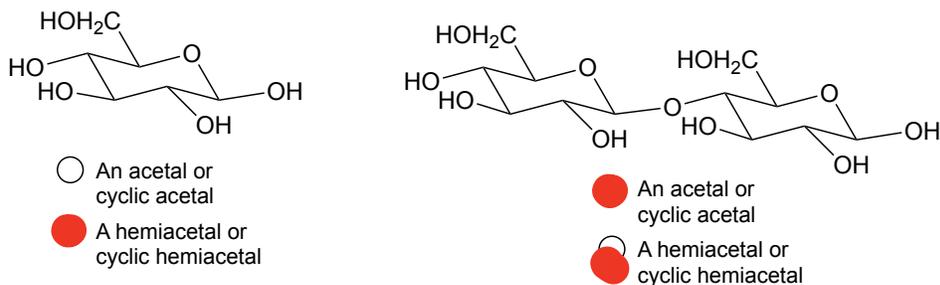
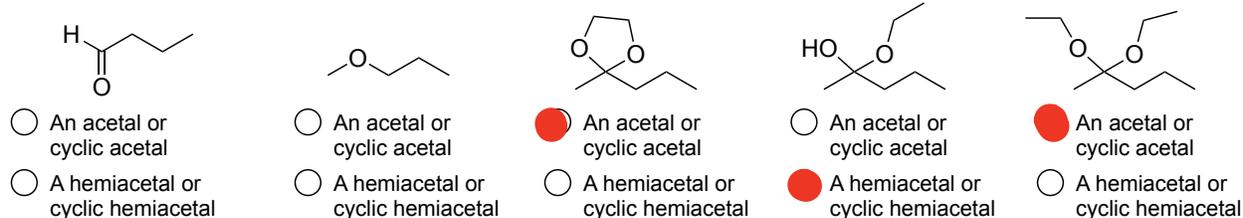


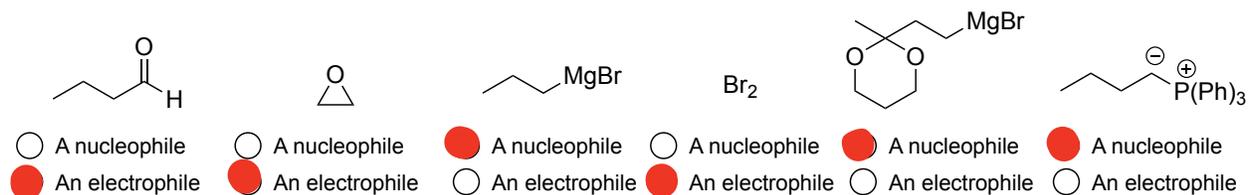
1) Fill in the circle next to the statement that most accurately reflects your approach to this class.

- I am here primarily to get points on exams so I can get a good grade in this class.
- I am here primarily to understand and learn Organic Chemistry because in the future I will need to know what I am understanding and learning now.

2) Among the following molecules, fill in appropriate circles to indicate which molecules contain acetals/cyclic acetals or hemiacetals/cyclic hemiacetals. The correct answer might have none, one or even two circles filled in.



3) For reaction mechanisms we have seen already this semester, indicate which species is a nucleophile and which is an electrophile. To be correct, one circle will be filled in under each structure. These could also be acids or bases in some contexts, but we will ignore that for this problem.

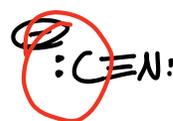
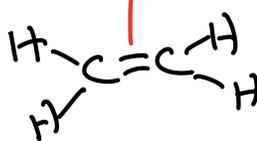
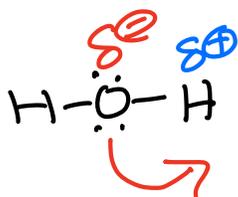
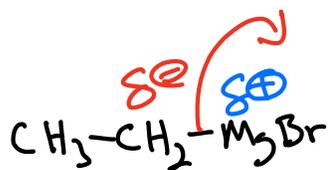


Nucleophiles react with electrophiles to MAKE A BOND

When trying to recognize nucleophiles:

Area of high electron density

Lone pair or bond AND they can make a new bond that is STABLE

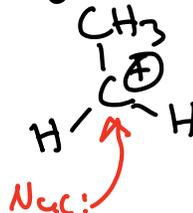
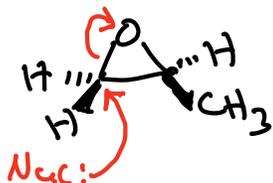
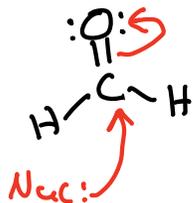
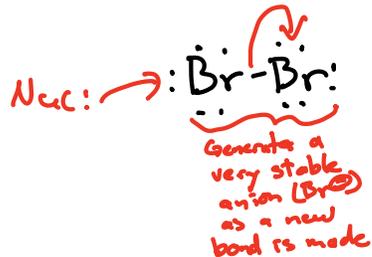


The O atom of a carbonyl is NOT a nucleophile because reacts at the lone pair and cannot make a stable bond

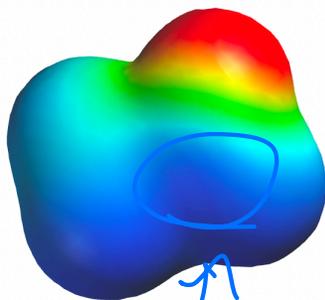
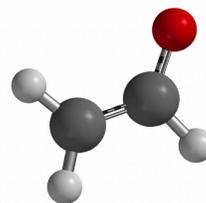
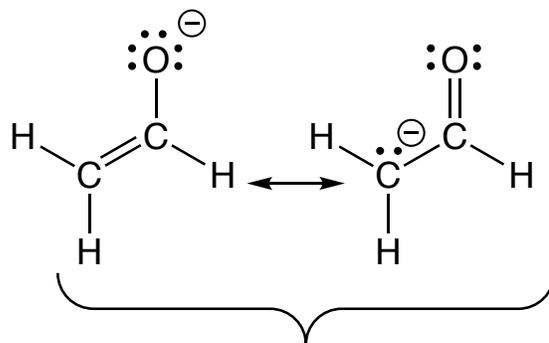
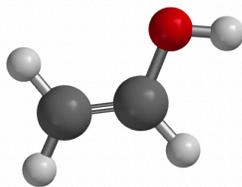
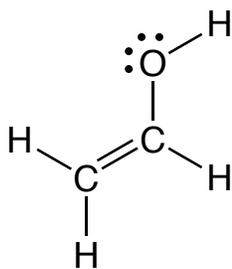
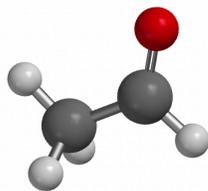
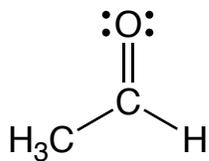
When trying to recognize electrophiles:

Often an area of low electron density

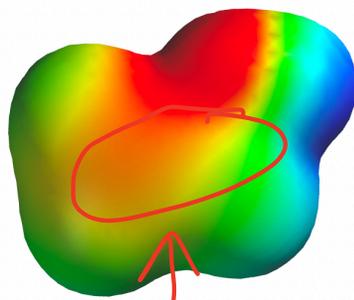
Can accept a new bond that is stable



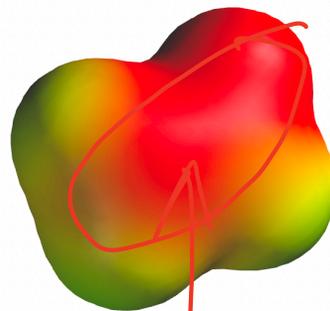
# Changing Personality:



electrophile



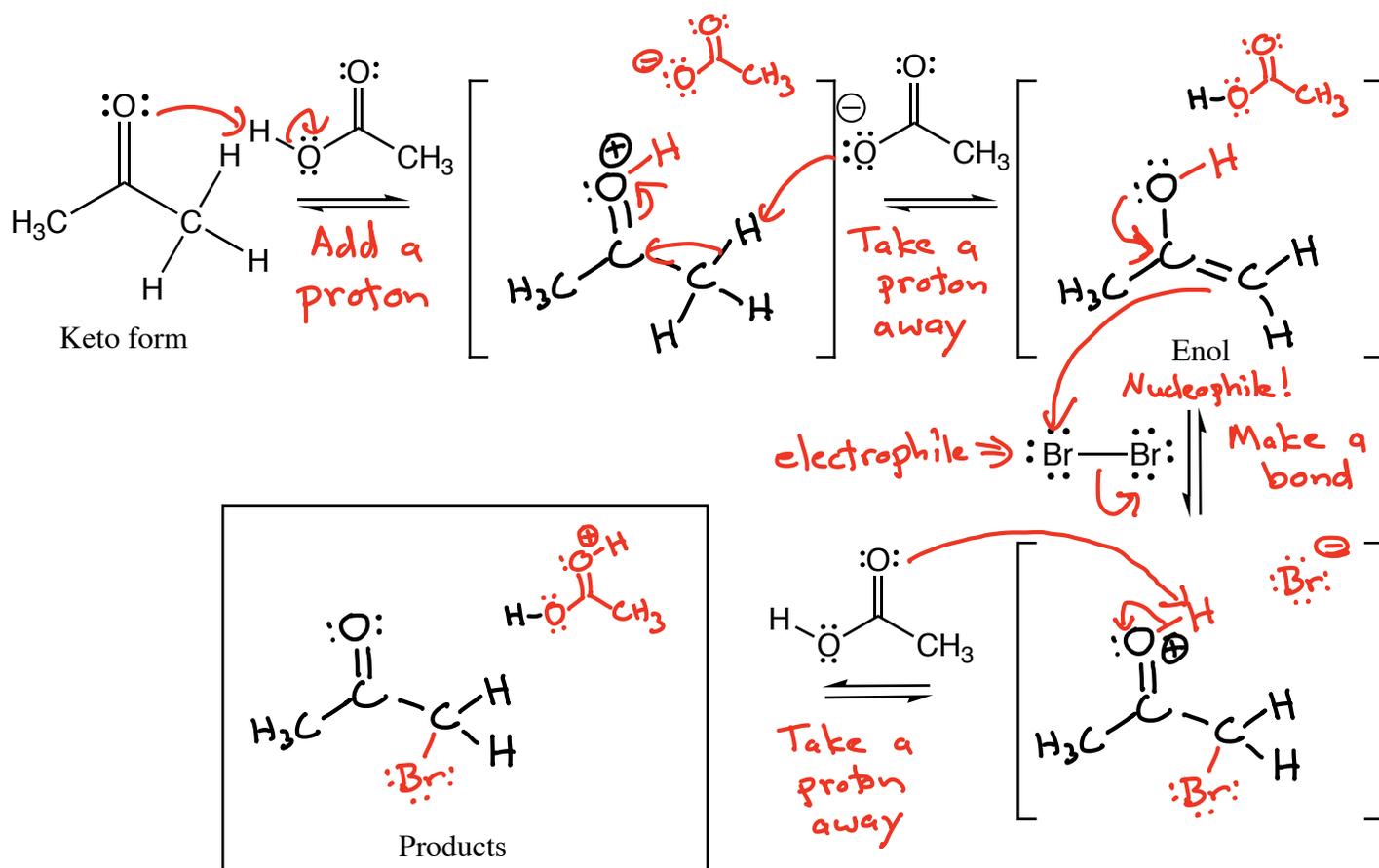
nucleophile



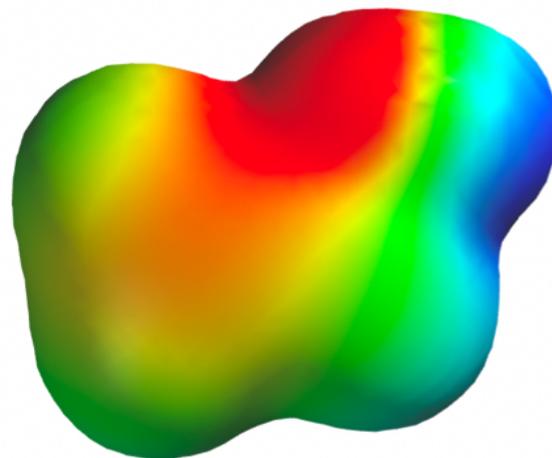
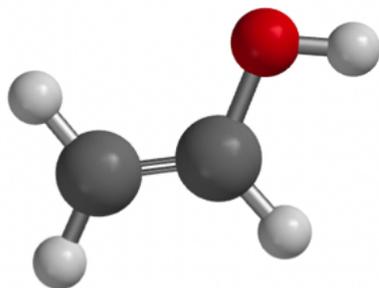
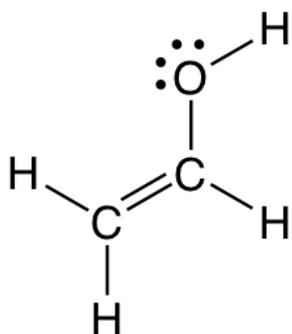
strong nucleophile



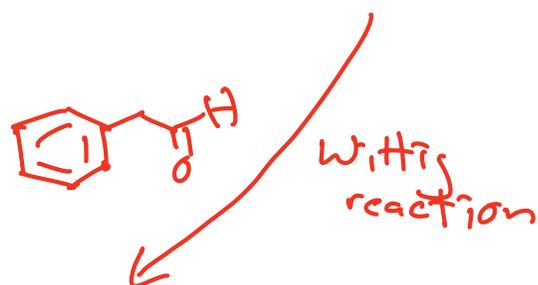
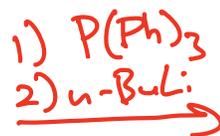
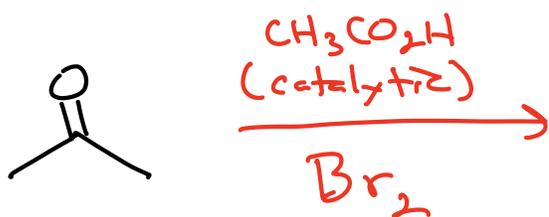
## $\alpha$ -Halogenation of an Aldehyde or Ketone Catalyzed by Acid

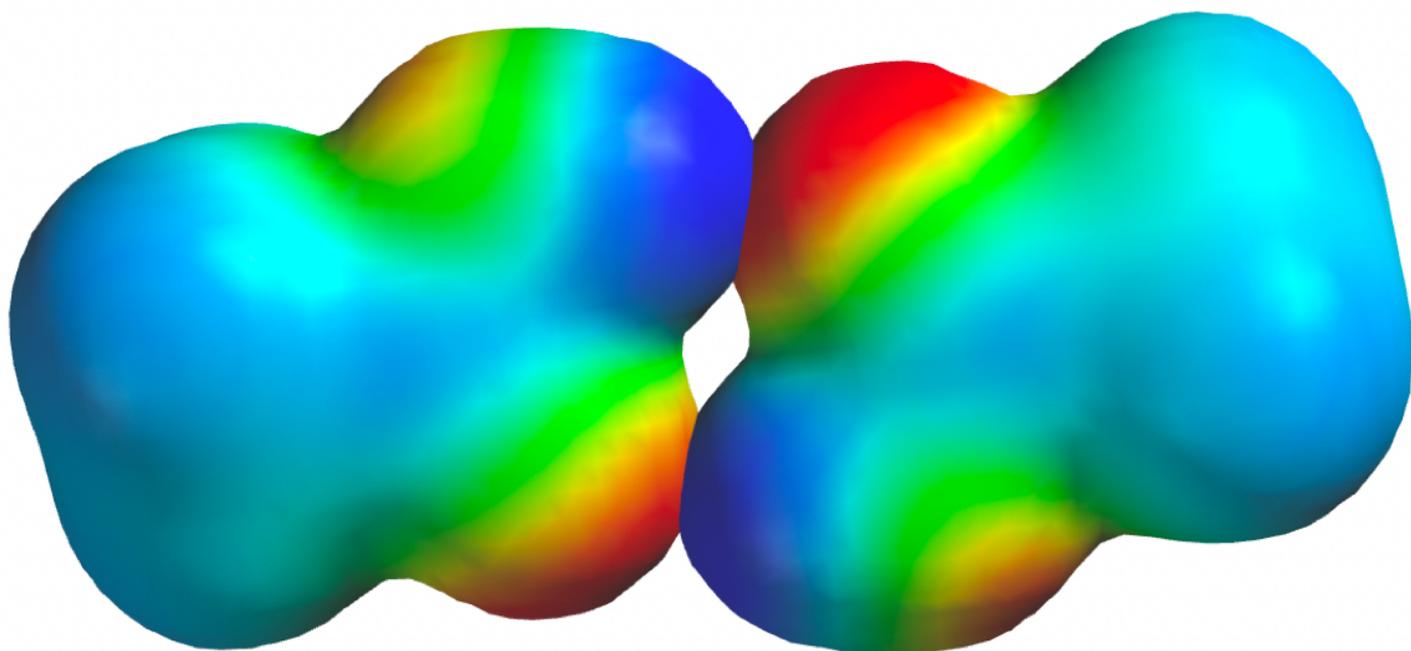
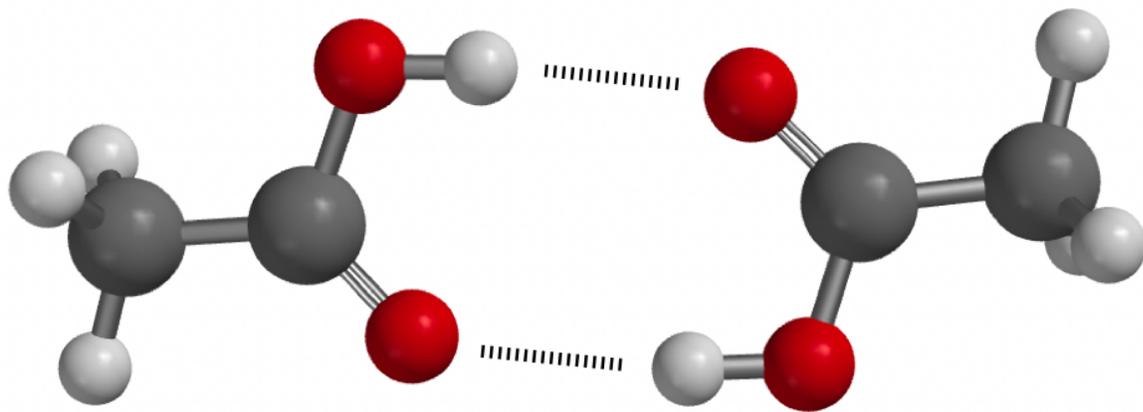
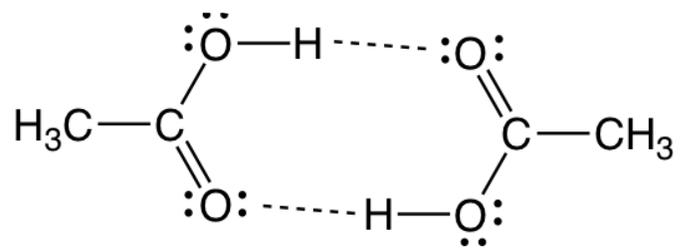


Note: For unsymmetrical ketones, **METHYL GROUPS** react in preference to all other types of alkyl groups  $\rightarrow$  Steric

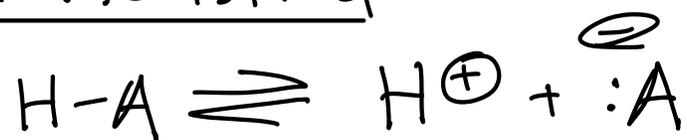


# Example



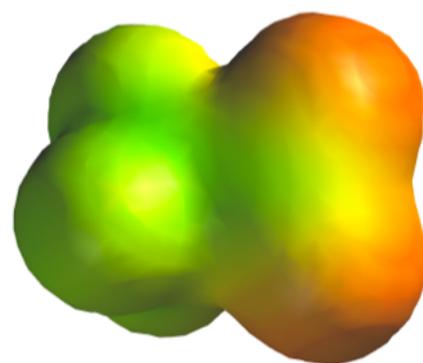
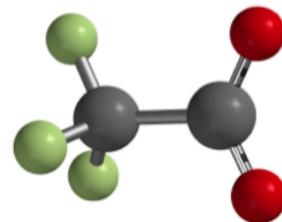
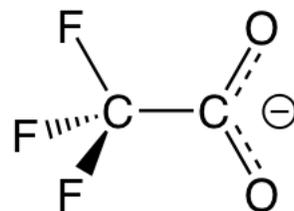
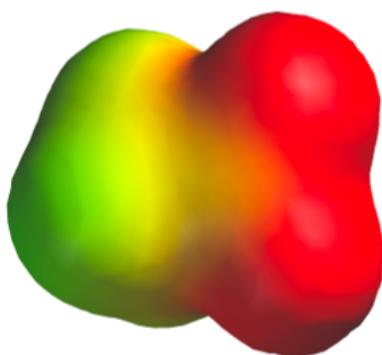
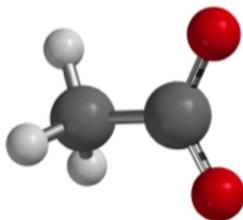
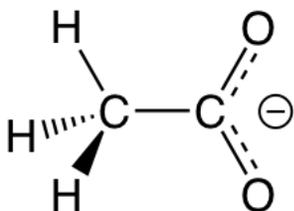
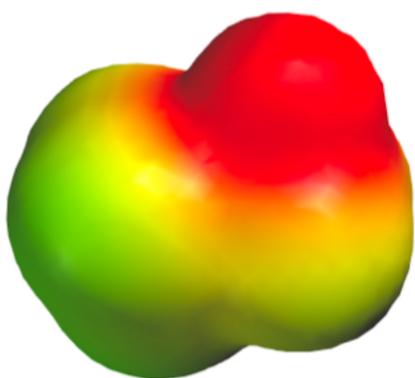
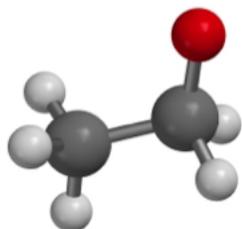
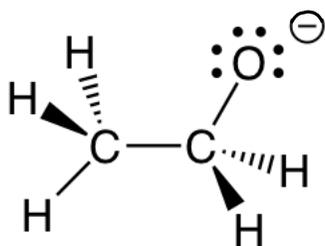


## Acidity Revisited

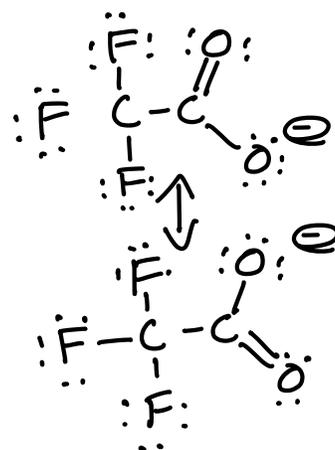
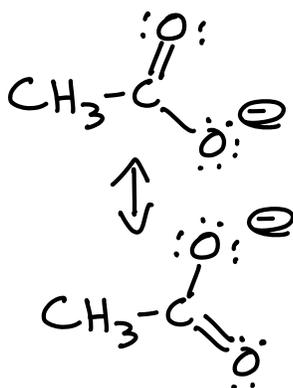
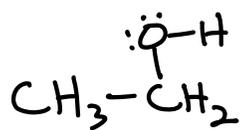
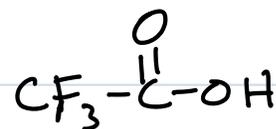
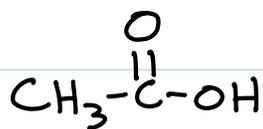
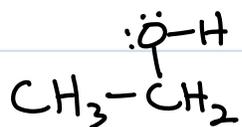


$$K_a = \frac{[\text{A}^{\ominus}][\text{H}^{\oplus}]}{[\text{HA}]}$$

$$\text{p}K_a = -\log_{10} K_a$$



Parent Acids



For an acid H-A

$$K_a = \frac{[A:^{\ominus}][H^{\oplus}]}{[HA]}$$

$$pK_a = -\log_{10} K_a$$

$$pH = -\log_{10} [H^{\oplus}]$$

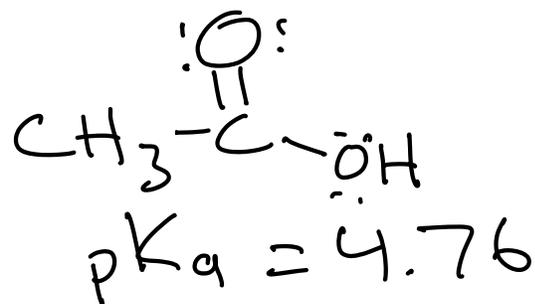
$$\frac{K_a}{[H^{\oplus}]} = \frac{[A:^{\ominus}]}{[HA]} = 10^{(pH - pK_a)}$$

If  $pH = 7$  and  $pK_a = 3$

$$\frac{[A:^{\ominus}]}{[HA]} = 10^{(pH - pK_a)} = 10^{(7-3)} = 10^4$$

1) If the pH of a solution is above (larger) than the  $pK_a$  of an acid, the acid will be largely deprotonated

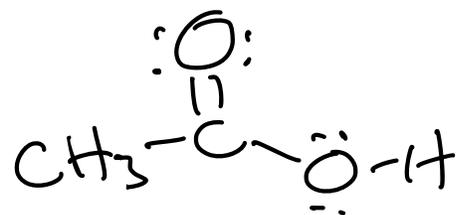
2) If the pH of a solution is below (smaller) than the  $pK_a$  of an acid, the acid will be largely protonated



at pH 7.0



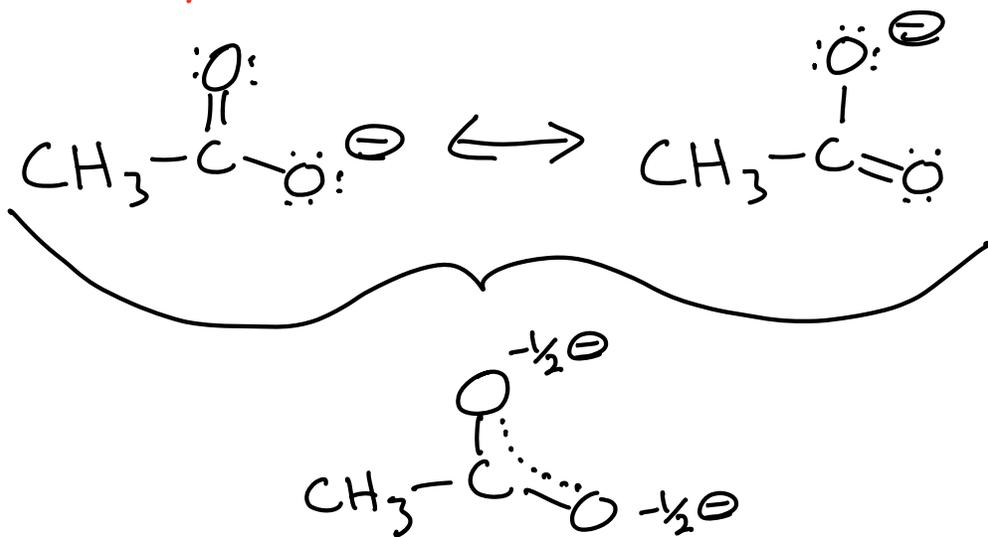
at pH 2.0



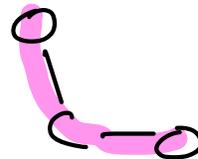
In biochemistry  $\rightarrow$  at or near neutral pH, carboxylic acids are deprotonated and negatively charged!

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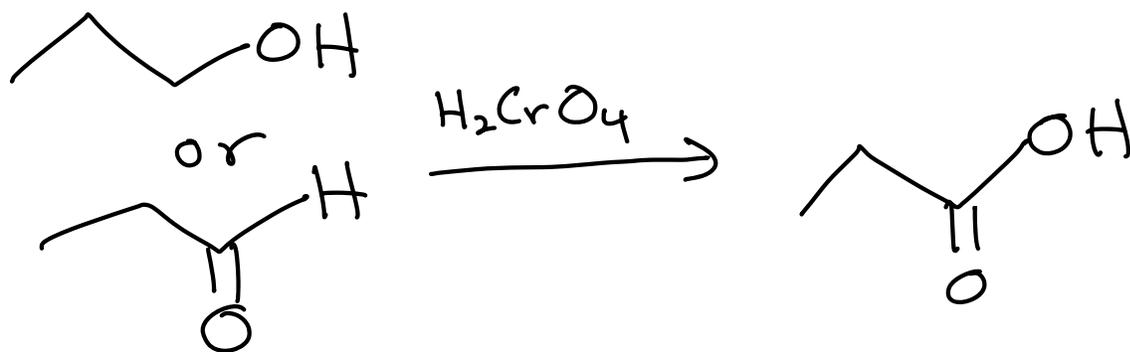
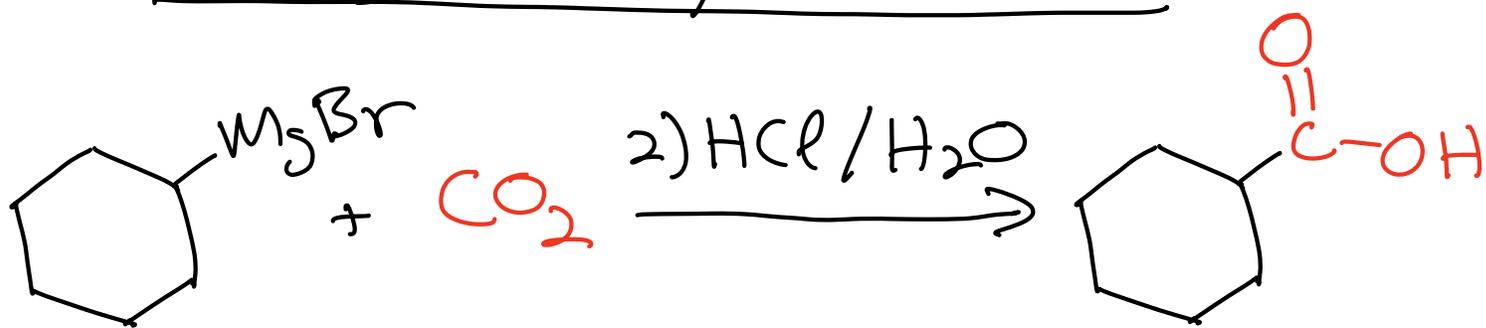
## Stability of anion Part II



Not only is the negative charge split between both O atoms, there is a "π-way", namely a π bond that extends over 3 atoms



# Making Carboxylic Acids



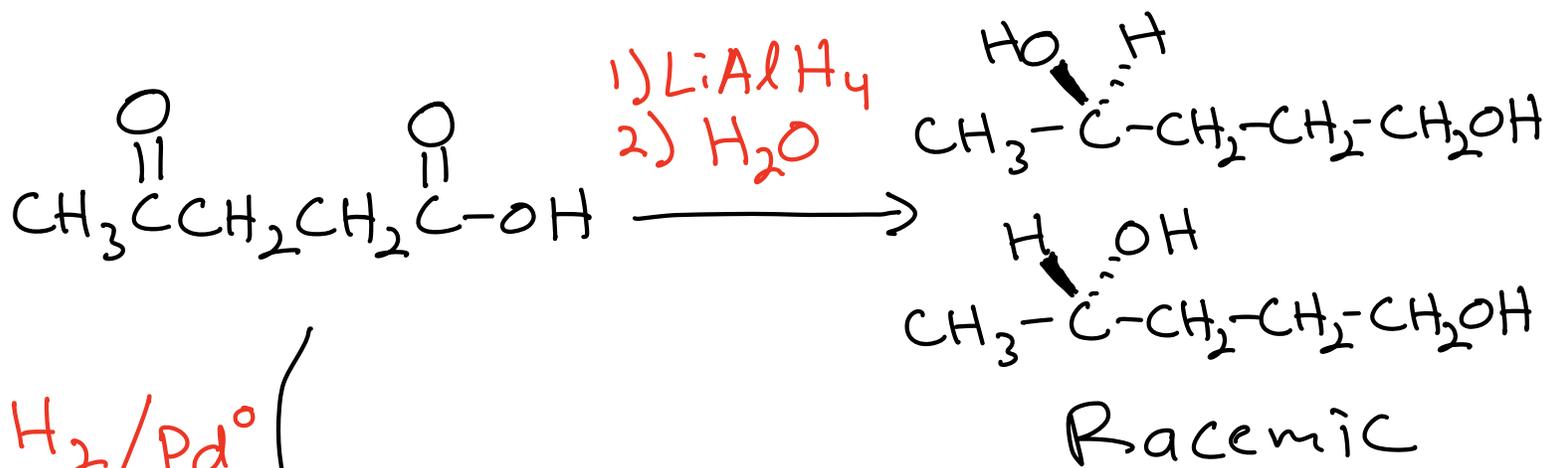
## Reactions of Carboxylic Acids

Reduction  $\rightarrow \text{H}_2 / \text{Pd}^\circ$  or

1)  $\text{NaBH}_4$  2)  $\text{H}_2\text{O}$  will  
NOT reduce a carboxylic  
acid

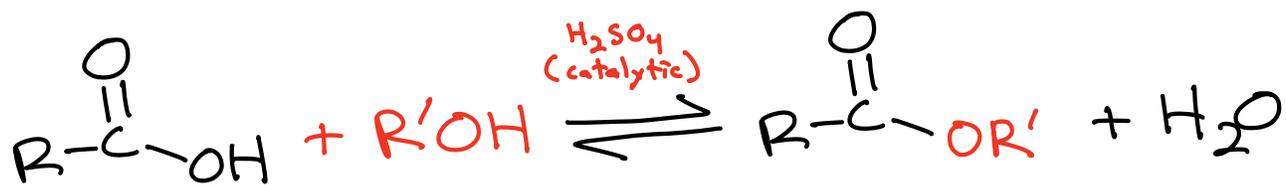
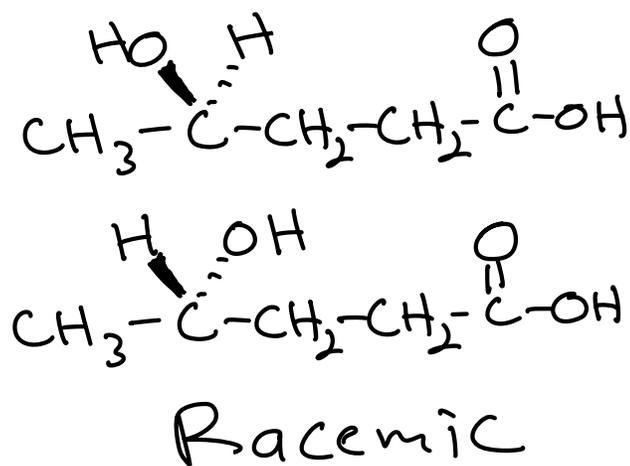
NOT responsible  
for mechanism

1)  $\text{LiAlH}_4$  2)  $\text{H}_2\text{O}$  DOES  
reduce a carboxylic acid to  
a primary alcohol

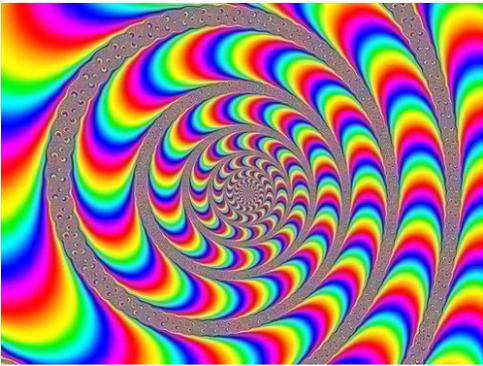
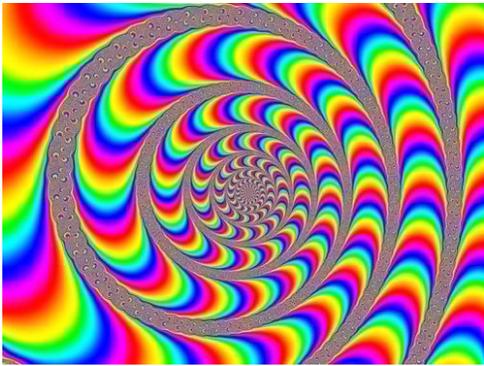
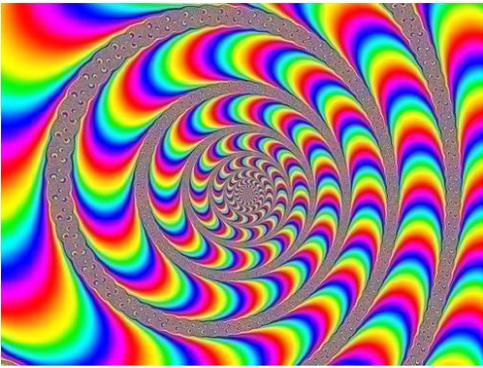
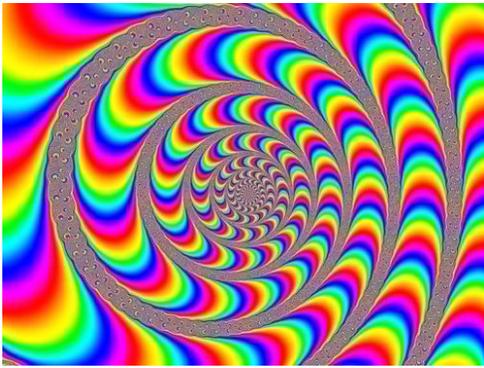


$\text{H}_2/\text{Pd}^\circ$   
or

1)  $\text{NaBH}_4$   
2)  $\text{H}_2\text{O}$



Time Capsule →  
This is  
Reversible

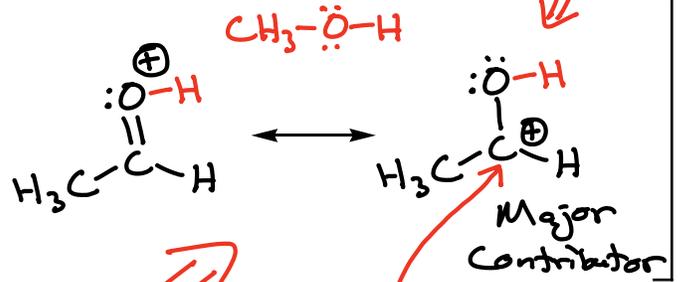
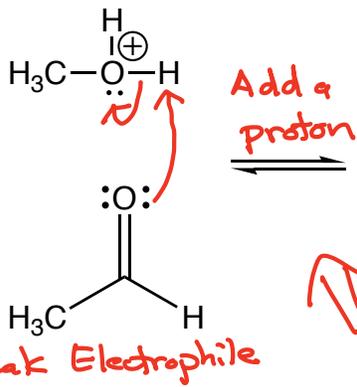
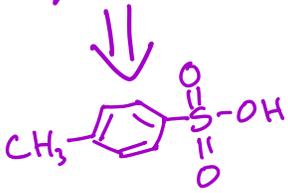


TsOH or H<sub>2</sub>SO<sub>4</sub>

Tosylic Acid

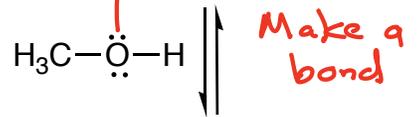
# Acid Catalyzed Hemiacetal and Acetal Formation From an Aldehyde or Ketone

"Hey, does that thing have a hemi in it?" "SWEET!"

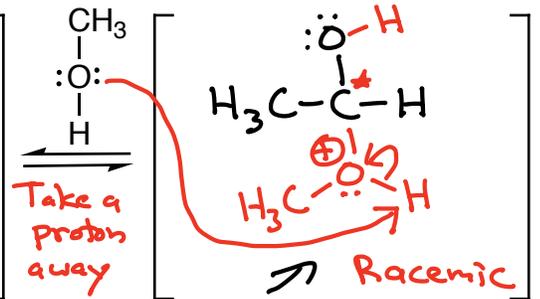
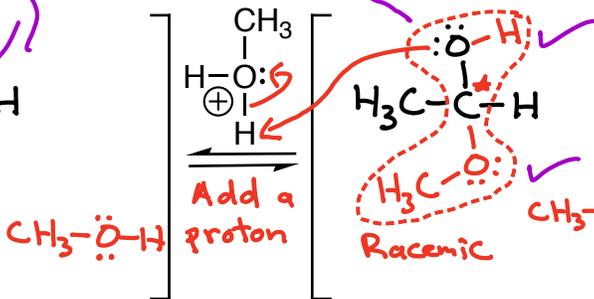
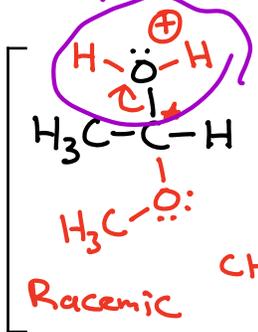


Red Hot Electrophile

Mechanism

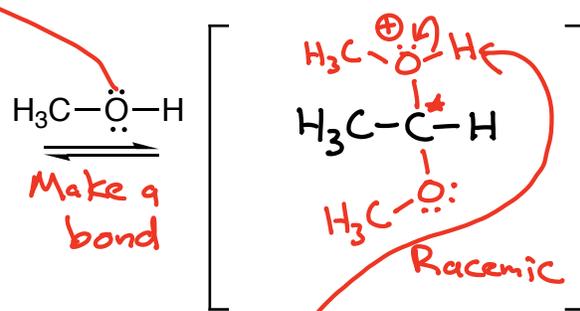
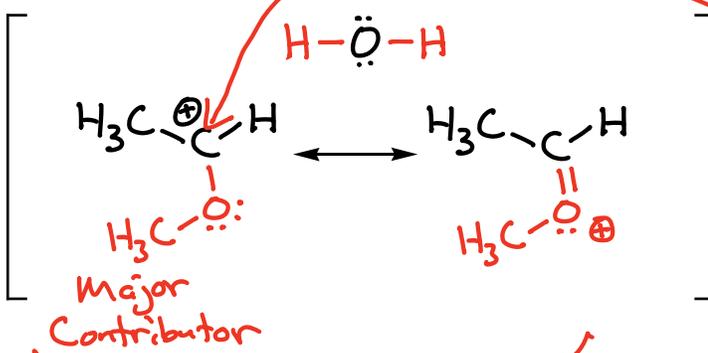


-OH and -OR on the same sp<sup>3</sup> C atom



Break a bond

Not stable

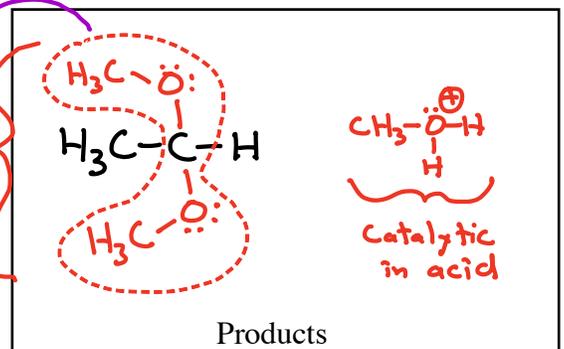


Key Recognition Element (KRE):

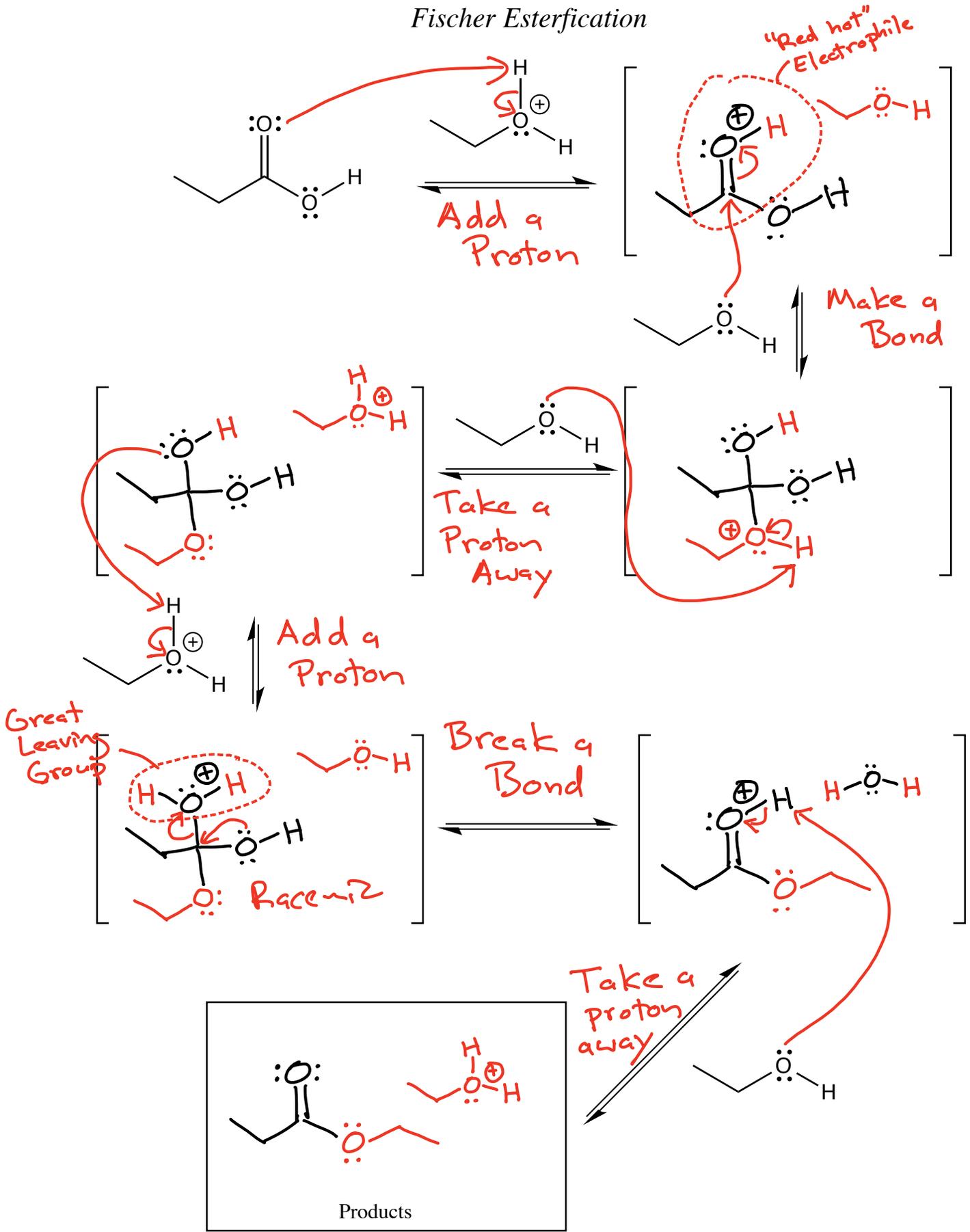
Two -OR on the same sp<sup>3</sup> C atom

Two bonds to ether O atoms to an sp<sup>3</sup> C atom

An acetal



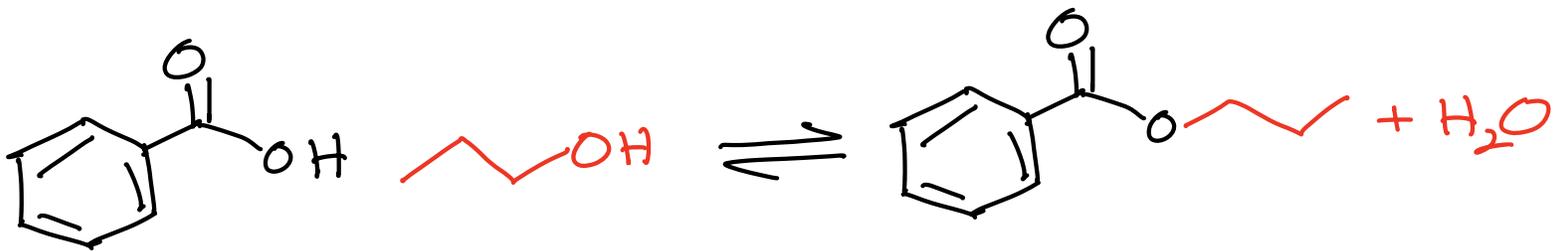
# Fischer Esterification



$K_{RE} \rightarrow$  An ester is formed



New Bond 



Time Capsule  $\rightarrow$

This is reversible

$\rightarrow$  The position of equilibrium depends on the ratio of alcohol to water