

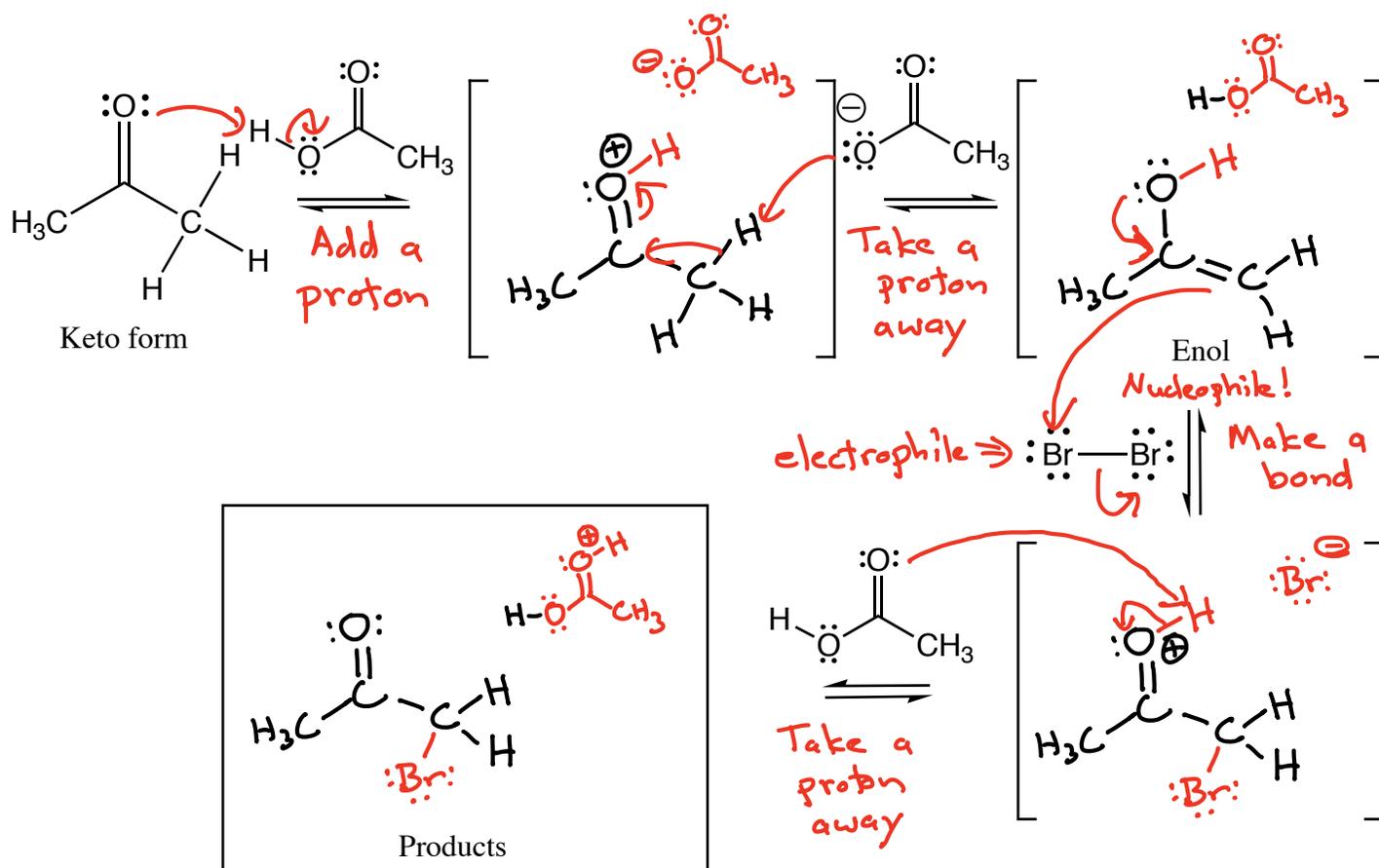




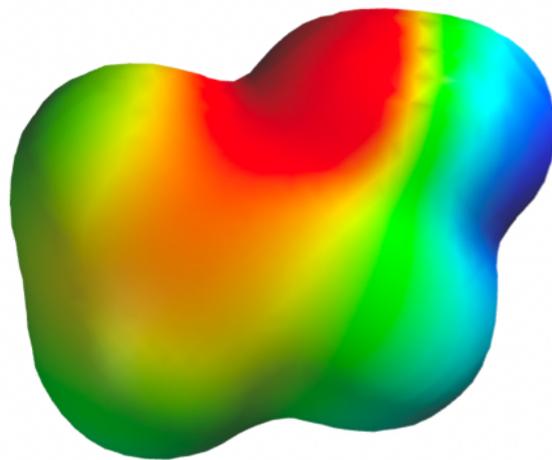
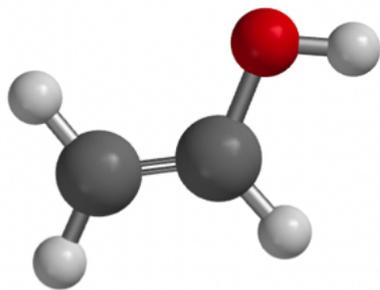
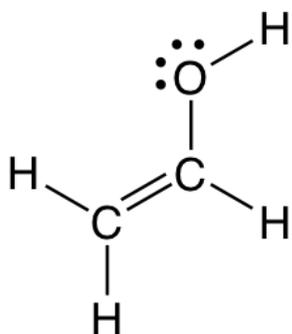
Exam Information:

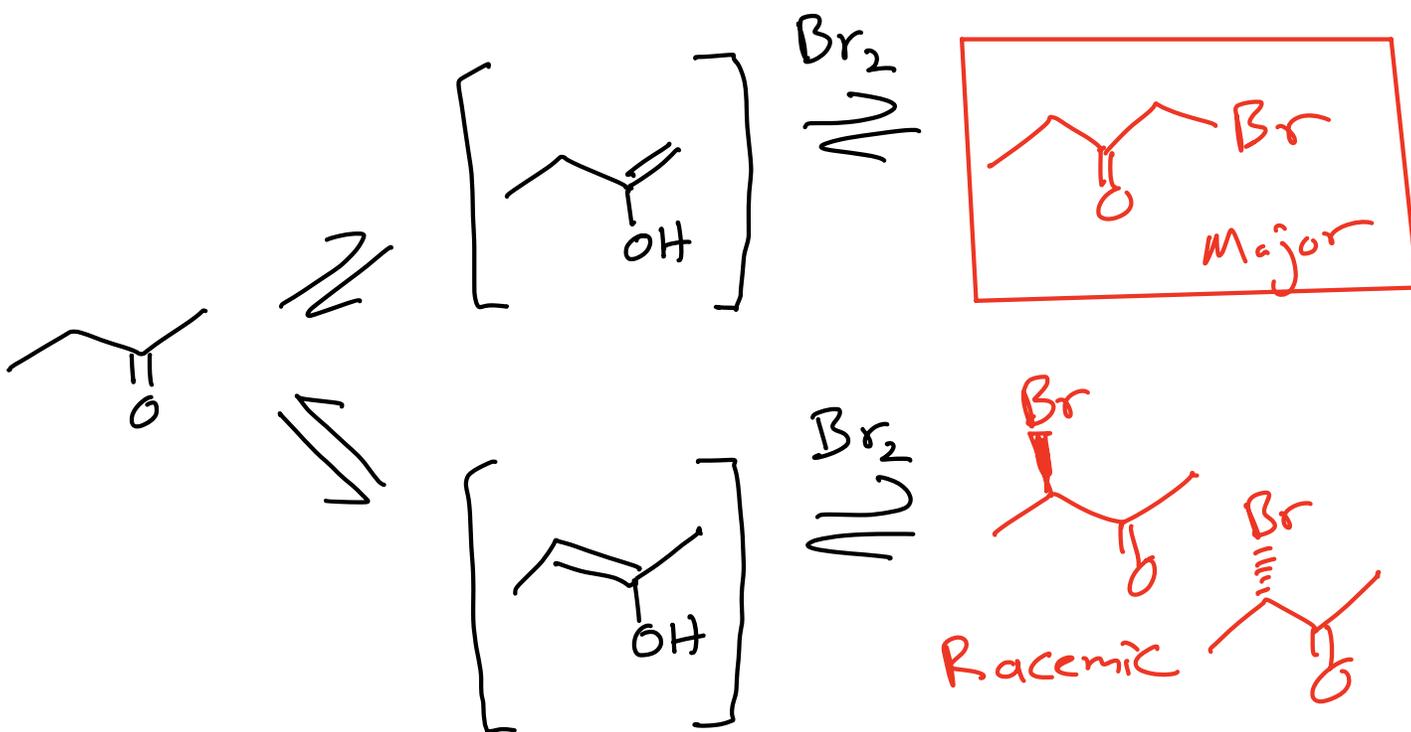
Concepts	70 points
Nomenclature	12 points
Mechanisms	76 points
Reactions ("Box" Problems)	53 points
Synthesis	43 points
MCAT Question	8 points
	<hr/>
	262 points

α -Halogenation of an Aldehyde or Ketone Catalyzed by Acid

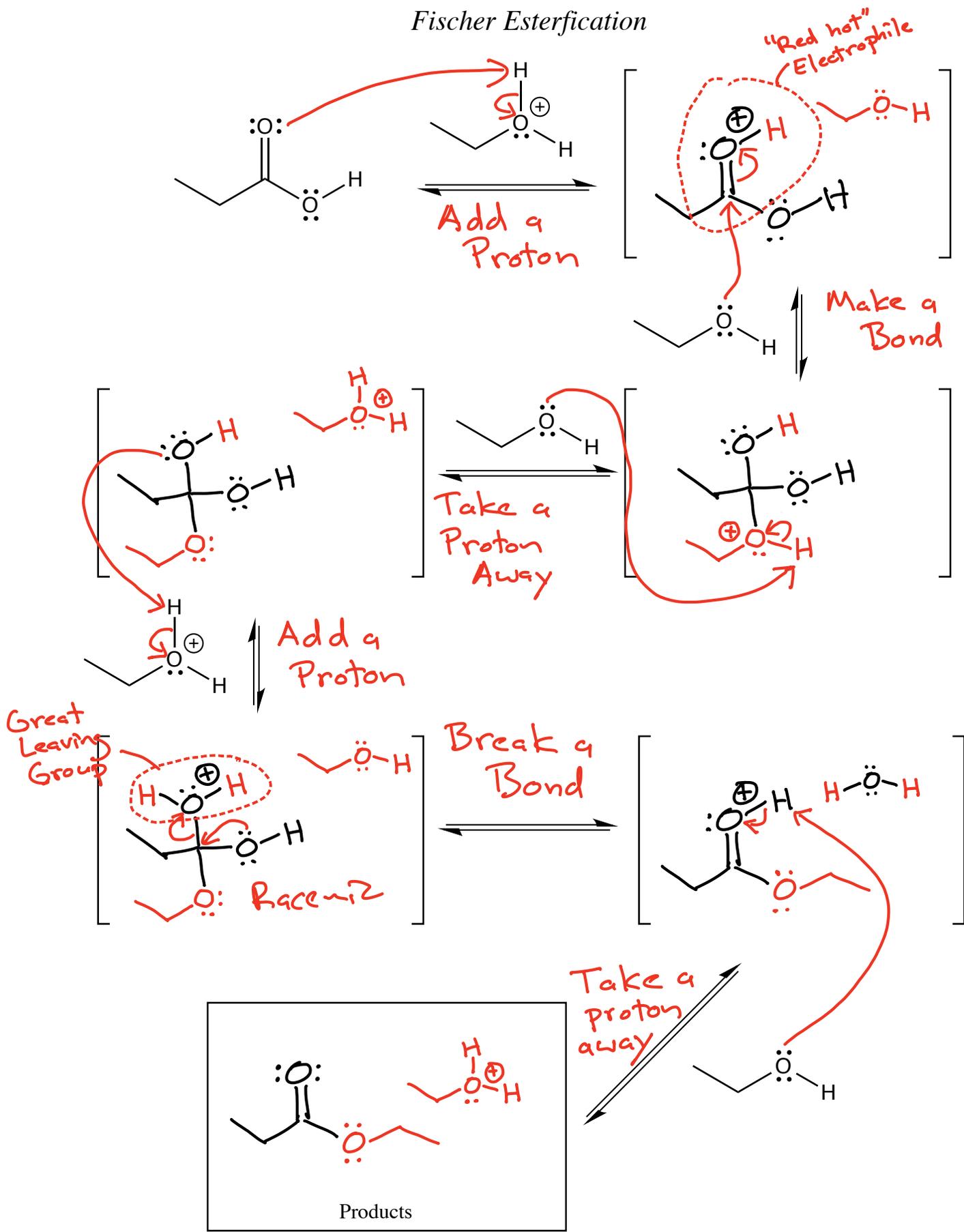


Note: For unsymmetrical ketones, METHYL GROUPS react in preference to all other types of alkyl groups \rightarrow Steric





Fischer Esterification

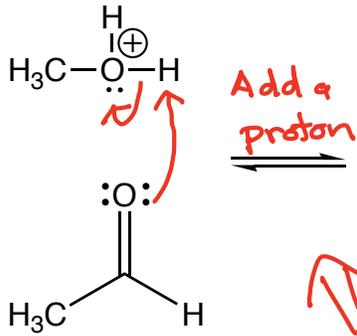
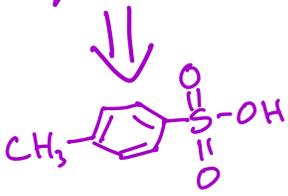


TsOH or H₂SO₄

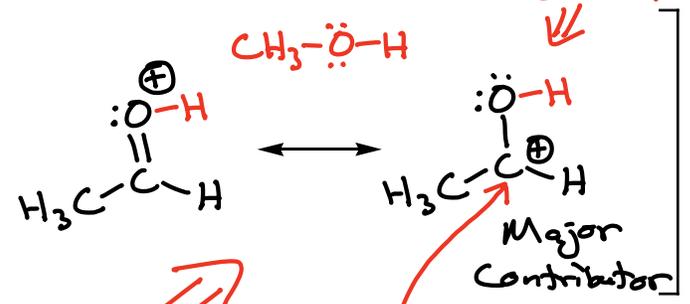
Tosylic Acid

Acid Catalyzed Hemiacetal and Acetal Formation From an Aldehyde or Ketone

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



Add a proton

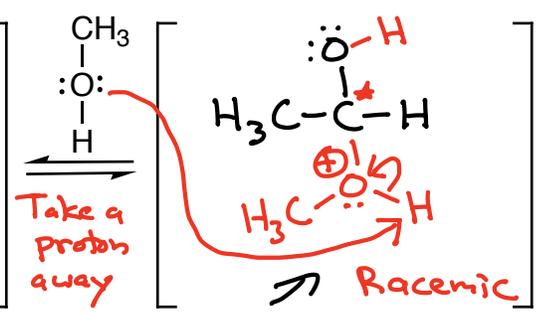
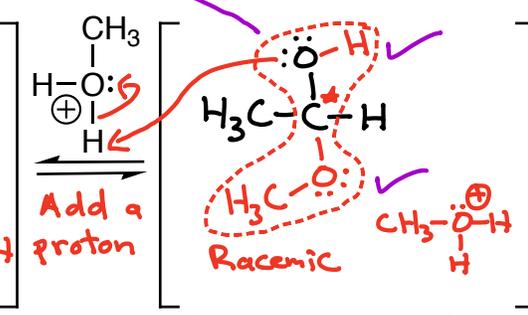
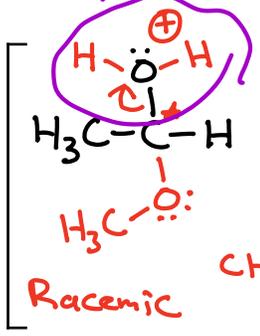


Red Hot Electrophile

Mechanism

Make a bond

-OH and -OR on the same sp³ C atom

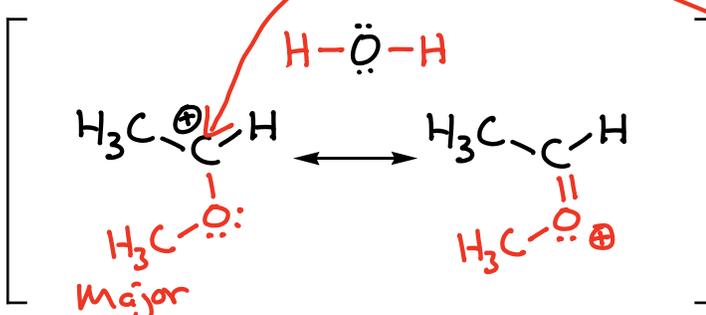


Add a proton

Take a proton away

Break a bond

Not stable



Make a bond

Take a proton away

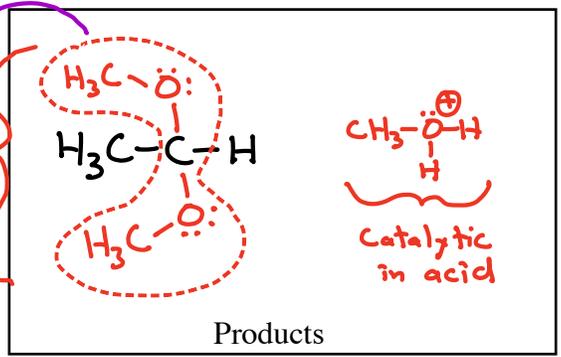
Stabilized by Charge Delocalization

Key Recognition Element (KRE):

Two -OR on the same sp³ C atom

Two bonds to ether O atoms to an sp³ C atom

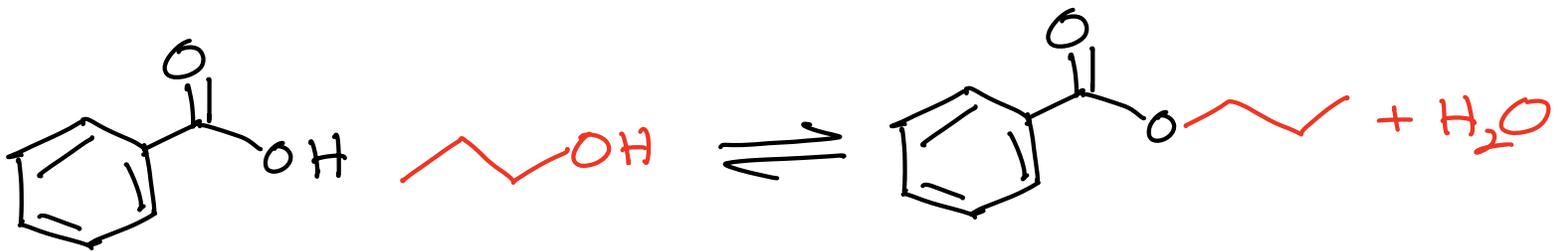
An acetal



KRE \rightarrow An ester is formed



New Bond \nearrow



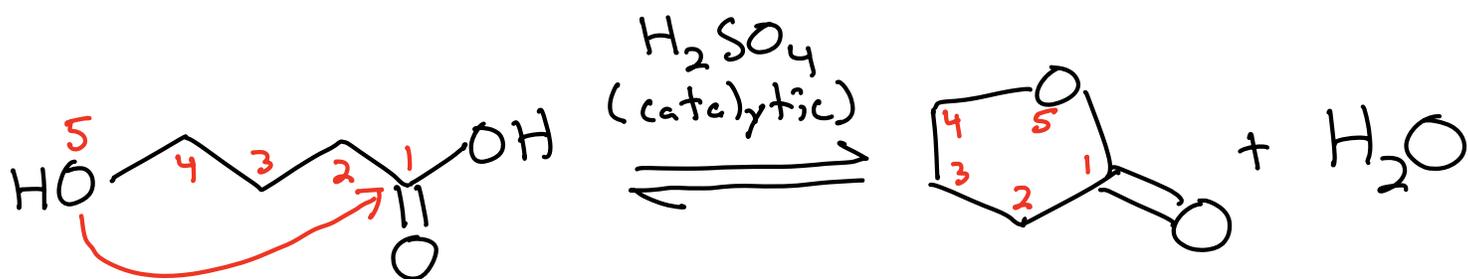
Time Capsule \rightarrow

This is reversible

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

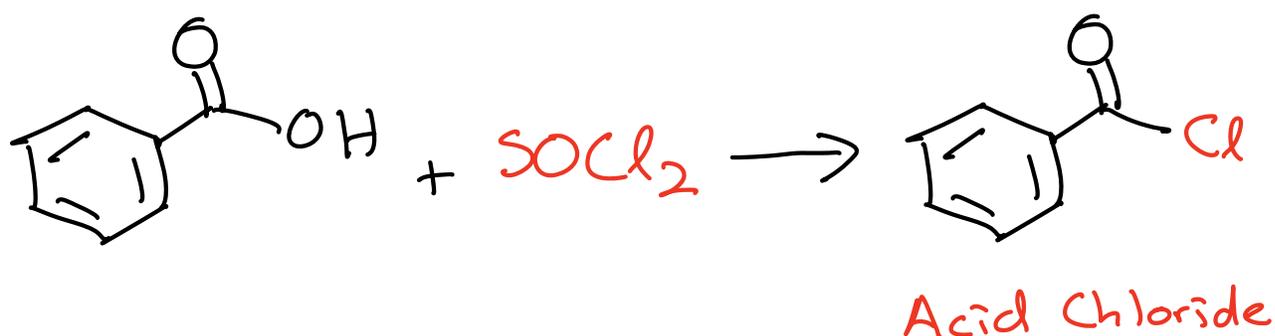


You can make cyclic esters called Lactones



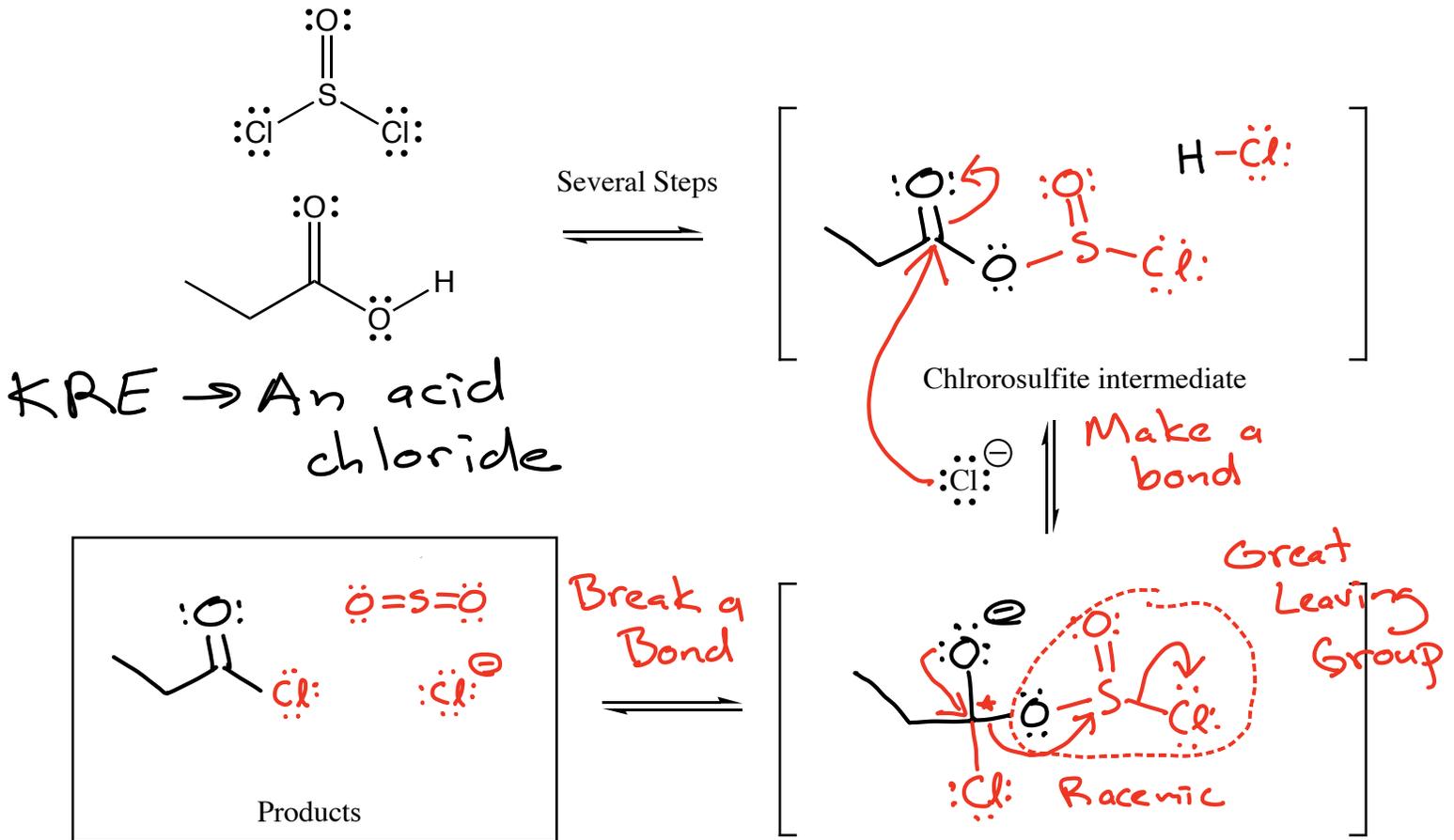
Pro tip: Always put numbers on the atoms when a ring is involved

Carboxylic Acid and SOCl_2
Thionyl Chloride

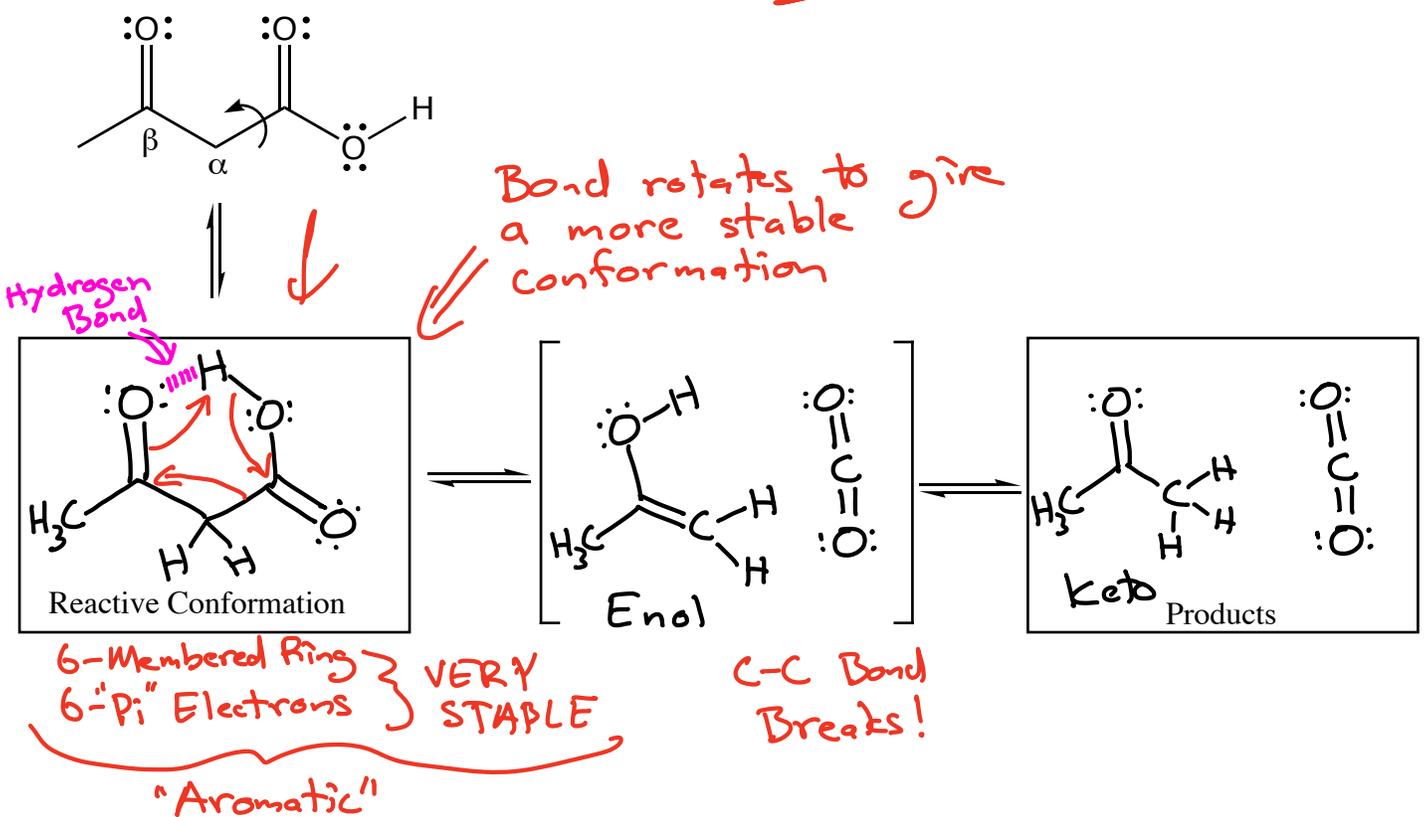


Time capsule →
You can make
all of the other
carboxylic acid
derivatives from
acid chlorides

Reaction with Thionyl Chloride



Decarboxylation of a β -Keto Acid

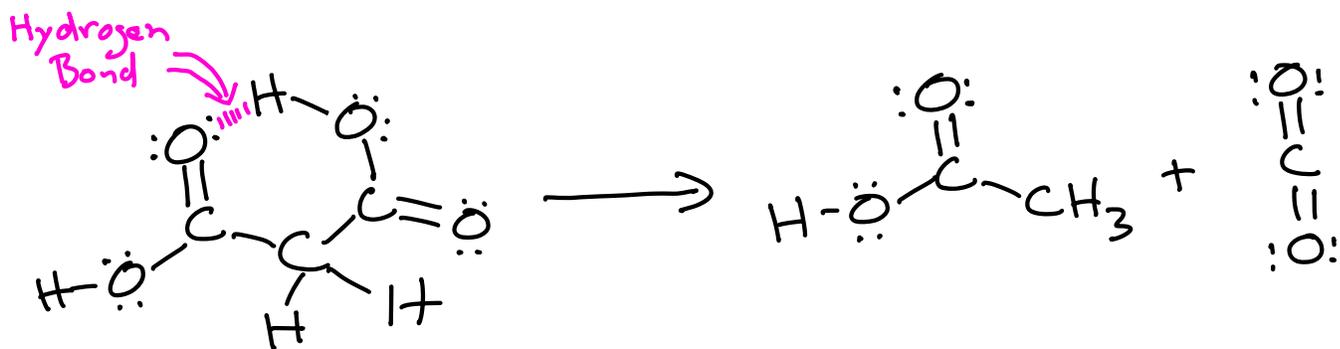


KRE → Ketone and CO₂
Broke a C-C Bond!



Time capsule →
Important for
products of Claisen
reaction!

This also works with β -diacids





Broke a C-C bond

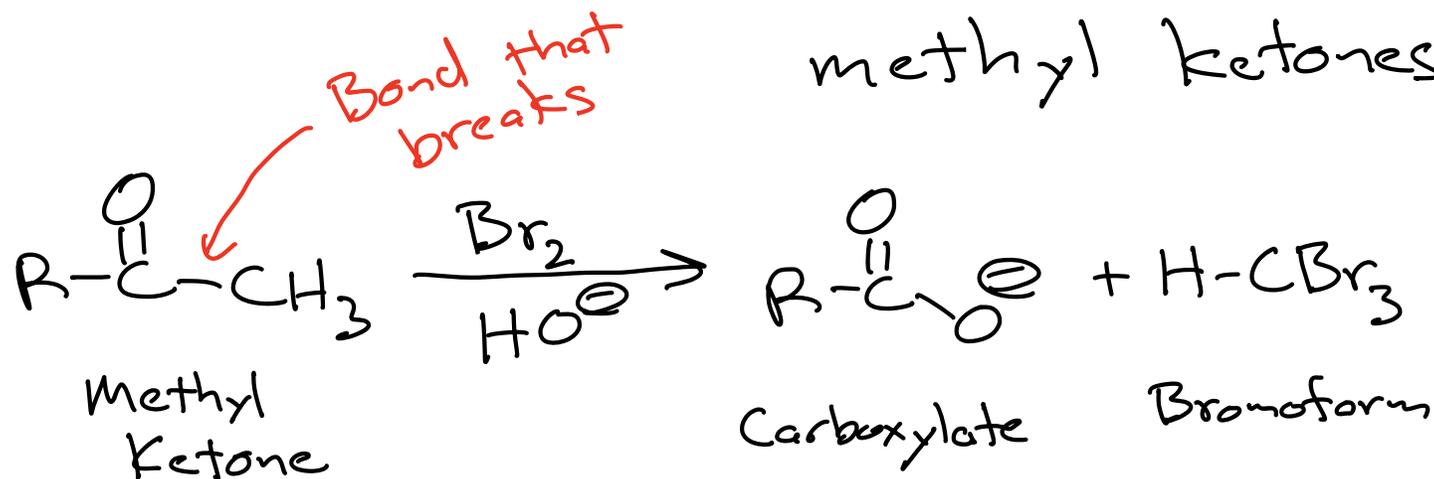
Time Capsule:

This is important
for the Claisen
condensation
reaction.



diacids
react
the same

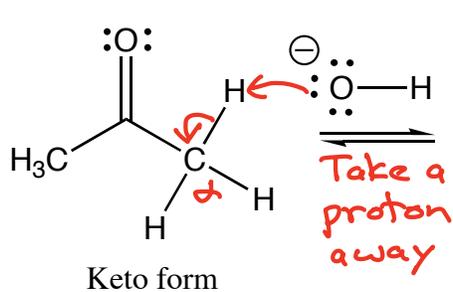
The haloform reaction \rightarrow uses methyl ketones



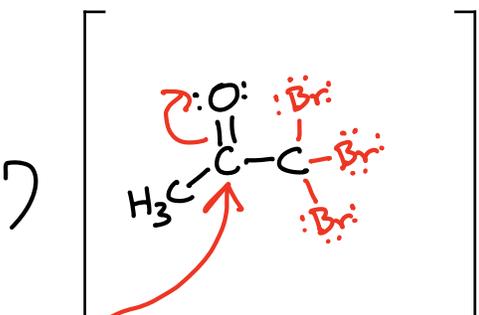
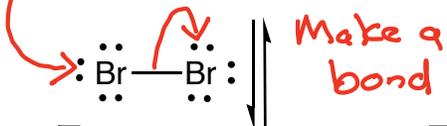
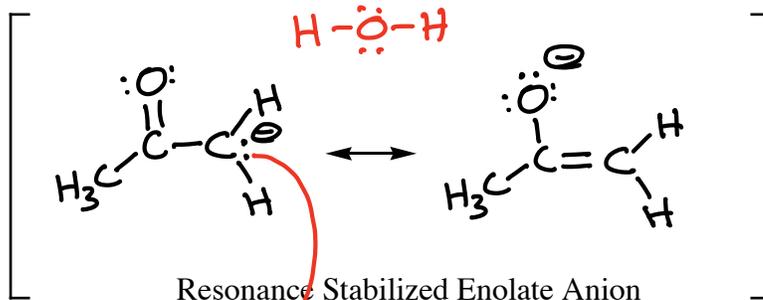
Not that useful for synthesis,
however the mechanism contains
three elements that are
important to second semester
organic chemistry

- 1) acidity of α -hydrogen
- 2) enolate nucleophile
- 3) Mechanism B

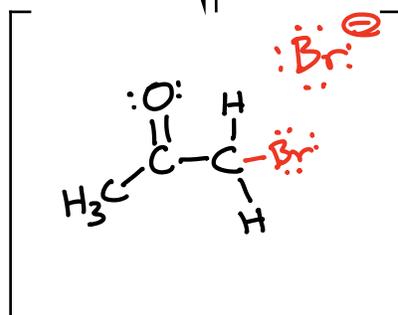
The Haloform Reaction



α -hydrogen $pK_a = 18-20$

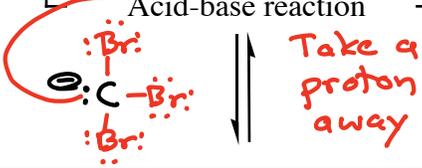
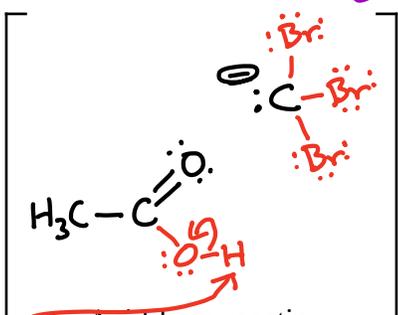
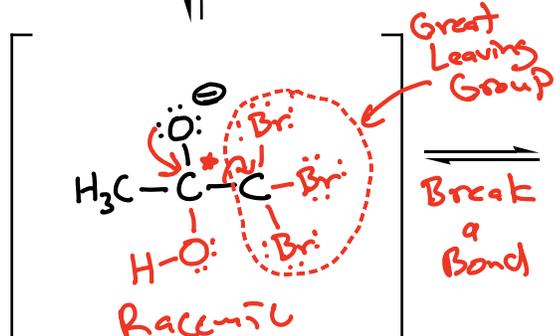


Two more times

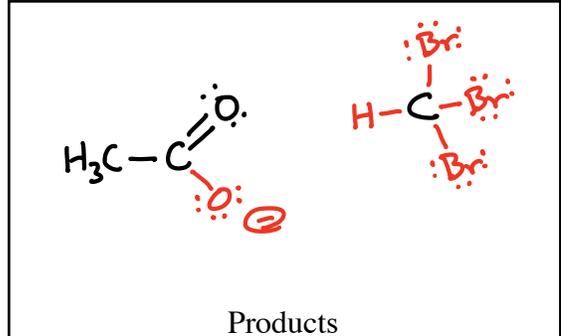


Mechanism B

The inductive effect stabilizes the \ominus explaining why $\ominus:C(Br)_3$ is such a good leaving group

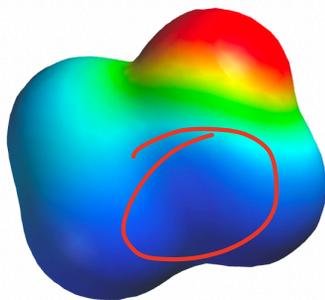
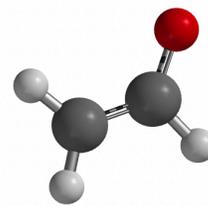
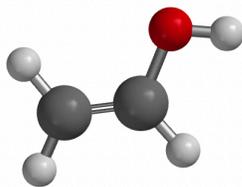
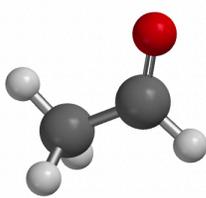
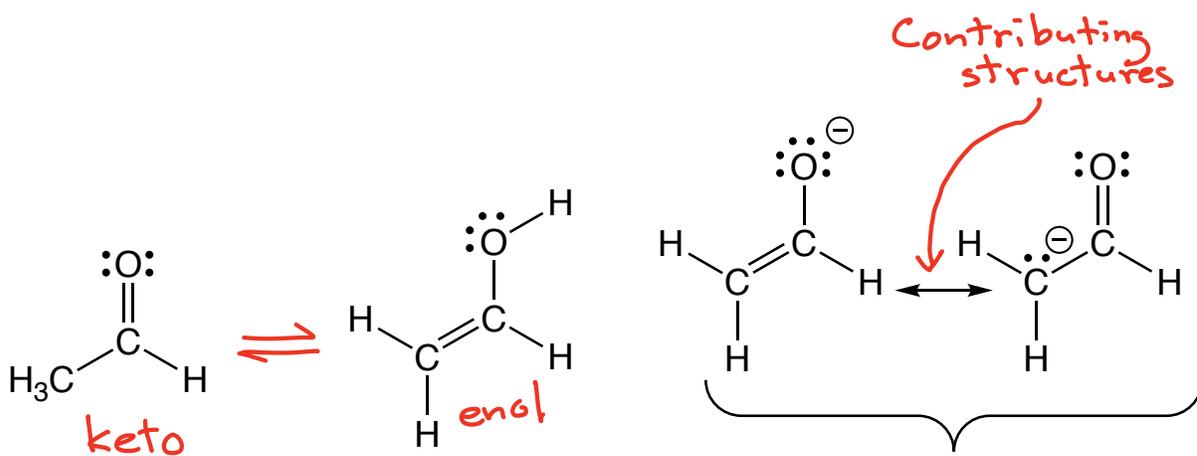


KRE → Break the C-C bond to give a carboxylate and haloform product

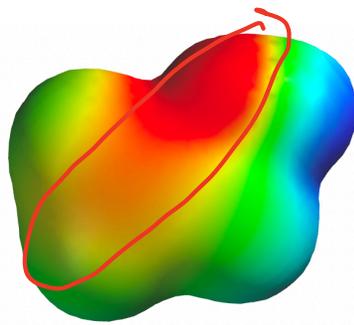




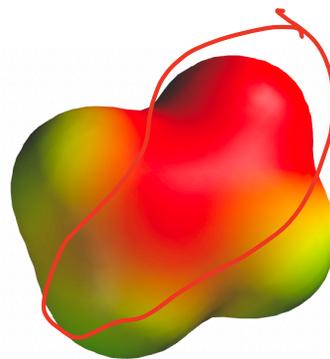
Be Careful: Do
not confuse
keto-enol
equilibrium
with
enolate
contributing
structures!



Electrophile



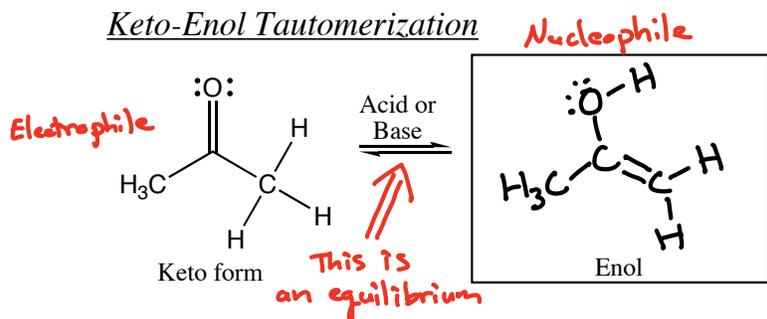
Nucleophile



Strong Nucleophile

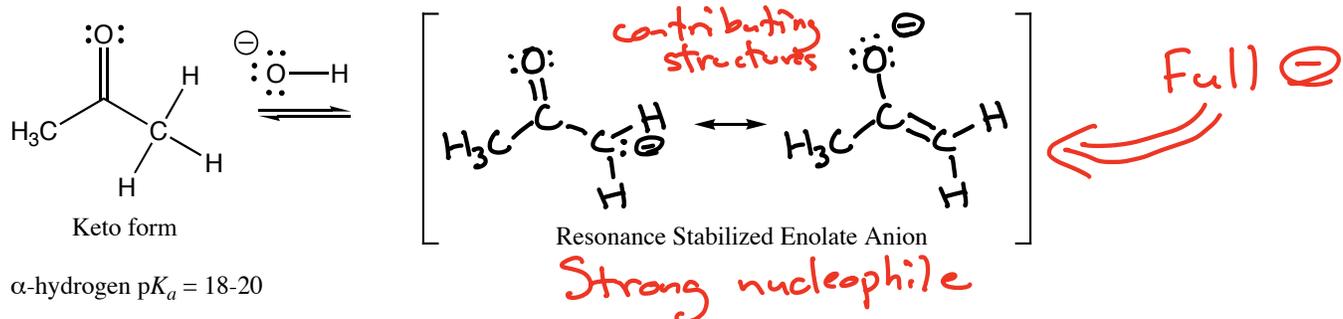
Keto-Enol Tautomerization vs. Enolate Resonance

Keto-Enol Tautomerization

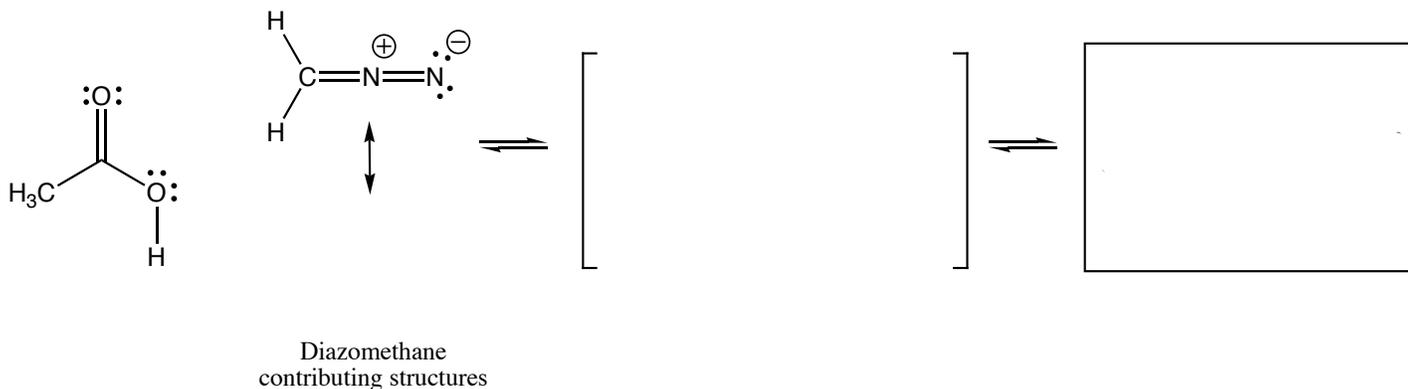


These are both neutral!

Enolate Resonance



Diazomethane reaction



Amide Resonance VERY IMPORTANT!!!!!!

