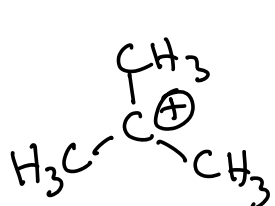
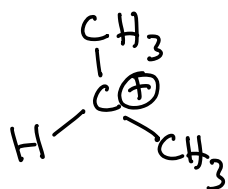


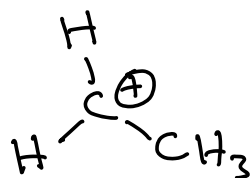
Carbocation stability  $\rightarrow$  the more C atoms bonded to the  $C^{\oplus}$  the more stable



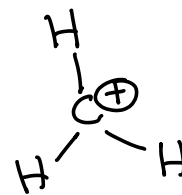
$3^{\circ}$   
(tertiary)



$2^{\circ}$   
(secondary)



$1^{\circ}$   
(primary)



methyl

$\leftarrow$  Hyperconjugation stabilization

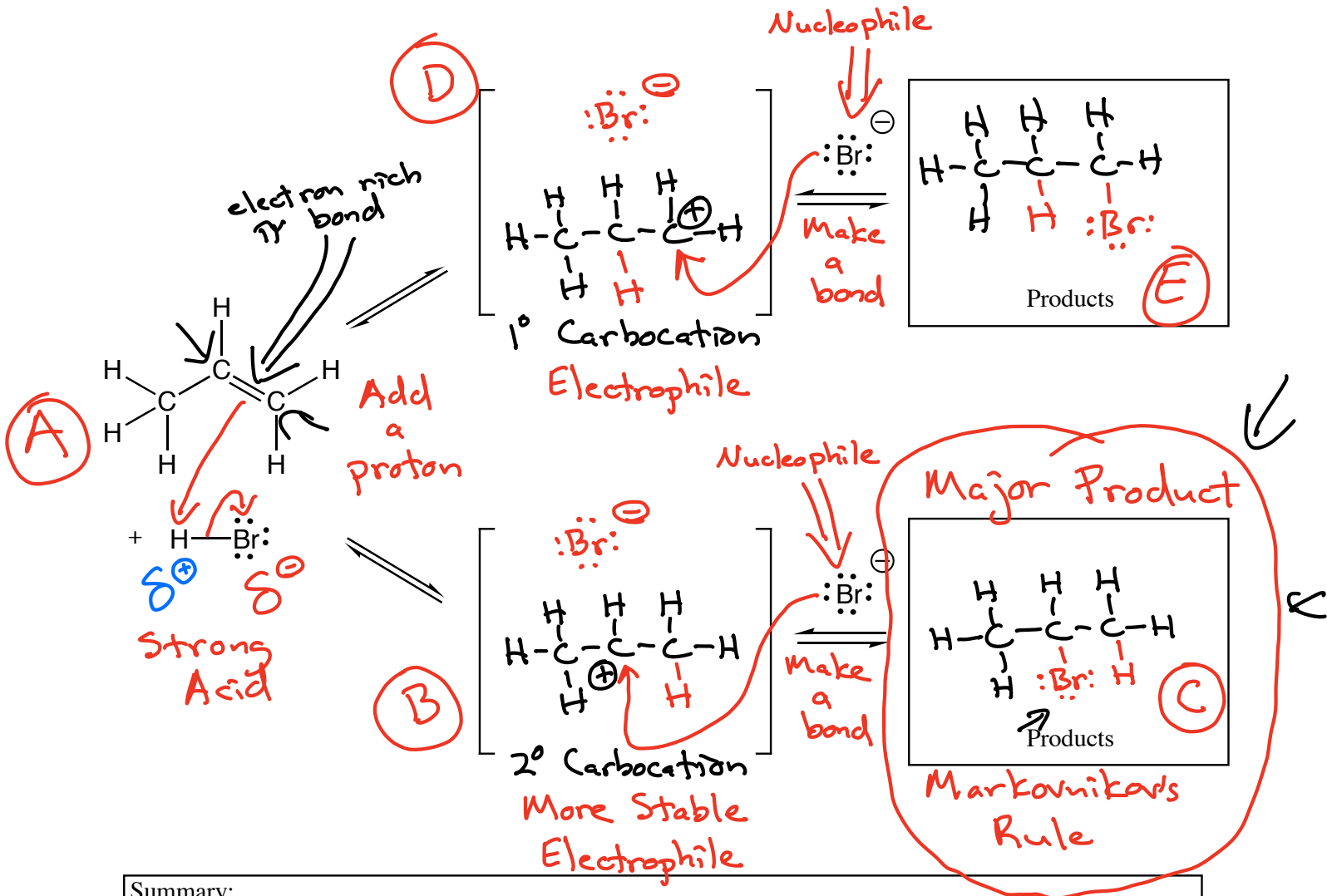
$\leftarrow$  Inductive effect stabilization

$\leftarrow$  Carbocation Stability

Markovnikov's Rule  $\rightarrow$  For alkene reactions involving a carbocation intermediate the nucleophile (ex.  $:\ddot{\text{Br}}:^{\ominus}$ ) will make a bond to the more substituted C atom  $\rightarrow$  derived from the more stable carbocation

Addition of H-X to an Alkene

X = Cl, Br, I  
but not F

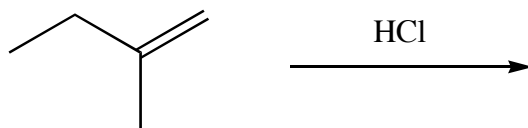


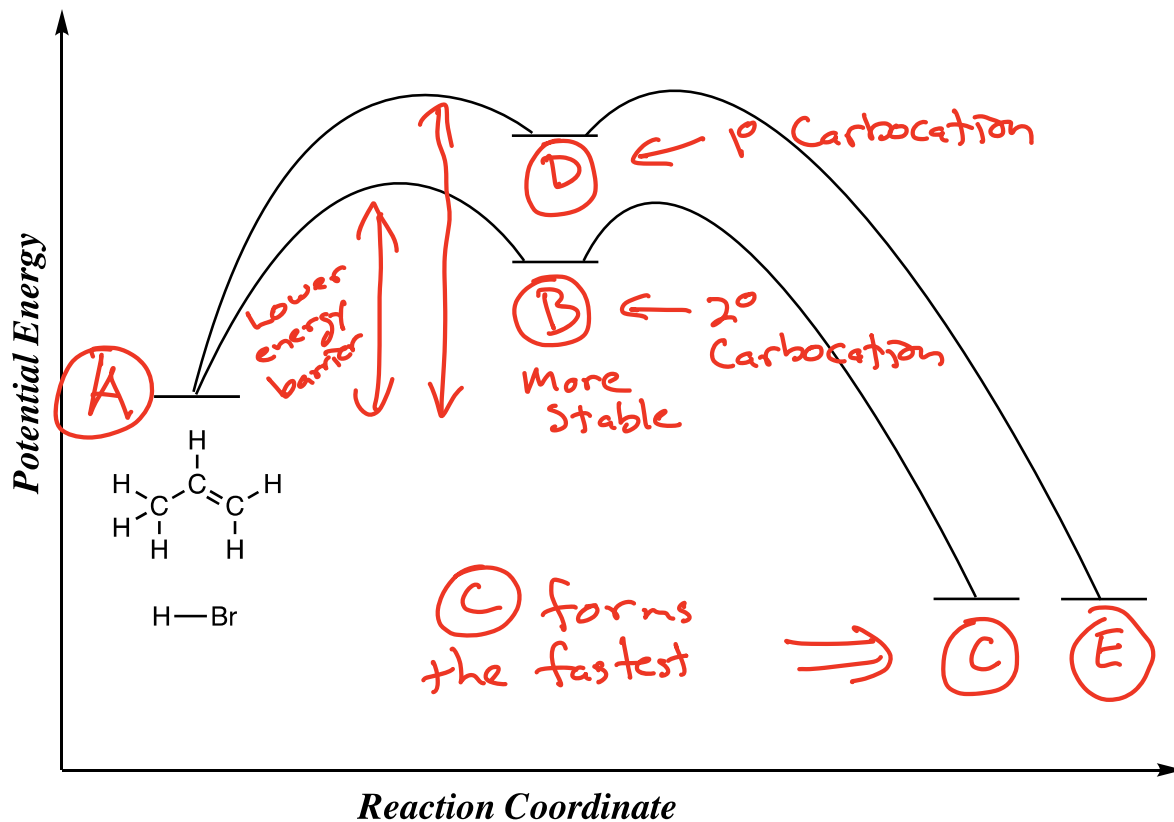
Summary:

Regiochemistry:

Stereochemistry:

Example:





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

Regiochemistry → Which constitutional isomer is made in largest amounts in a reaction

→ For H-X addition this is explained by Markovnikov's Rule



Stereochemistry → Which of the possible stereoisomers are formed?

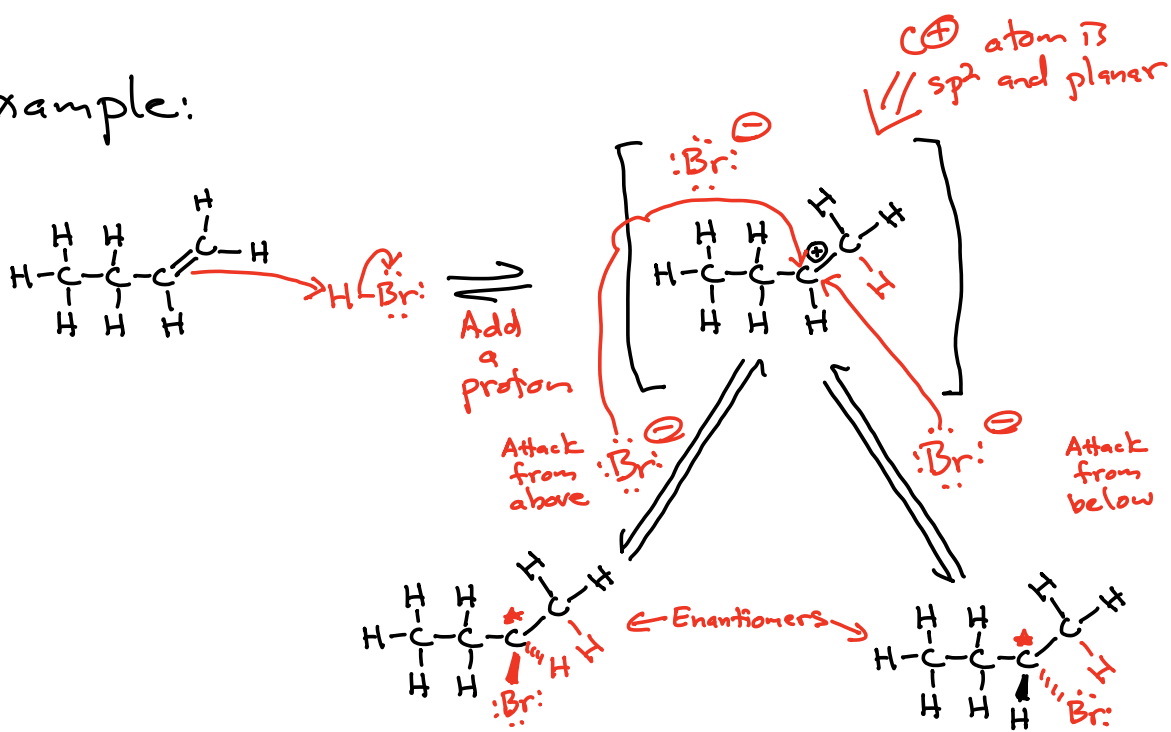
→ If a new chiral center is made from a molecule (the alkene) that itself is NOT chiral → You end up with a racemic mixture.



Time capsule → The stereochemistry of H-X addition to an alkene is MIXED as H and X can end

up on both the same (cis, syn) and opposite (trans, anti) sides of the original double bond

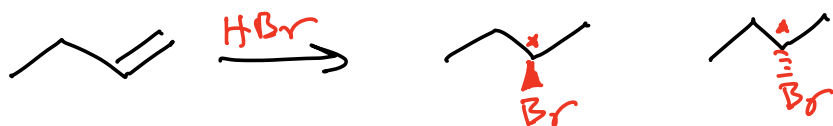
Example:



Racemic Mixture

It is equally likely to make either enantiomer

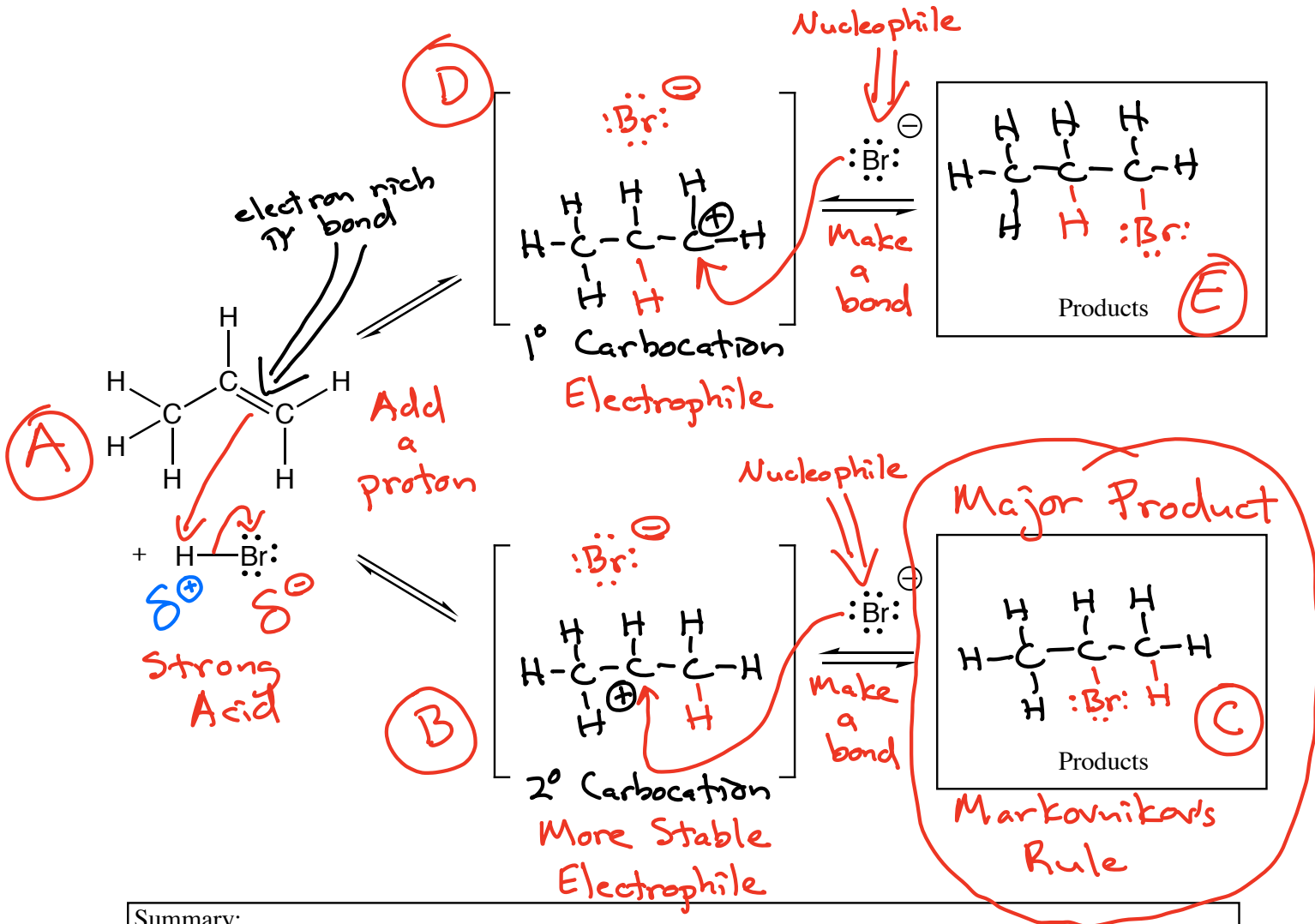
Also written as



Racemic Mixture

Addition of H-X to an Alkene

X = Cl, Br, I  
but not F



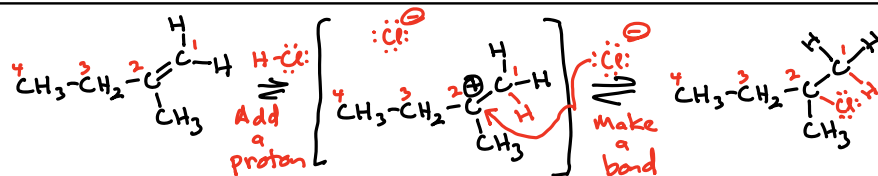
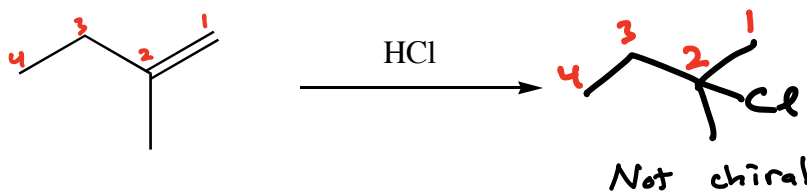
Summary:

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

Regiochemistry: **Markovnikov's Rule**

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

Example:



Google Search: "Andre the Giant holding  
Willie Shoemaker"

Go to "Images"

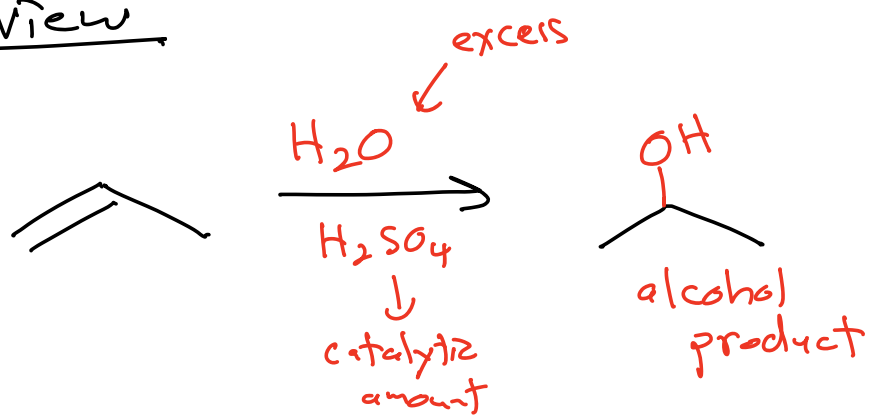
Select a high resolution black & white photo  
of a tall man holding a smaller one,  
then Zoom in on the smaller one.

Sorry!

YOU CANNOT UNSEE  
THIS!

New Reaction: → "same song,  
different verse"

Overview





# 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?

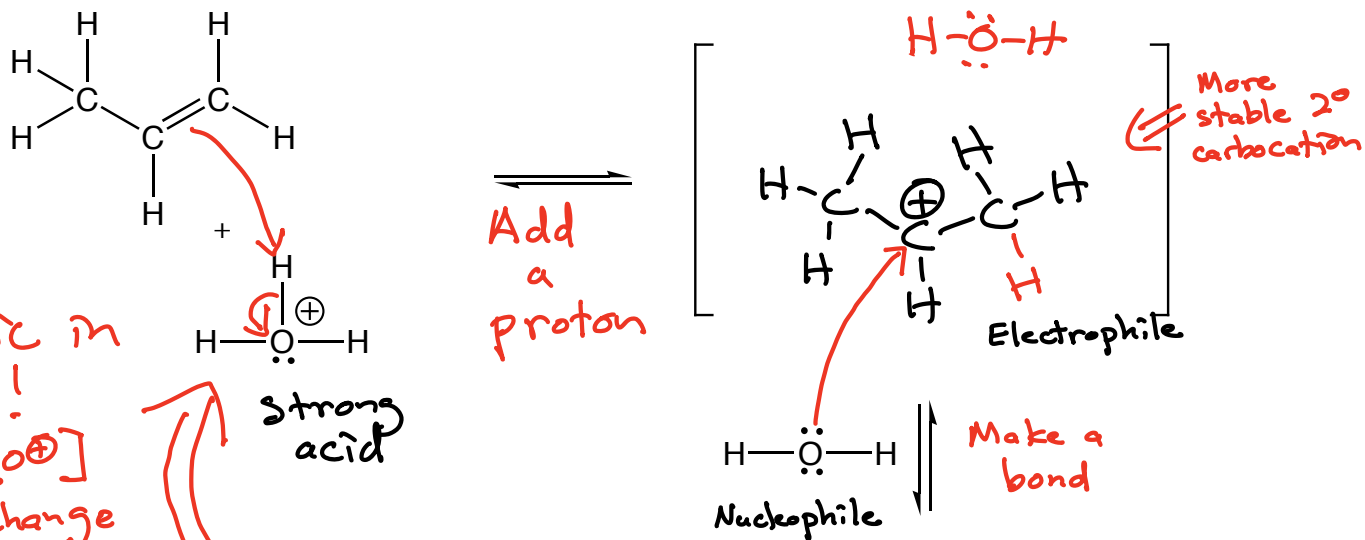
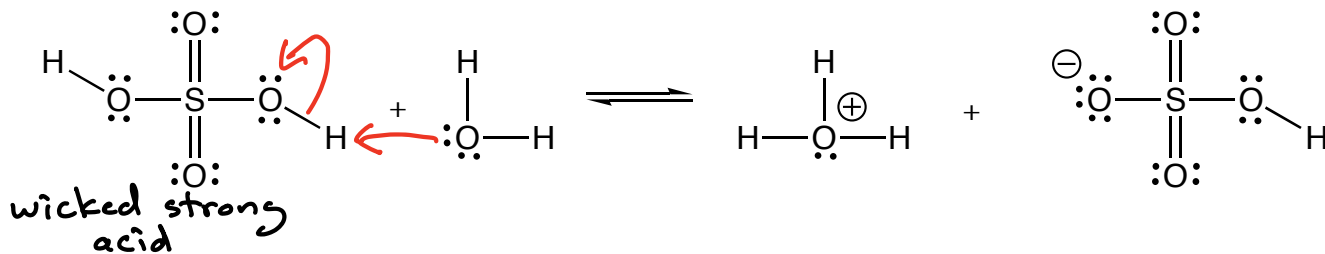
**YES** →

**Break a bond**

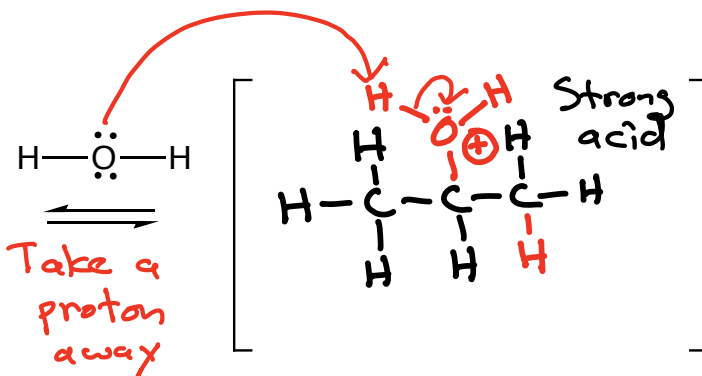
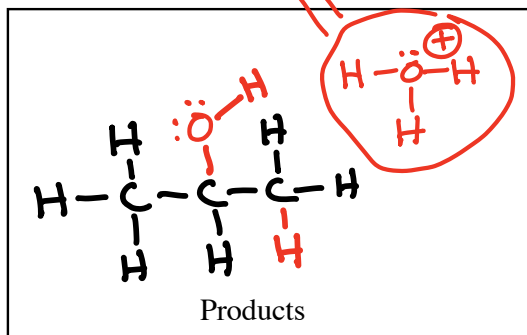
↓ **NO**

Think about alternative mechanistic elements

## Acid-catalyzed Hydration of an Alkene



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

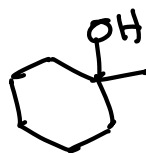
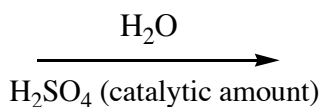
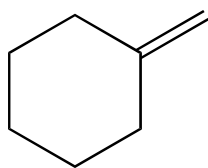


Summary: Proton adds to make a carbocation intermediate, water attacks to make a new bond, take a proton away to make the product alcohol. Catalytic in  $\text{H}_3\text{O}^+$

Regiochemistry: **Markovnikov's Rule**

Stereochemistry: **Mixed (time capsule)**

Example:



(Not chiral)

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

**Organic Chemistry is the study of carbon-containing molecules.**

**This class has two points.**

***The first point of the class is to understand the organic chemistry of living systems. We will teach you how to think about and understand the most amazing things on the planet!!***

Water is essential for life, you will learn why water has such special properties. 8/25/2022

You will learn the secret structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life. 9/6/22

You will learn why when you take Advil for pain, exactly half of what you take works, and the other half does nothing. 9/20/22

You will learn how toothpaste works. 9/29/22

You will learn how a single chlorofluorocarbon refrigerant molecule released into the atmosphere can destroy many, many ozone molecules, leading to an enlargement of the ozone hole.

You will learn how medicines like Benadryl, Seldane, and Lipitor work.

You will learn how Naloxone is an antidote for an opioid overdose.

You will learn why Magic Johnson is still alive, decades after contracting HIV.

You will learn how MRI scans work.

***The second point of organic chemistry is the synthesis of complex molecules from simpler ones by making and breaking specific bonds.***

You will learn how to understand movies of reaction mechanisms like alkene hydration. 10/4/22

You will learn reactions that once begun, will continue reacting such that each product molecule created starts a new reaction until all the starting material is used up.

You will learn reactions that can make antifreeze from vodka.

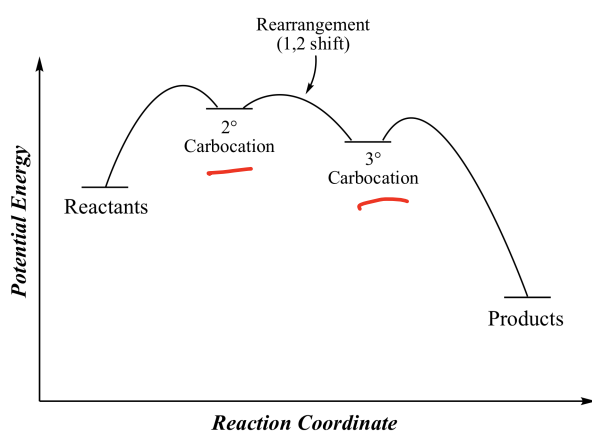
You will learn a reaction that can make nail polish remover from rubbing alcohol.

You will learn how to look at a molecule and accurately predict which atoms will react to make new bonds, and which bonds will break during reactions.

You will learn how to analyze a complex molecule's structure so that you can predict ways to make it via multiple reactions starting with less complex starting molecules.



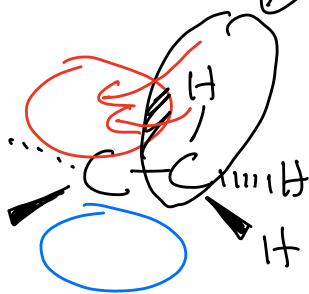
Carbocation intermediates can sometimes rearrange (Called 1,2 Shift) If a carbocation intermediate of equal or greater stability can be produced by shifting an adjacent H atom (or rarely an alkyl group), **rearrangement** will compete with product formation to give a mixture of products.



**Motive** → A 3° (tertiary) carbocation is more stable than a 2° (secondary) carbocation

Opportunity → The mechanism is really just hyperconjugation "taken to the extreme"

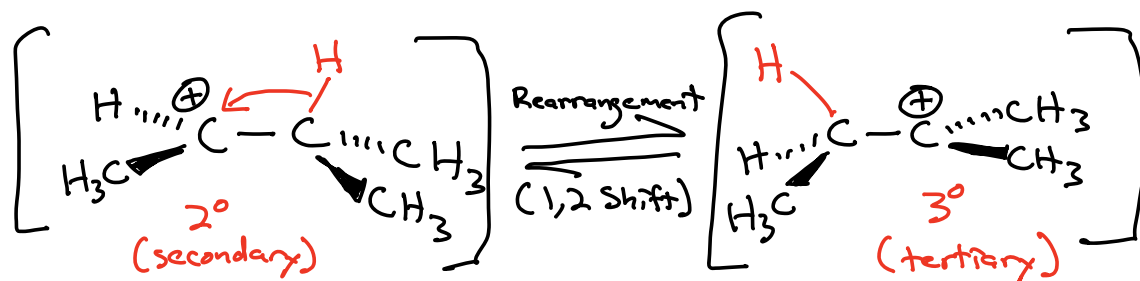
1) Hyperconjugation → overlap of adjacent  $\sigma$  bonding electron density with the empty 2p orbital of a carbocation



delocalizes the  $\oplus$  charge

Some electron density of the C-H  $\sigma$  bond is pulled into the empty 2p orbital

(red arrows in the figure)



More Stable  
Carbocation