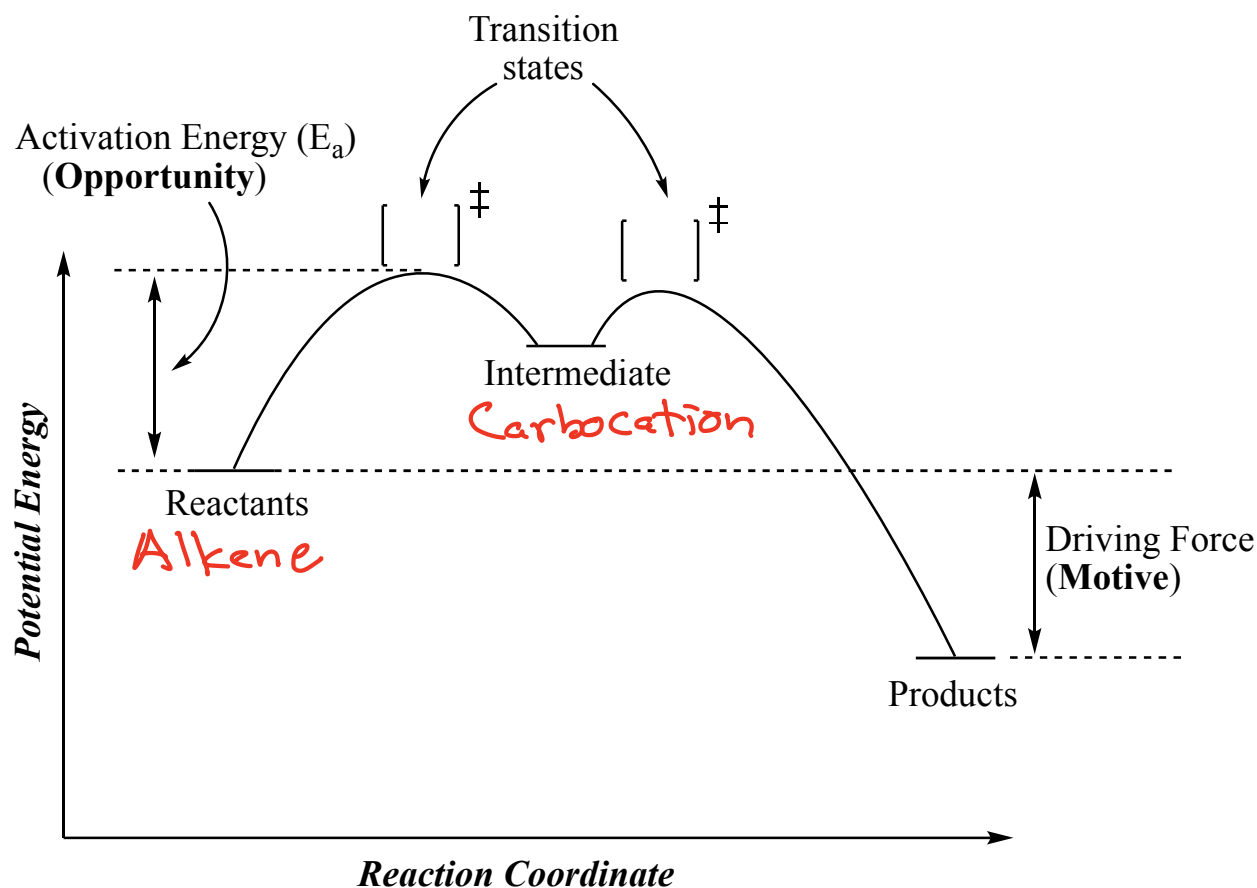
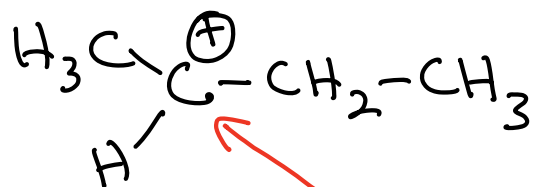




During reactions we often encounter intermediates $\rightarrow$ relatively high energy species that are formed between reactants and products

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

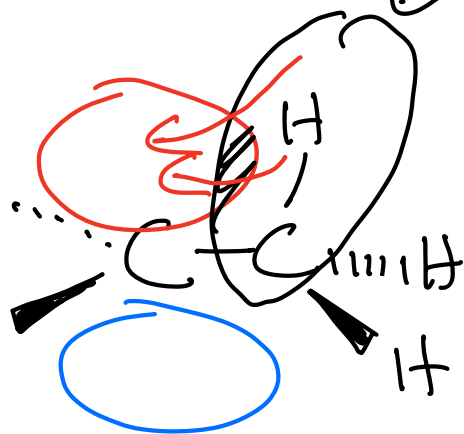
Carbocations $\rightarrow$ positive charge on a carbon atom



sp^2 hybridized
with an empty 2p orbital

Alkyl groups stabilize carbocations by 2 different mechanisms

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



delocalizes the $\oplus$ charge

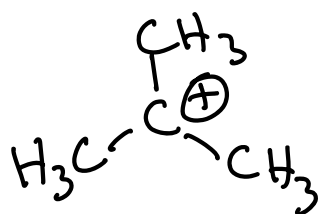
Some electron density of the C-H σ bond is pulled into the empty 2p orbital

(red arrows in the figure)

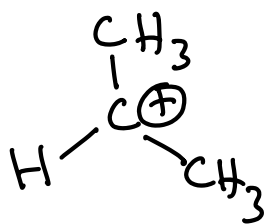
2) Inductive effect $\rightarrow$ the electron density is drawn through the σ bonds to the C^+

$\hookrightarrow$ The C^+ is very electronegative!

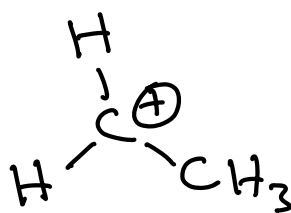
Carbocation stability $\rightarrow$ the more C atoms bonded to the C^+ the more stable



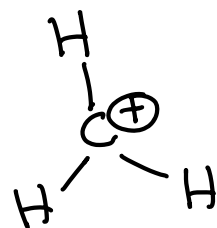
3°
(tertiary)



2°
(secondary)



1°
(primary)

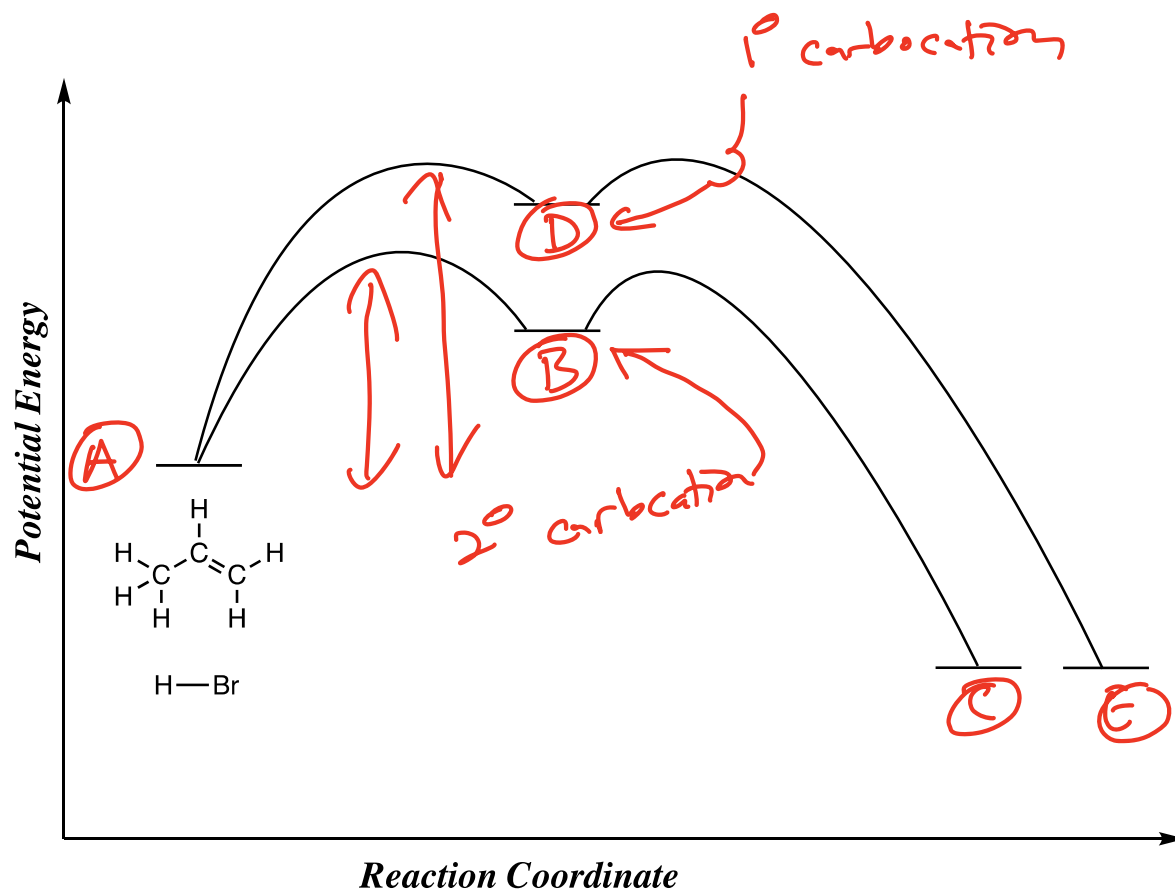


methyl

$\leftarrow$ Hyperconjugation stabilization

$\leftarrow$ Inductive effect stabilization

$\leftarrow$ Carbocation Stability

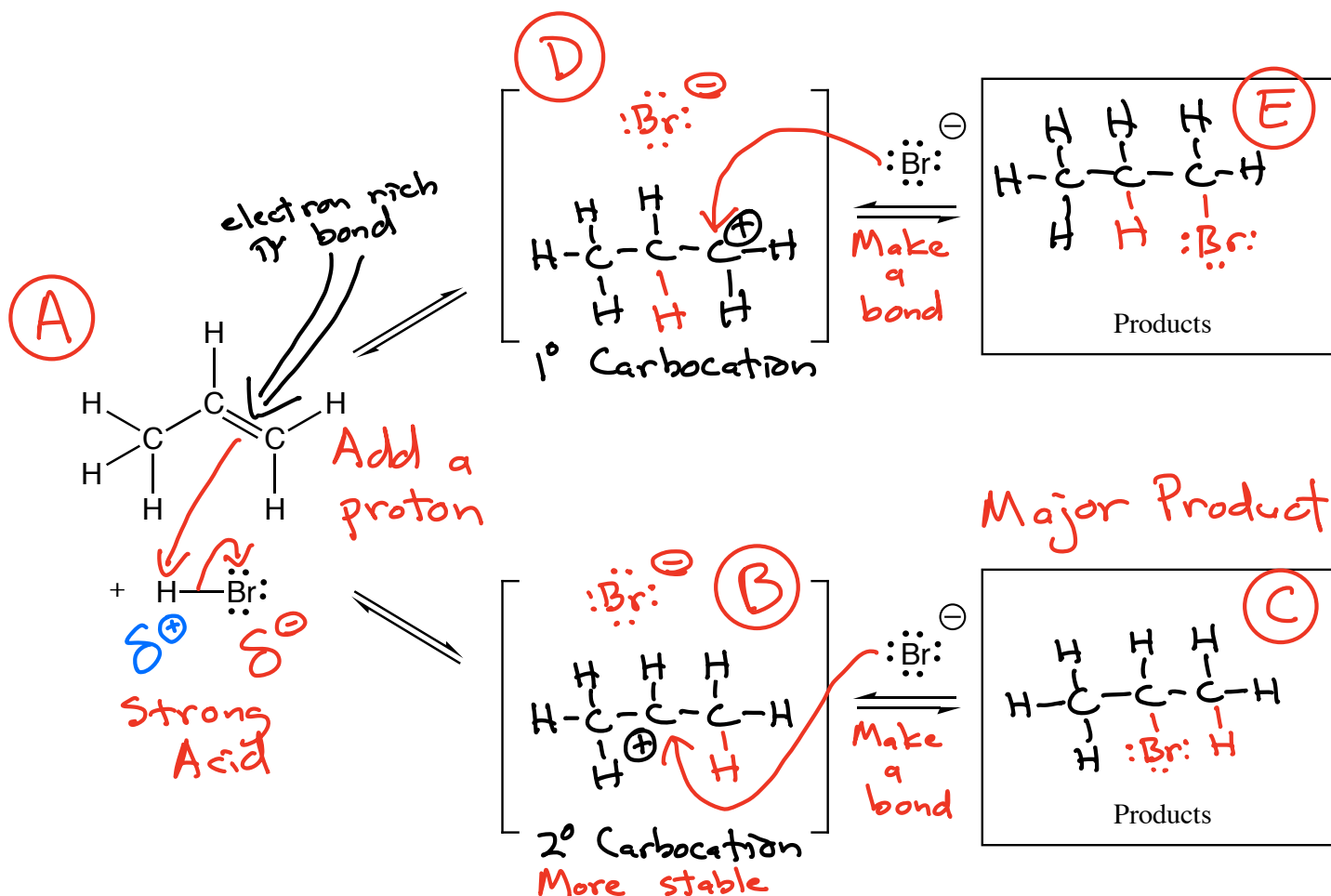


Creation of **B** has a lower energy barrier and it forms faster → We get more **C** product

Markovnikov's Rule $\rightarrow$ For alkene reactions involving a carbocation intermediate -

Addition of H-X to an Alkene

X = Cl, Br, I
but not F

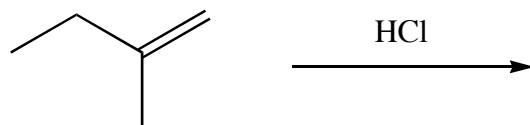


Summary:

Regiochemistry:

Stereochemistry:

Example:



Regiochemistry →



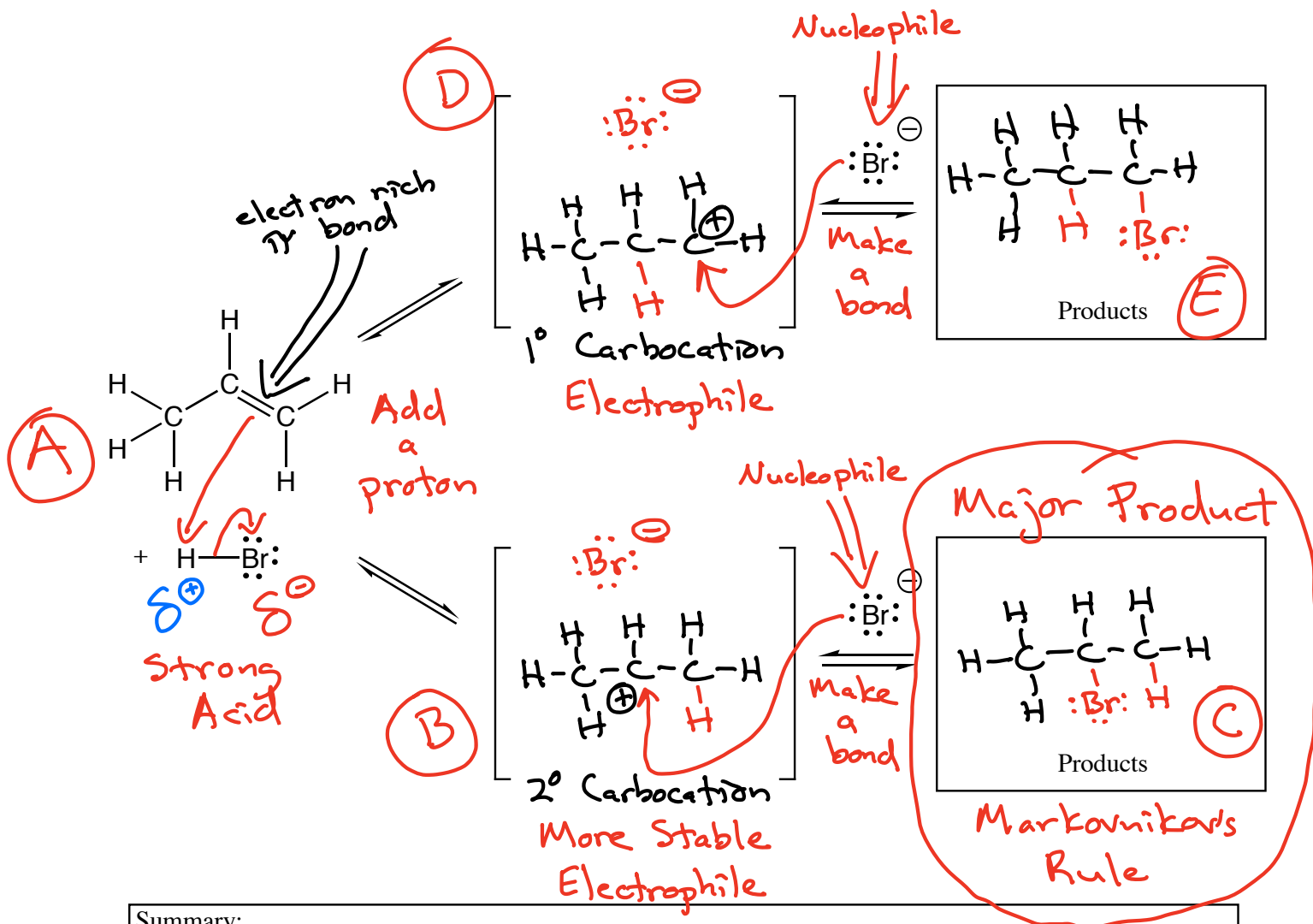
Stereochemistry → Which of the possible stereoisomers are formed?



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

Addition of H-X to an Alkene

X = Cl, Br, I
but not F

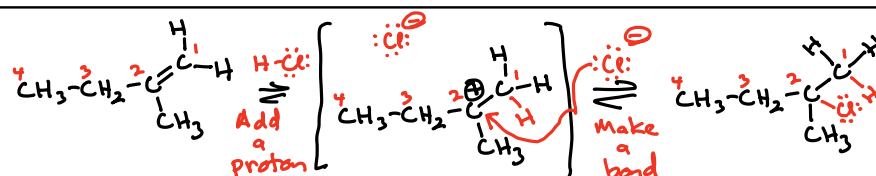
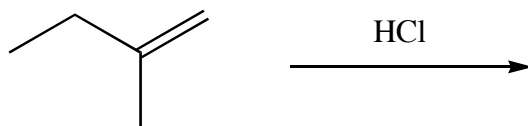


Summary:

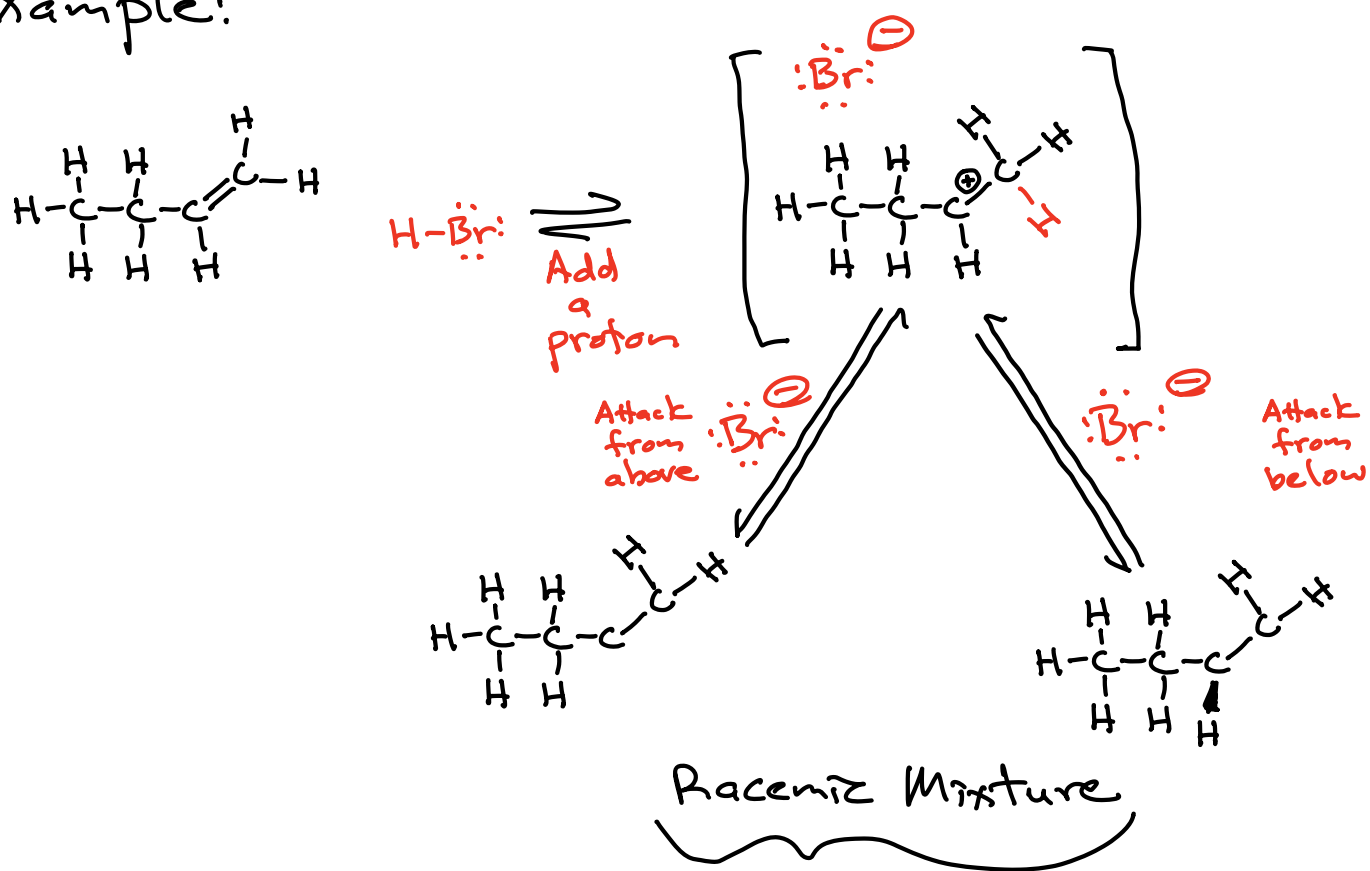
Regiochemistry:

Stereochemistry:

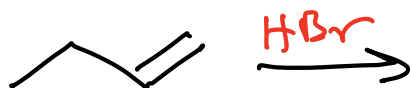
Example:



Example:

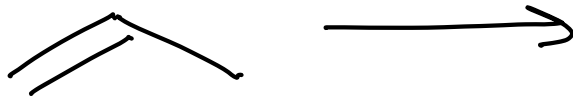


Also written as



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.

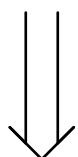
Mechanism Summary

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

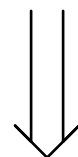


NO

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

YES
⇒

Take a proton away

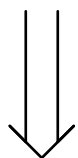


NO

Are there a nucleophile and electrophile present?

YES
⇒

Make a bond

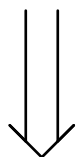


NO

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

YES
⇒

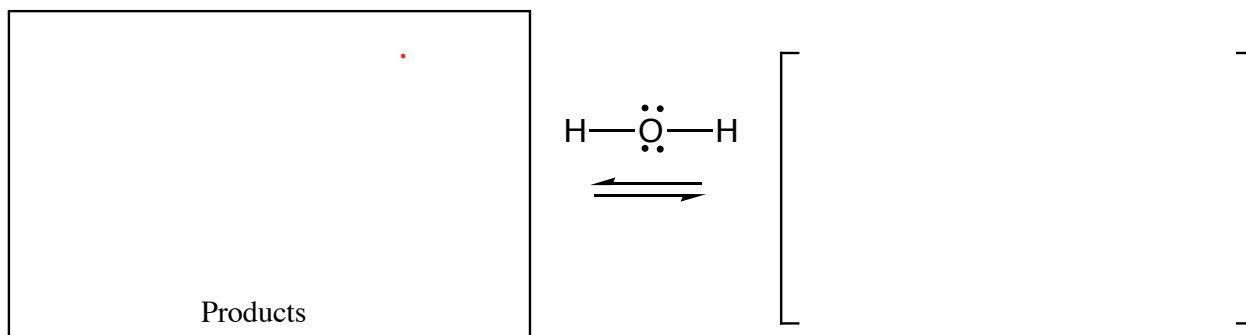
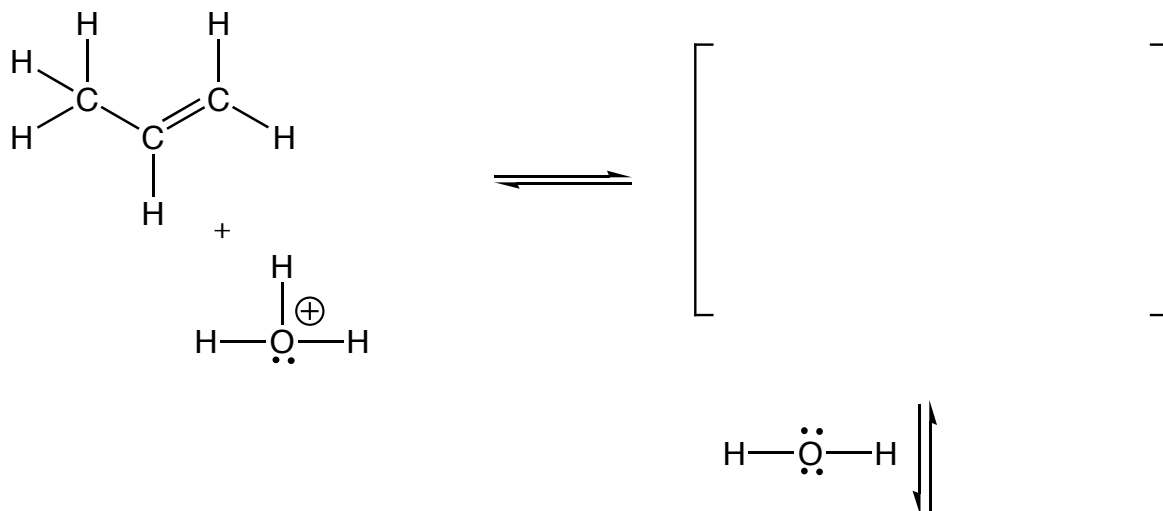
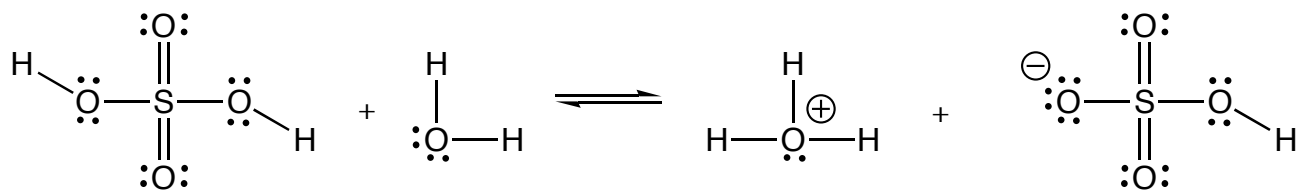
Break a bond



NO

Think about alternative mechanistic elements

Acid-catalyzed Hydration of an Alkene

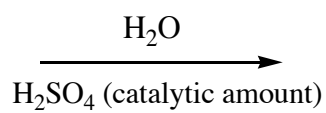
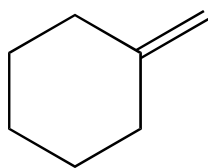


Summary:

Regiochemistry:

Stereochemistry:

Example:



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. 8/26/26

You will learn the secret structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life. 9/9/26

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

You will learn how toothpaste works. 9/21/26
9/30/26

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.

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.

Google Search: "Andre the Giant holding
Willie Shoemaker"

Go to "Images"

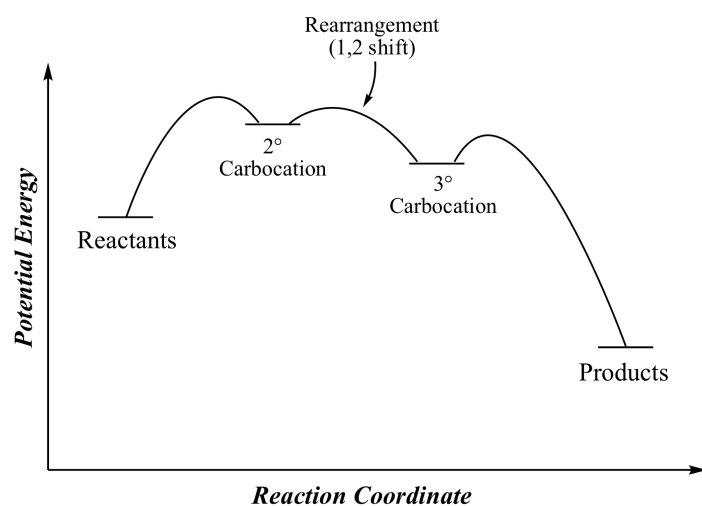
Select a high resolution black & white photo
of a tall man holding a smaller one,
then Zoom in on the smaller one.

Sorry!

YOU CANNOT UNSEE
THIS!



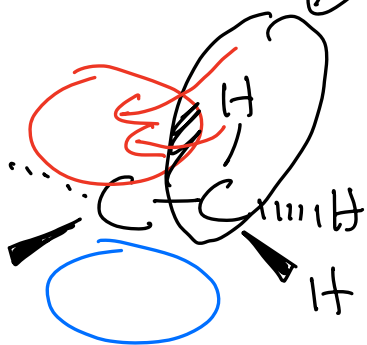
Carbocation intermediates
can sometimes rearrange
(Called 1,2 Shift)



Motive →

Opportunity →

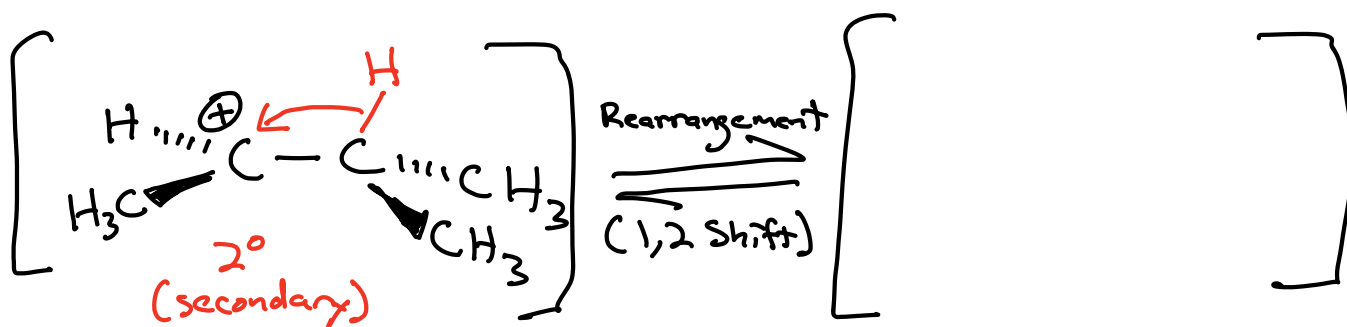
1) Hyperconjugation → overlap of adjacent C bonding electron density with the empty 2p orbital of a carbocation



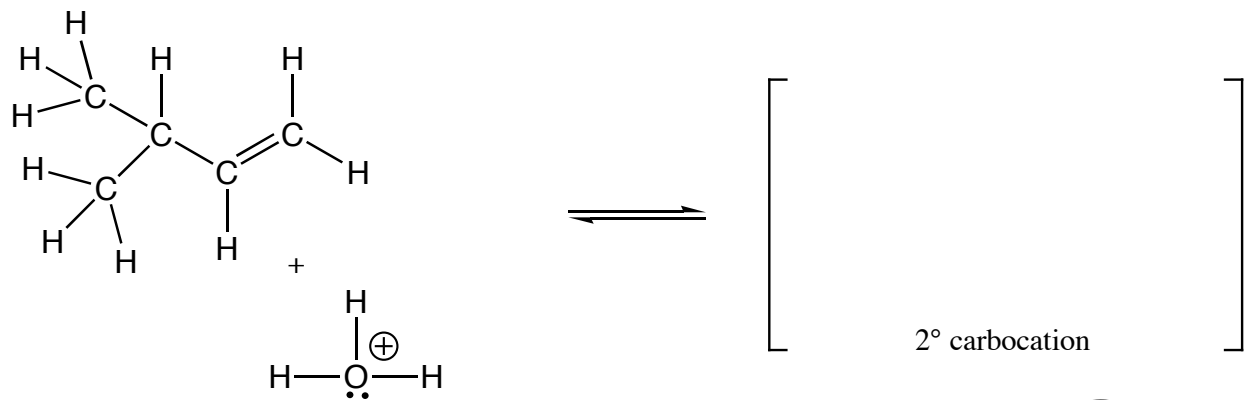
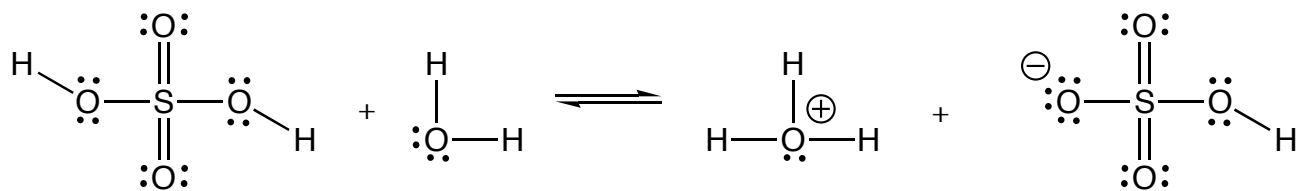
delocalizes the $\oplus$ charge

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

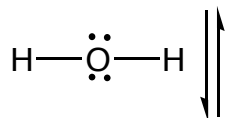
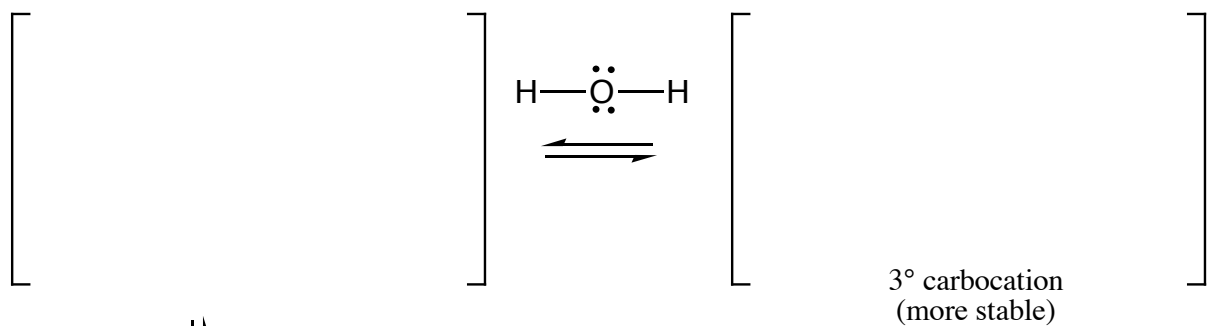
(red arrows in the figure)



Cation Rearrangement

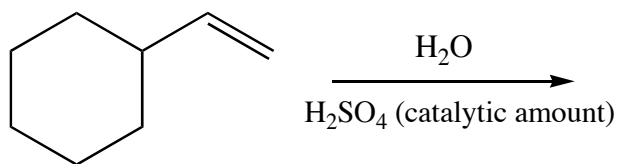


Rearrangement $\rightleftharpoons$ 



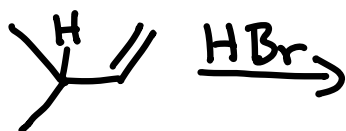
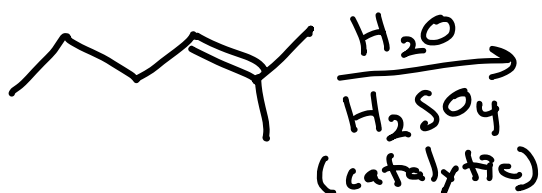
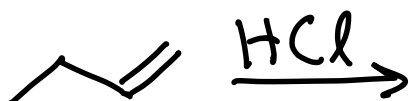
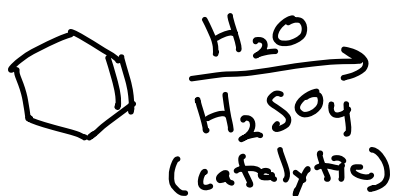
Products

Example:



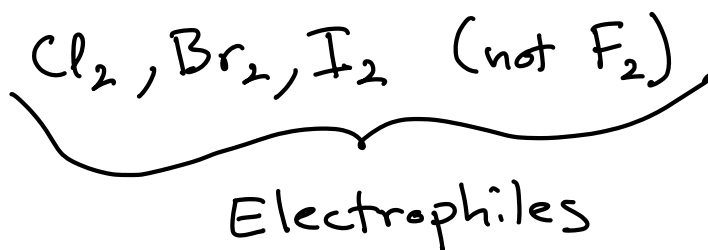
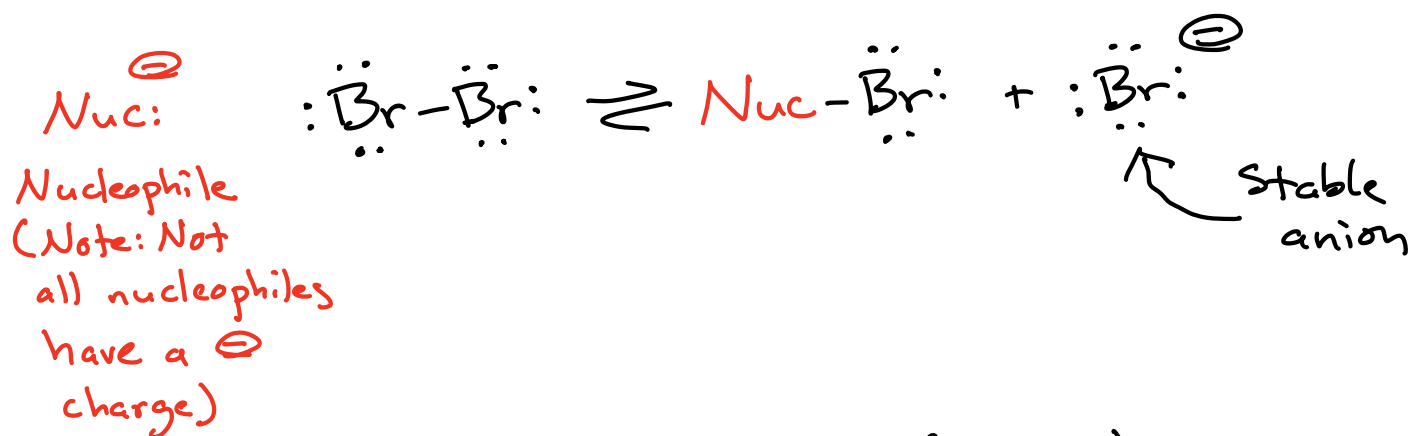


Examples

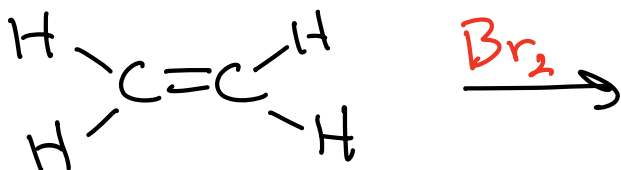


(Only draw
the rearranged
product)

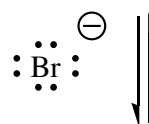
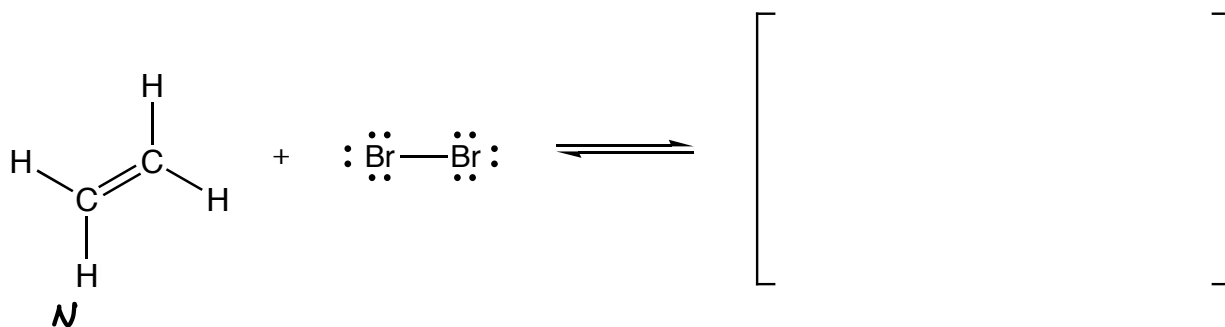
New definition of an electrophile $\rightarrow$
a relatively weak bond that can
break to create a stable anion



Overall) New Reaction



Alkene Halogenation



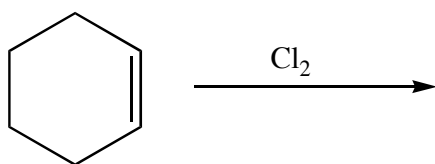
Products

Summary:

Regiochemistry:

Stereochemistry:

Example:



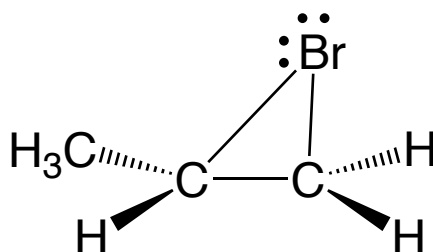
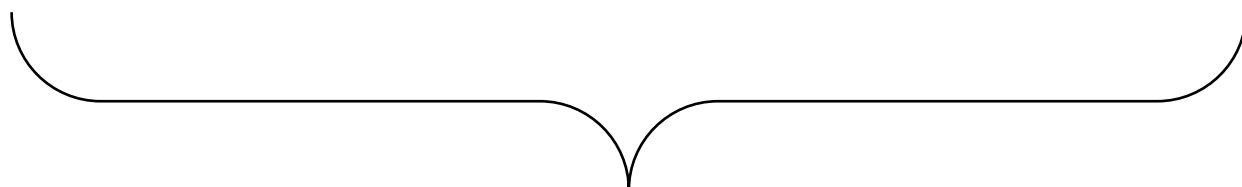
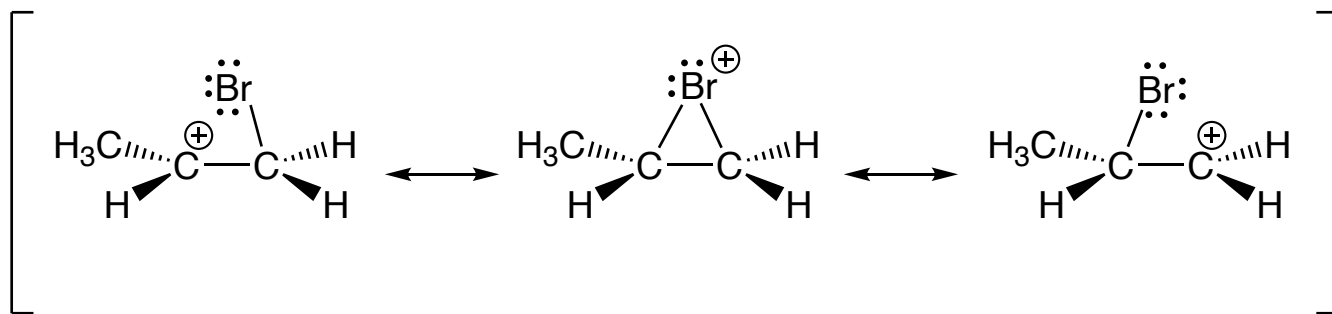
Alkene Reaction Stereochemistry Possibilities

Anti →

Syn →

Mixed →

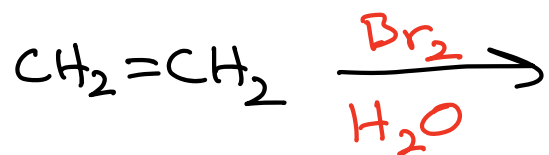
How to think about unsymmetrical
halonium ions



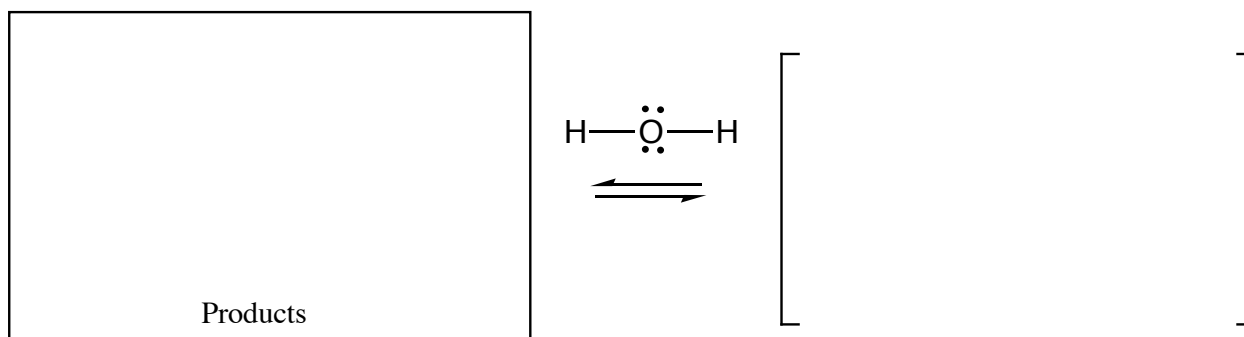
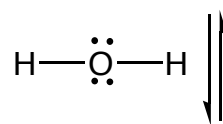
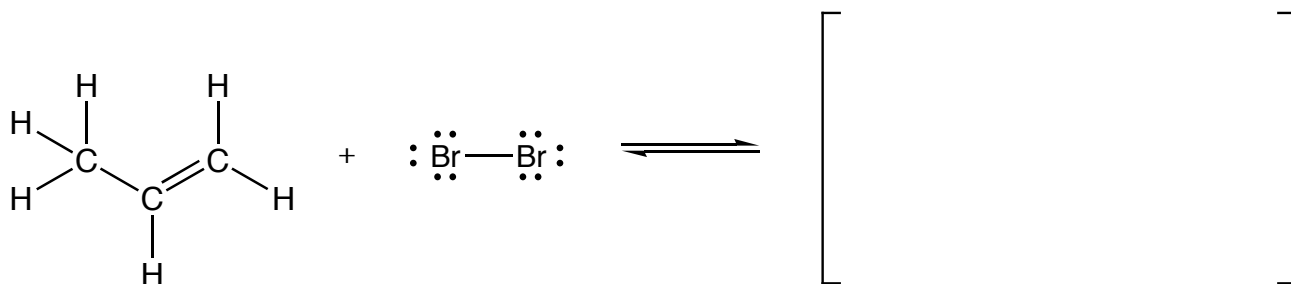
Complication $\rightarrow$ Some intermediates and products are chiral

Solution $\rightarrow$

New overall reaction: Halohydrin Formation



Alkene Hydrohalogenation

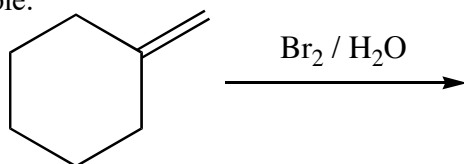


Summary:

Regiochemistry:

Stereochemistry:

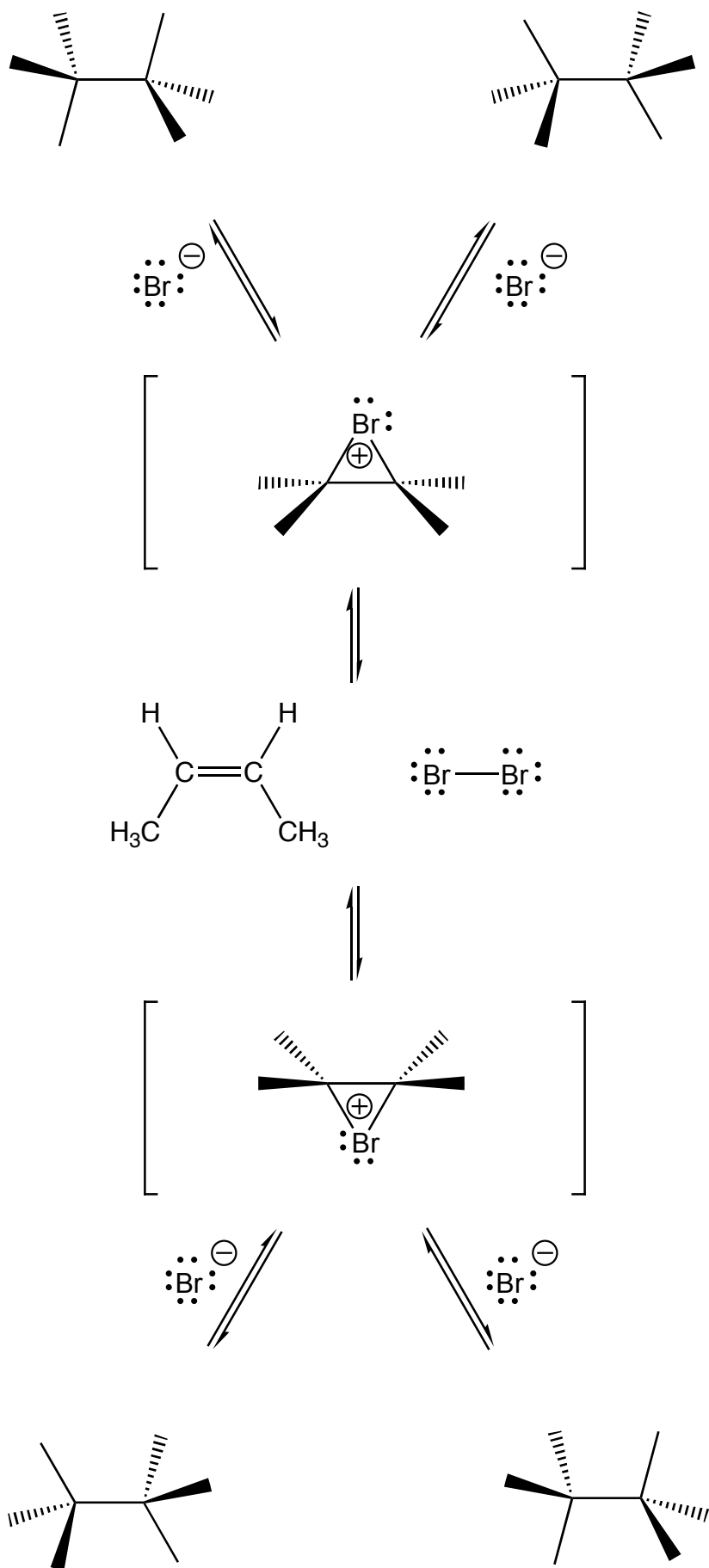
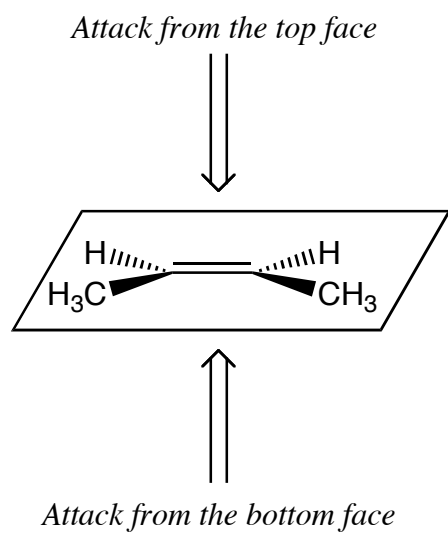
Example:

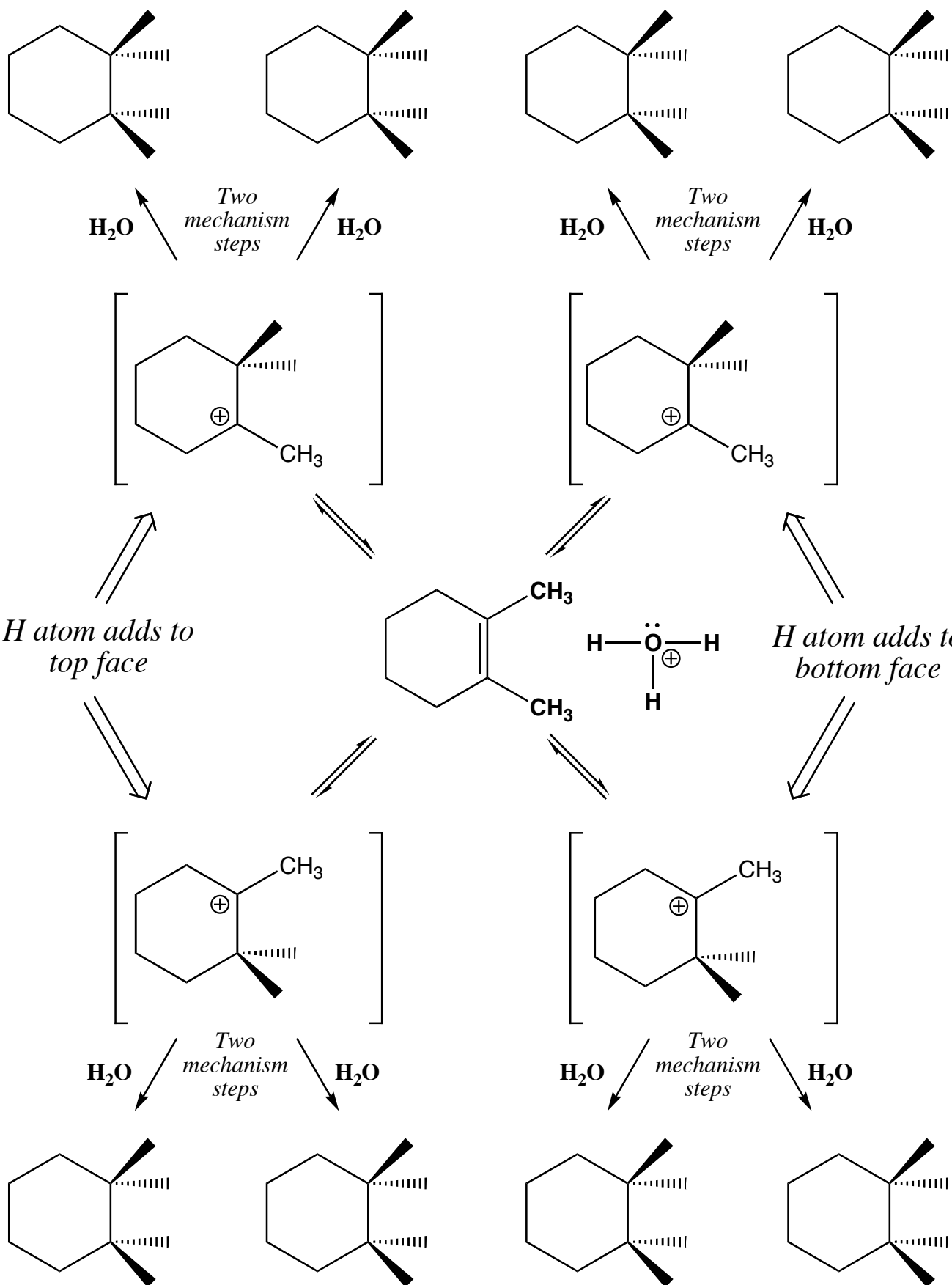


Only carbocations rearrange!

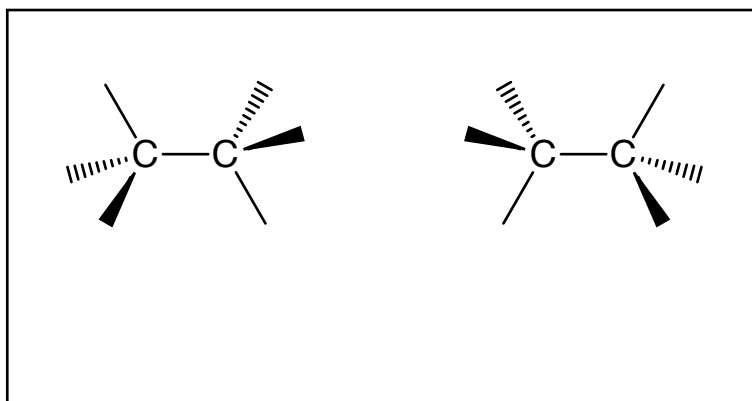
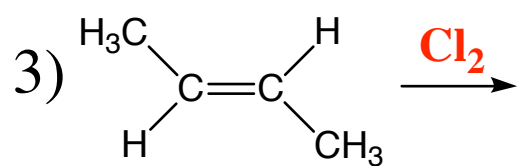
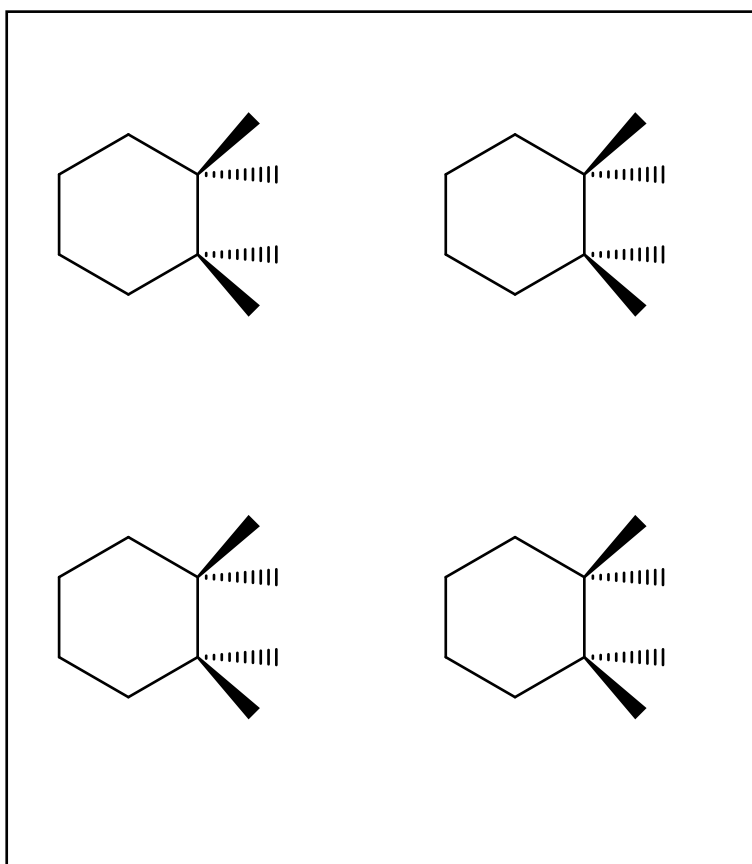
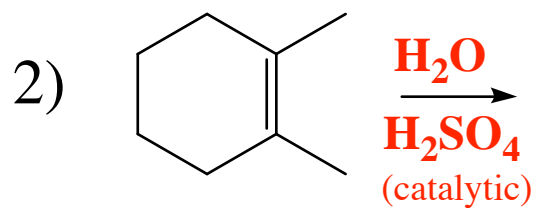
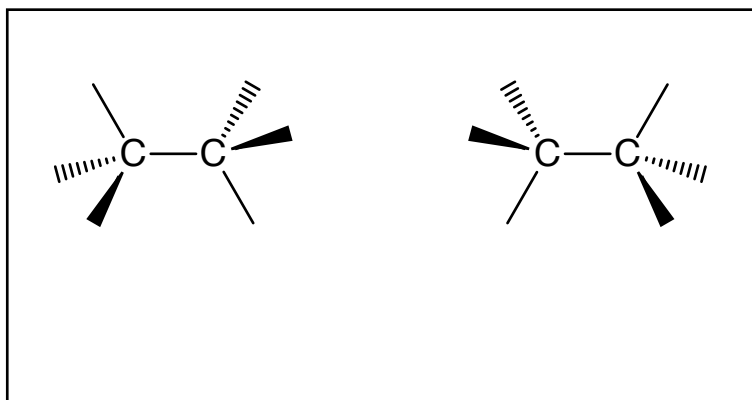
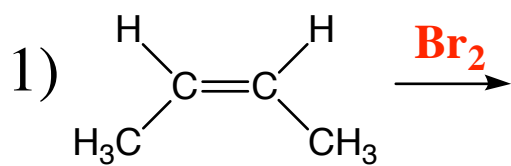


To get stereochemistry
correct when predicting
reaction products,





Examples



More Examples

