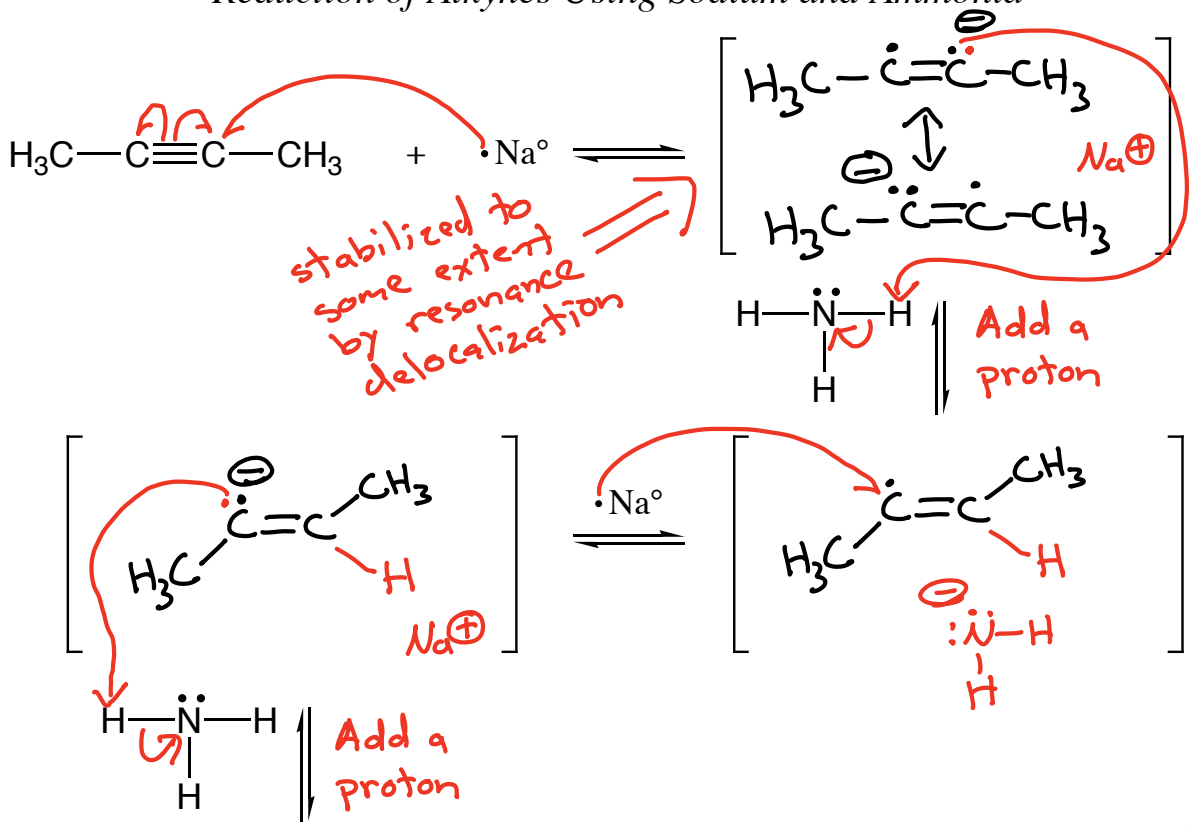


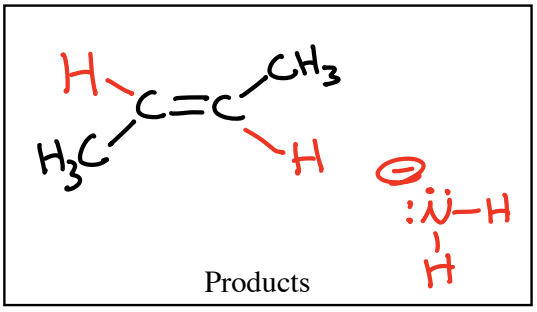
1. $(sia)_2BH$

2. H_2O_2 / $HO^{\ominus}$



Reduction of Alkynes Using Sodium and Ammonia





This reaction makes the more stable E alkene

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

Regiochemistry: N/A

Stereochemistry: Anti → E products

Example: