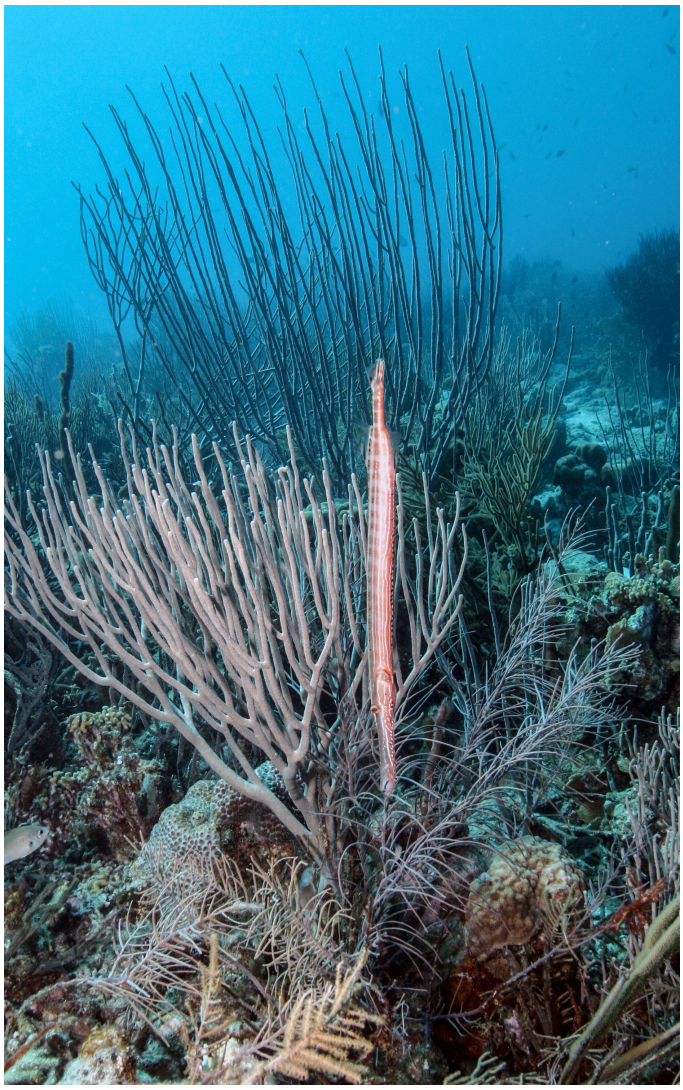
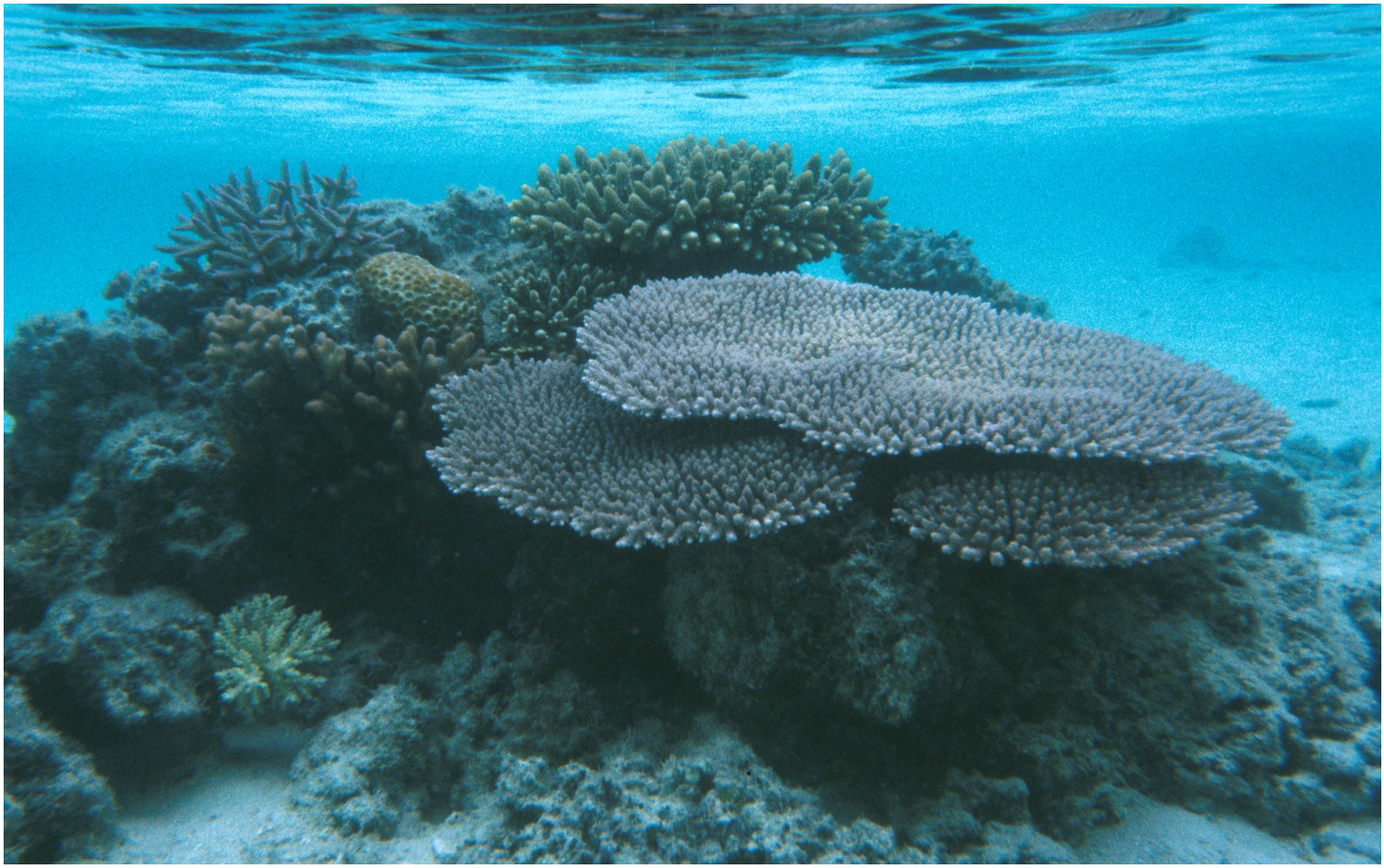




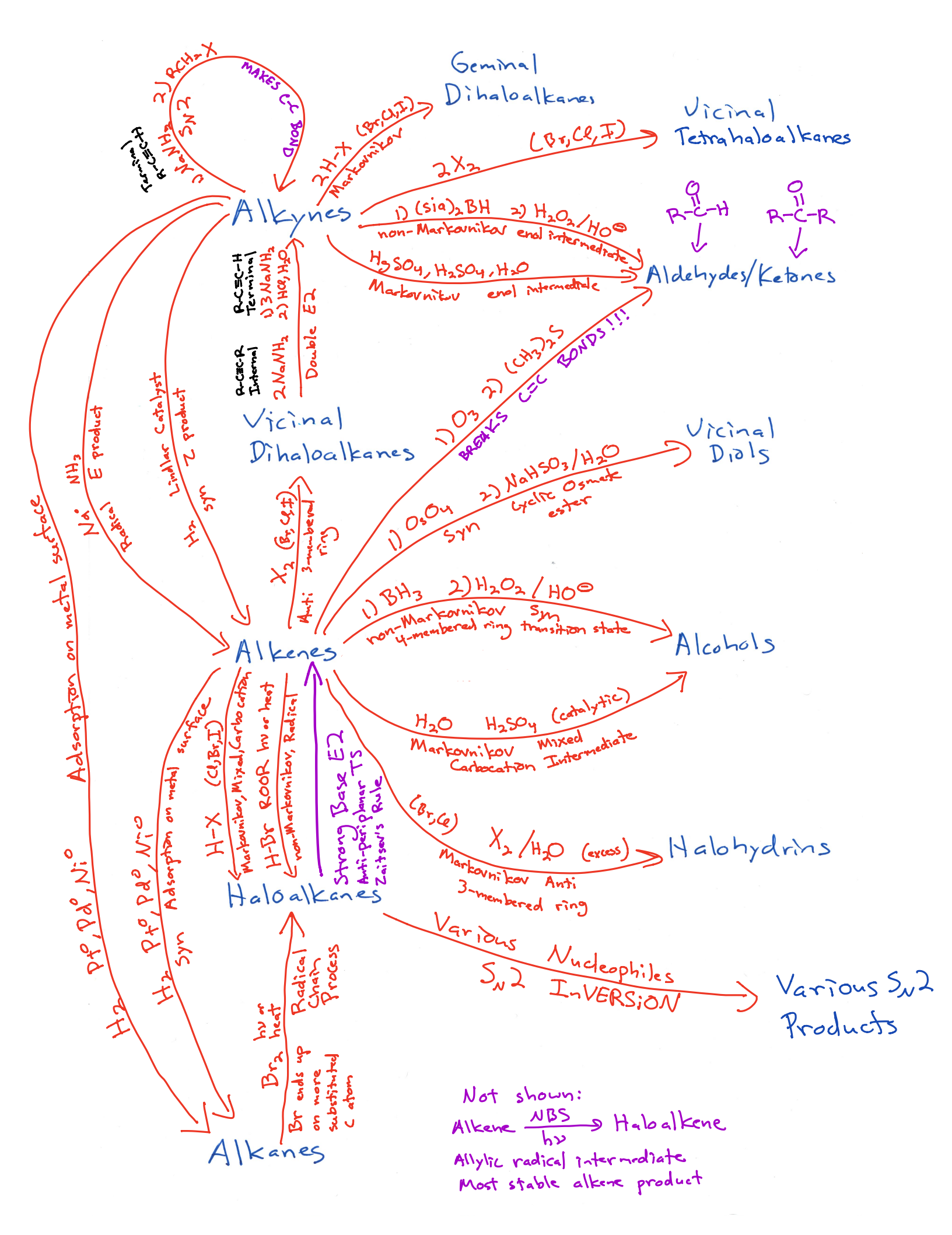


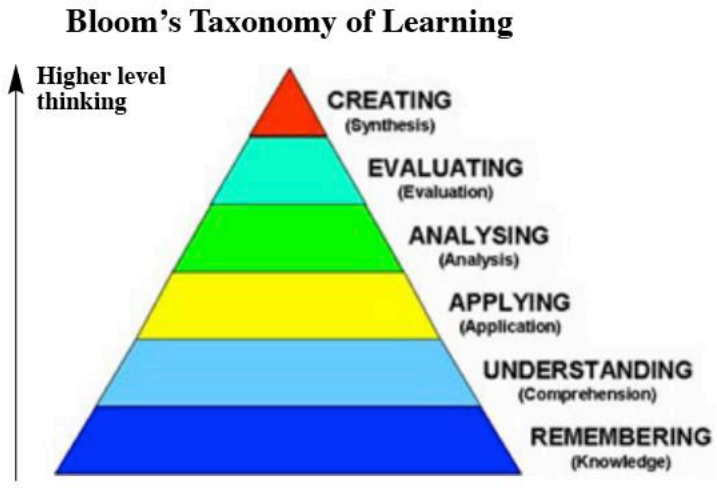


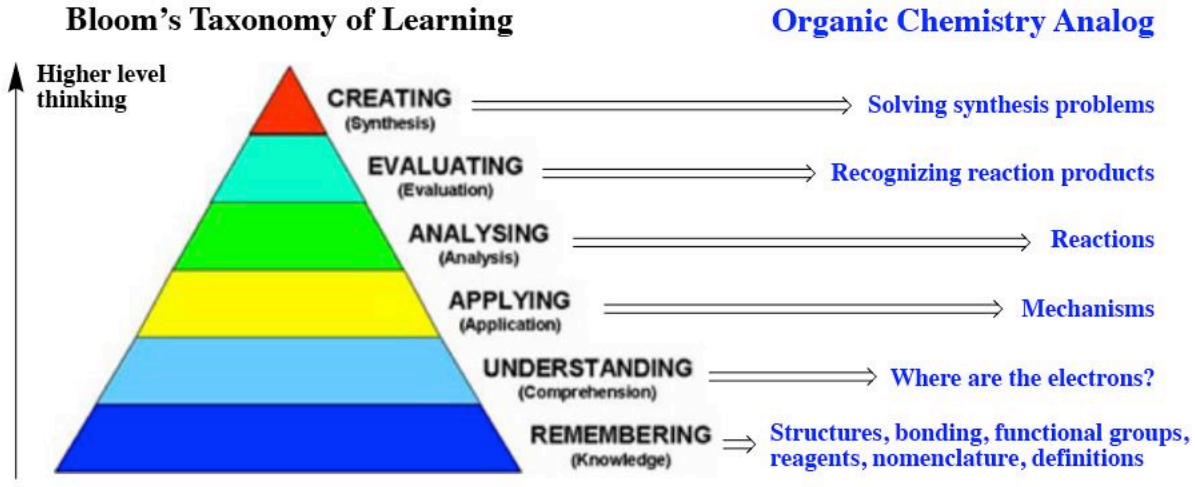





WELCOME TO OUR
REACTION
FESTIVAL


Alkynes
Terminal R-C≡C-H
1) NaNH2 2) RCH2X SN2
MAKES C-C
ANOTHER
2H-X (Br,Cl,I) Markovnikov
Geminal Dihaloalkanes
2X2 (Br,Cl,I)
Vicinal Tetrahaloalkanes
1) (sia)2BH 2) H2O2/HO⊖ non-Markovnikov enol intermediate
H2SO4, H2SO4, H2O Markovnikov enol intermediate
Aldehydes/Ketones
R-C(=O)-H
R-C(=O)-R
R-C≡C-H Terminal 1) 3NaNH2 2) HCl, H2O
R-C≡C-R Internal 2NaNH2
Double E2
Vicinal Dihaloalkanes
1) O3 2) (CH3)2S BREAKS C=C BONDS!!!
1) OsO4 2) NaHSO3/H2O syn cyclic Osmate ester
Vicinal Diols
X2 (Br, Cl, I) Anti 3-membered ring
Alkenes
1) BH3 2) H2O2/HO⊖ non-Markovnikov syn 4-membered ring transition state
Alcohols
H2O H2SO4 (catalytic) Markovnikov Mixed Carbocation Intermediate
(Br,Cl) X2/H2O (excess) Markovnikov Anti 3-membered ring
Halohydrins
H-X (Cl,Br,I) Markovnikov, Mixed, Carbocation
H-Br ROOR hv or heat non-Markovnikov, Radical
Strong Base E2 Anti-periplanar TS Zaitsev's Rule
Haloalkanes
Various Nucleophiles SN2 INVERSION
Various SN2 Products
Adsorption on metal surface
Pt°, Pd°, Ni°
H2 syn
Ni° NH3 Radical E product
Lindlar Catalyst H2 syn Z product
Br2 hv or heat Radical Chain Process
Br ends up on more substituted C atom
Alkanes
Not shown:
Alkene NBS hv Haloalkene
Allylic radical intermediate
Most stable alkene product





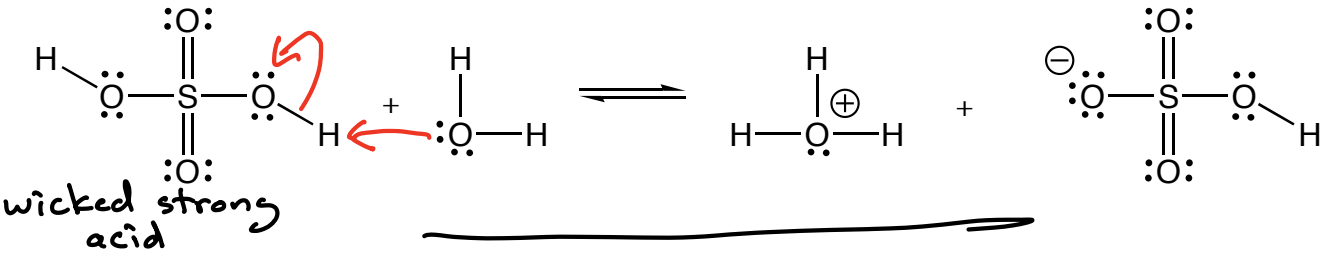
A) **You must have your entire roadmap learned** so you can recite the NIRRS parameters for each reagent, i.e. Nature of overall transformation ("locations" on the roadmap), the Intermediate or transition state (carbocation, anti-periplanar etc.), the Reagents and how to designate them, as well as any Regiochemistry (Markovnikov, etc.) and any appropriate Stereochemistry (syn, anti, InVERSiON, scrambled, etc).

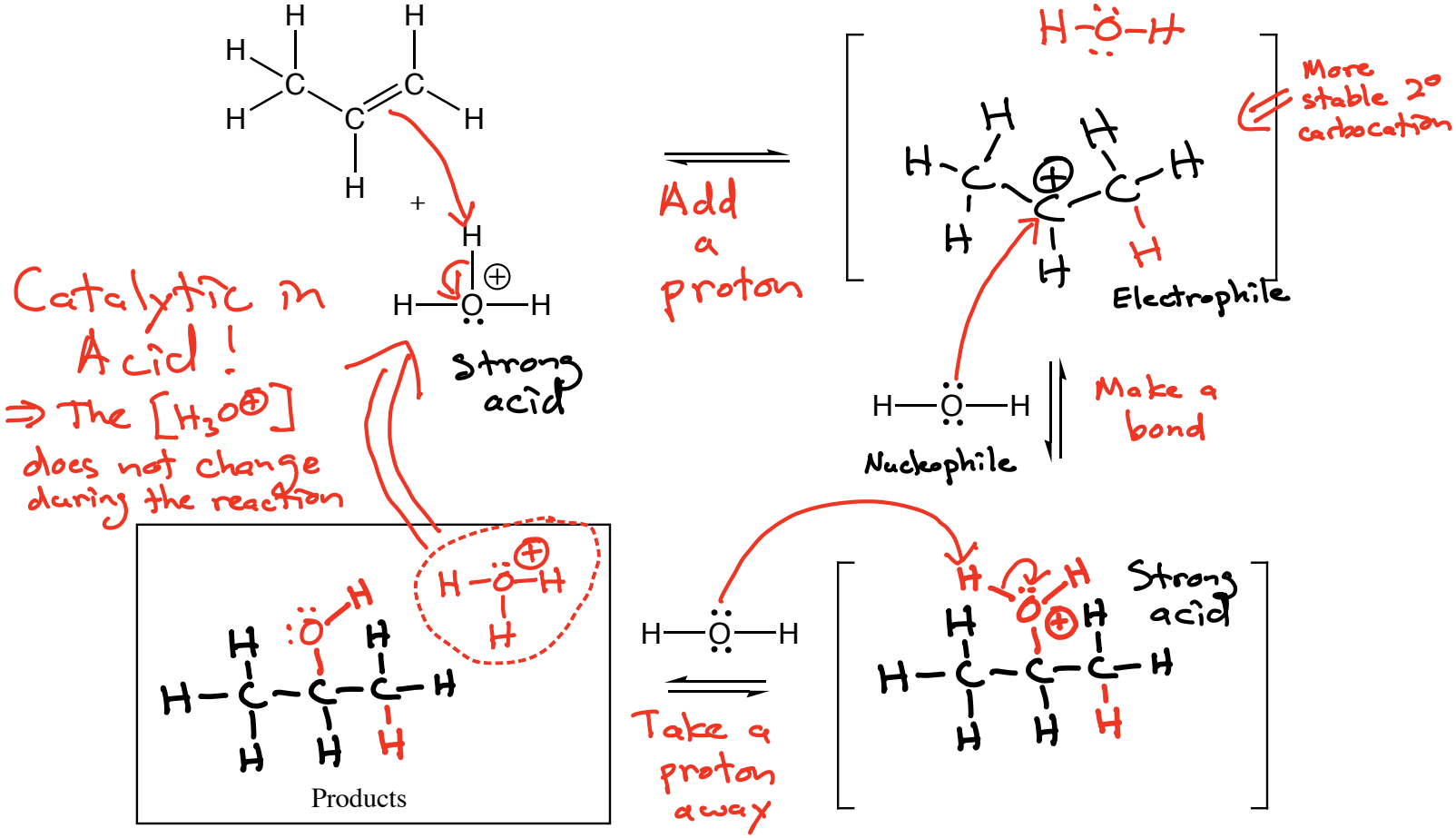
B) **Work backwards** (learn to RECOGNIZE the appropriate reagents and starting materials by looking at the products) from the final product. DO NOT try to work forward from the starting materials. Please trust me on this.

C) **Count carbons** in the starting material(s) and product(s) to see if any carbon-carbon bonds need to be broken or made, thereby zeroing in on key steps. This will be far more important next semester, so you should get used to doing this now.

D) **Pretty much all synthesis problems in OChem 1 involve traveling "north or south" on the so-called "I-35"** reactions (alkanes SA, haloalkanes NB/SM, alkenes ATX, vicinal dihaloalkanes Waco, alkynes DFW) at least part way at some point during the synthesis. This is not a promise or a rule, just an observation.

Acid-catalyzed Hydration of an Alkene



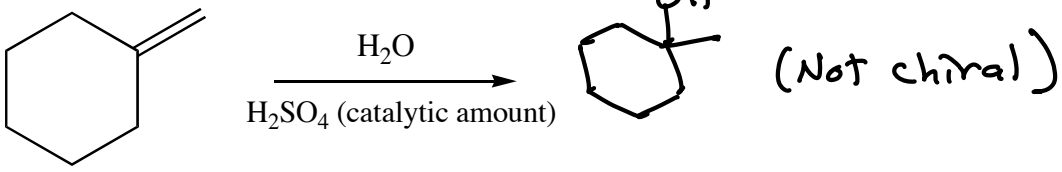


Summary: Proton adds to make a carbocation intermediate, water attacks to make a new bond, take a proton away to make the product alcohol. Catalytic in $H_3O^{\oplus}$

Regiochemistry: Markovnikov's Rule

Stereochemistry: Mixed (time capsule)

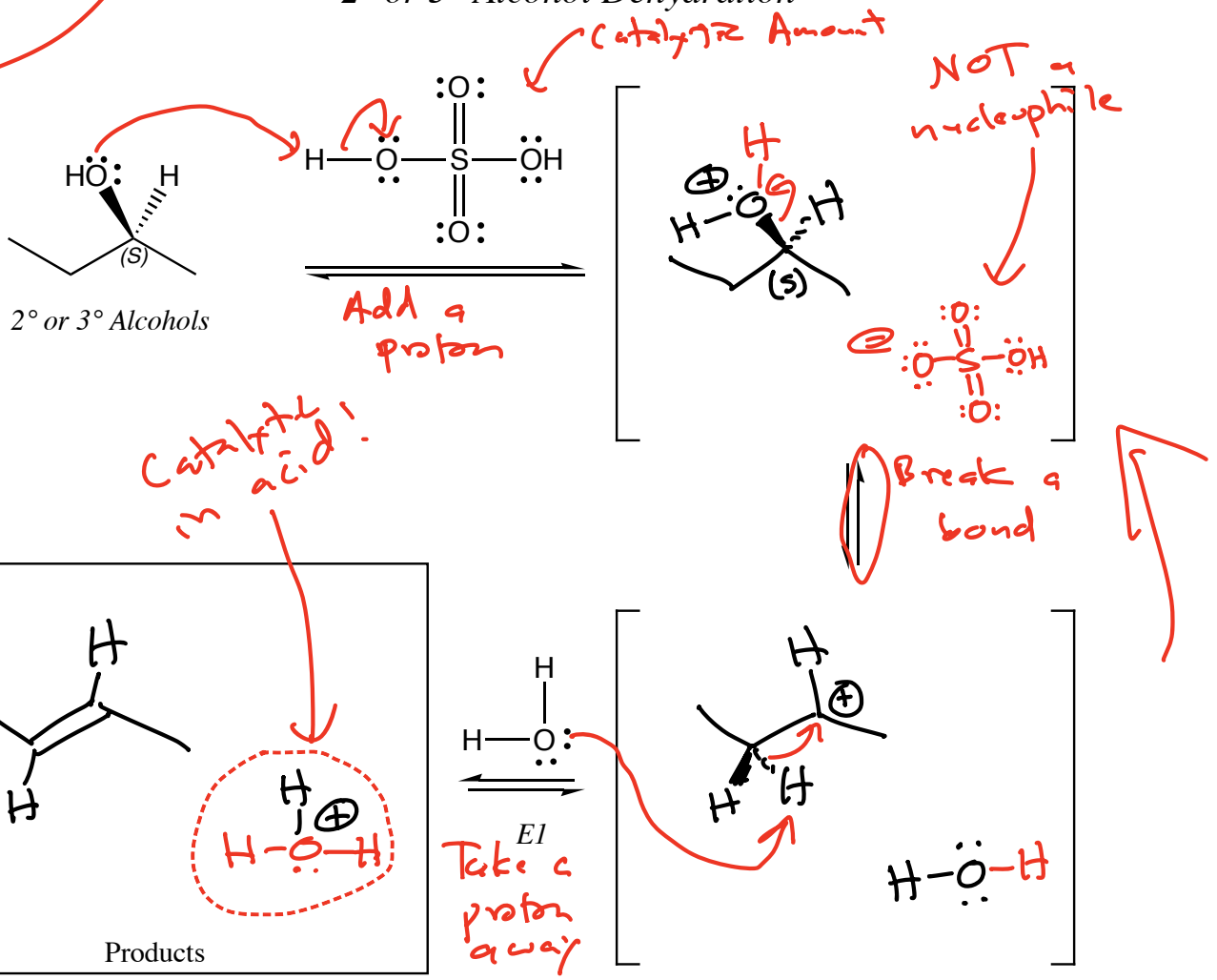
Example:



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

1° alcohols react via E2

2° or 3° Alcohol Dehydration

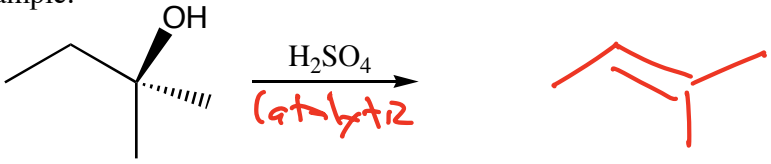


Summary: The OH group is protonated in strong acid to make a good leaving group (H_2O), which breaks a bond to give a carbocation that has a proton taken away → E1 (No S_N1!)

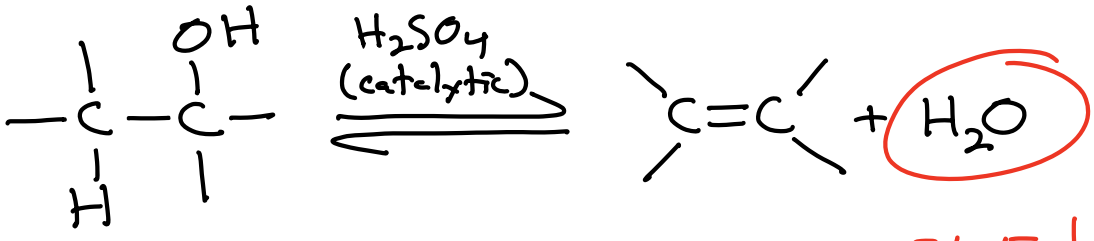
Regiochemistry: Zaitsev's Rule

Stereochemistry: N/A

Example:



Microscopic Reversibility → Reversible reaction mechanisms have the same intermediates in both directions → compare the last two mechanisms!



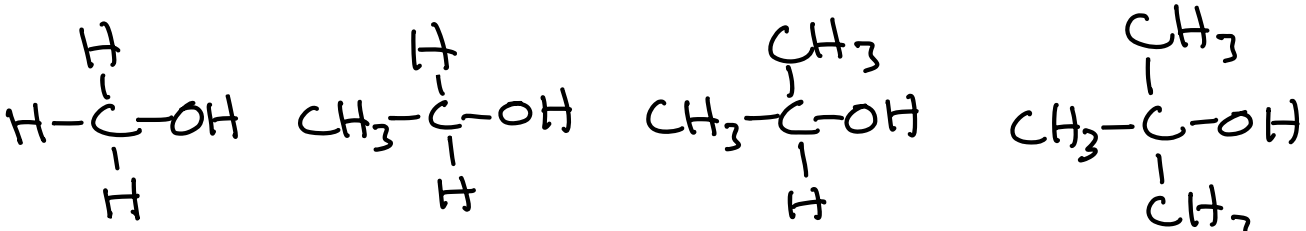
This reaction REVERSIBLE!

Le Chatlier's Principle ⇒

If we add water → we drive reaction to the alcohol product

If we remove the water as it is formed → we drive reaction to the alkene product

Alcohols → Reaction mechanisms depend on the number of alkyl groups attached on the C atom of C-OH bond.

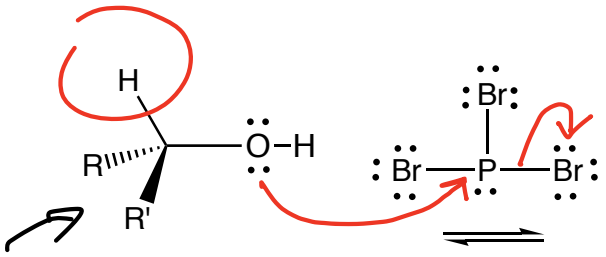


methyl 1° 2° 3°

The -OH is not a leaving group but several reactions involve conversion of the -OH group into a good leaving group

Recall, the -OH group is a weak nucleophile and weak base (in strong acid)

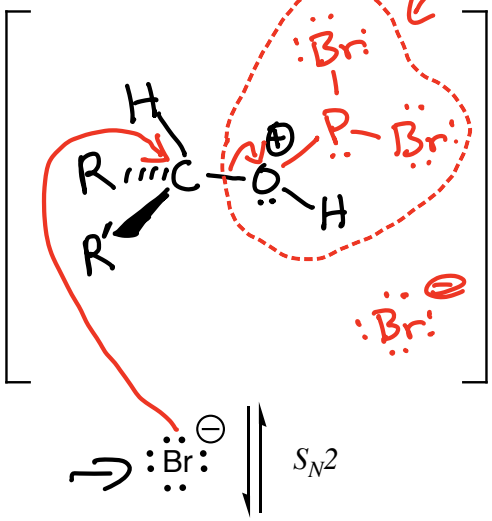
Alcohols + PBr_3



1° or 2° Alcohols

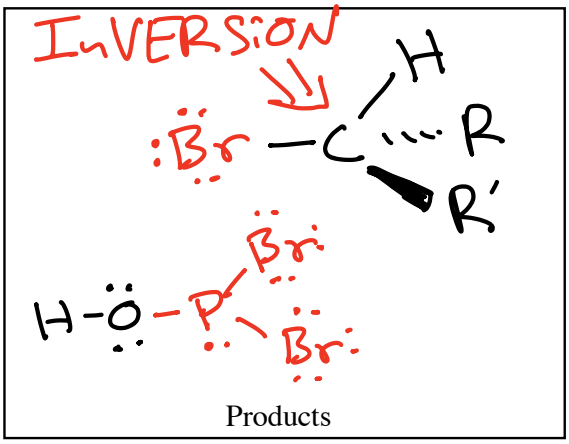
S_N2

Great leaving group



Does NOT work with 3° alcohols

There is an analogous reaction with $SOCl_2$ that converts an -OH group into -Cl, also with INVERSION of stereochemistry

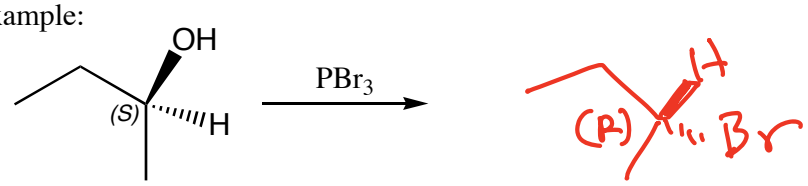


Summary: 1° or 2° alcohols react with PBr_3 via an S_N2 reaction at the P atom to create a great leaving group that undergoes an S_N2 reaction with $Br^{\ominus}$ at the C atom

Regiochemistry: N/A

Stereochemistry: INVERSION

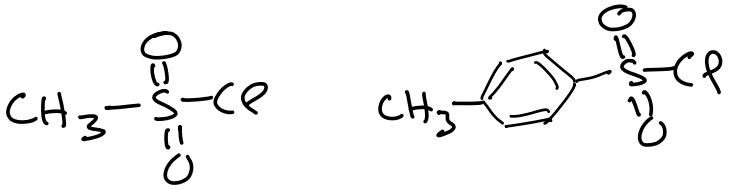
Example:





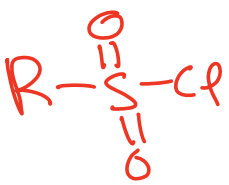


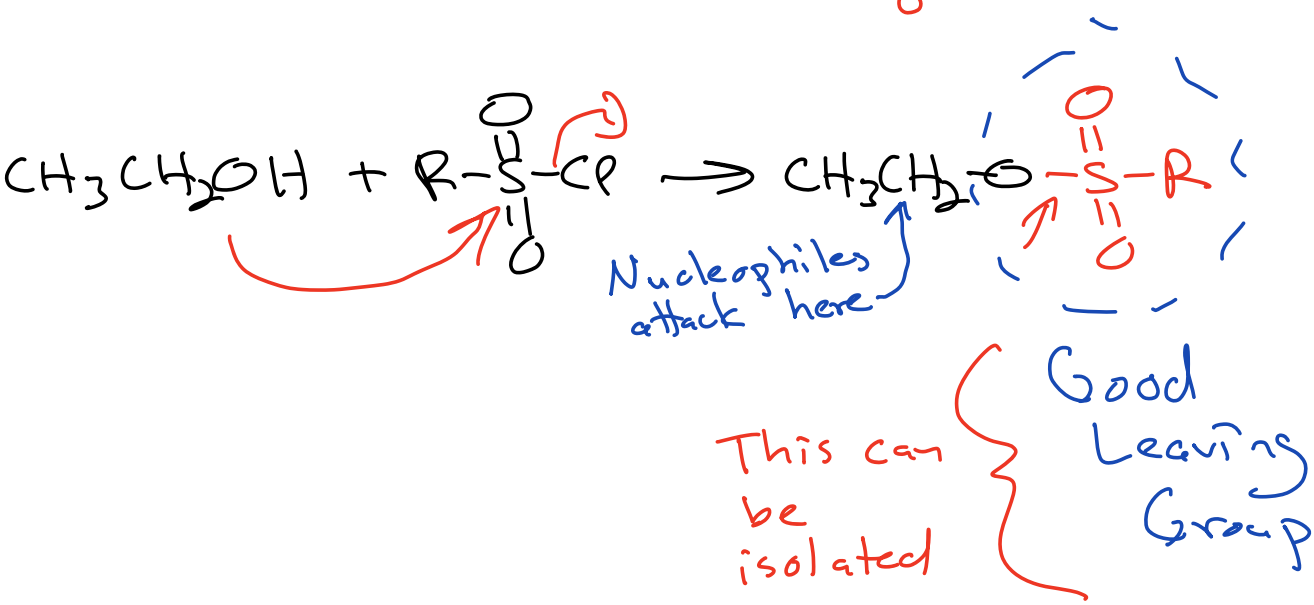
Alkyl Sulfonates



Methanesulfonyl Chloride

p-Toluenesulfonyl Chloride



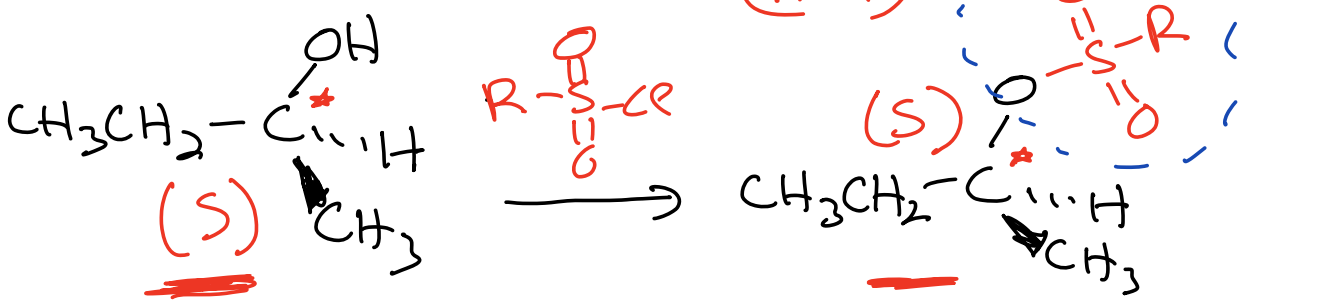


Stereochemistry

Byproduct of the reaction

(HCl)

This reacts like -Br



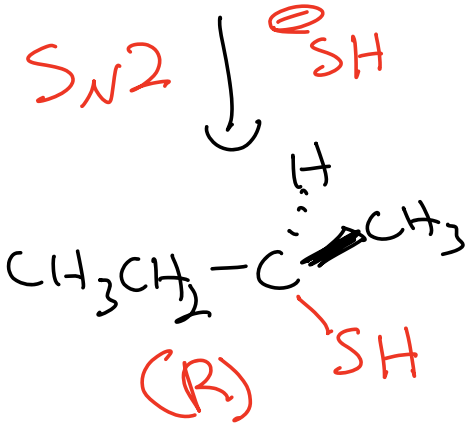
(S)

(S)

Net ⇒

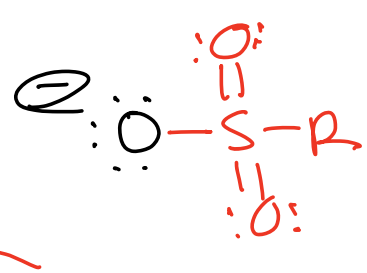
INVERSION

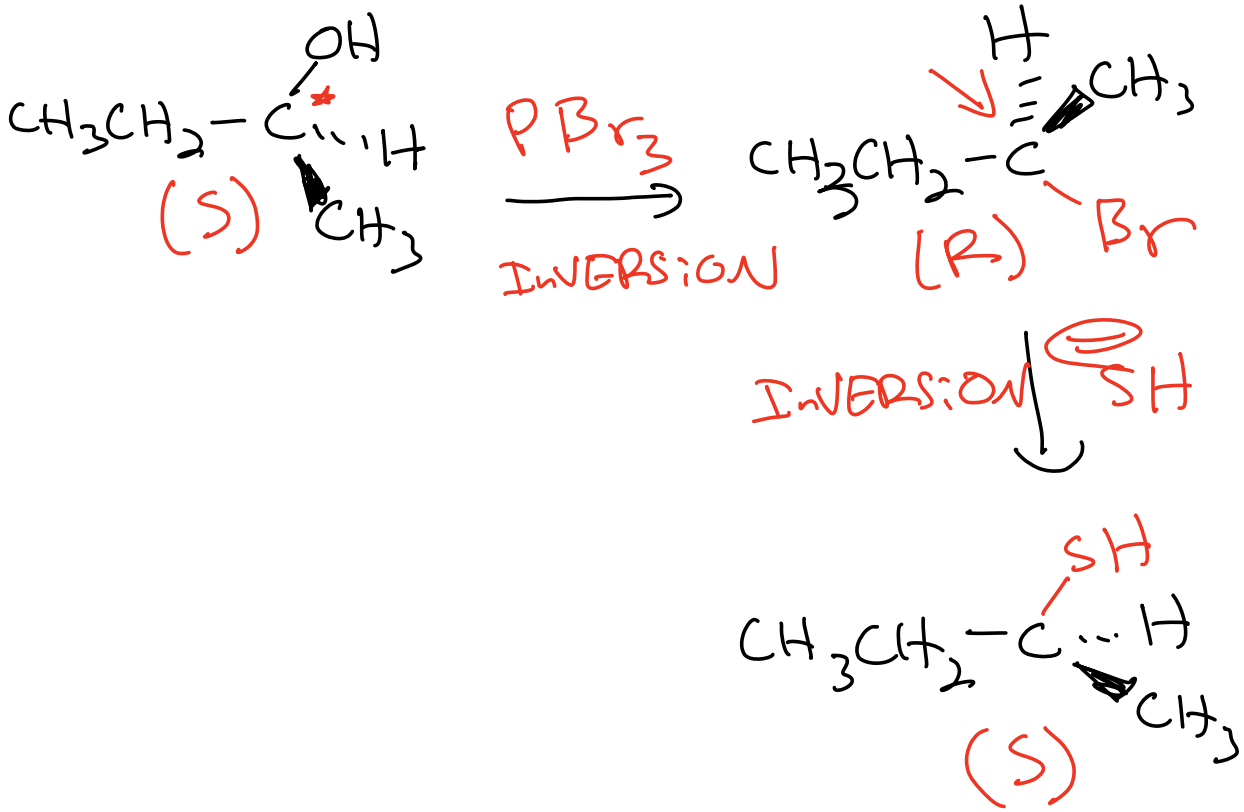
S_N2



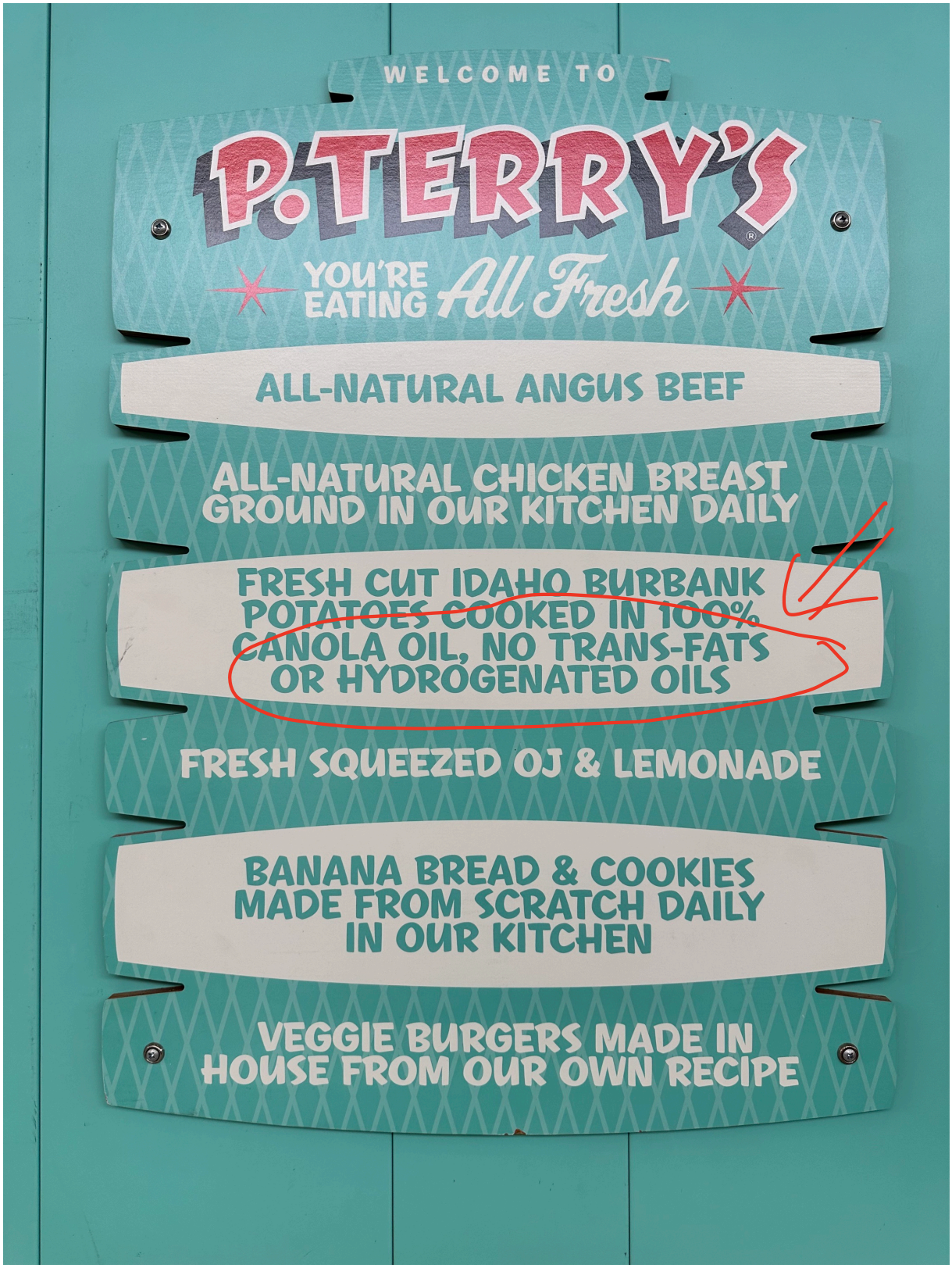
(R)

stabilized by resonance delocalization ⇒ relatively stable anion, explaining why it is such a good leaving group





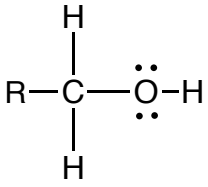
⟹ You can not invert or retain the stereochemistry of a chiral alcohol taking part in S_N2 reactions


WELCOME TO
P.TERRY'S
YOU'RE EATING All Fresh
ALL-NATURAL ANGUS BEEF
ALL-NATURAL CHICKEN BREAST GROUND IN OUR KITCHEN DAILY
FRESH CUT IDAHO BURBANK POTATOES COOKED IN 100% CANOLA OIL, NO TRANS-FATS OR HYDROGENATED OILS
FRESH SQUEEZED OJ & LEMONADE
BANANA BREAD & COOKIES MADE FROM SCRATCH DAILY IN OUR KITCHEN
VEGGIE BURGERS MADE IN HOUSE FROM OUR OWN RECIPE

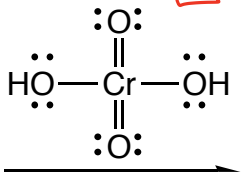
Chromic Acid Oxidation of Alcohols

Called "Jones Reagent" ($CrO_3 + H_2O$ or K_2CrO_7) + H_2SO_4

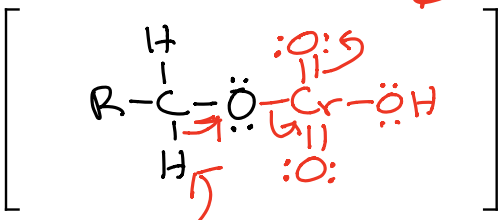
Not responsible for first step

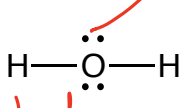


1° Alcohols



"H_2CrO_4" or "Chromic Acid"

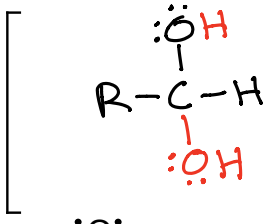




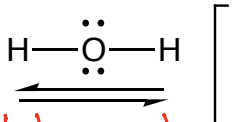
Take a proton away and break a bond

Aldehyde

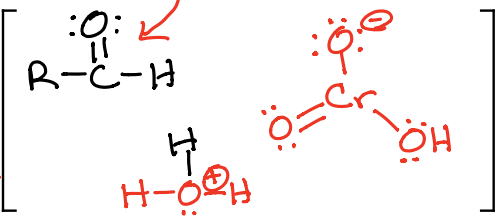
Not responsible for this step

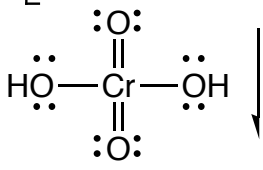


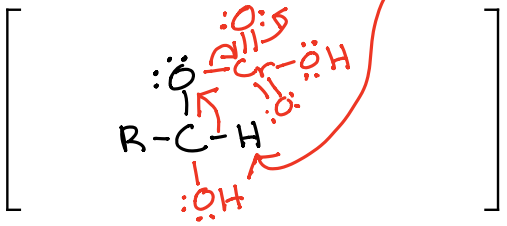
Called a geminal diol

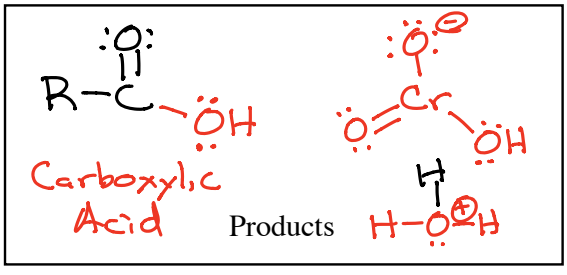


Water reacts with aldehyde – will learn next semester





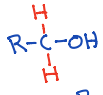




Carboxylic Acid

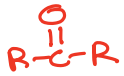
Products

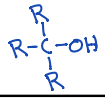
Summary:



1° alcohols ⇒ Carboxylic Acid → 



2° alcohols ⇒ Ketone → 

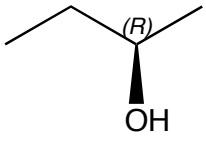


3° alcohols ⇒ NO REACTION

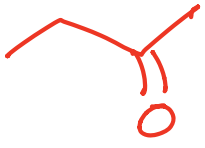
Regiochemistry: N/A

Stereochemistry: N/A

Example:

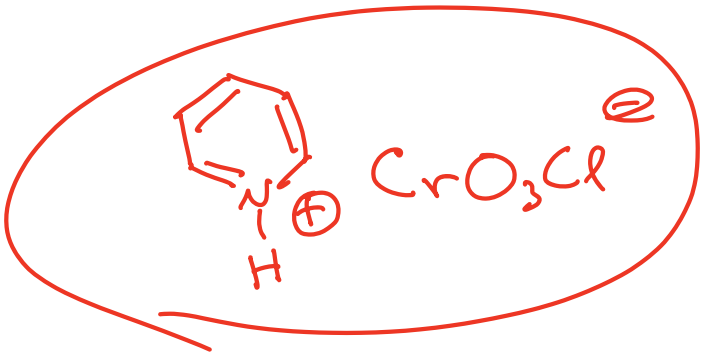


H_2CrO_4

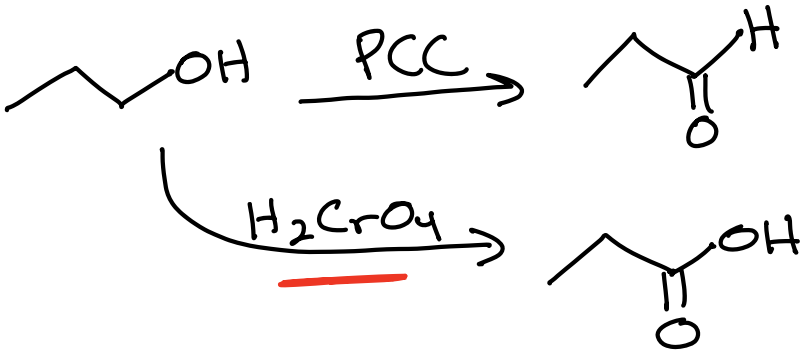


Ketone

A chromic acid-like reagent WITHOUT WATER will stop at the aldehyde when using a primary alcohol as starting material



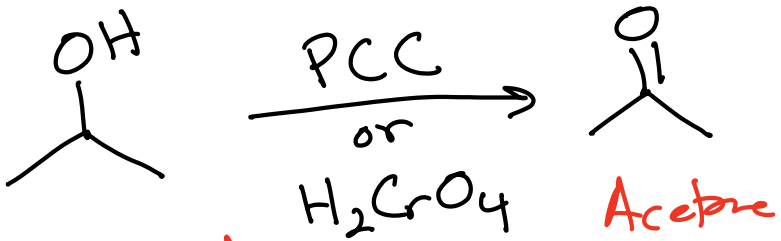
PCC



Aldehyde

Carboxylic Acid

Rubbing Alcohol



2-propanol

Acetone

Nail Polish Remover

<u>Organic Chemistry</u> 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. 8/25/26

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. 10/26/26

You will learn how medicines like Benadryl, Seldane, and Lipitor work. 11/9/26

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. 10/5/26

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. 10/26/26

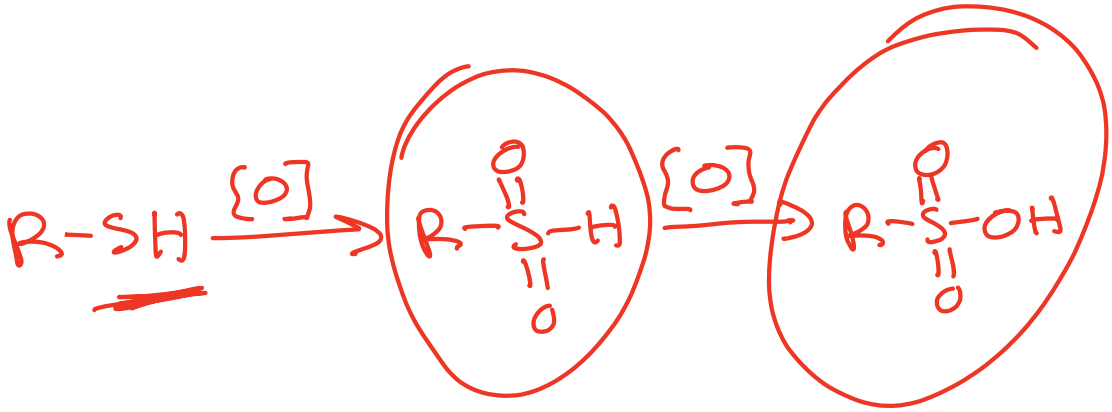
You will learn reactions that can make antifreeze from vodka. 11/9/26

You will learn a reaction that can make nail polish remover from rubbing alcohol. 11/11/26

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.

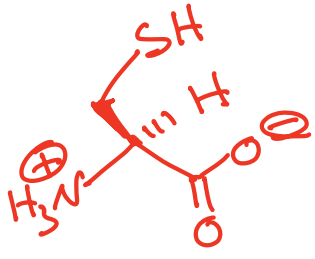
Thiols → R–S–H



In the presence of O_2:

$$2\ R\text{-}SH + \tfrac{1}{2}O_2 \longrightarrow R\text{-}S\text{-}S\text{-}R + H_2O$$

Dissulfide Bond



The amino acid cysteine (Cys)

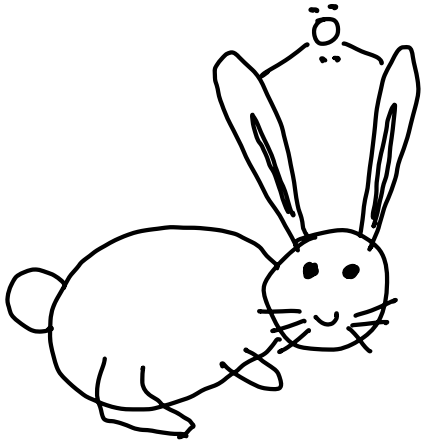
Dissulfide bonds between cysteine residues that are far apart in the sequence, but overlap in three-dimensions, provide covalent links that stabilize folded protein structures

Ethers → R–Ö–R

↳ Unreactive under most conditions



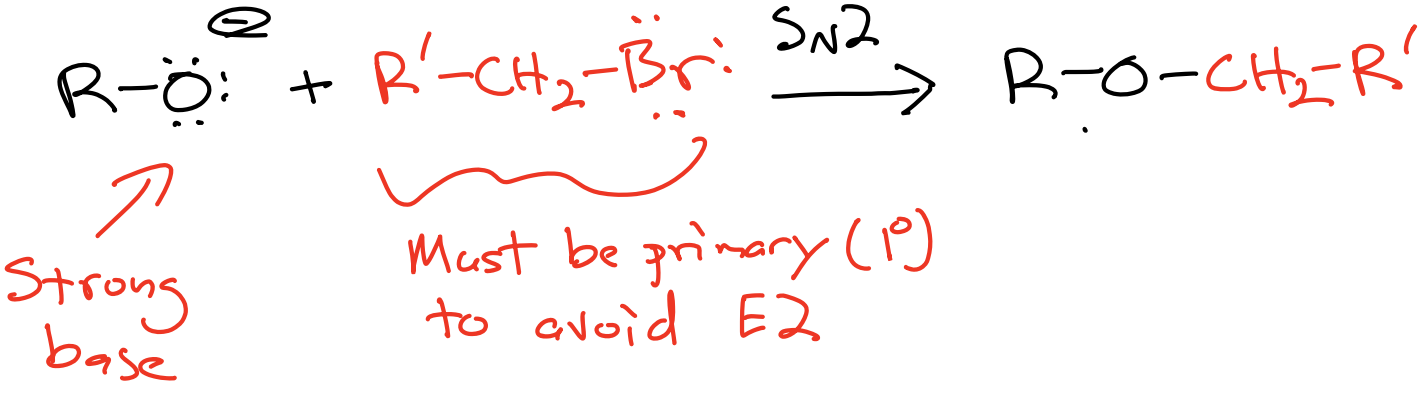
Diethyl ether



Ether Bunny

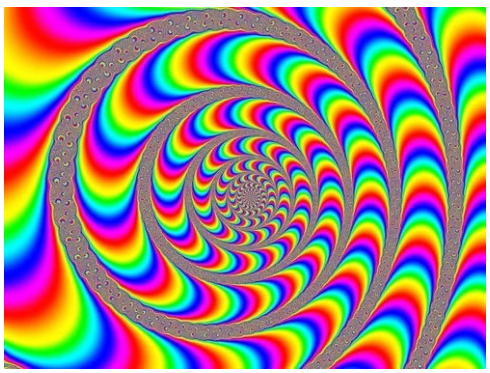
How to make ethers

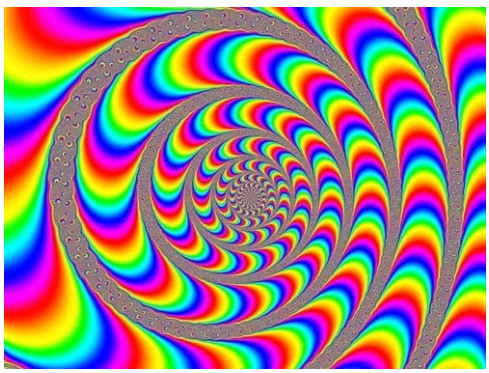
Williamson Ether Synthesis



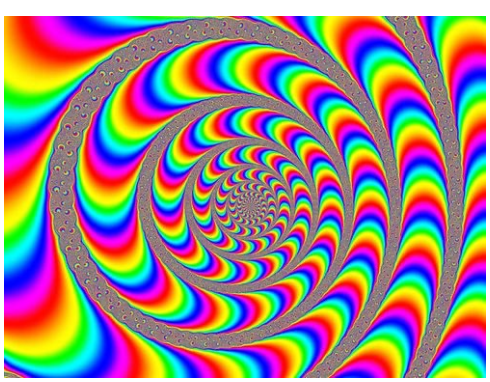
You can also react alkenes with alcohols in the presence of catalytic amounts of H_2SO_4 to make ethers:

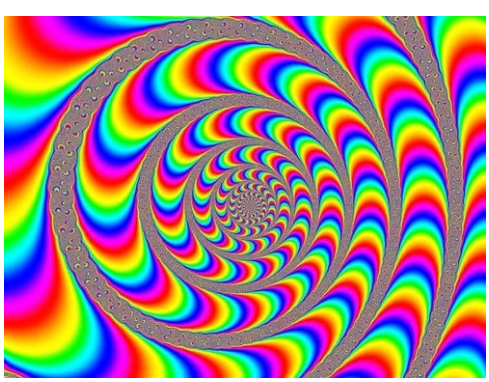
Flashback!!





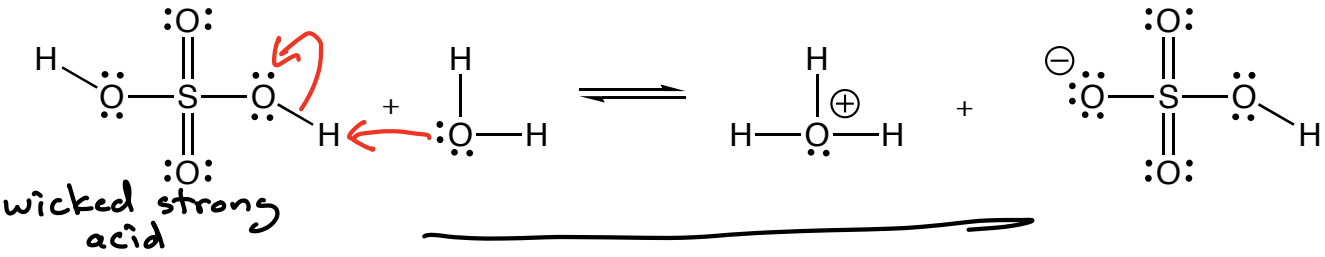


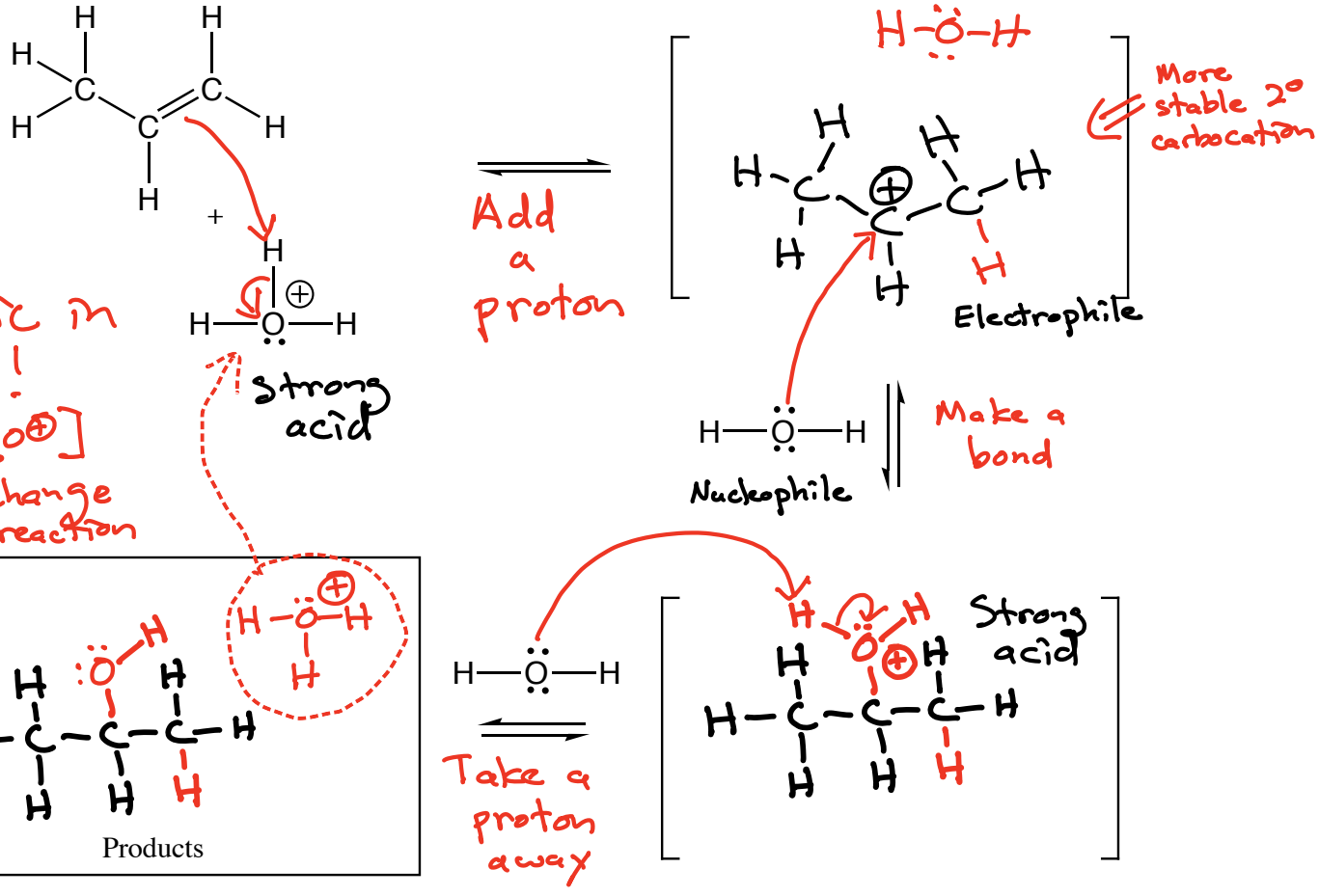




Flashback!!

Acid-catalyzed Hydration of an Alkene



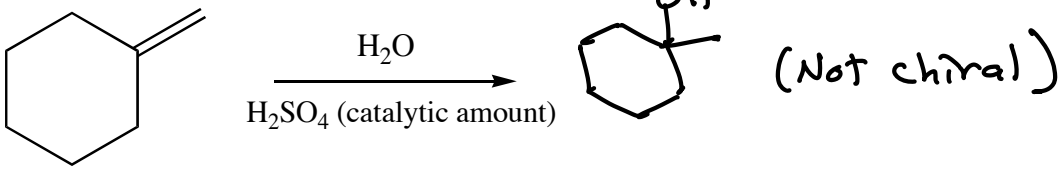


Summary: Proton adds to make a carbocation intermediate, water attacks to make a new bond, take a proton away to make the product alcohol. Catalytic in $H_3O^{\oplus}$

Regiochemistry: Markovnikov's Rule

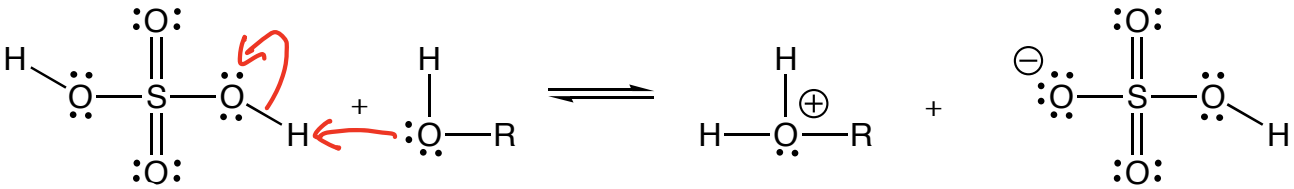
Stereochemistry: Mixed (time capsule)

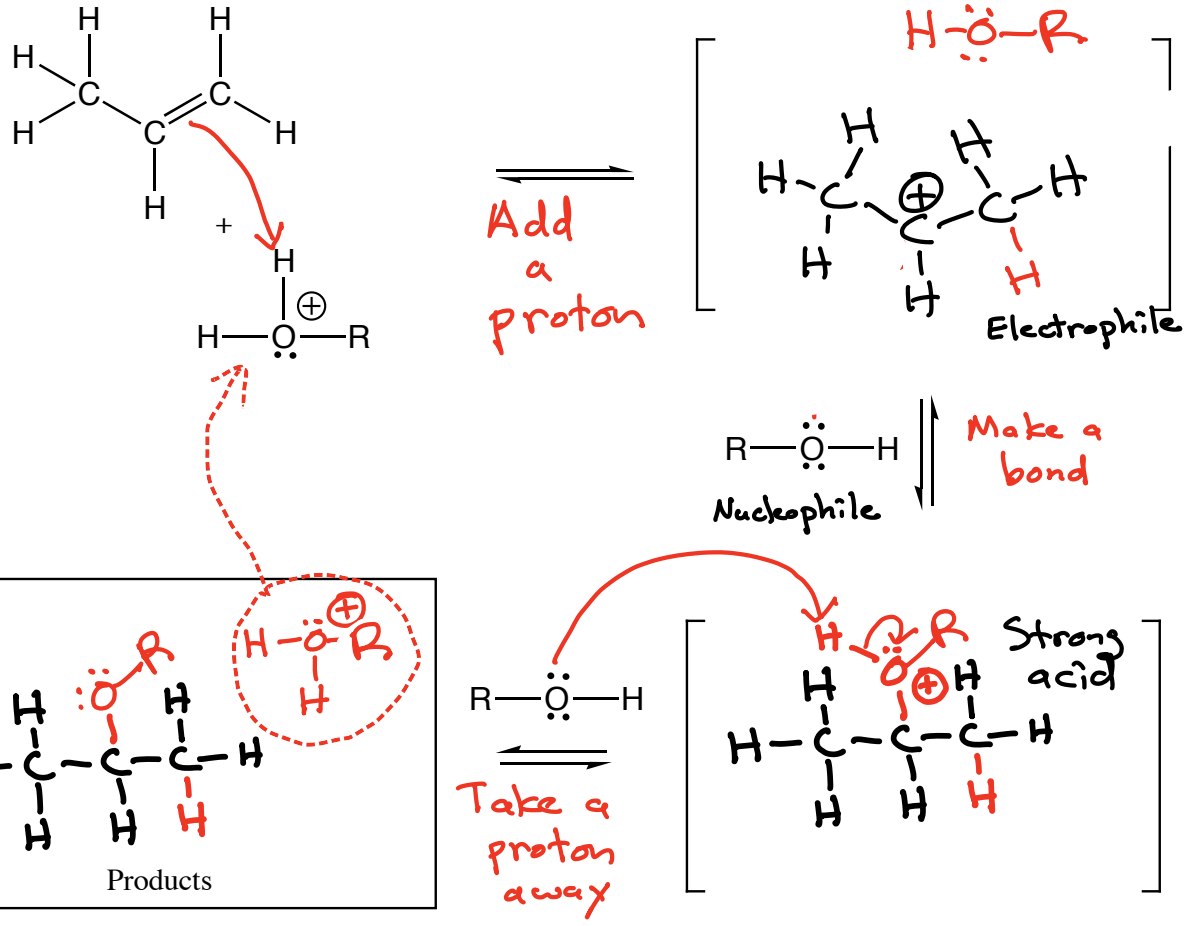
Example:



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

Acid-catalyzed Reaction of an Alcohol with an Alkene



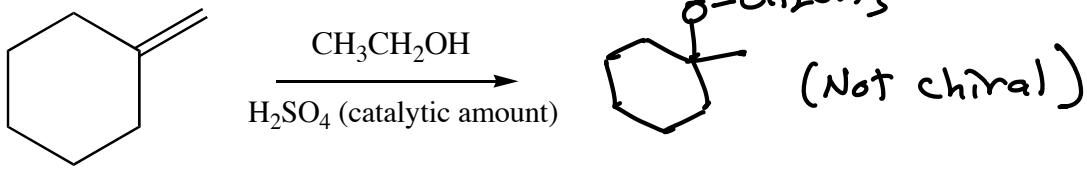


Summary: Proton adds to make a carbocation intermediate, alcohol attacks to make a new bond, take a proton away to make the product ether. Catalytic in $H_3O^{\oplus}$

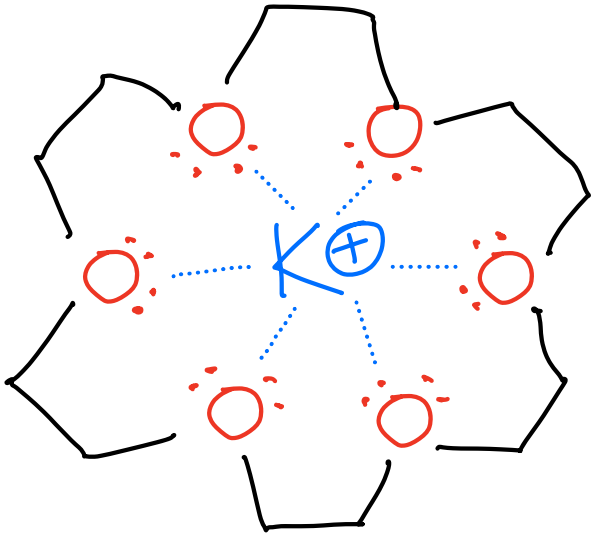
Regiochemistry: Markovnikov's Rule

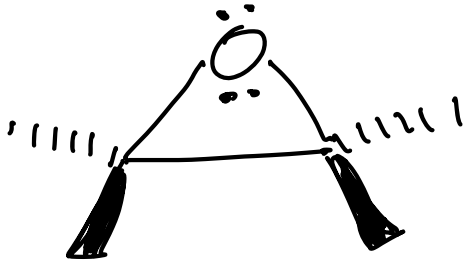
Stereochemistry: Mixed

Example:



Crown Ethers → bind cations based on size of cation → For 18 crown 6 → $K^{\oplus}$ (and $H_3O^{\oplus}$) fits the best.





Epoxide

Important because they can be formed from alkenes or halohydrins AND

Epoxides are also involved in a number of biological processes including oxidative damage