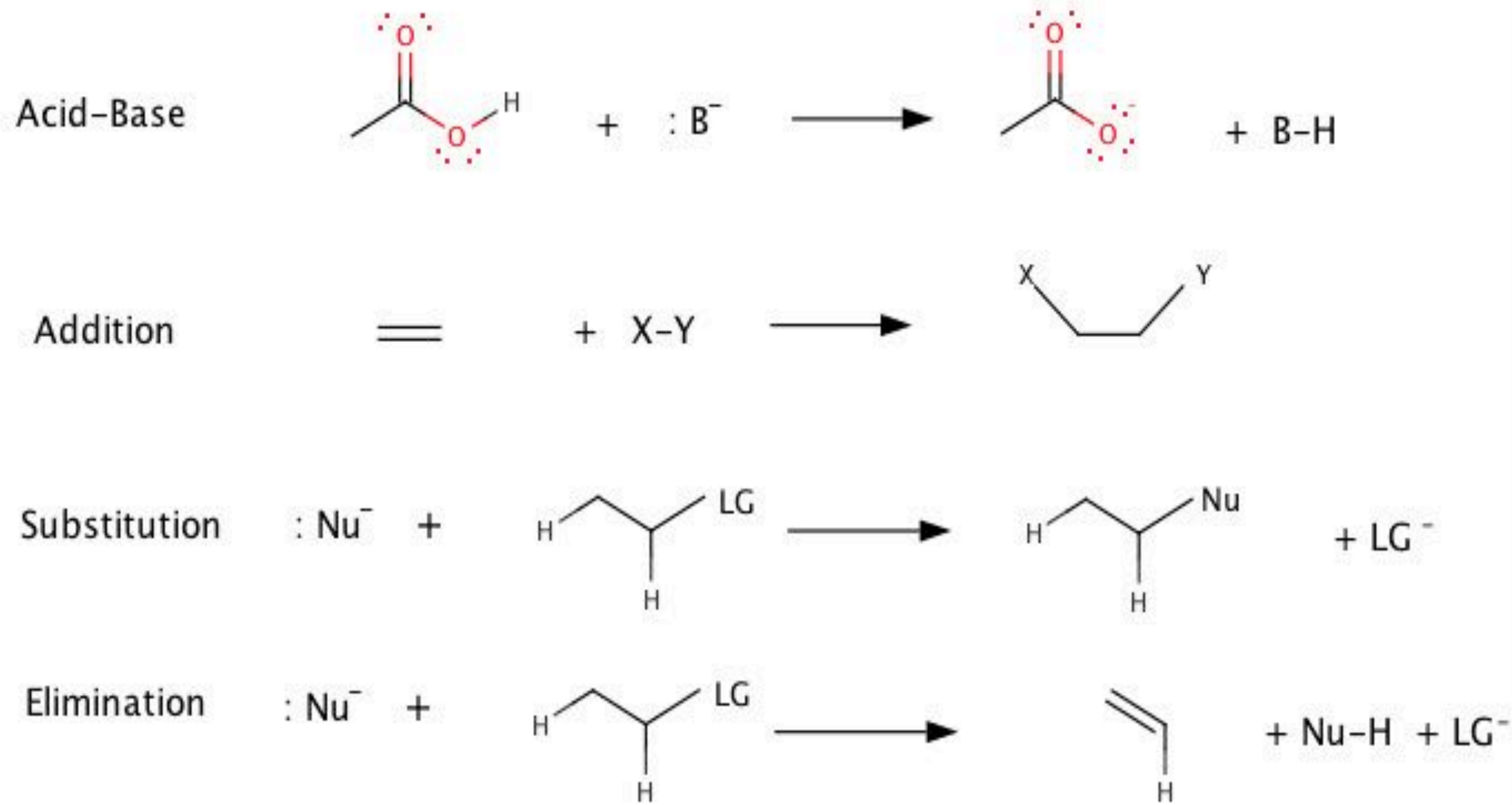
Objective 12

Apply Reactivity Principles to Electrophilic Addition Reactions 1: Alkenes

Identify structural features (pi bond) and electrophiles

Use curved arrows to predict product

4 Types of Organic Polar Reactions



Alkenes are Used as Starting Materials for Many Compounds
Alkenes Undergo Addition Reactions

Functional group/Bonding/Structure/Reactivity:

C=C-H **C=C π bond = Nu:⁻**, can react with E^+ (addition rxn)(compare to C-C bond)

H = E^+, can react with base (acid-base rxn)

What is pK_a? Is this H a strong or weak E^+?

Uses: Biology - found in fats and oils, C_2H_4 plant hormone

Petroleum - fuel, starting material for many compounds

Preparation: R-OH -- H^+ catalyst --> alkene (Elimination rxn)

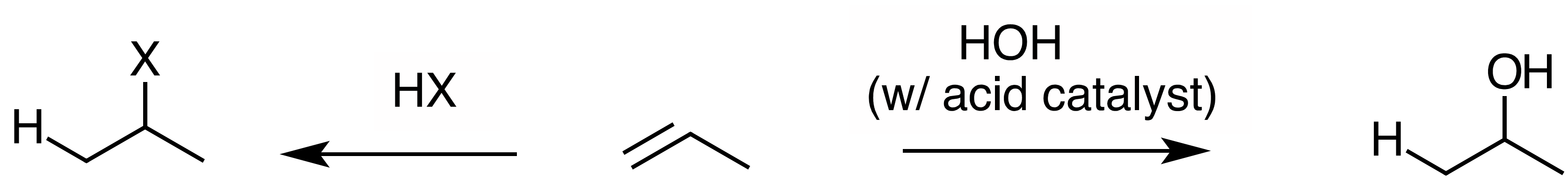
R-X + base --> alkene (Elimination rxn)

Reactions: addition reactions

polymerization

Alkene Addition Reactions Make Different Functional Groups

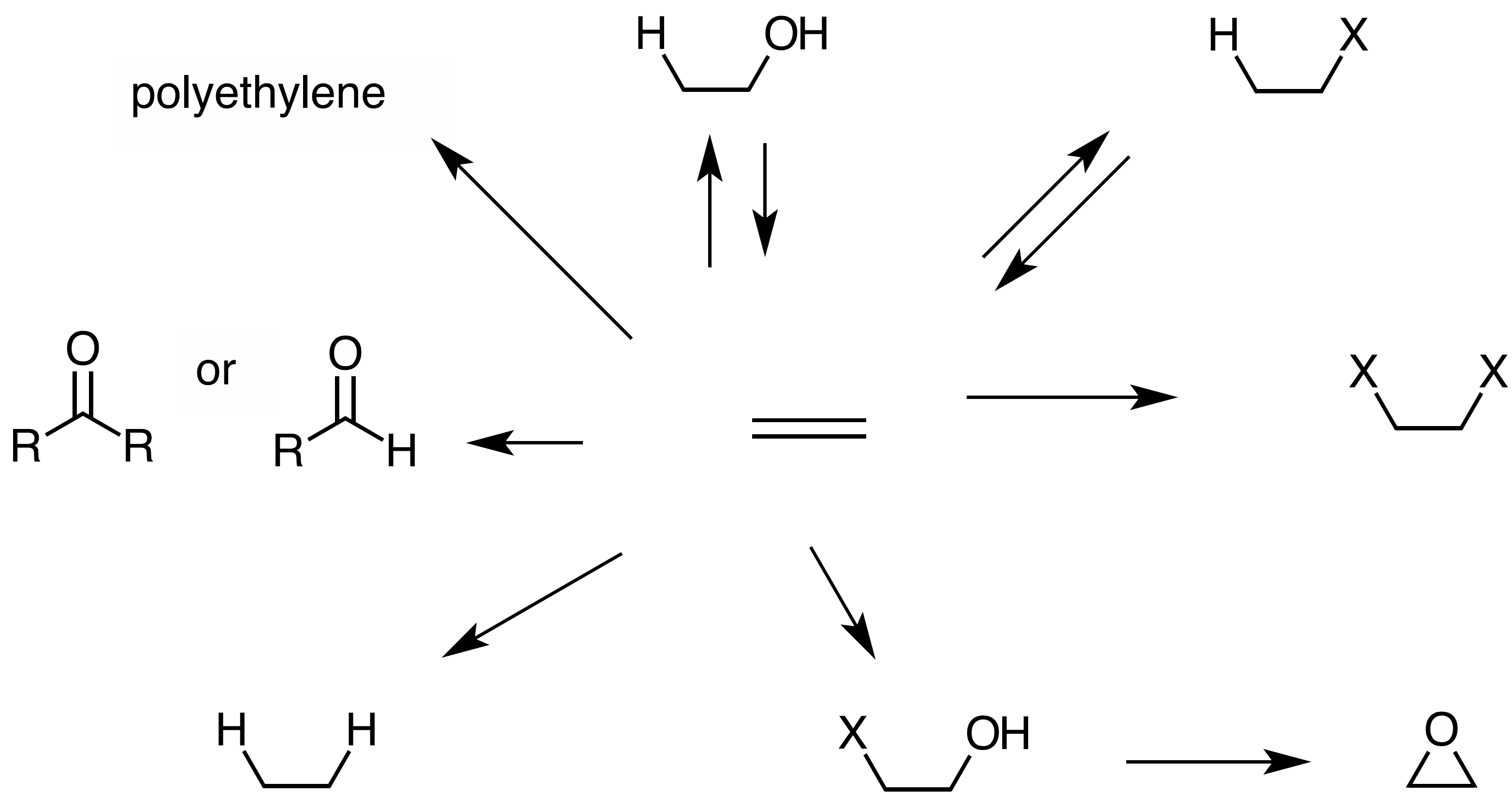
Polar Additions: alkene + HX --> alkyl halide
alkene + HOH ---> alcohol



Propylene

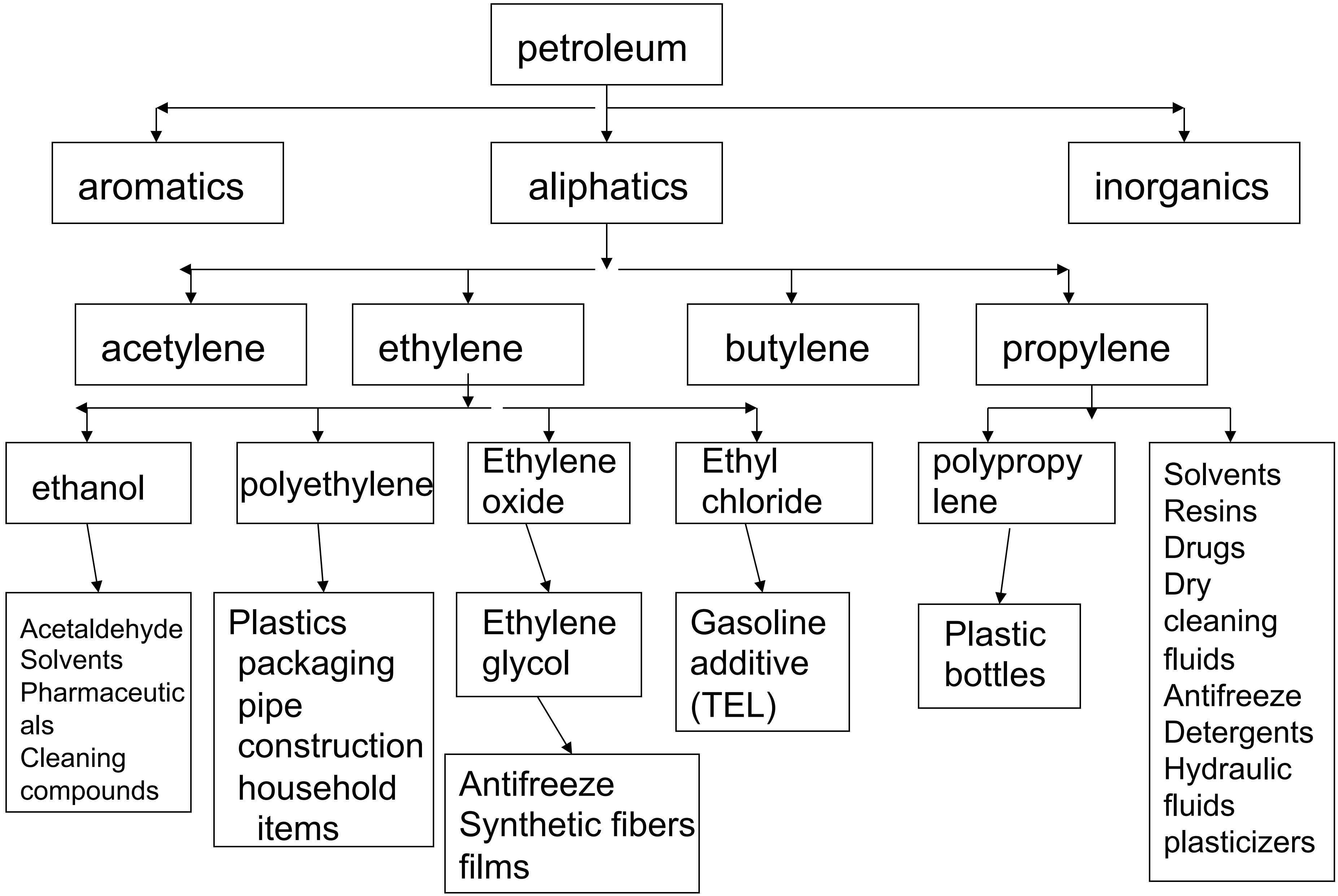
Isopropanol
Rubbing alcohol

Ethylene is used to make Other Functional Groups

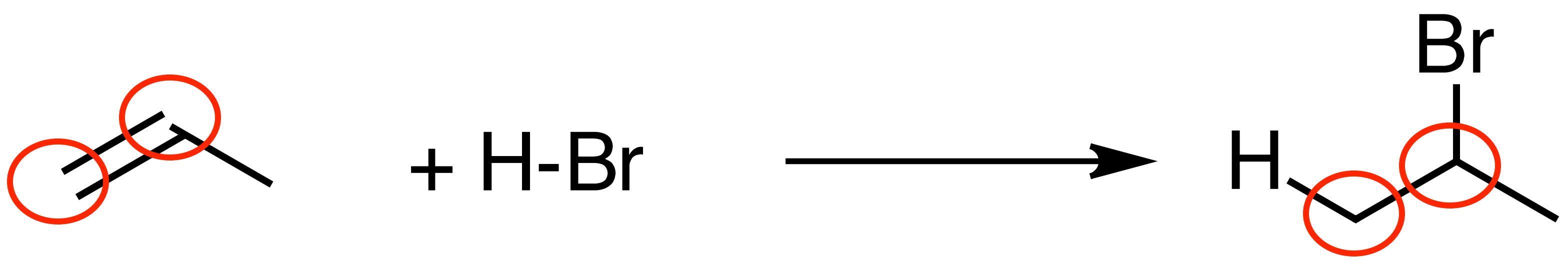


Many of these reactions are ***addition reactions*** (polar):

Ethylene and Propylene are used to make many products



Addition Reaction: pi bond Nucleophile reacts with Electrophile.
Pi bond breaks to form a new functional group.
2 atoms or groups forms bond (ADDS) to each vinylic C.



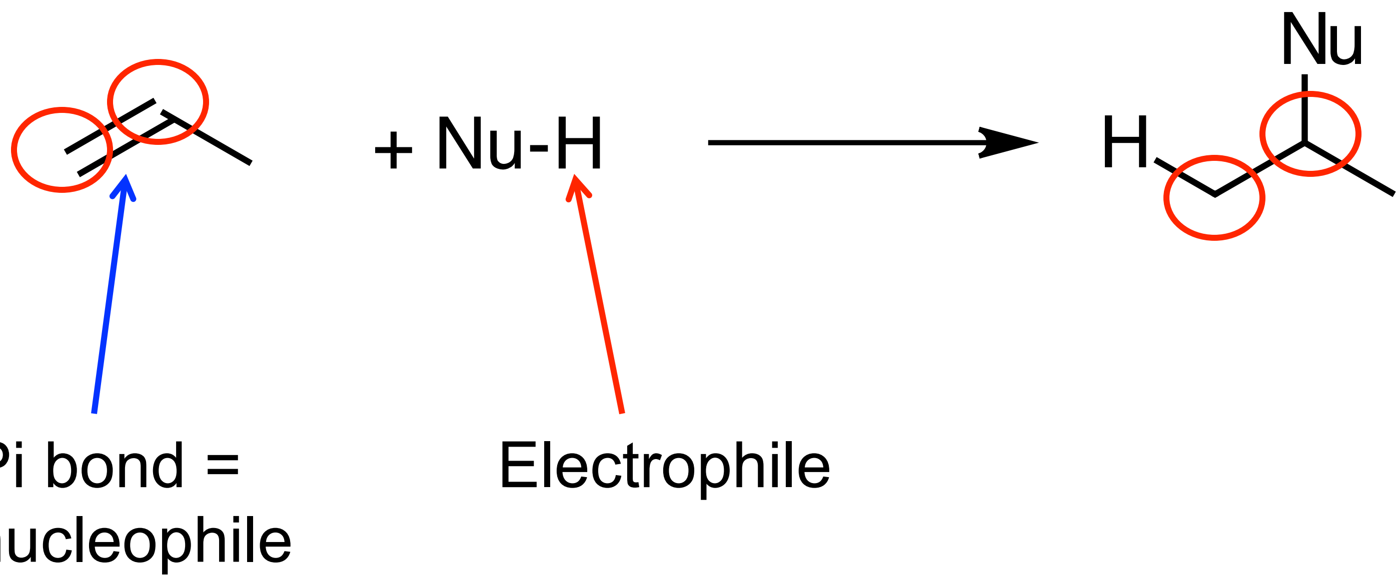
Synthesis: a good way to make a different functional groups from a pi bond

Structural Features *for* ***Addition Reactions***

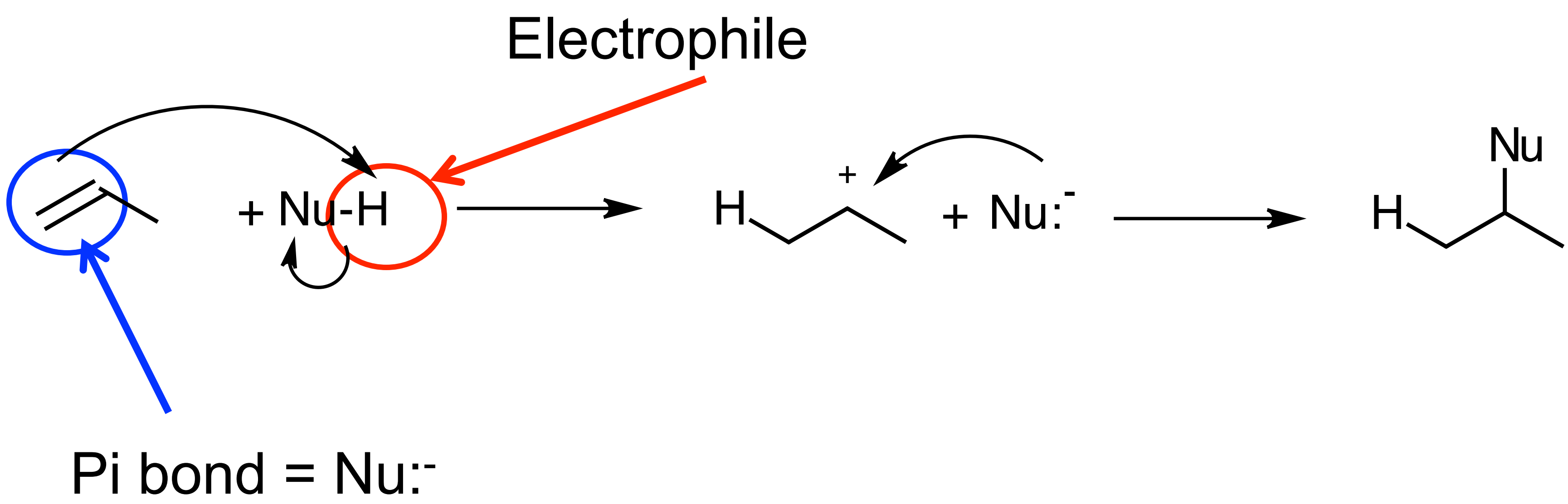
Need a:

1. Nucleophile ($Nu:^-$) = Pi bond
2. Electrophile (E^+)

The **Nucleophile Reacts with Electrophile. 2 atoms or groups adds to each vinylic C**.



Addition Reaction: pi bond Nucleophile reacts with Electrophile. Pi bond breaks. 2 atoms or groups adds to each vinylic C.



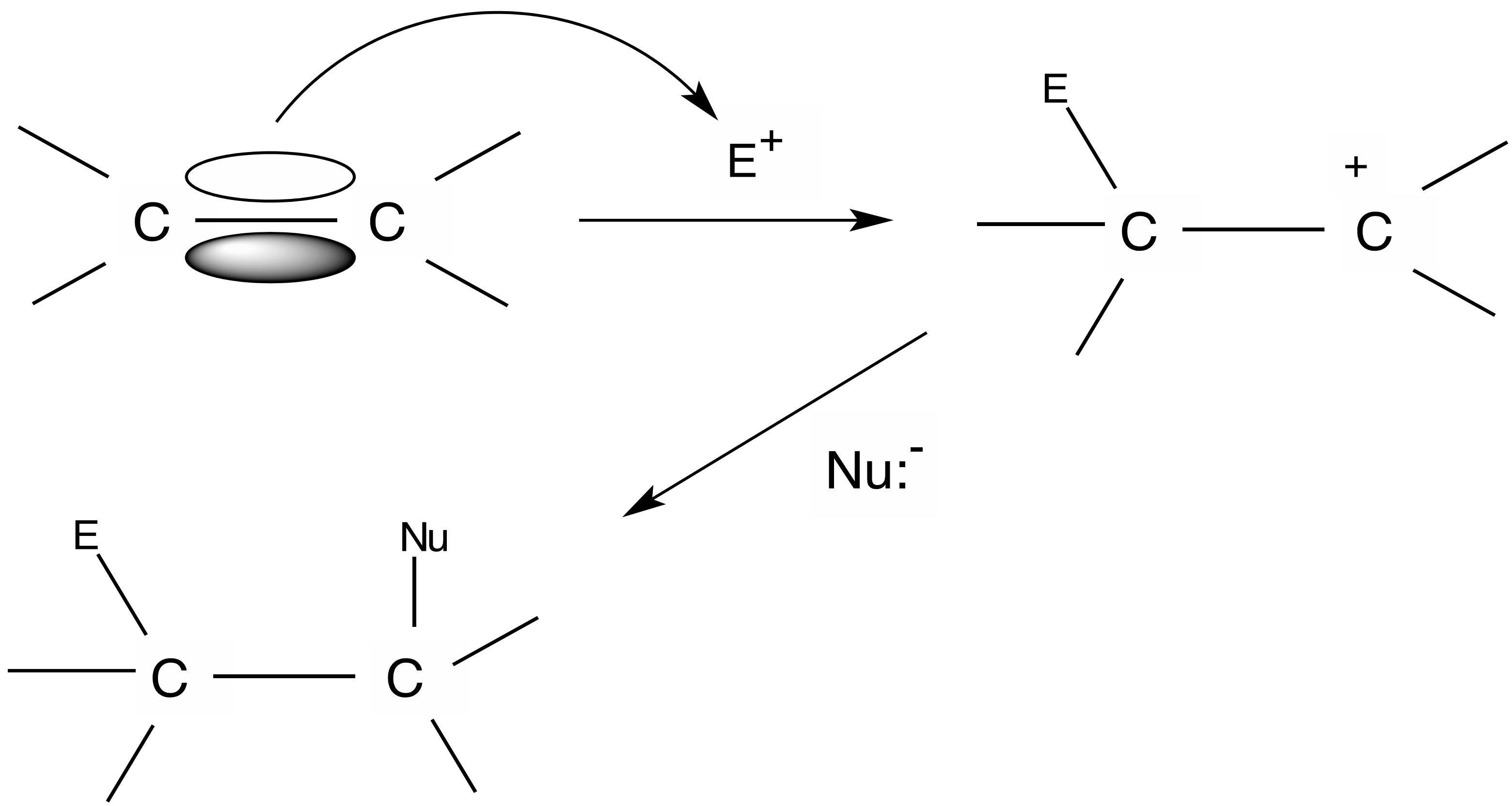
A CARBOCATION intermediate forms.
Another type of carbocation intermediate can form. Draw this carbocation.
What is the bond making process in the 2nd step?

Alkene Addition of HX or HOH is a Polar Mechanism

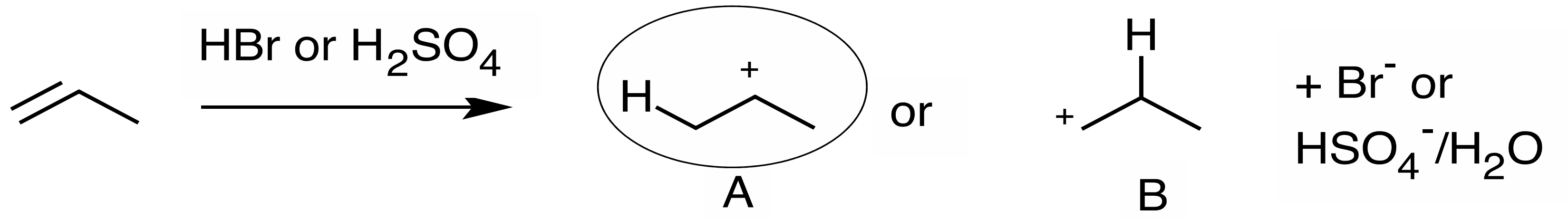
Alkene = π bond = Nu:$^-$ reacts with E$^+$ to form a ______ intermediate.

HX addition: ***E$^+$ = H in HX***

HOH addition: ***E$^+$ = H in H_2SO_4*** (H_2SO_4 is an acid catalyst)



The Stability of the _______ Intermediate Determines the Product.

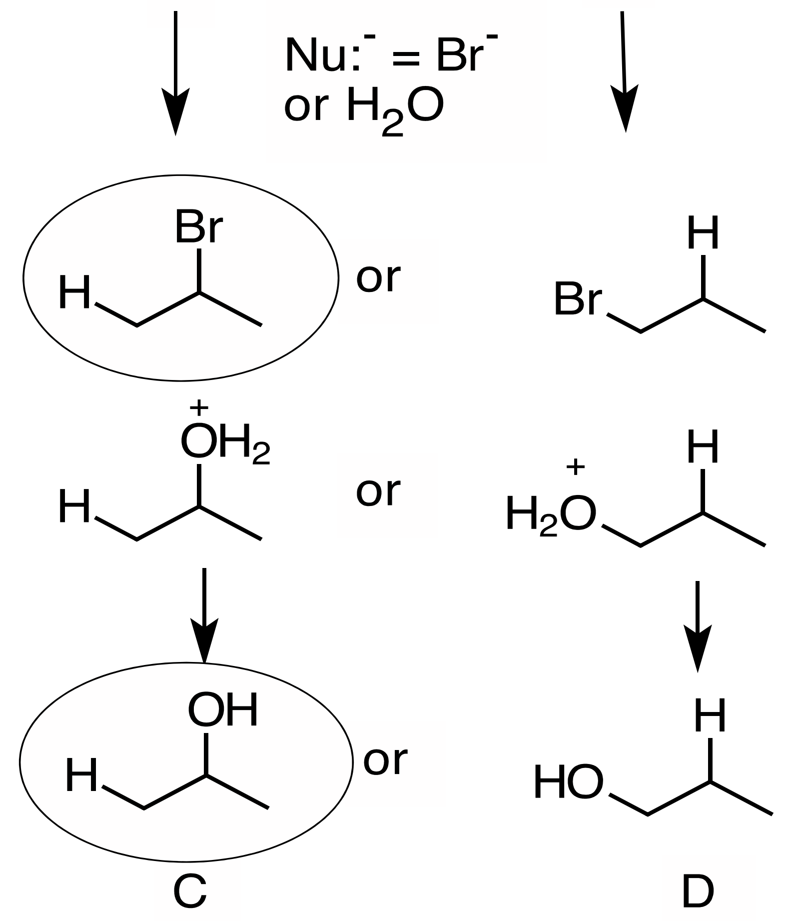


Markovnikov's rule:

E^+ adds to less substituted C in double bond

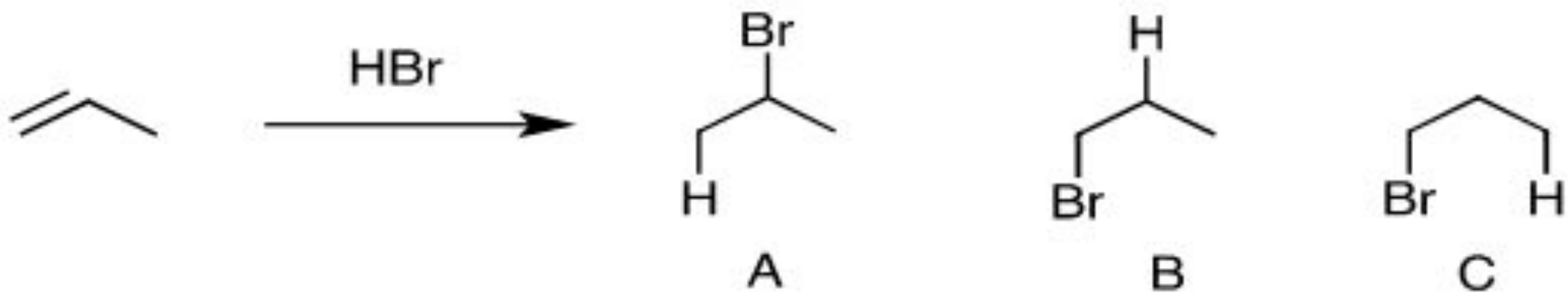
A is more stable

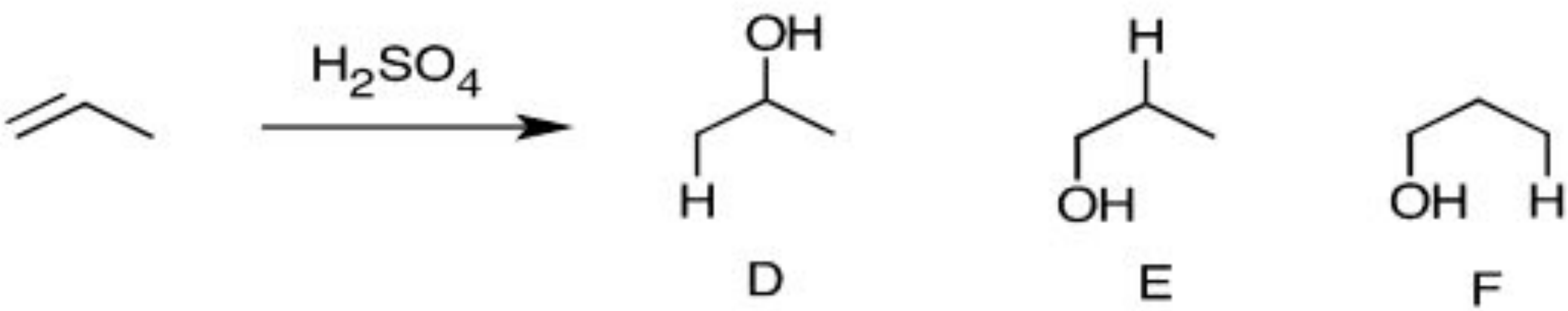
C is the product



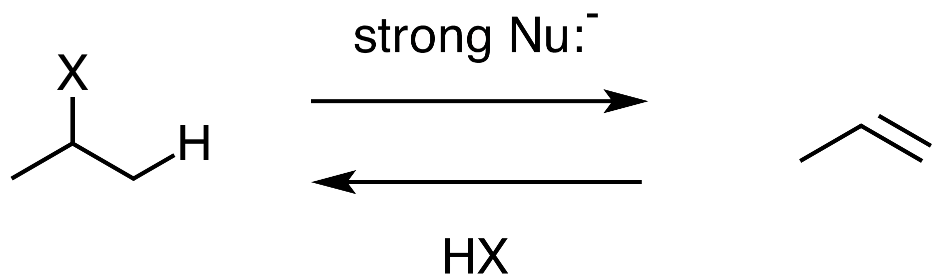
Alkenes undergo Addition Reactions

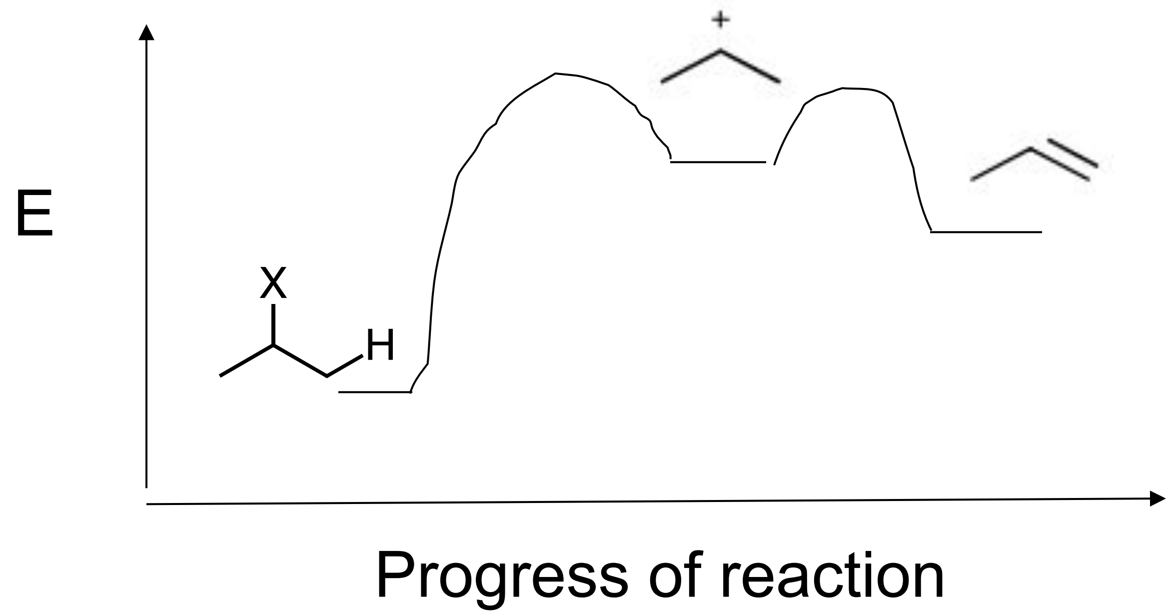
Predict the product of each reaction:





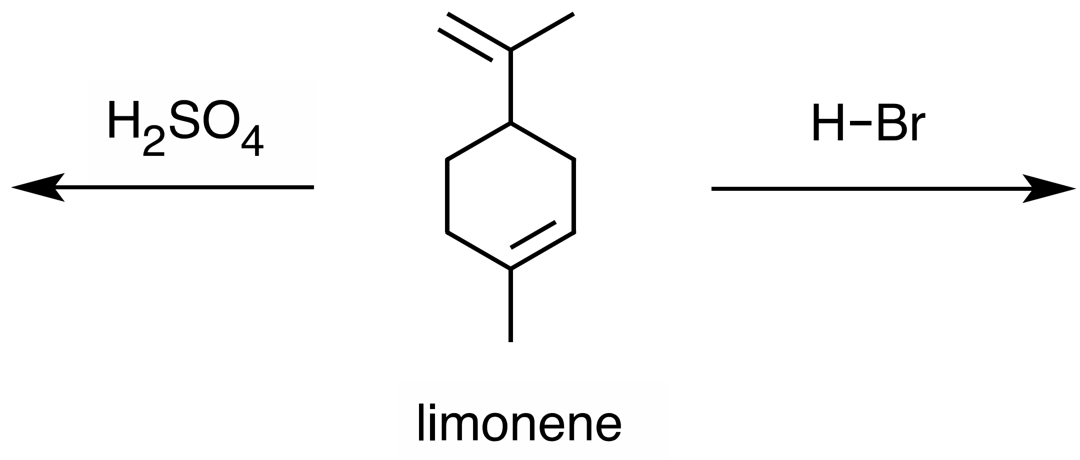
Addition Reaction of HX or HOH is the ***REVERSE*** of an Elimination Reaction ***(Use this in Organic Synthesis!)***





Which reaction requires high T? Why?

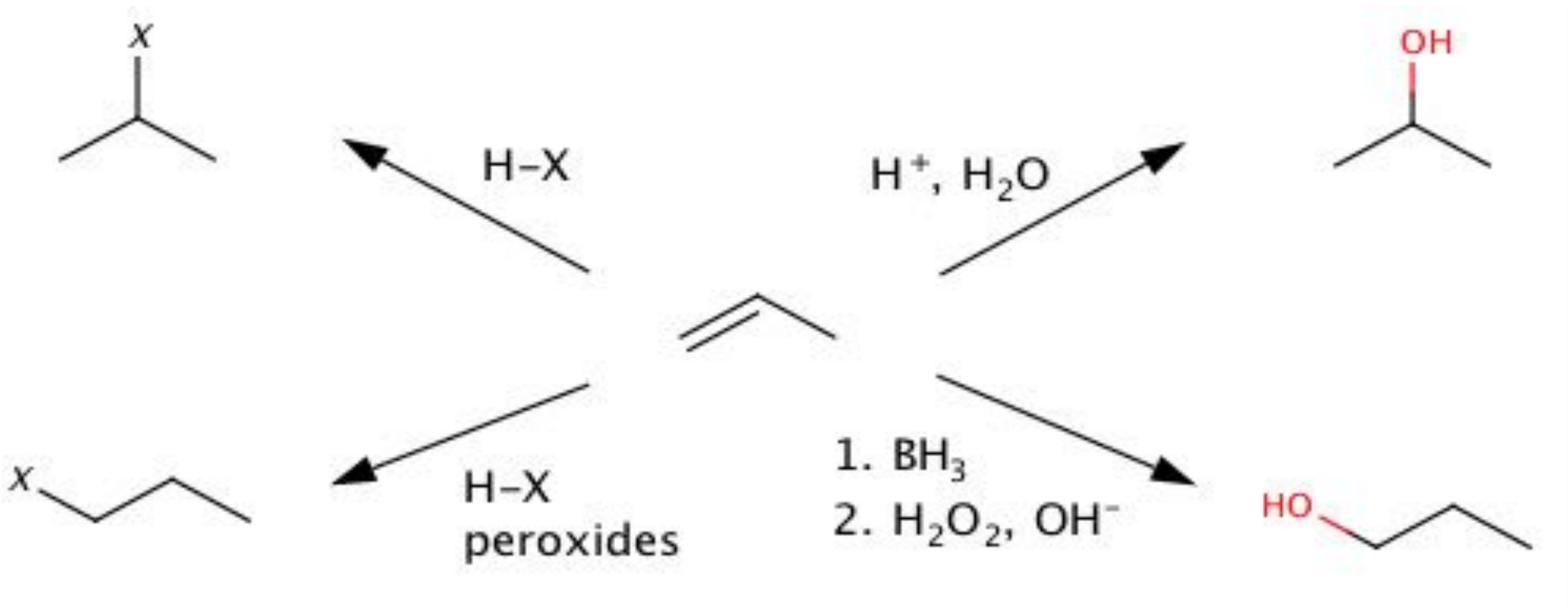
Predict the product of each reaction:



What if you want to add −OH or −X to the other C?

Reaction Conditions Determine the Product

Alkyl halide <---------   alkene ----------> Alcohol



Peroxides - radical reaction

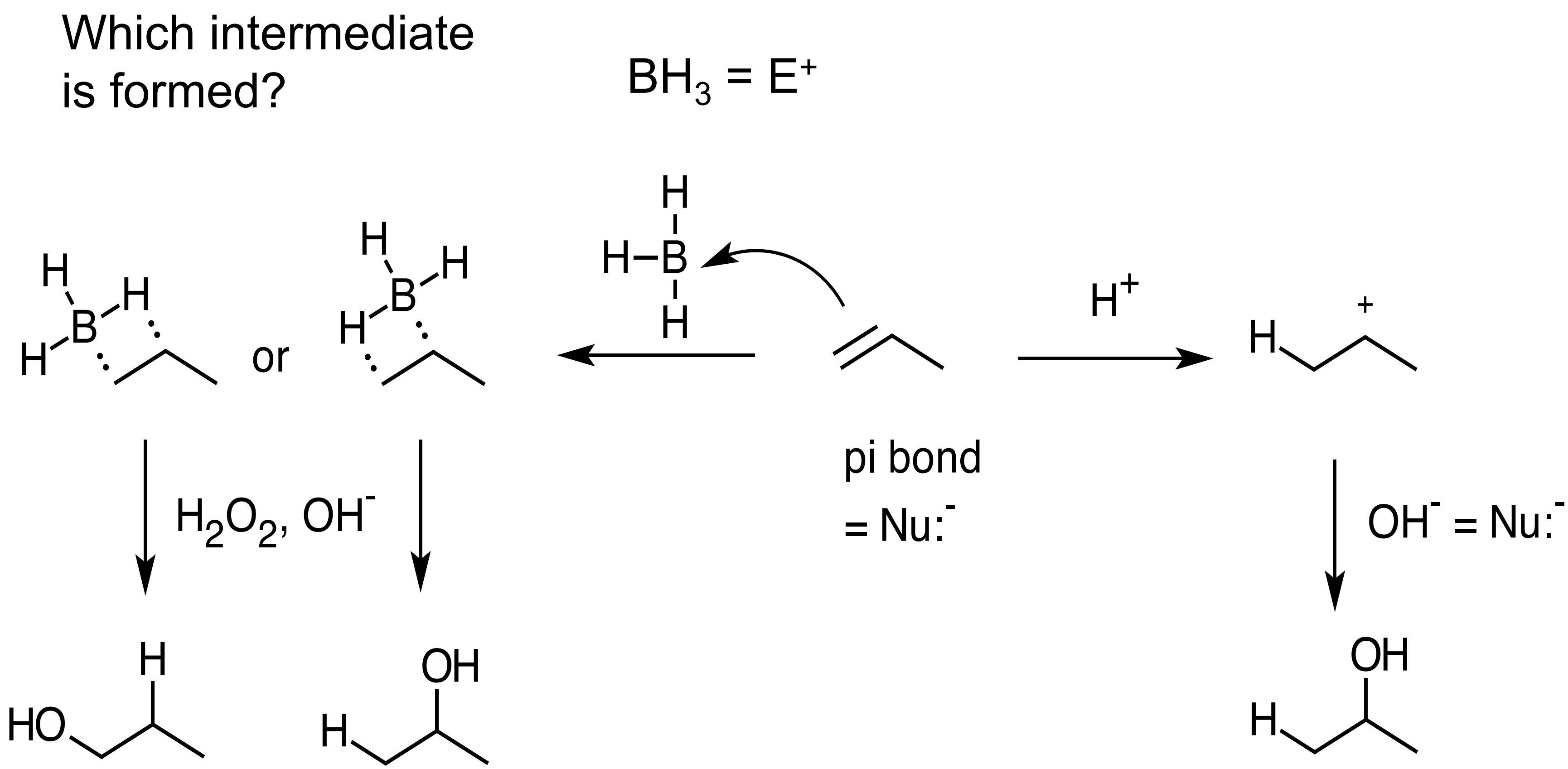
E^+ = B in BH_3

Which conditions produce the Markovnikov product?
Which conditions produce the non-Markovnikov product?

Alkene to Alcohol: What if you want to add –OH to *other* C?

1. H_2SO_4 (acid catalyzed hydration - Markovnikov)
2. BH_3/ H_2O_2, OH^- (hydroboration - anti-Markovnikov)

What is the *mechanism*?



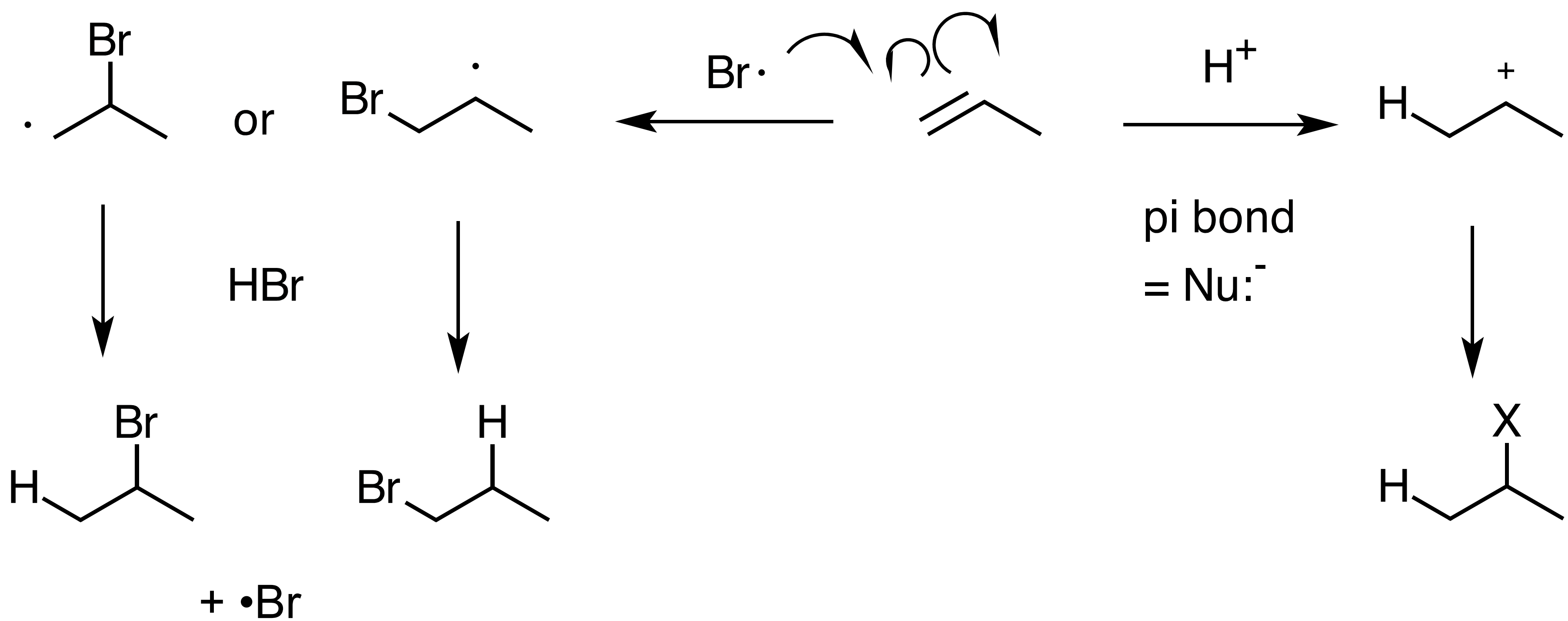
Alkene to Alkyl Halide: What if you want to add −Br to *other* C?

1. HX (hydrohalogenation - Markovnikov)
2. HX/ ROOR (hydrohalogenation - anti-Markovnikov)

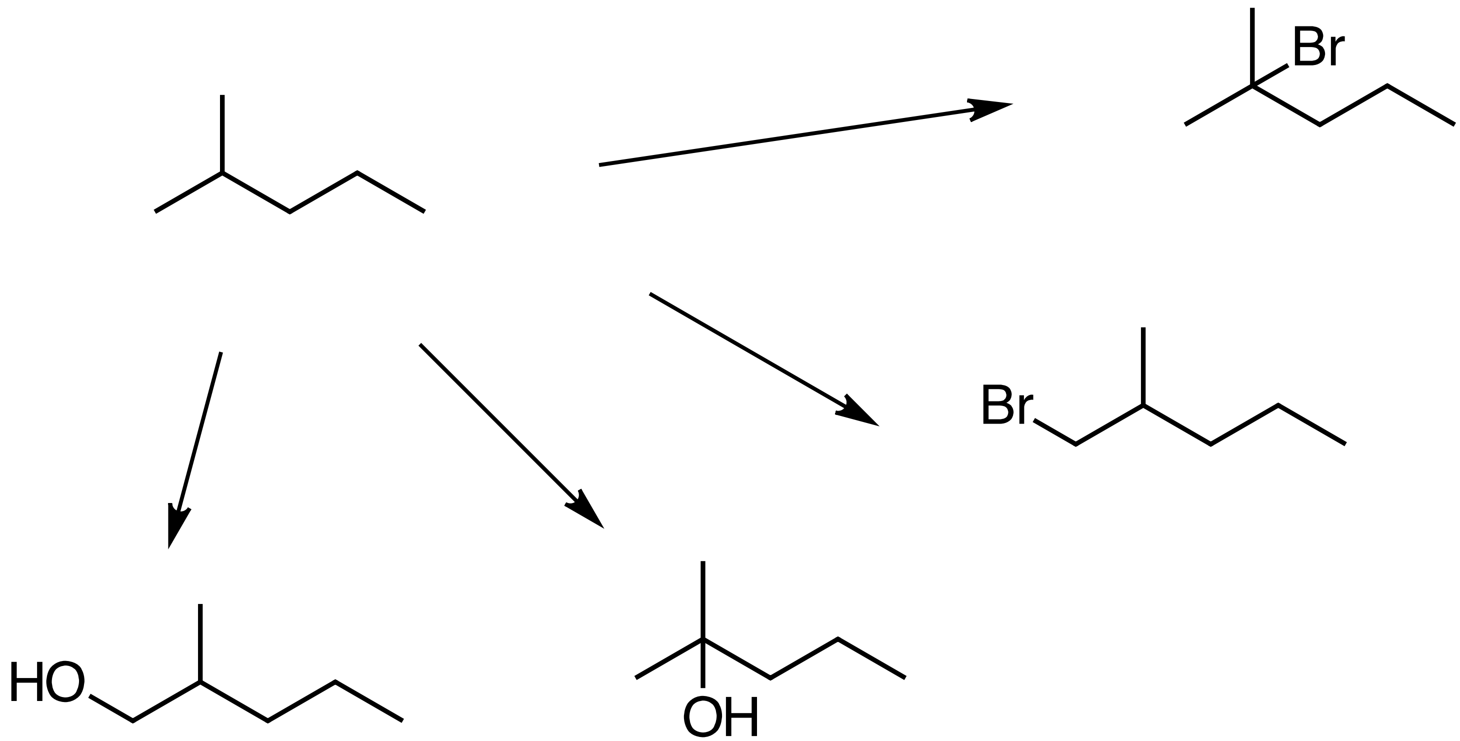
Radical mechanism. See Klein, Chapter 11.10

Peroxide: ROOR --> 2 RO•
HBr + RO• --> ROH + •Br
•Br + alkene --> alkyl radical

Which intermediate is formed?



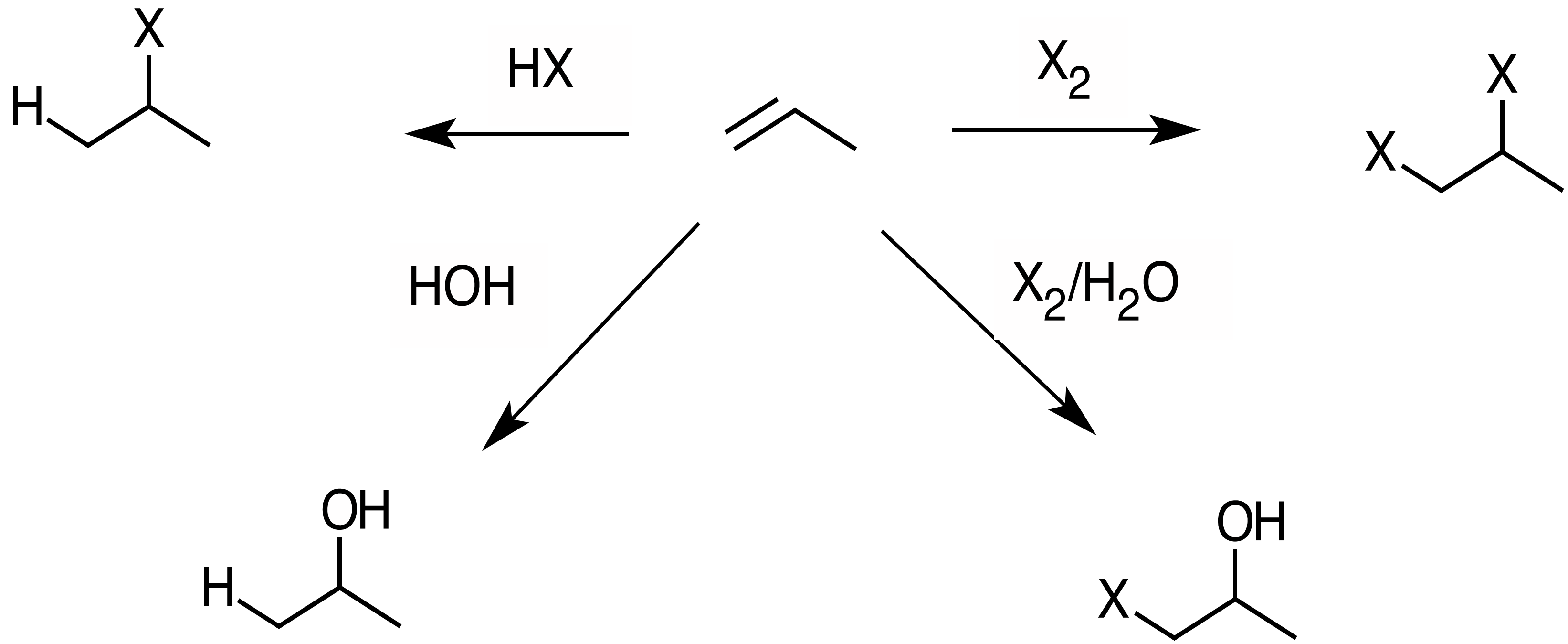
Which reagent would you use for each reaction?



Alkene Addition Reactions Make Different Functional Groups

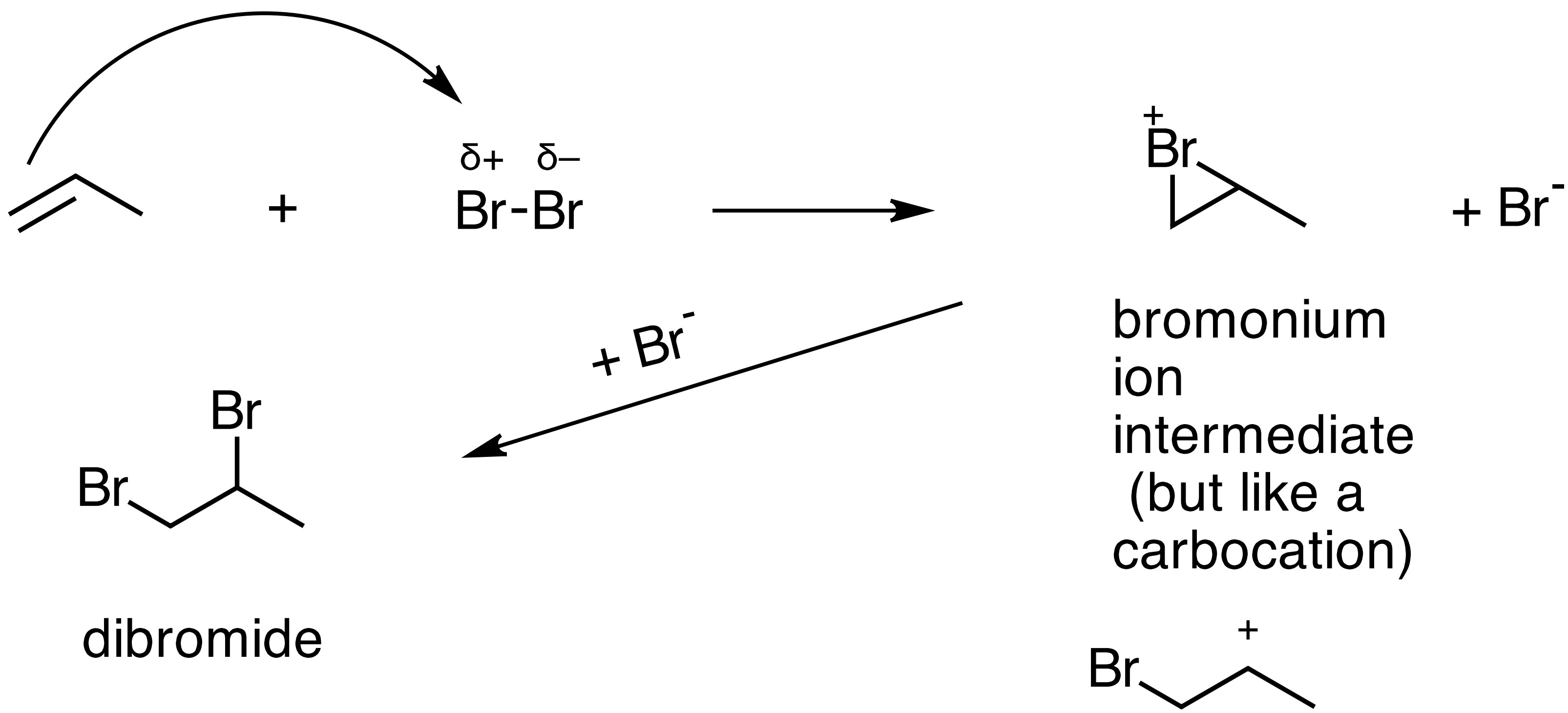
Polar Additions:

alkene + HX --> alkyl halide
alkene + HOH ---> alcohol
alkene + X_2 ---> dihalide
alkene + X-OH ---> halohydrin



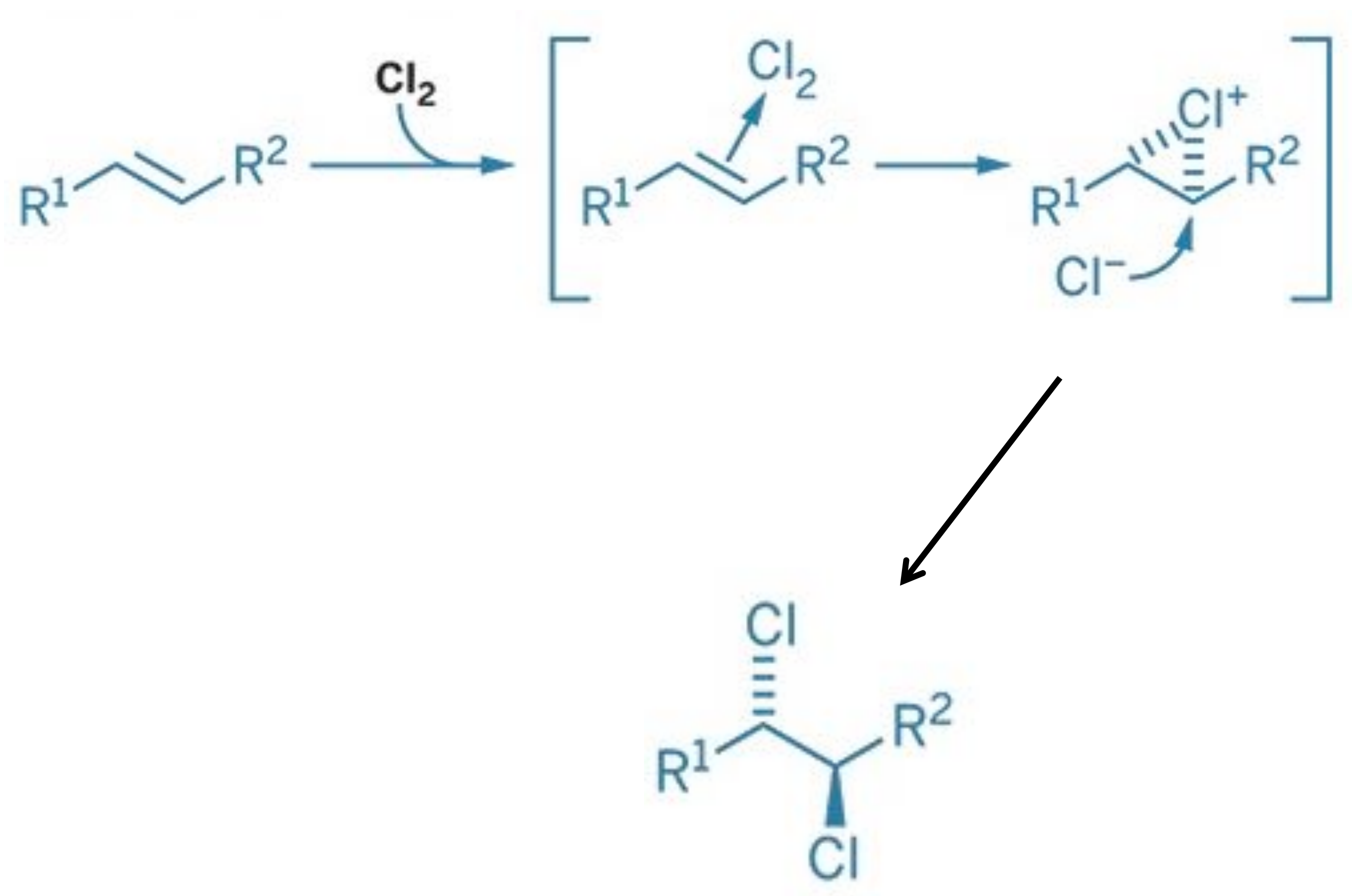
Identify functional group.
What reaction type occurs with this functional group?
At what atom(s) does this reaction type occur?
What reagent is needed for this reaction type to occur?

Alkene addition of X_2, e.g.,Br_2, forms a ***dihalide***.
Br_2 is non-polar, but at one instant in time, Br is E^+



Alkene Addition of X_2 is a Polar Mechanism

Alkene Halognenation Stereochemistry



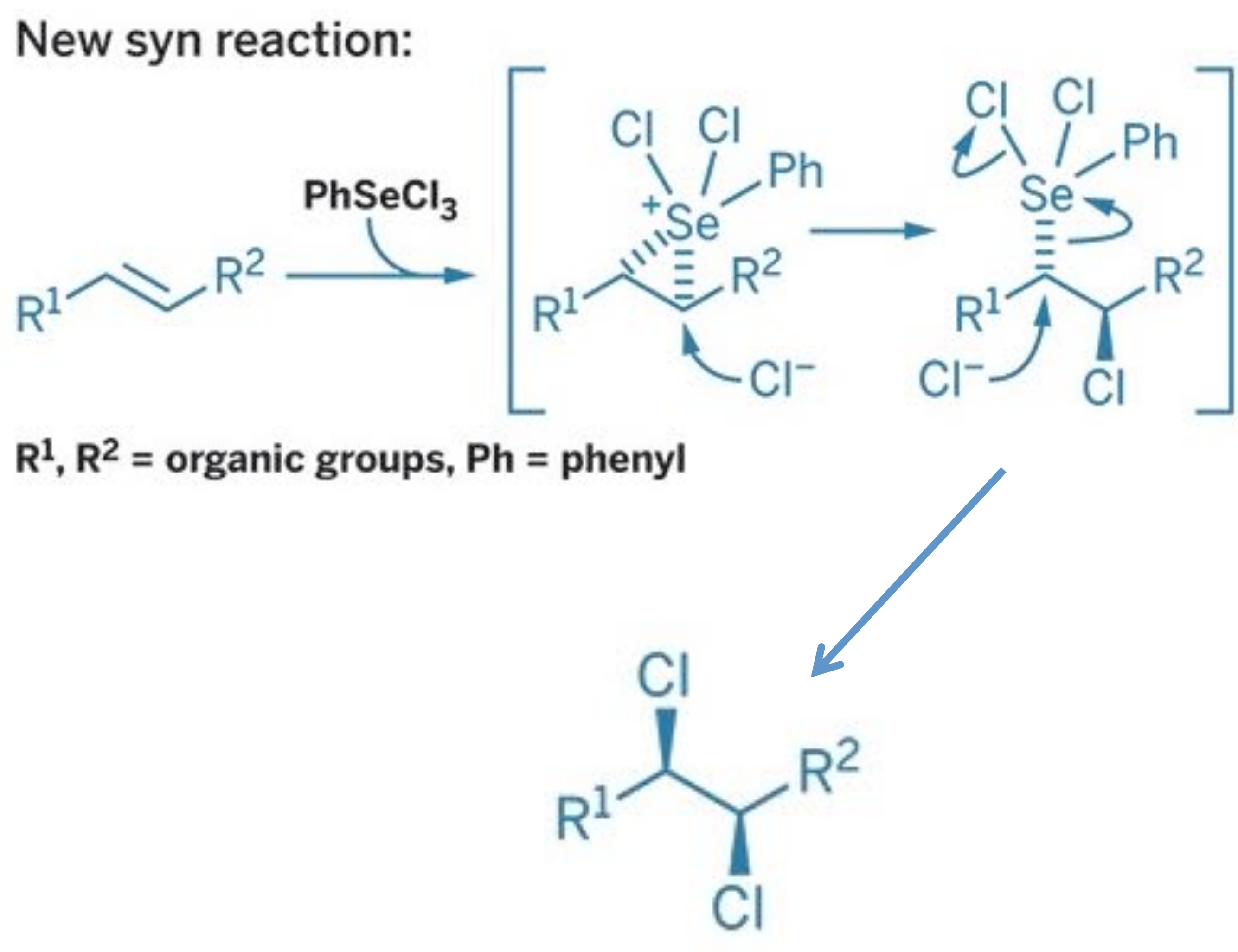
syn or *anti*?

CEN, 1/19/15, p. 5

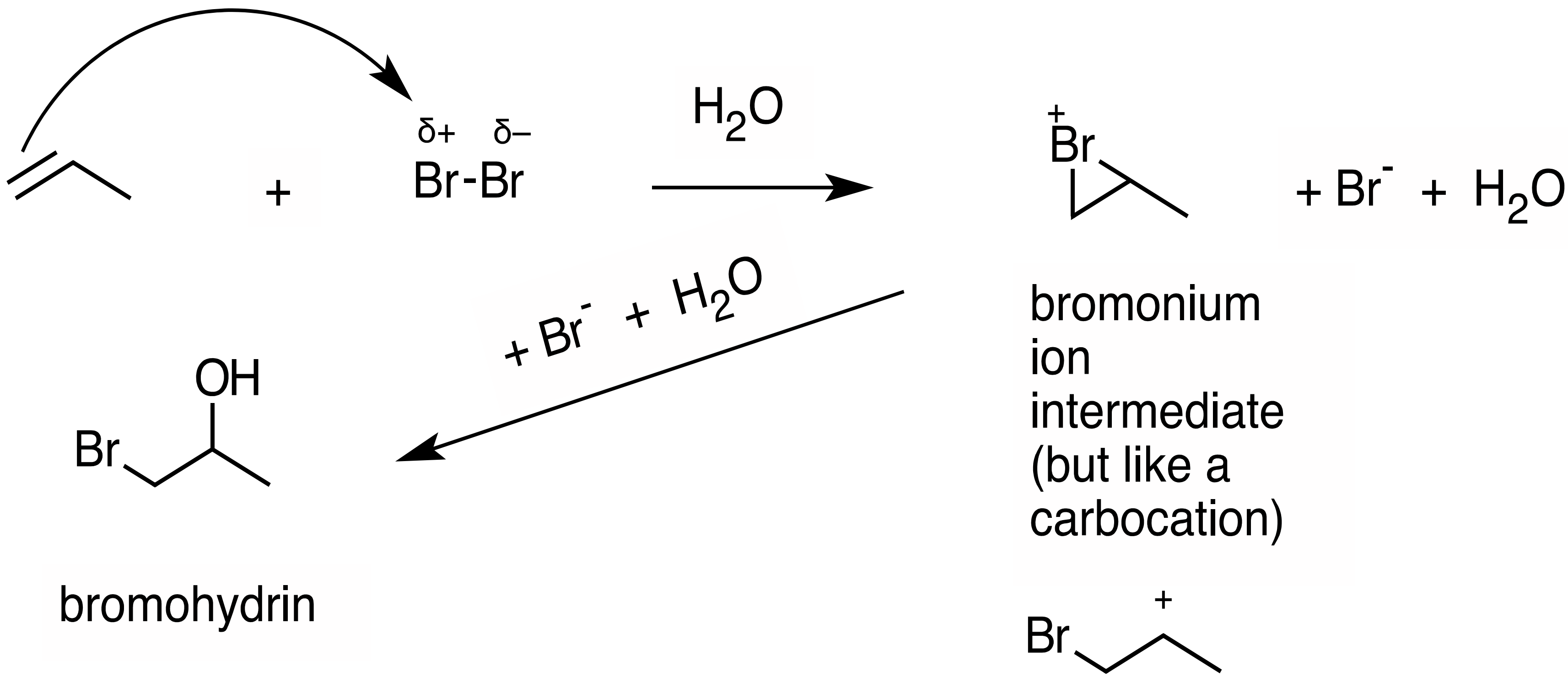
Alkene Halognenation Stereochemistry

http://cen.acs.org/articles/93/i3/Classic-Addition-Reaction-Makeover.html

CEN, 1/19/15, p. 5 New catalyst – *syn* addition (instead of *anti*)



Alkene addition of X_2 and H_2O forms a ***halohydrin***.

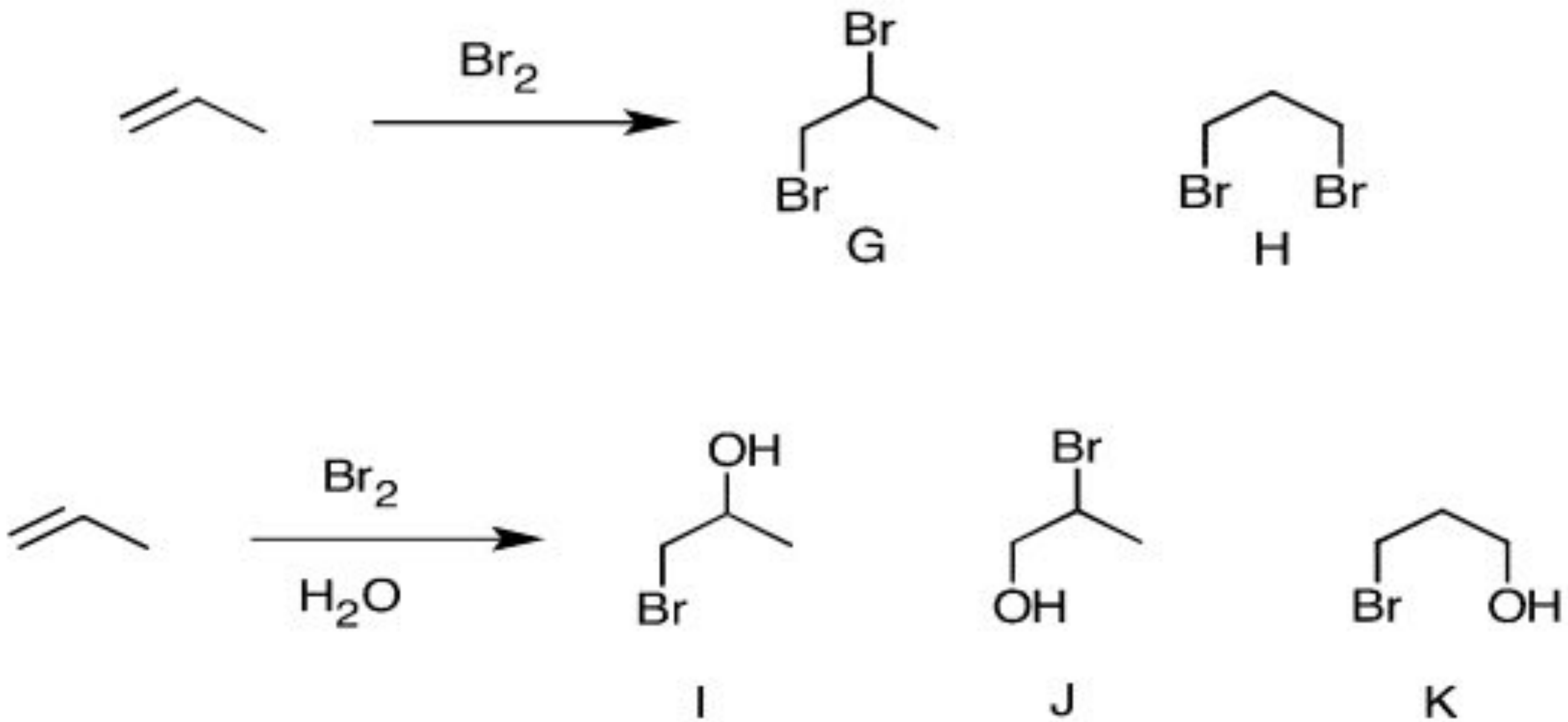


Why does H_2O react and not Br^-?

Polar mechanism

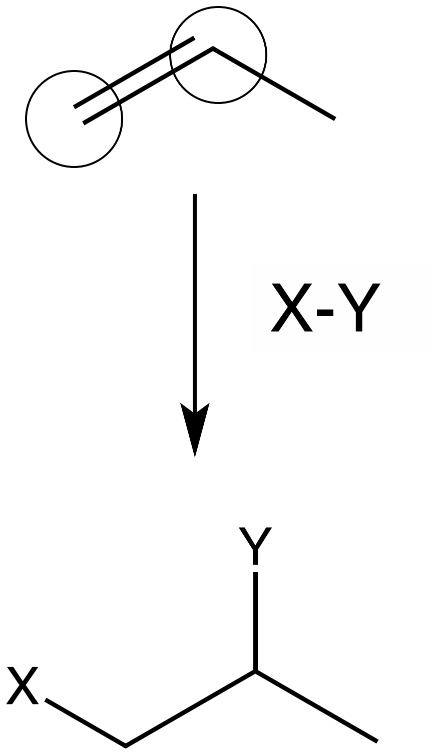
Alkenes undergo Addition Reactions

Predict the product:



Alkene Addition Forms Different Functional Groups

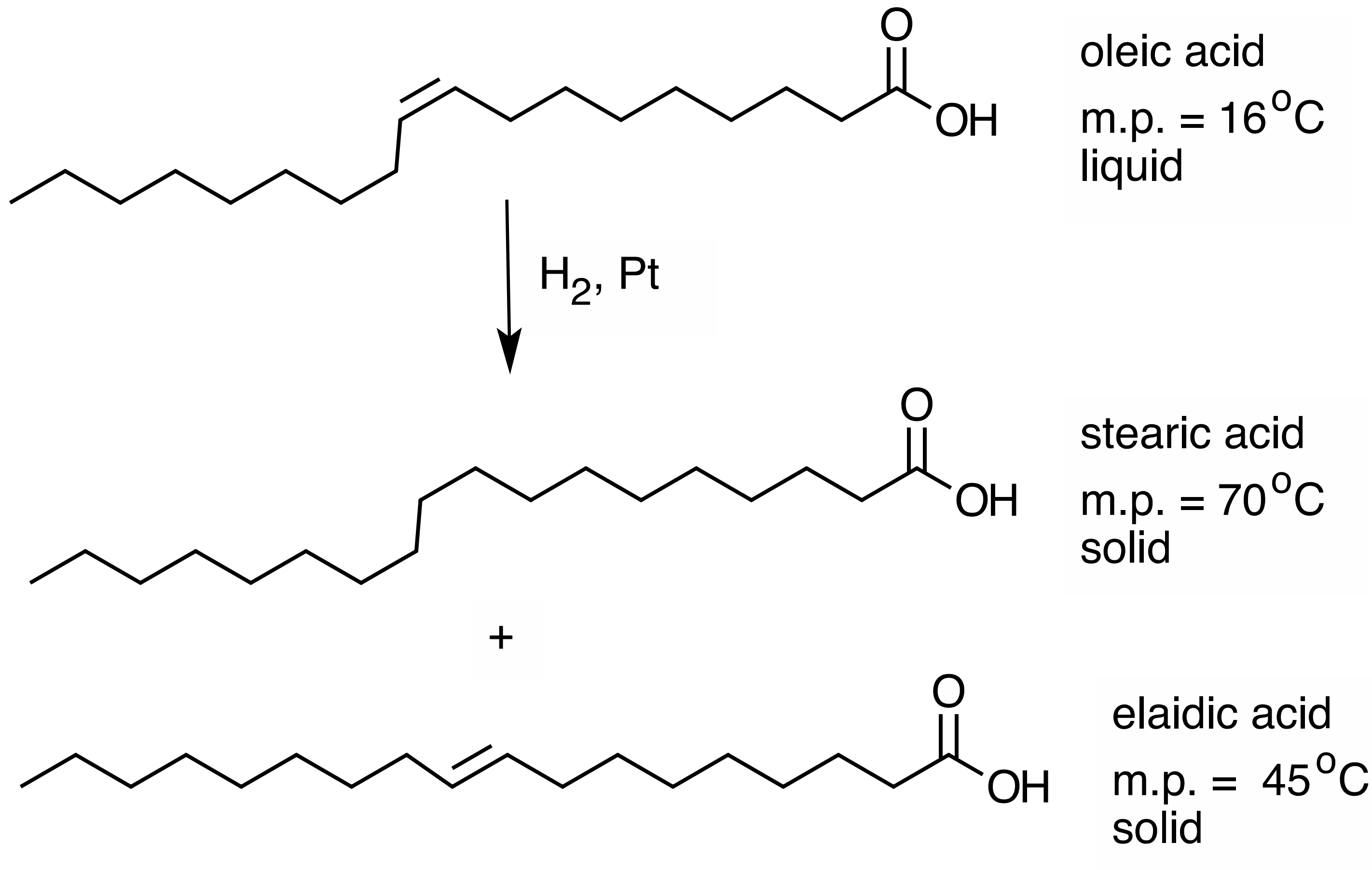
X-Y adds across C=C double bond



X	Y	Reaction Conditions	Product
H	X	HX (Markovnikov) HX/ROOR (Non-Markovnikov)	Alkyl halide
H	OH	H_2SO_4 (Markovnikov) 1. BH_3 2. H_2O_2, OH^- (Non-Markovnikov)	Alcohol
X	X	X_2	Dihalide
X	OH	X_2/H_2O	Halohydrin
H	H	H_2/Pd, Pt, Ni	Alkane
OH	OH	Peroxyacid/ H_3O^+	Diol

Very useful in organic synthesis

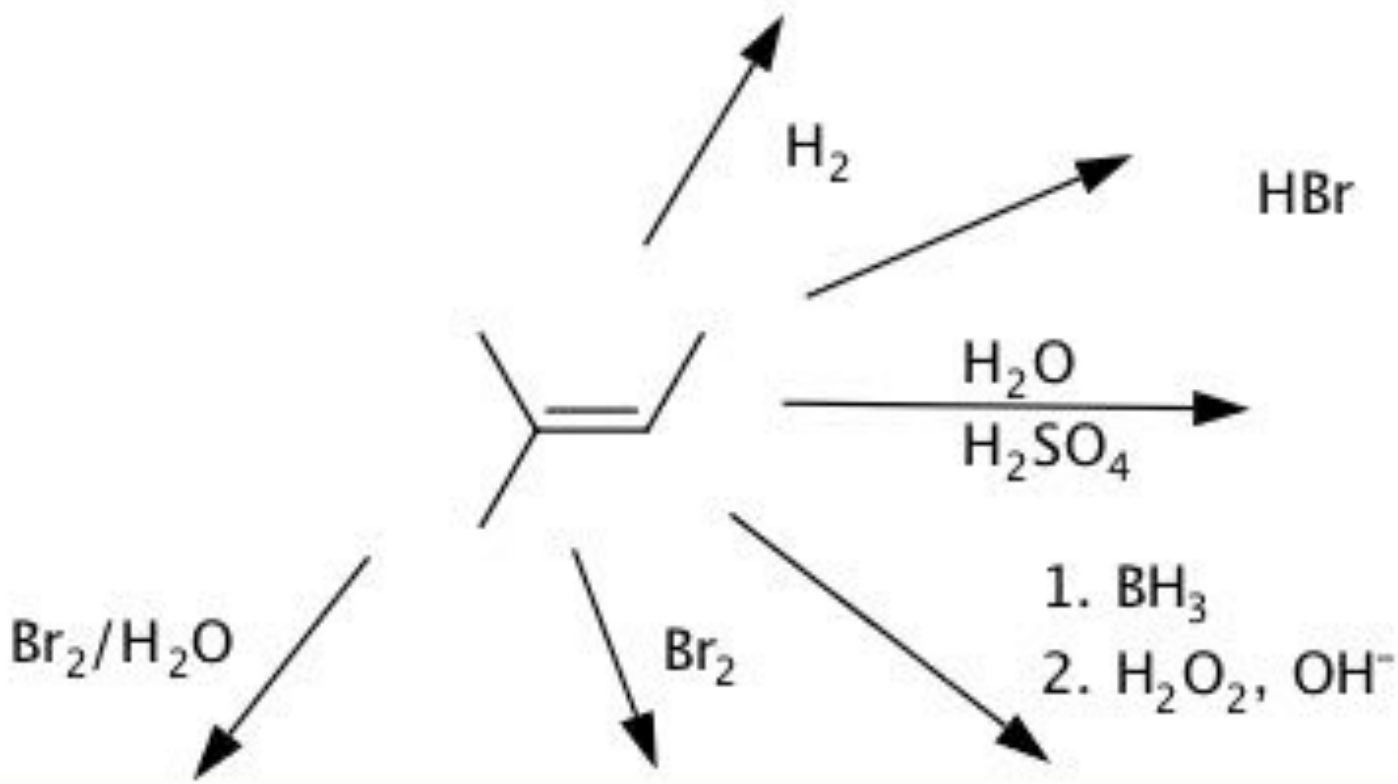
Convert an Unsaturated fat to a Saturated fat by Hydrogenation
But ***trans fats*** are also formed



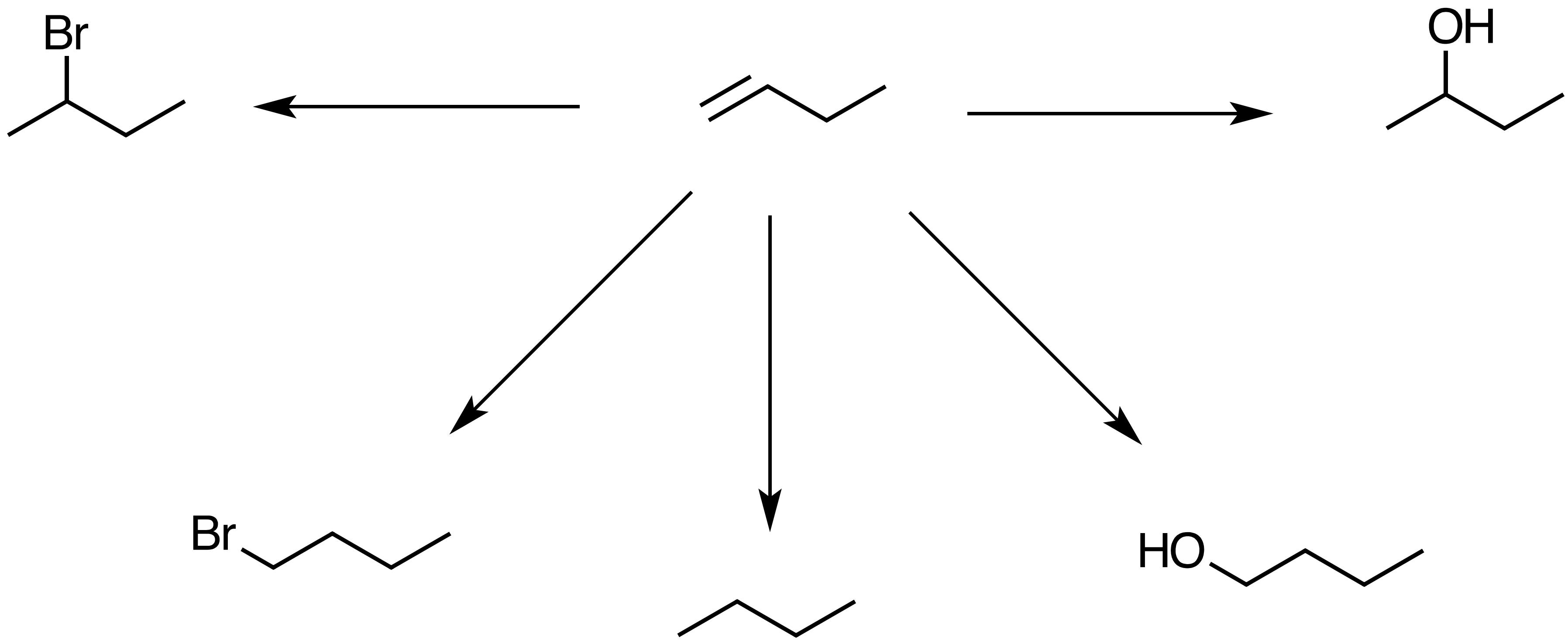
Also, polyunsaturated fat ---> monounsaturated fat

Why convert an unsaturated fat to a saturated fat?

Given the reaction conditions, predict the product (functional group):



How would you synthesis each compound from 1-butene?
Determine the reaction conditions for each reaction.
See Practice Problem 6b.



Choices: a. H_2SO_4

b. H_2O

c. HBr

d. NaOMe

e. HBr and peroxides

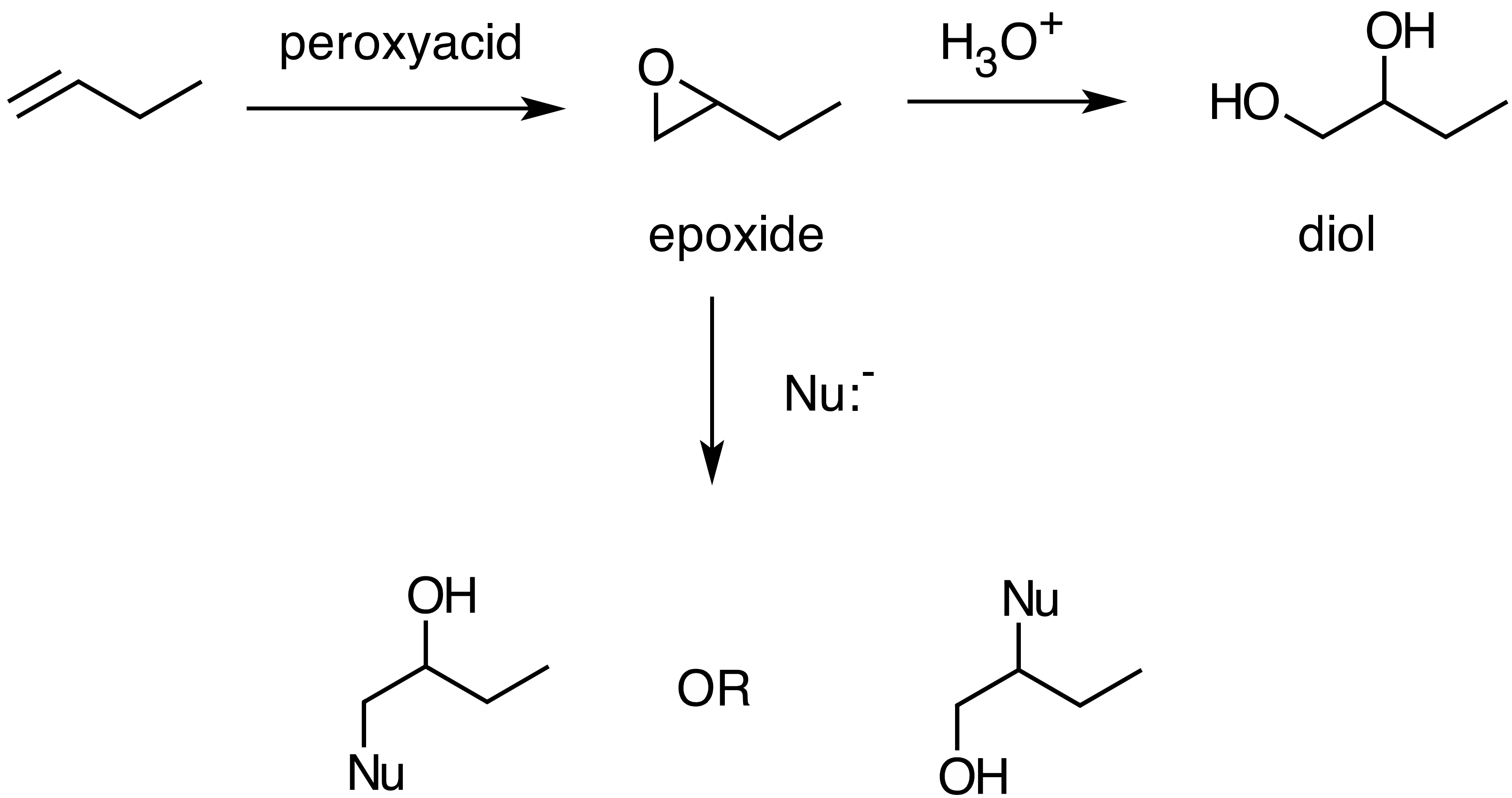
f. Br_2

g. BH_3/H_2O_2, OH^-

h. H_2/Pd

Alkene --> **EPOXIDE** --> Diol

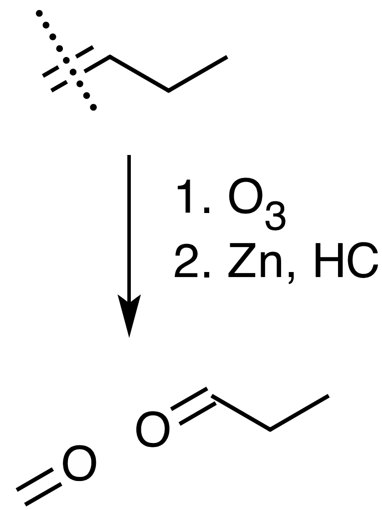
Epoxides are important intermediates in organic synthesis



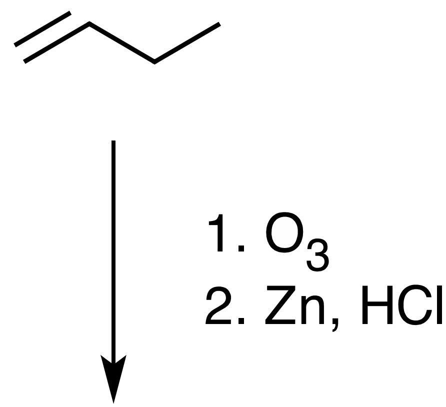
Which one?

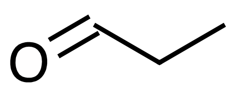
We will see Epoxides in Chem 12B.

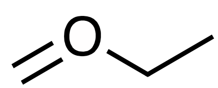
Make a smaller compound from a bigger one:
Use OZONOLYSIS
Ozonolysis cleaves (breaks) C=C bond
to form two C=O bonds

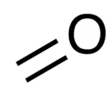


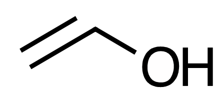
Predict the products:





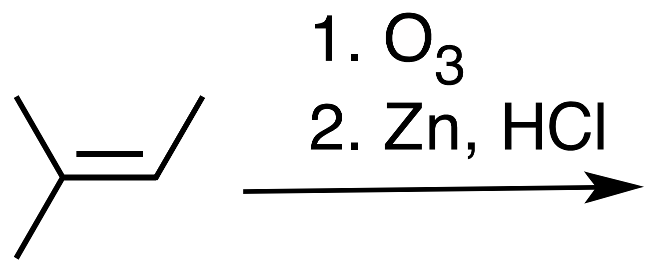


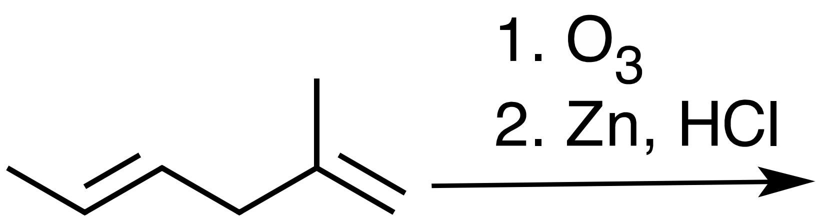




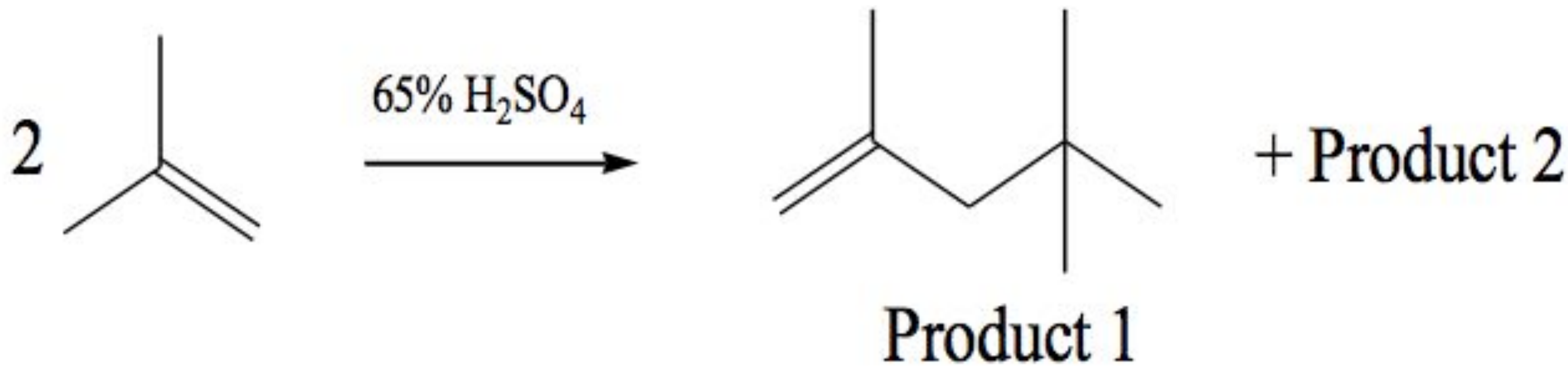
Make a smaller compound from a bigger one:
Use OZONOLYSIS

Predict the products:





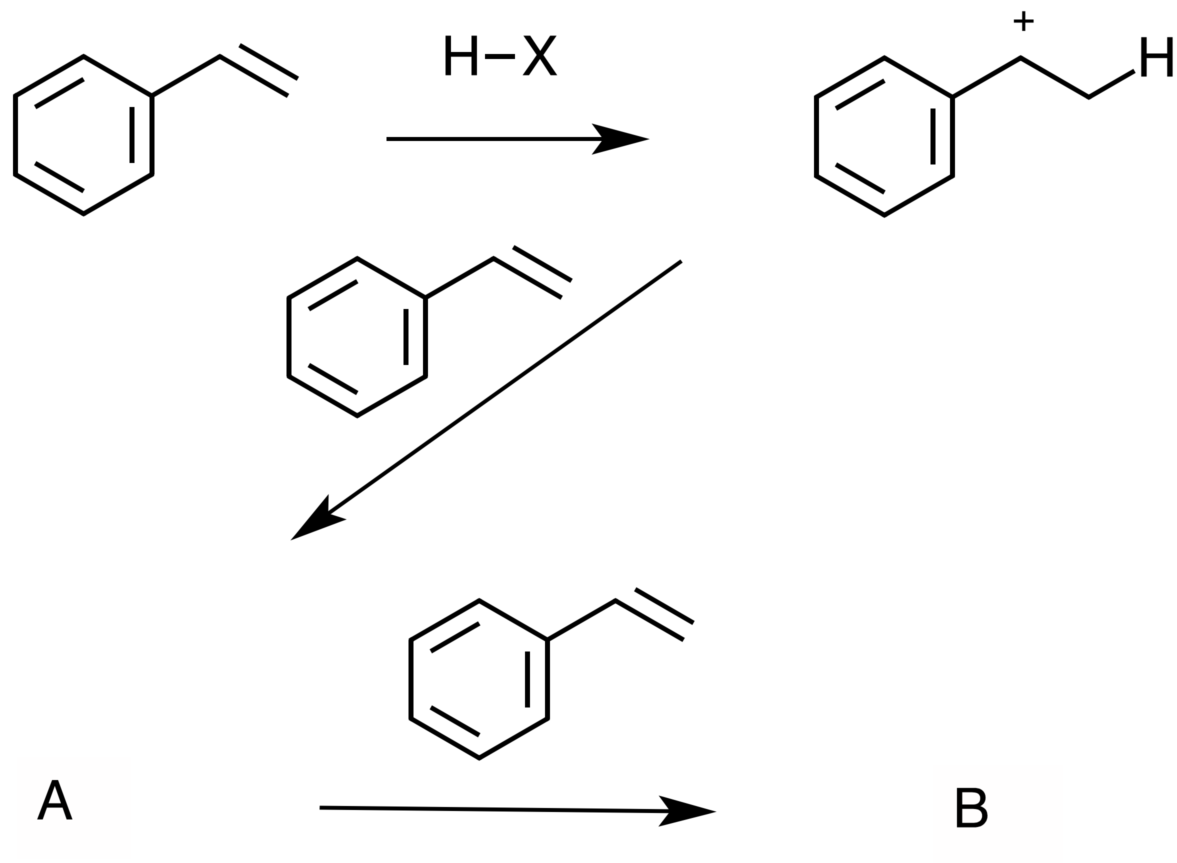
Make a Big Compound from a Small Compound
Explain how Product 1 is produced. Draw the structure of Product 2.



Hint: carbocation is a _____. Pi bond is a ______.
A Reaction Mechanism Describes How a Product is Produced

Once a carbocation forms, any Nu:$^-$ can react with it.

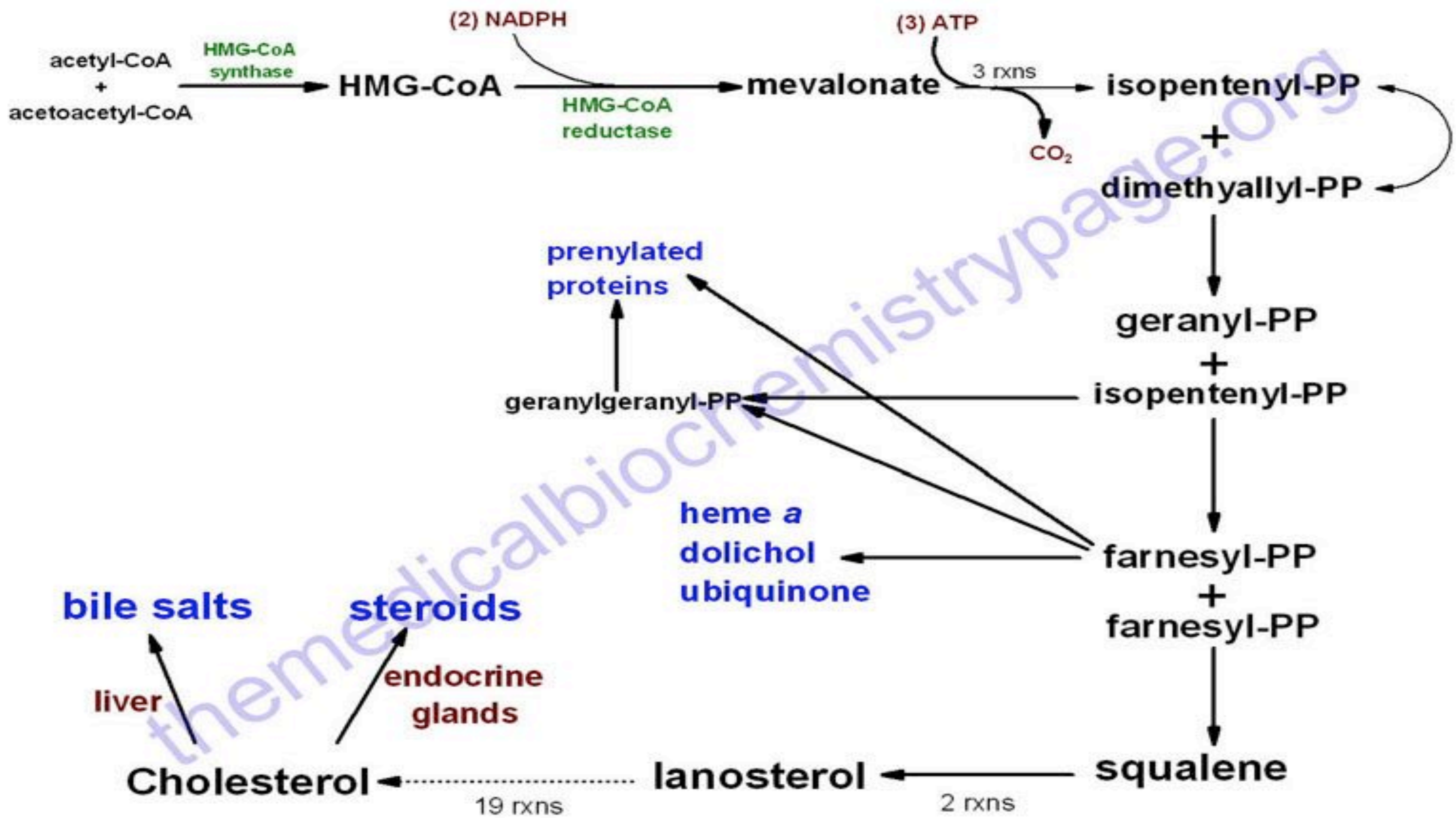
Cationic Polymerization: Styrene --> Polystyrene (Klein p. 405).
What is A and B?



(Use this reaction to make a larger molecule - ***lengthen carbon chain***)

Steroids, e.g., Cholesterol, are Made From ***Squalene*** (precursor)

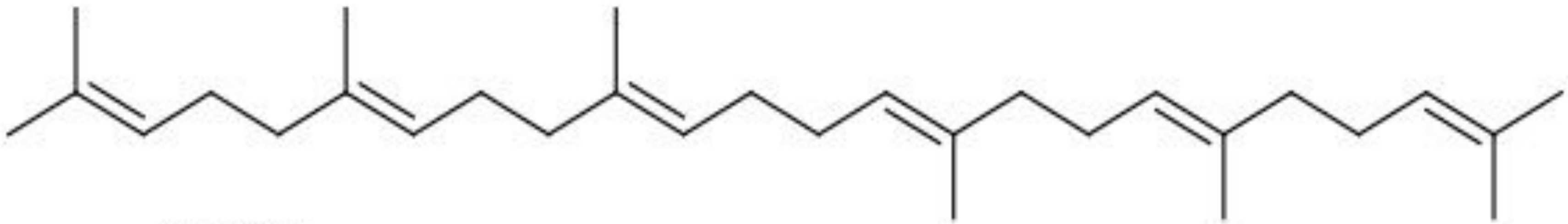
http://en.wikipedia.org/wiki/Squalene
http://en.wikipedia.org/wiki/Cholesterol
http://themedicalbiochemistrypage.org/cholesterol.html



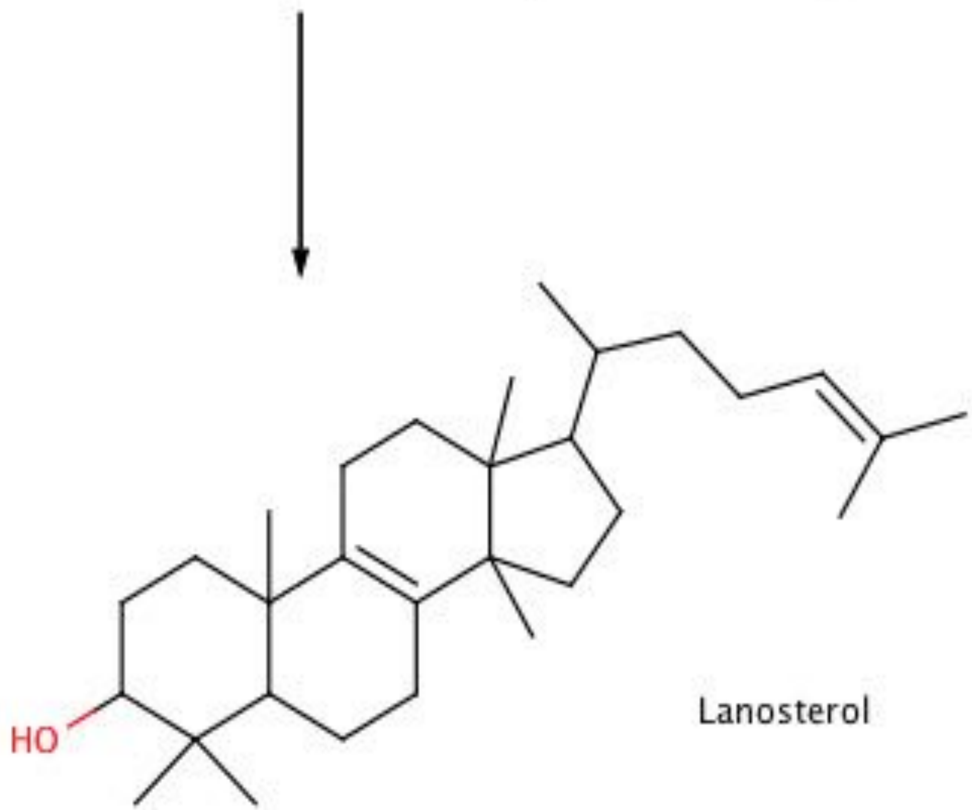
20-25% of total daily cholesterol production occurs in liver

Squalene is Converted to Lanosterol by ***<u>Alkene Addition</u>***

How is squalene (chain) converted to Lanosterol (rings)?



Squalene



Lanosterol

Squalene Undergoes ***Alkene Addition***, ***Rearrangements***, and ***Elimination*** to form Lanosterol