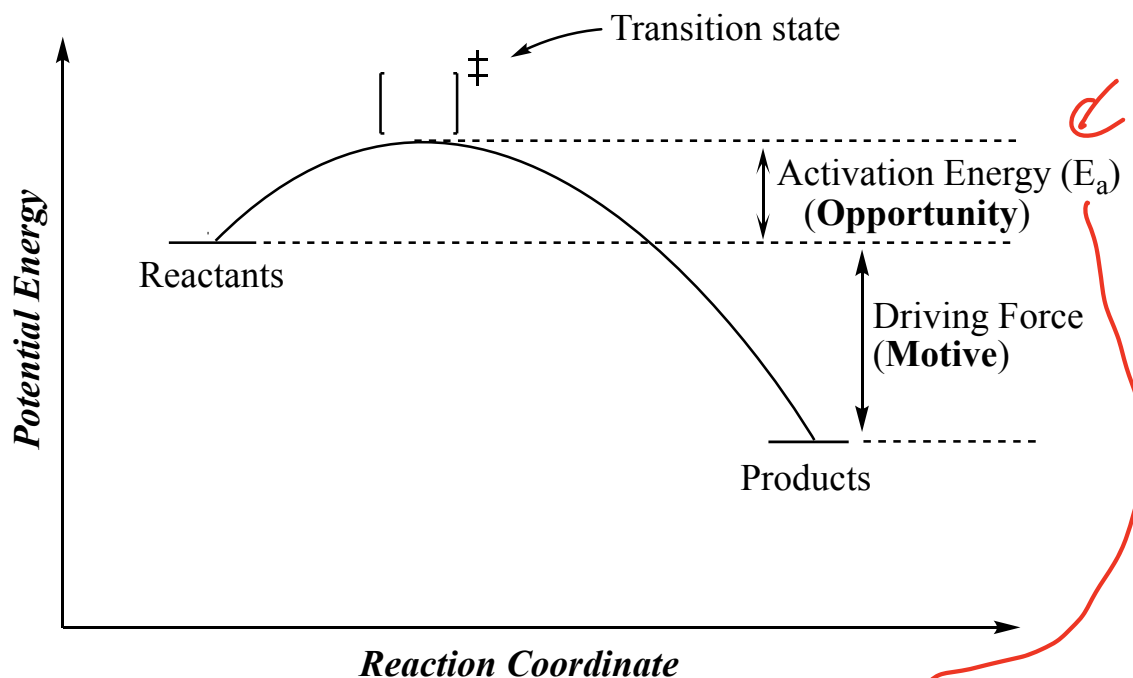
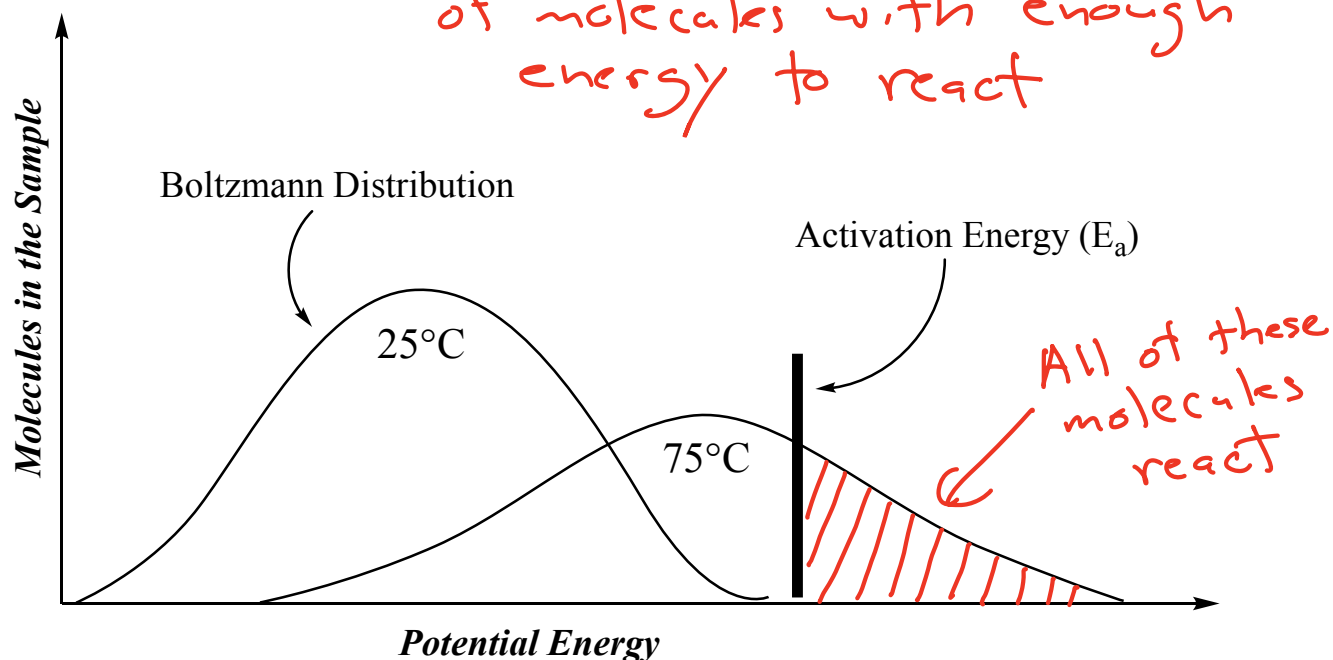
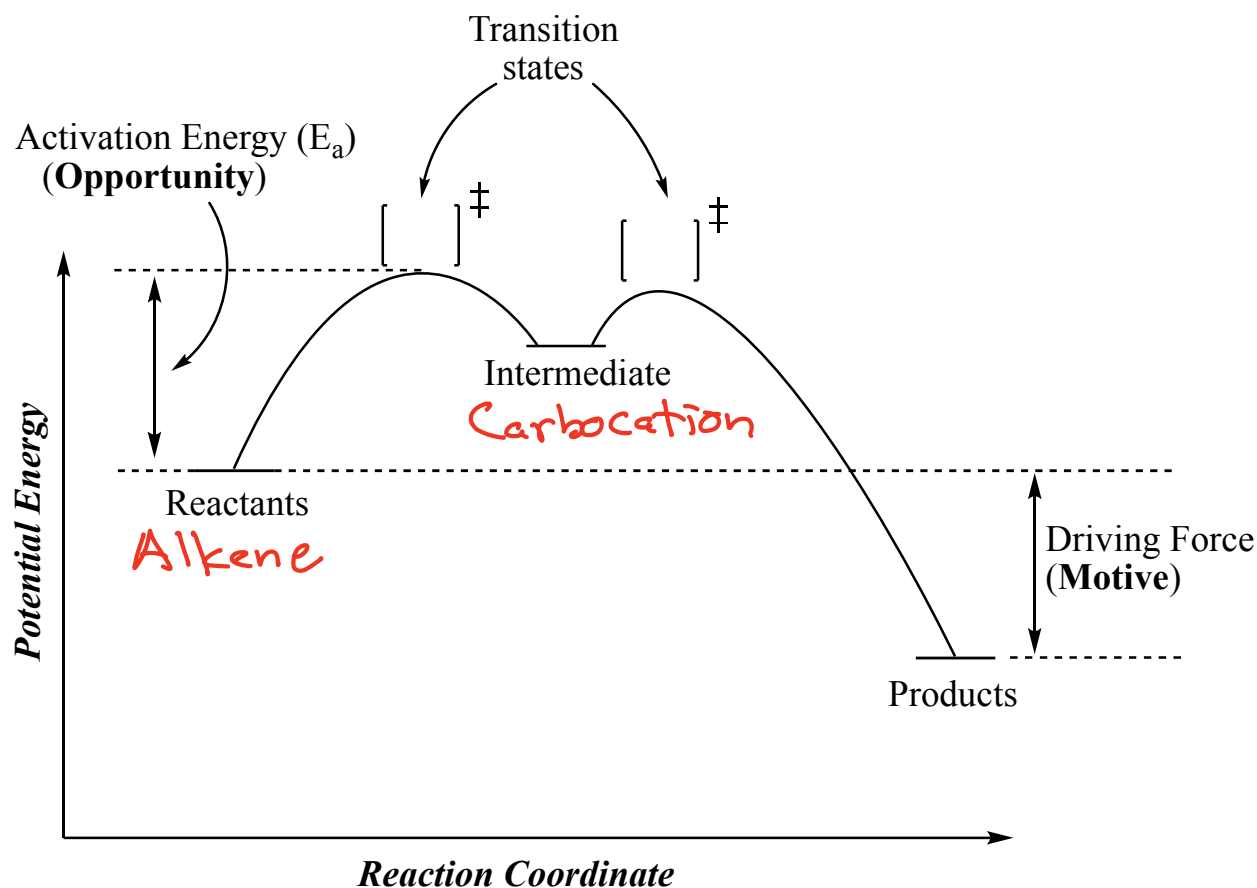




$$k = \text{reaction rate} = Ae^{-E_a/RT}$$

Increasing Temperature $\rightarrow$ increases the number of molecules with enough energy to react





During reactions we often encounter intermediates $\rightarrow$ relatively high energy species that are formed between reactants and products

When alkenes react with $H-X \rightarrow$ carbocation intermediate

The 4 Most Important Mechanistic Elements

The following are expressed from the point of view of the carbon-containing molecule taking part in a reaction

- 1) **Make a bond** between a nucleophile and electrophile.
⇒ A nucleophile and electrophile are both present and a bond can be made.
- 2) **Break a bond** to give stable molecules or ions.
⇒ None of the other possibilities are likely and the fragments produced are relatively stable
- 3) **Add a proton**
⇒ Acid is present or the molecule is a strong base.
- 4) **Take a proton away**
⇒ Base is present or the molecule is a strong acid.

Notice → 1) is the reverse of 2) and
3) is the reverse of 4) and vice versa

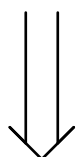
Mechanism Summary

The following questions and mechanistic elements are described from the point of view of the carbon-containing reagent, written in the form of a flowchart.

Is there a strong acid present or is the carbon-containing reagent a strong base?

YES
⇒

Add a proton

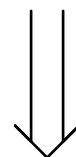


NO

Is there a strong base present or is the carbon-containing reagent a strong acid?

YES
⇒

Take a proton away

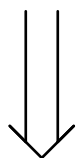


NO

Are there a nucleophile and electrophile present?

YES
⇒

Make a bond

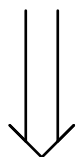


NO

Can a bond be broken to create stable molecules or ions?

YES
⇒

Break a bond

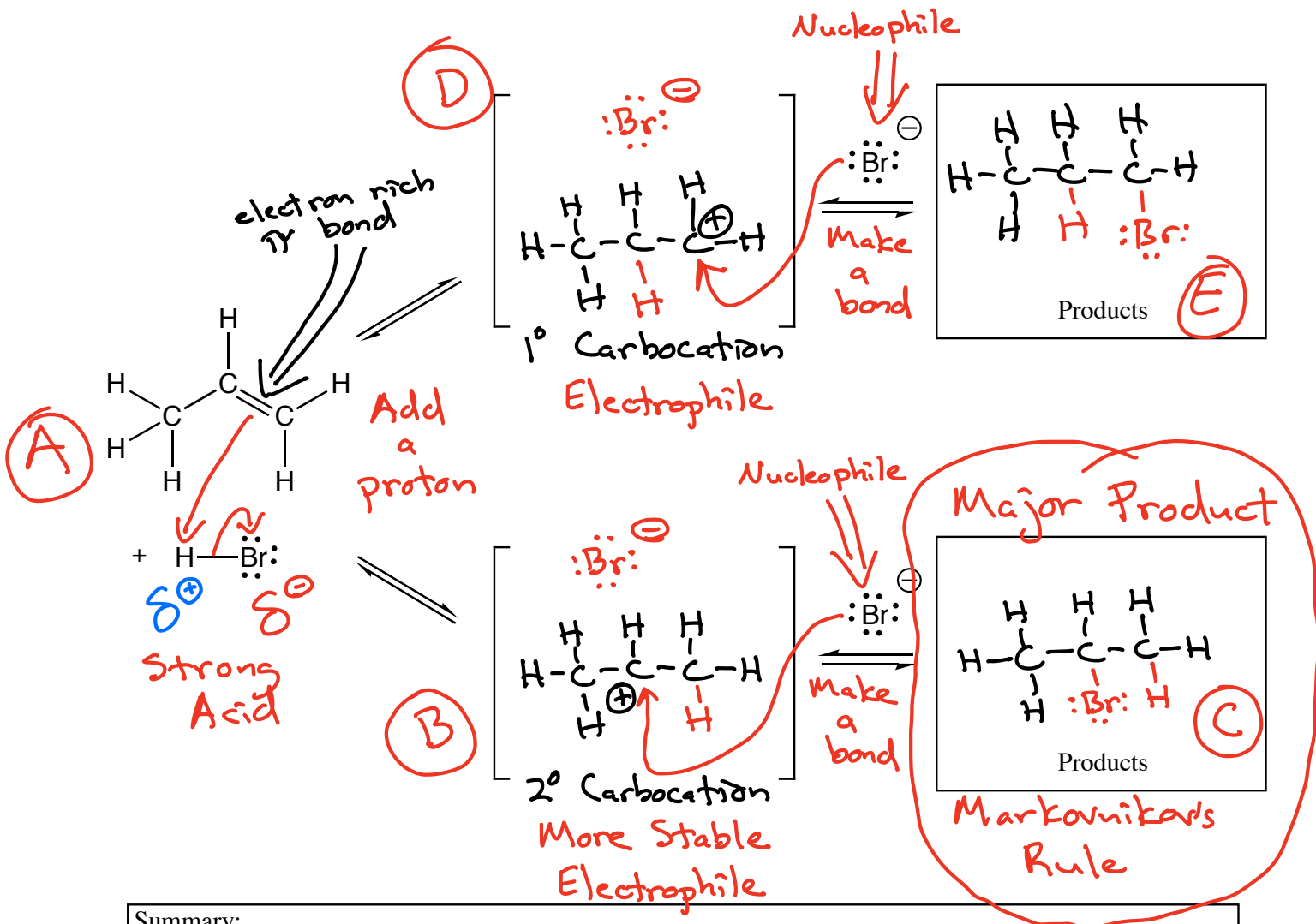


NO

Think about alternative mechanistic elements

Addition of H-X to an Alkene

X = Cl, Br, I
but not F



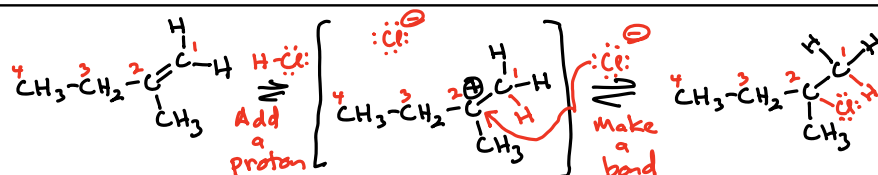
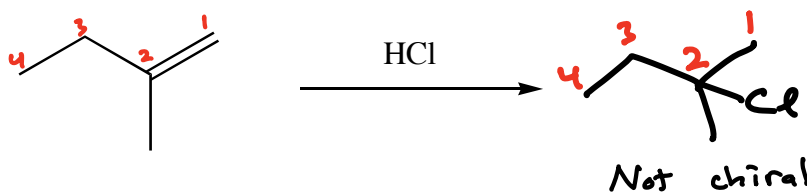
Summary:

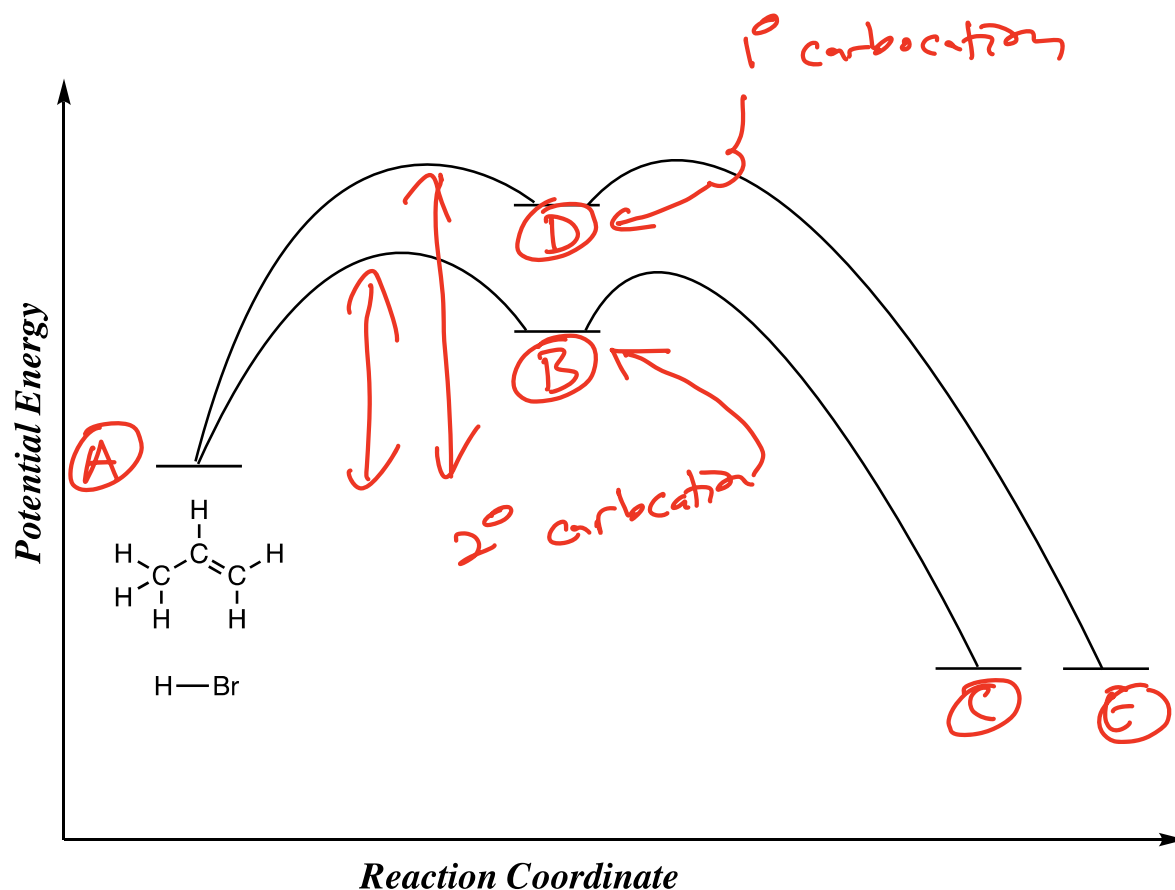
The alkene π bond reacts with H-X to add a proton to create a carbocation intermediate that makes a bond with X^- to give the product

Regiochemistry: **Markovnikov's Rule**

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

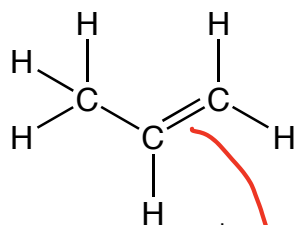
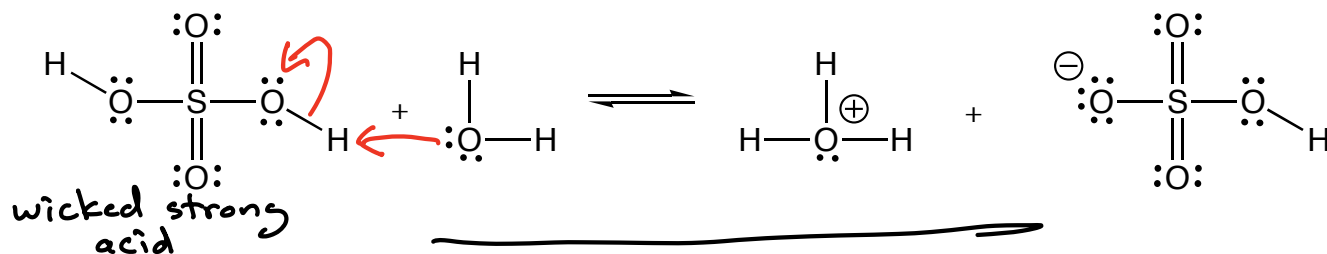
Example:



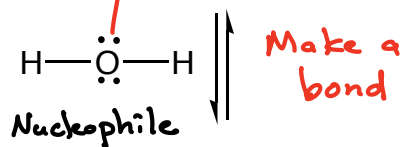
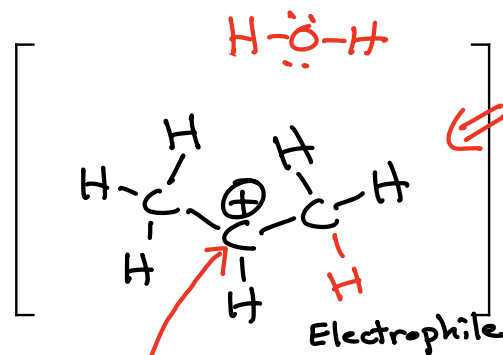


Creation of **B** has a lower energy barrier and it forms faster → We get more **C** product

Acid-catalyzed Hydration of an Alkene

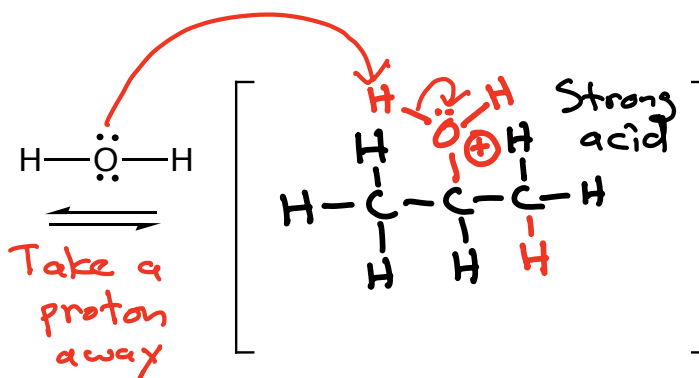
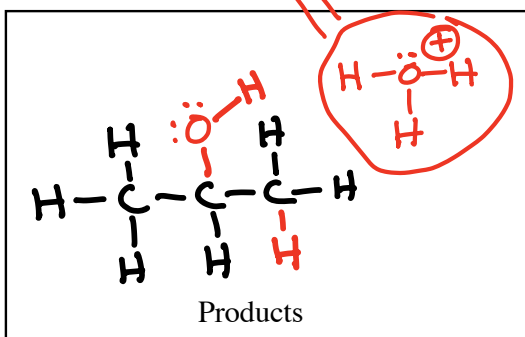


Add a proton



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

strong acid



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^+

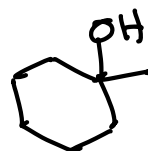
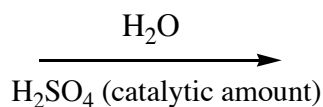
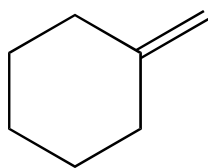
Regiochemistry:

Markovnikov's Rule

Stereochemistry:

Mixed (time capsule)

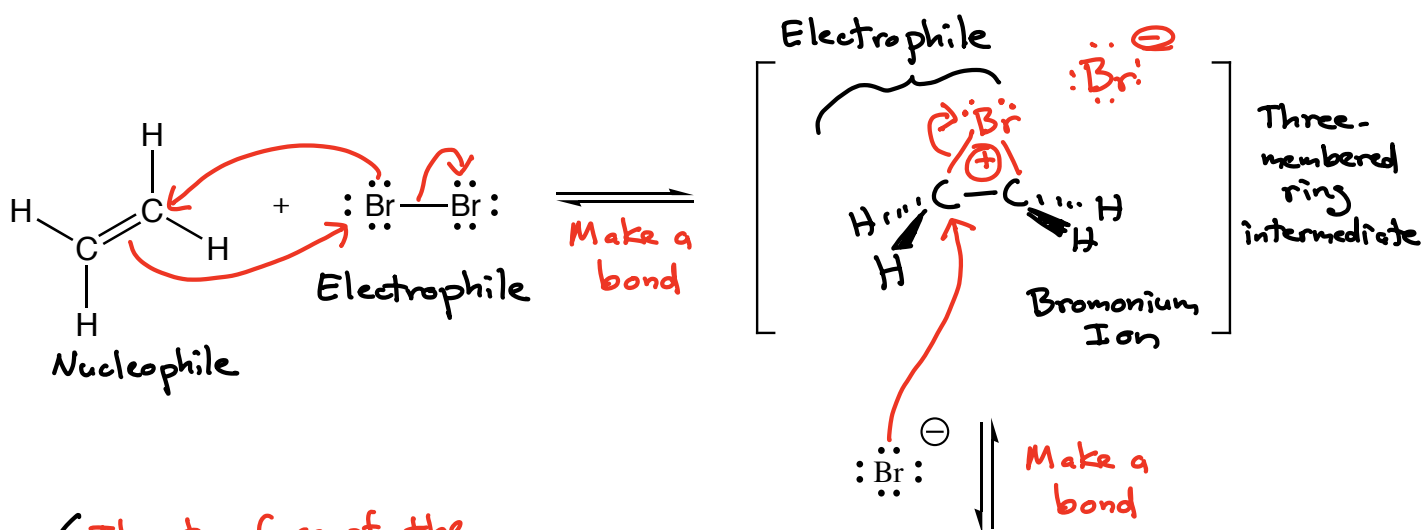
Example:



(Not chiral)

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

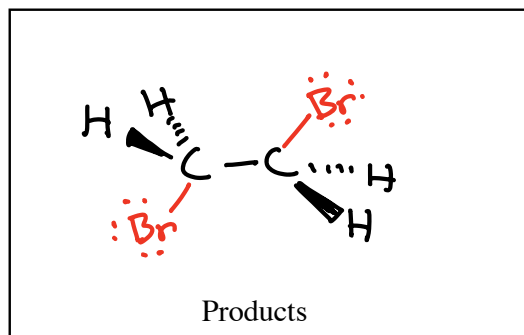
Alkene Halogenation



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"

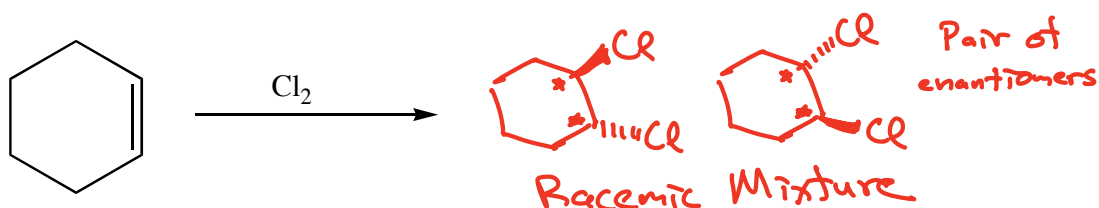


Summary: Alkenes react with X_2 to give a three-membered ring intermediate, then a new bond is made by X^- reacting from behind the C-X bond of the intermediate.

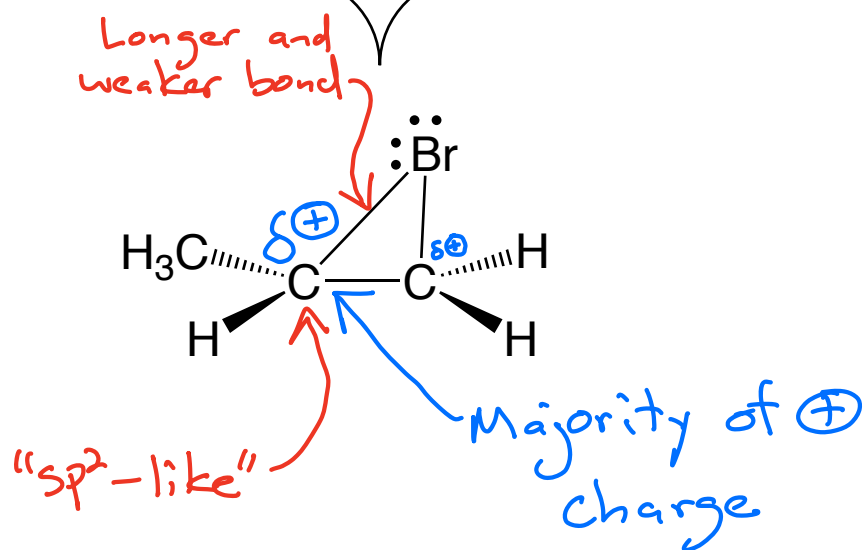
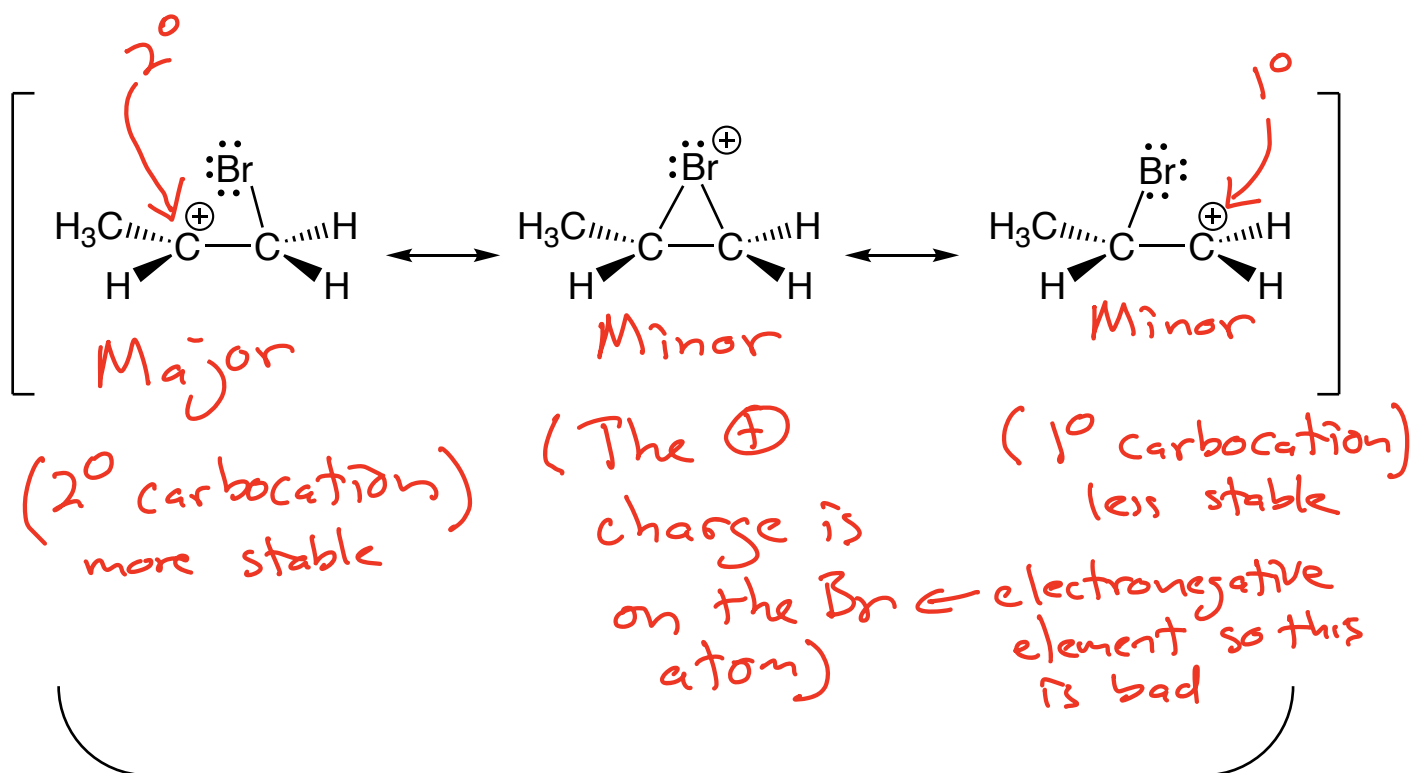
Regiochemistry: Not applicable → Br is on both atoms

Stereochemistry: Anti addition geometry → trans products

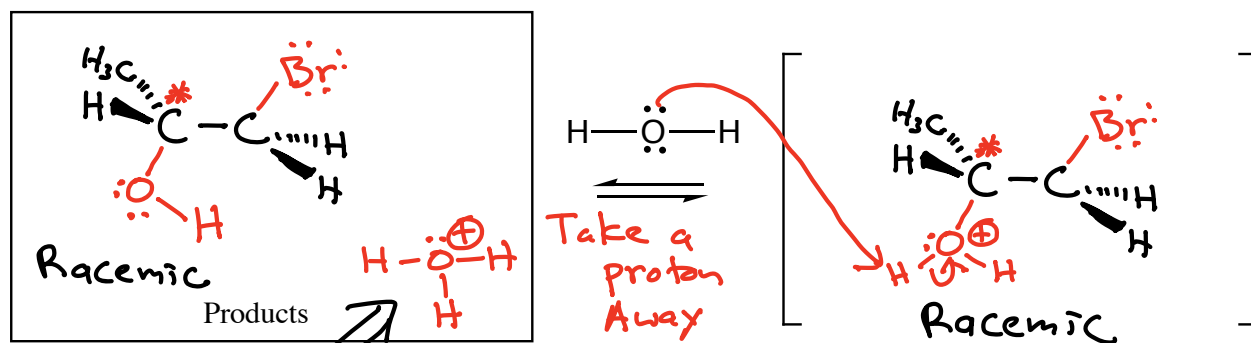
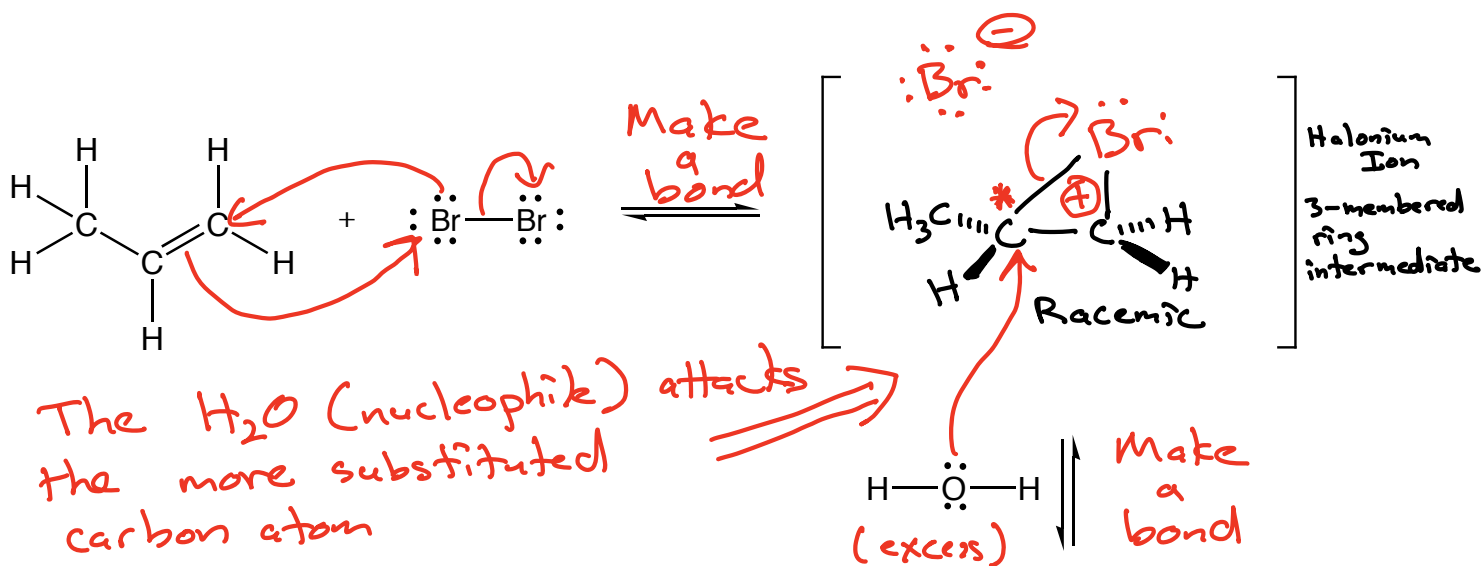
Example:



How to think about unsymmetrical halonium ions



Alkene Hydrohalogenation



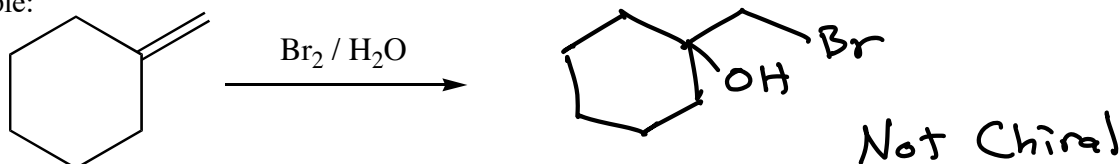
pH drops during the reaction!

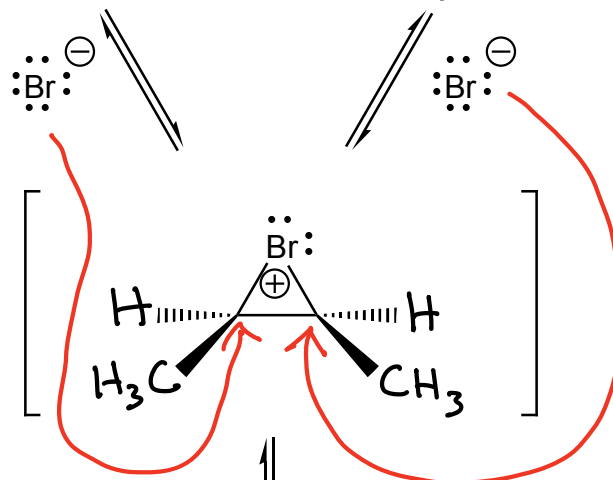
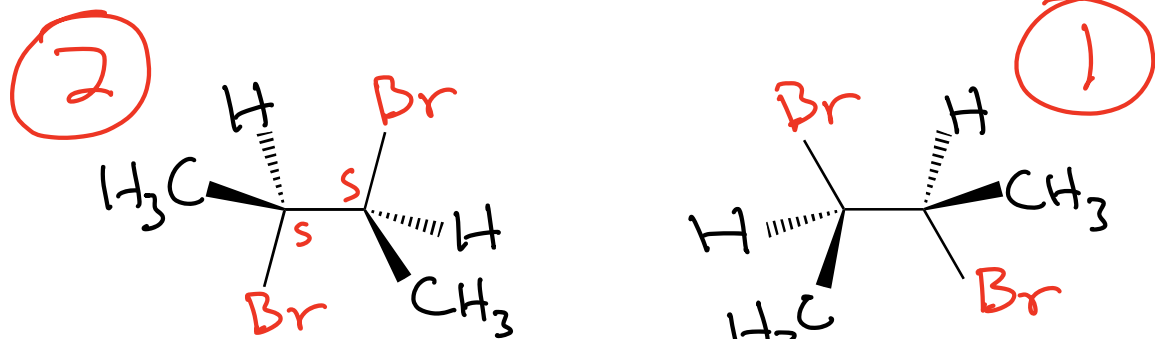
Summary: Alkene reacts with X_2 to give a 3-membered ring intermediate (halonium ion) $\rightarrow$ H_2O attacks the more substituted C atom and we take a proton away to give the halohydrin product.

Regiochemistry: Markovnikov (OH on more substituted C atom)

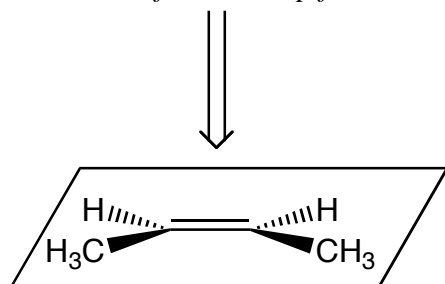
Stereochemistry: Anti

Example:

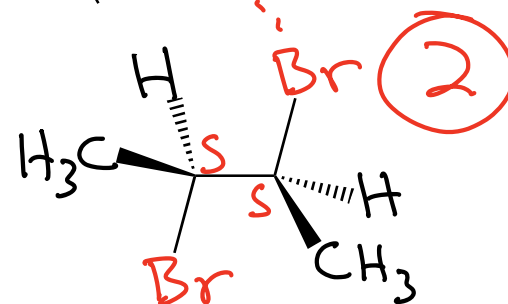
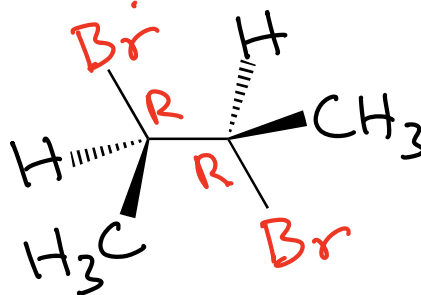
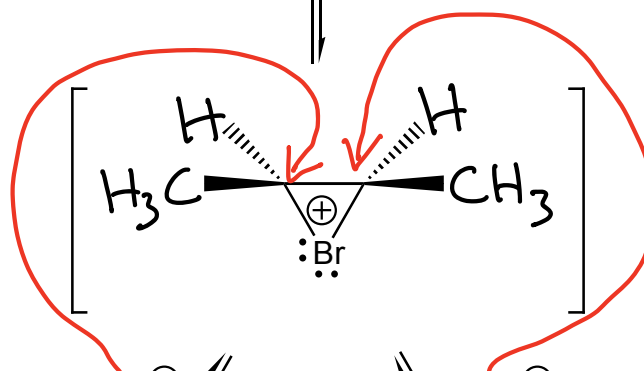
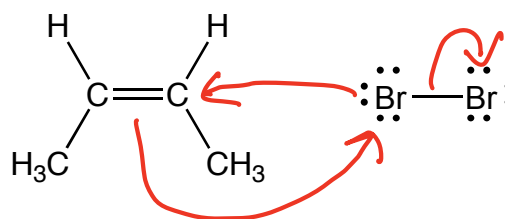


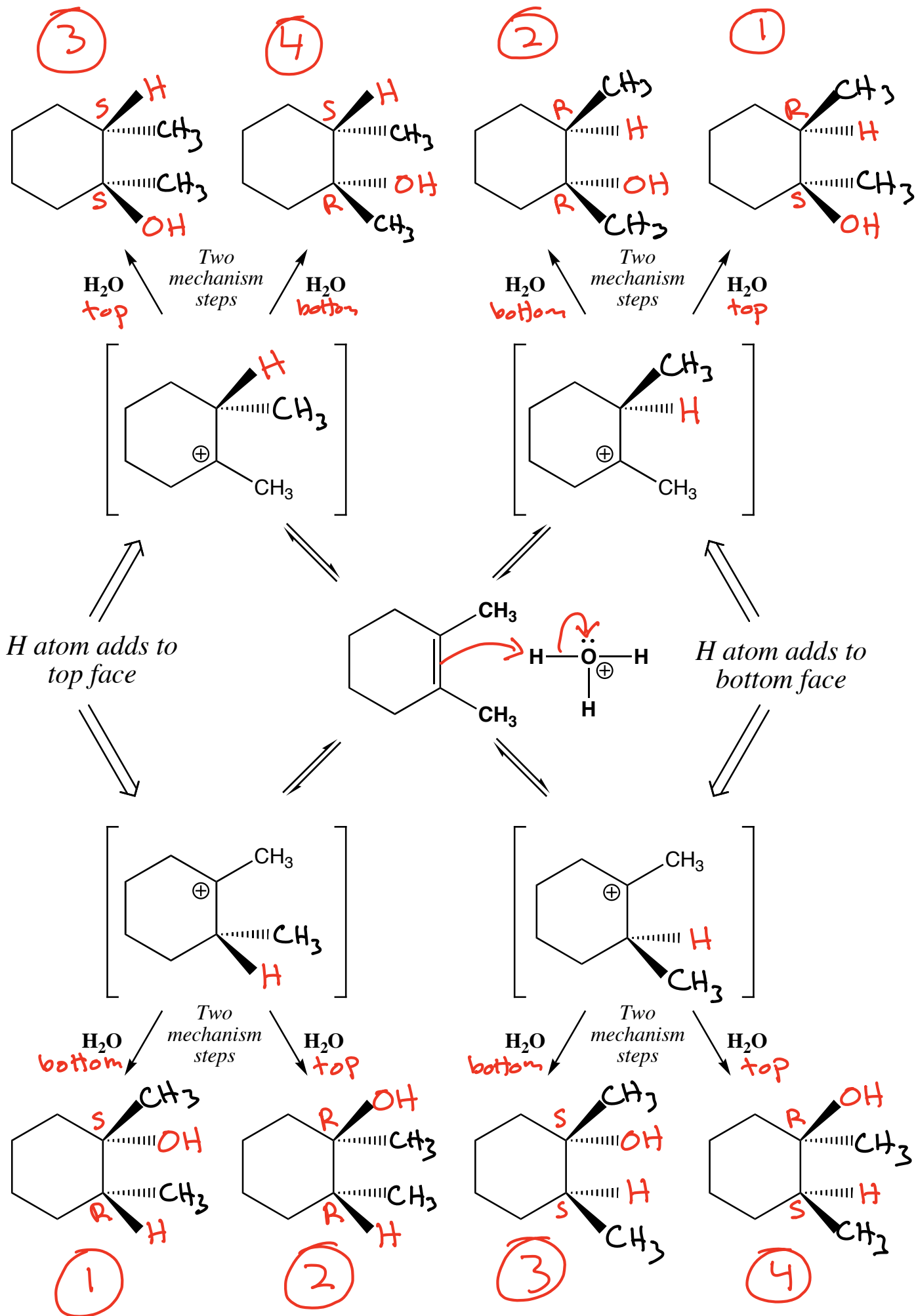


Attack from the top face

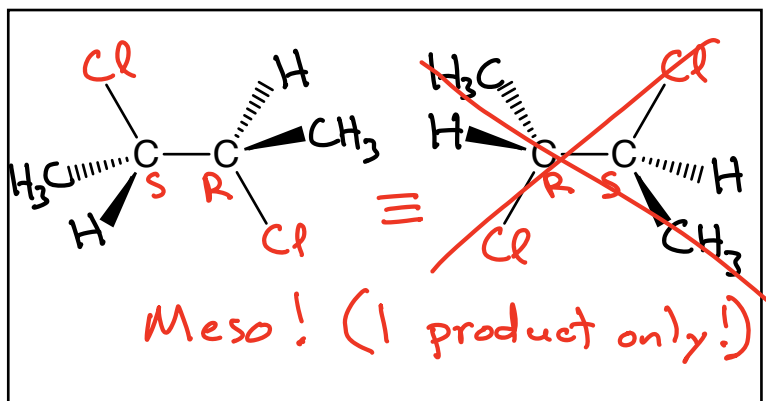
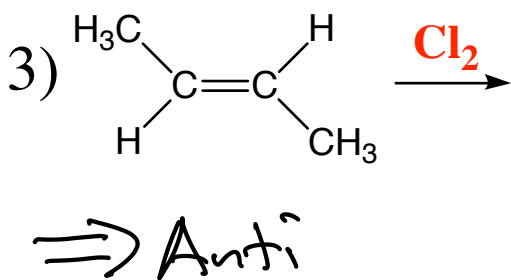
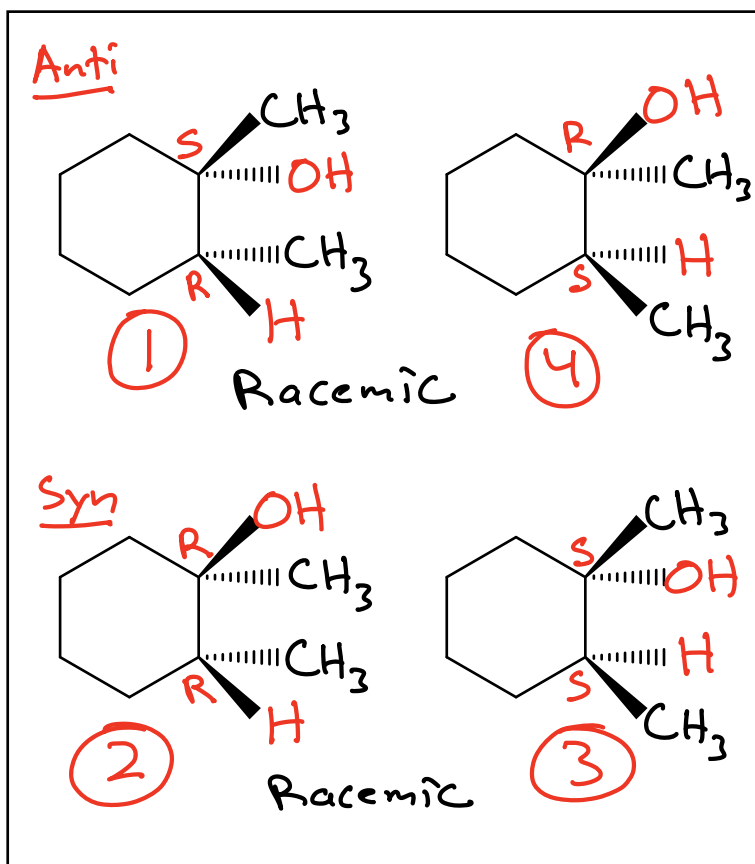
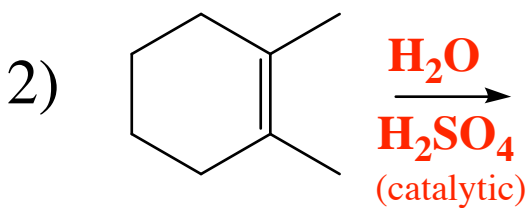
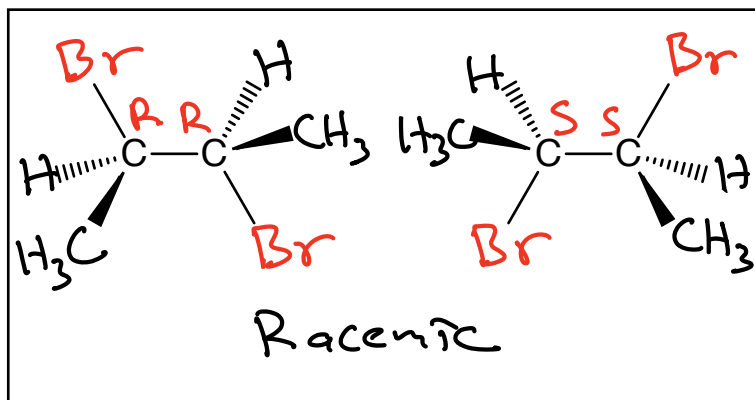
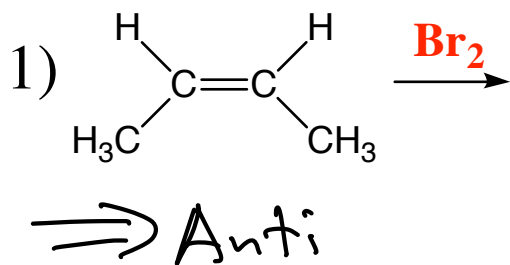


Attack from the bottom face

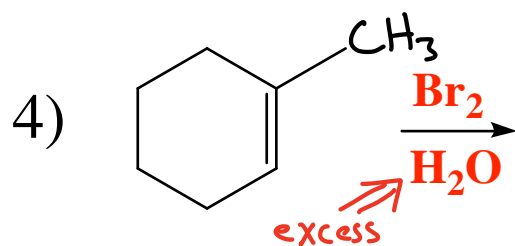




Examples

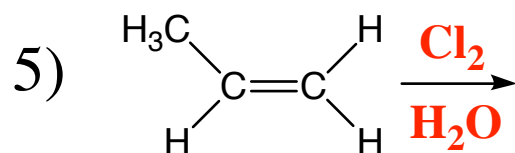
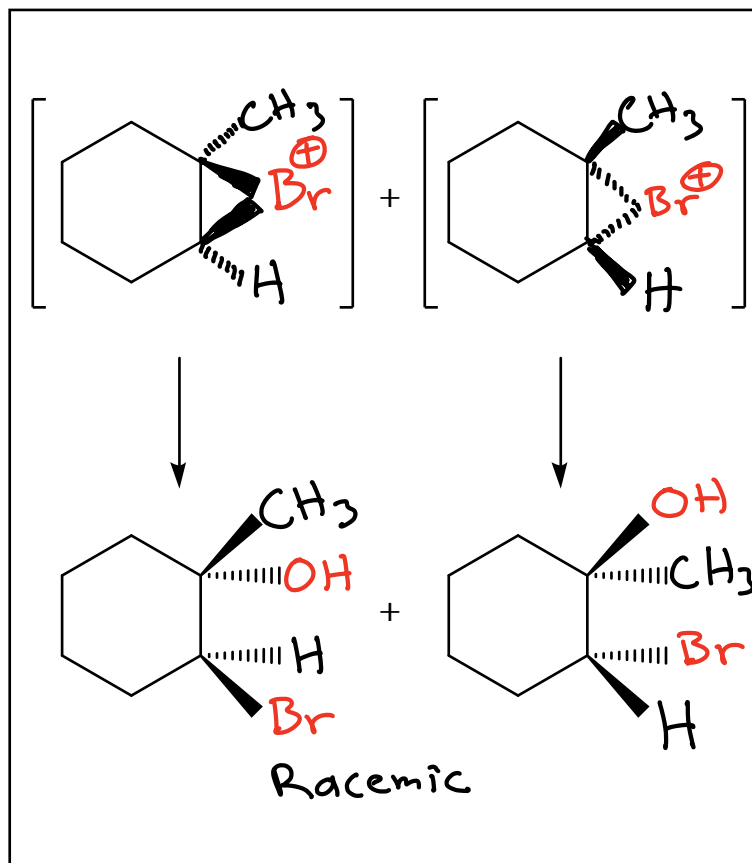


More Examples



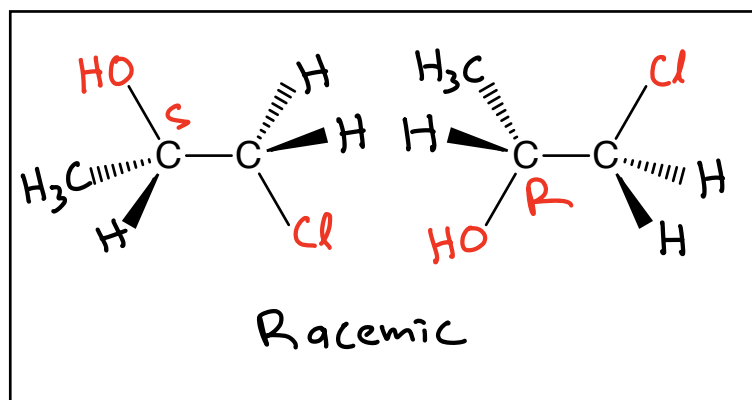
$\Rightarrow$ Markovnikov

$\Rightarrow$ Anti

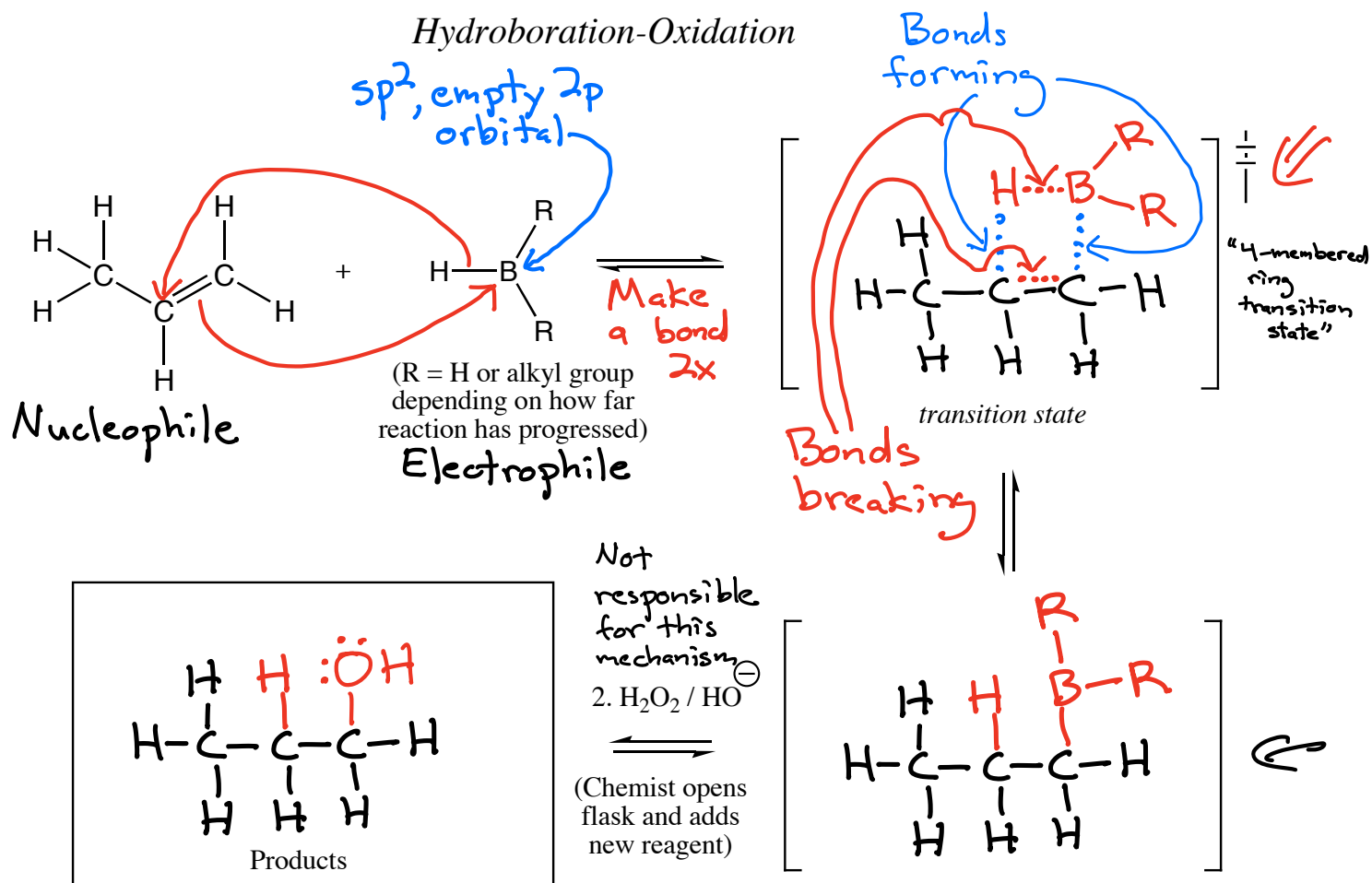


$\Rightarrow$ Mixed

$\Rightarrow$ Markovnikov



Hydroboration-Oxidation



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

} Steric strain in the first transition state

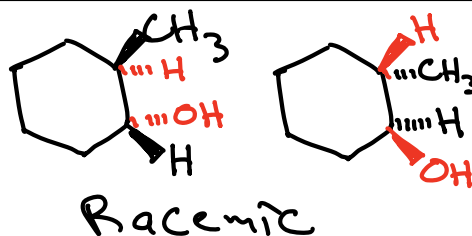
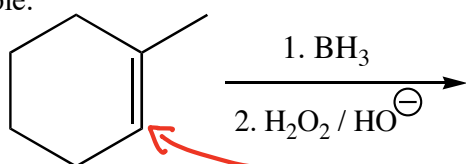
H and OH are syn

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

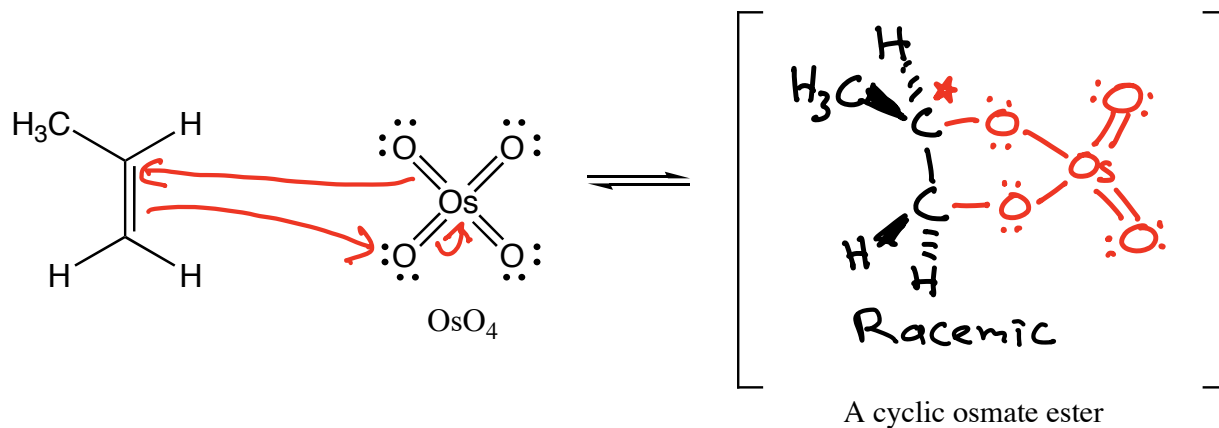
Example:



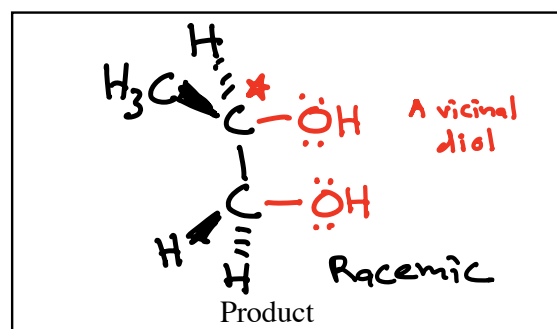
Less substituted C atom

Ozzy Osborne Reaction → "Sin" (Syn)

OsO_4 Partial Mechanism



2. $\text{NaHSO}_3 / \text{H}_2\text{O}$
(Chemist opens up flask) $\nparallel$ Not responsible for mechanism



Summary:

The mechanism involves a cyclic osmate ester, explaining the syn (sin!) stereochemistry of addition.

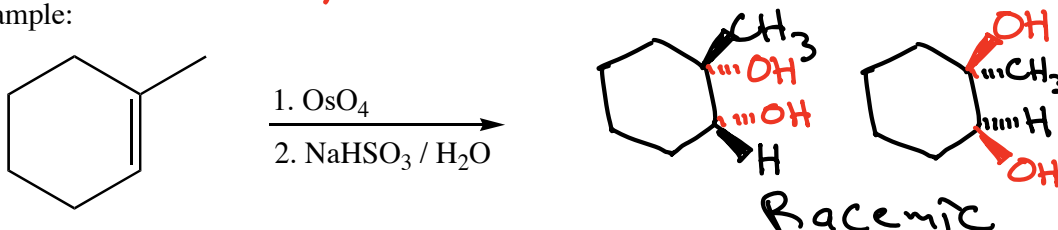
Regiochemistry:

N/A

Stereochemistry:

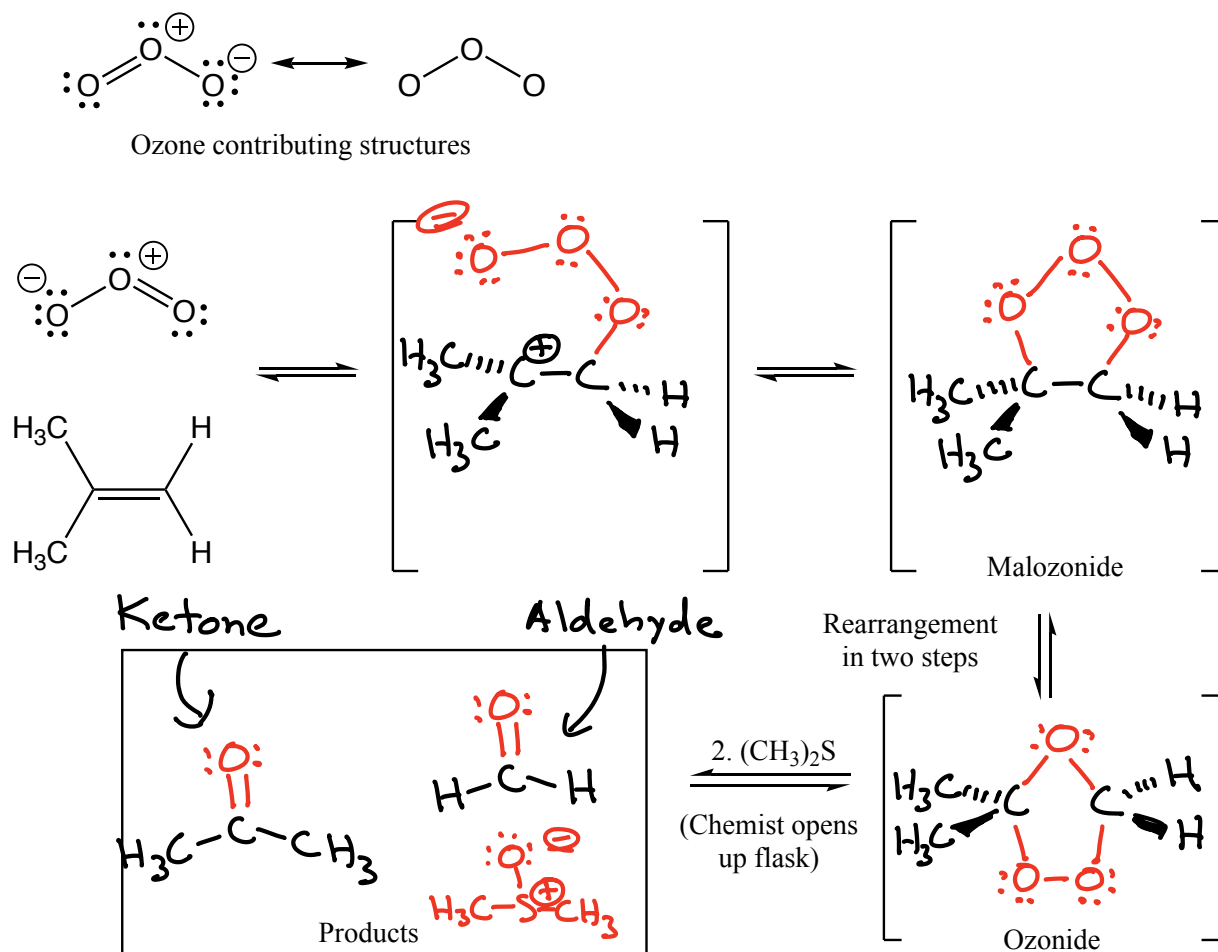
Syn (Sin!)

Example:



This reaction breaks a C=C bond!

Ozonolysis Partial Mechanism



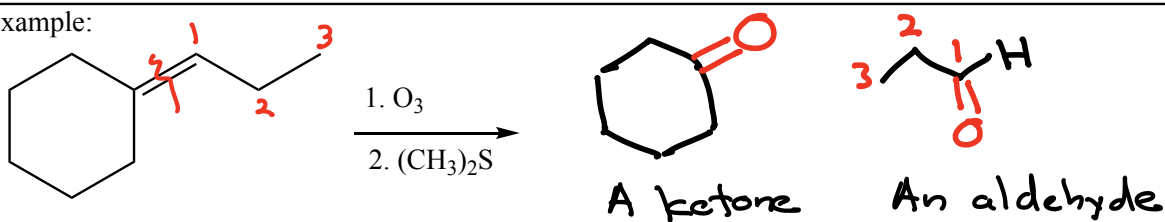
Summary:

Reaction of an alkene with O_3 gives a malozonide then 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

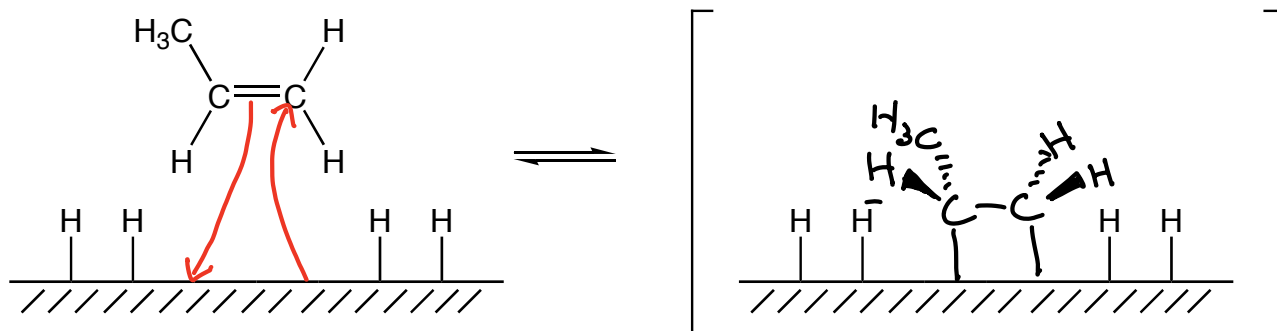
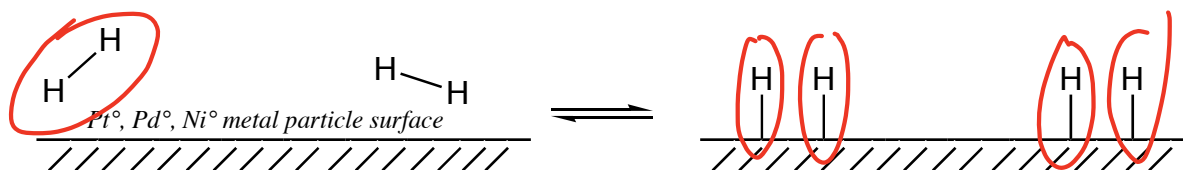
Stereochemistry: N/A

Example:

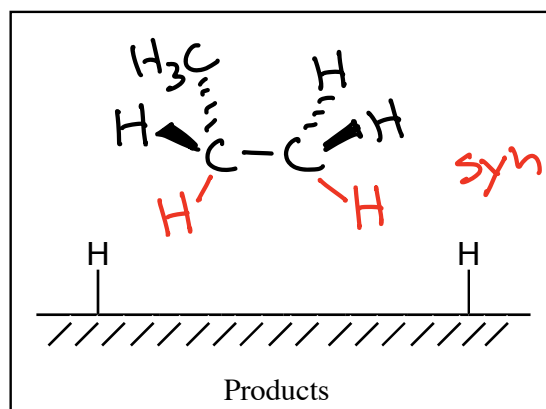


Hydrogenation: H_2 with Pt^0 , Pd^0 , Ni^0

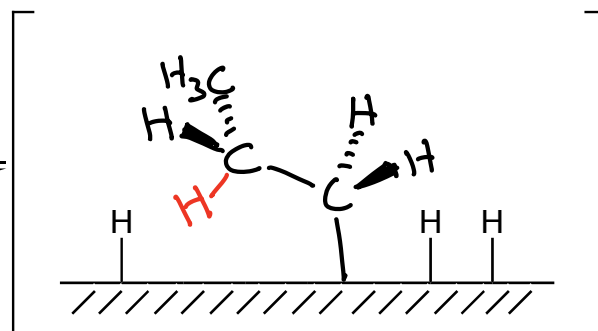
"In the elemental state - a metal"



Very fast



Very fast



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

Example:

