



For mechanisms, keep the following in mind:

1) Identify the bonds to be made and broken in the overall reaction

2) Avoid "mixed media errors"

a) In acid, all the intermediates are positively-charged or neutral

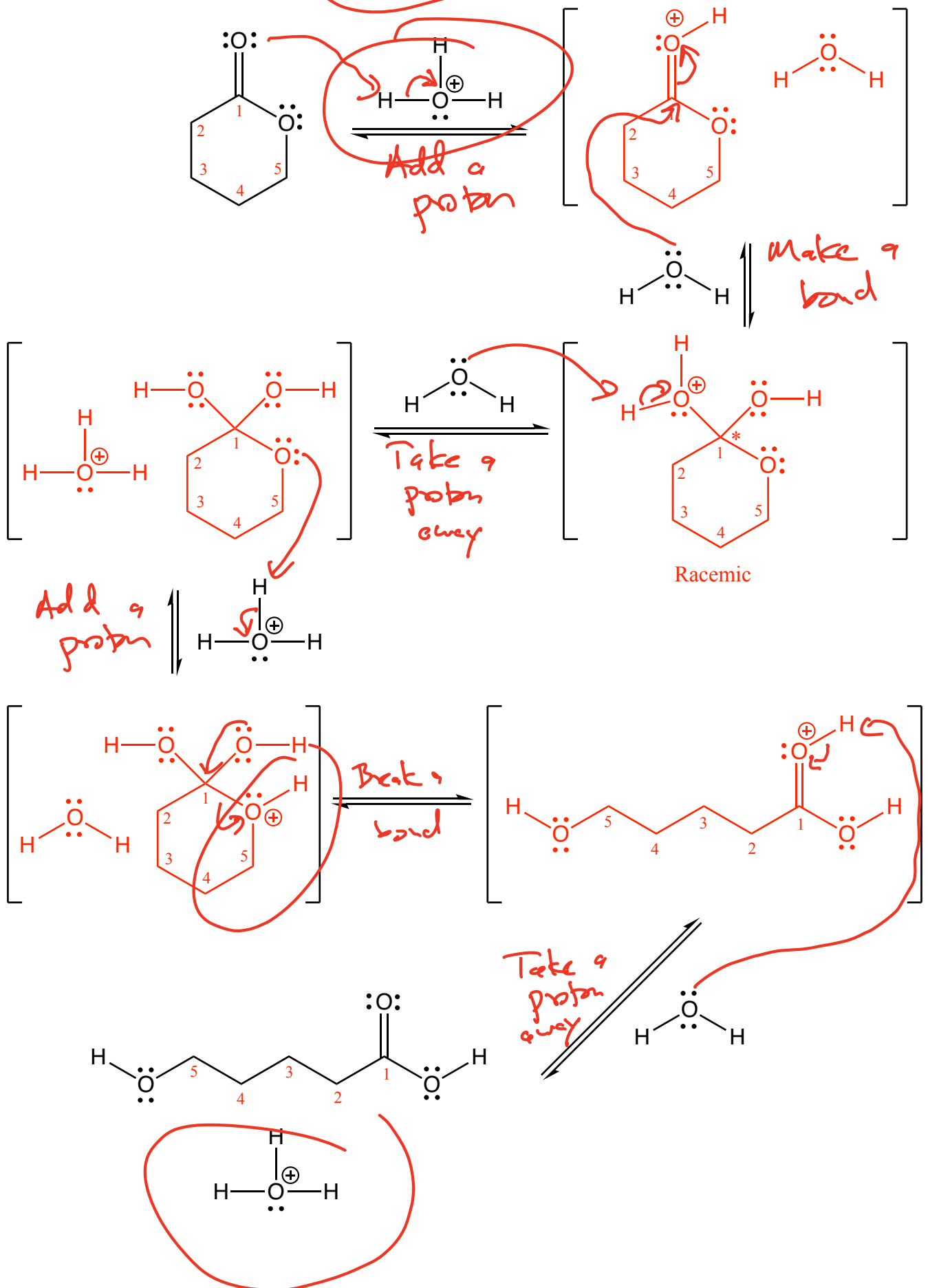
b) In base, all the intermediates are negatively-charged or neutral

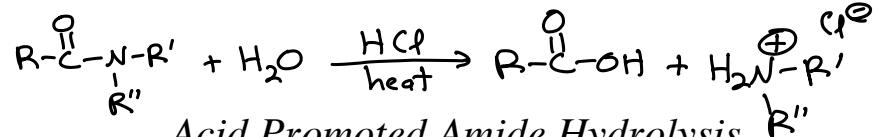
c) In neutral solution \rightarrow the intermediates could be positively-charged, negatively-charged or neutral

3) When in doubt transfer a proton \rightarrow protons move very fast

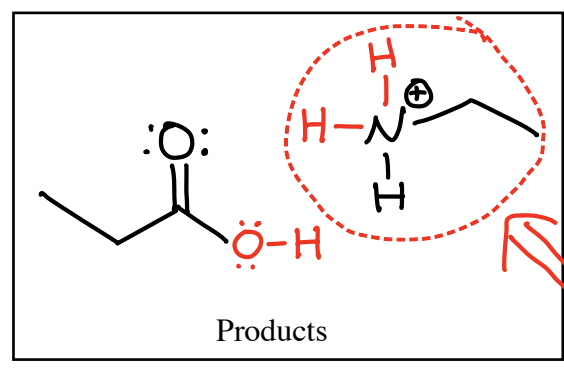
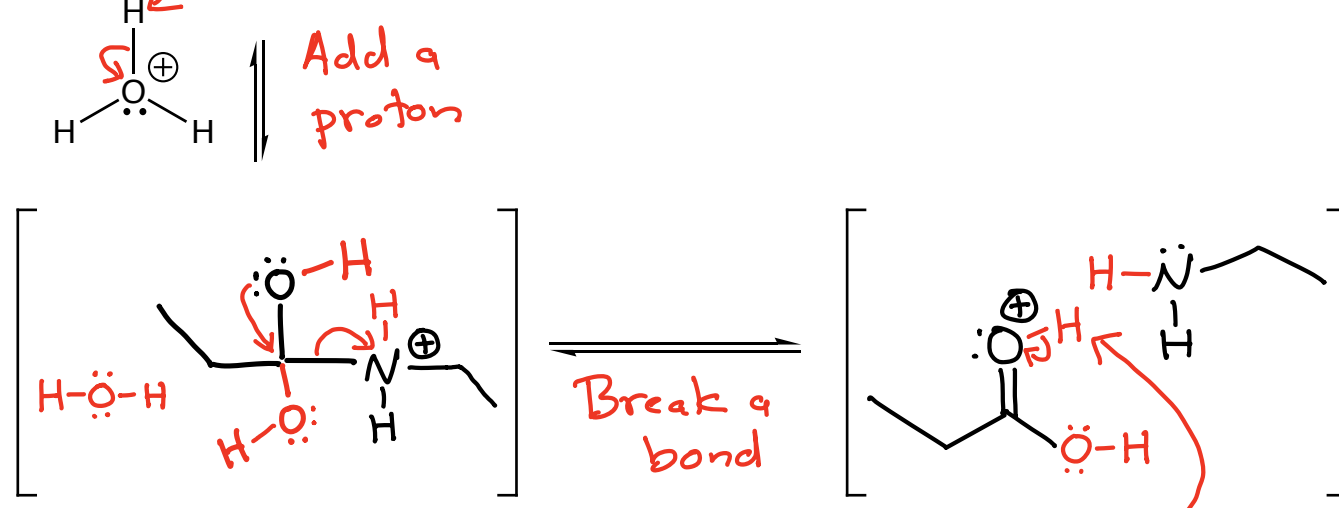
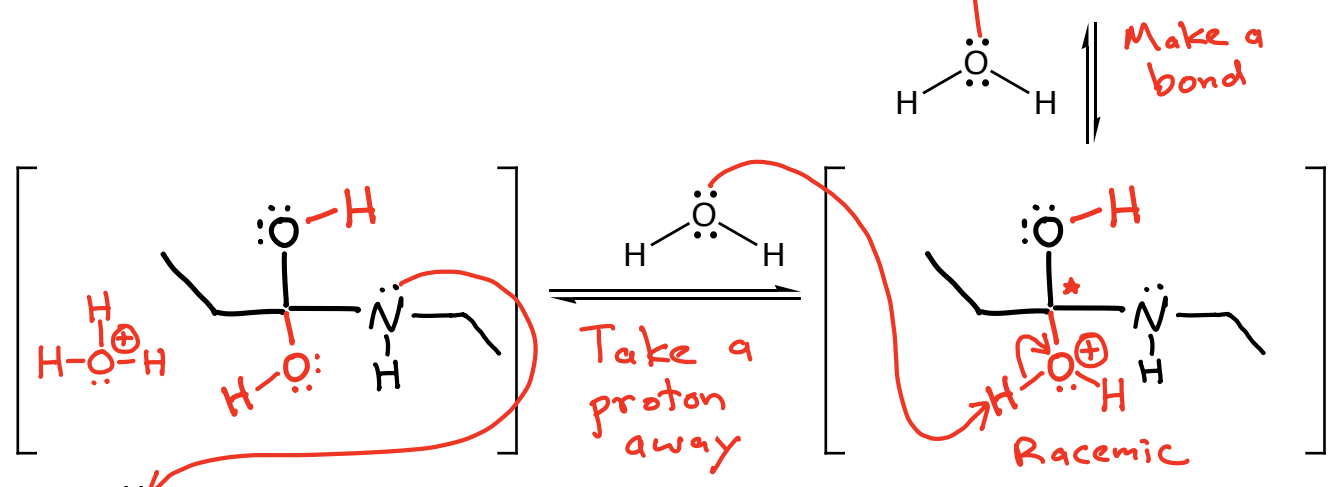
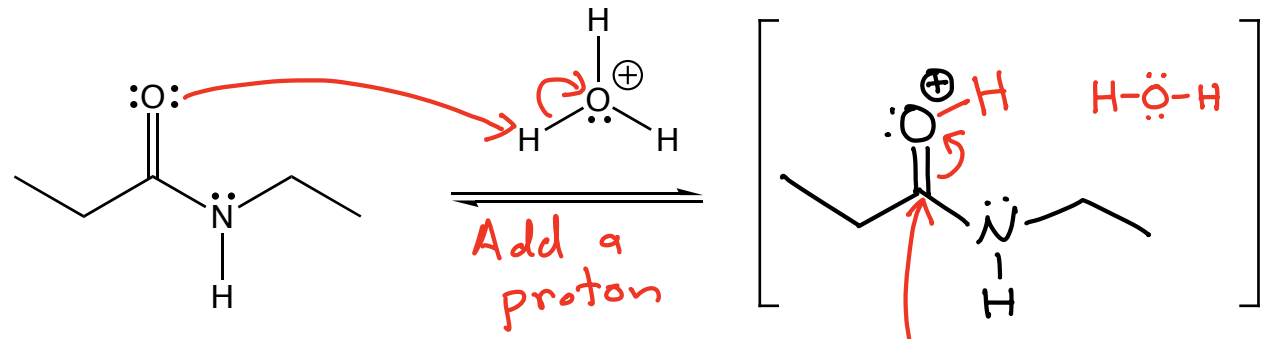
4) Analyze each intermediate carefully to predict the next step

Microscopic Reversibility: Acid Catalyzed Ester Hydrolysis-Fischer Esterification





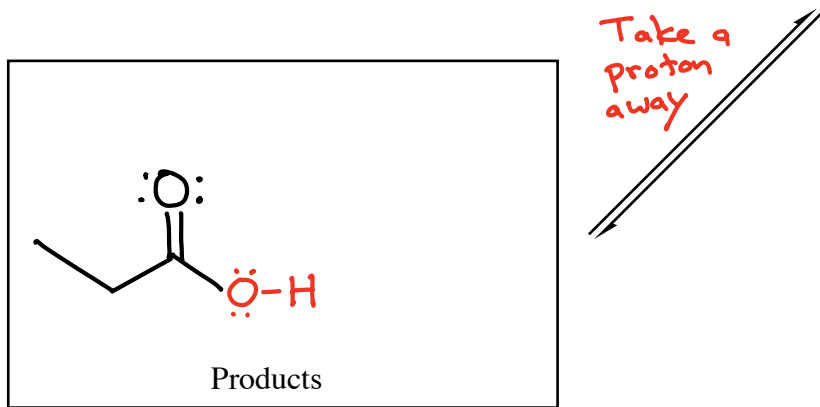
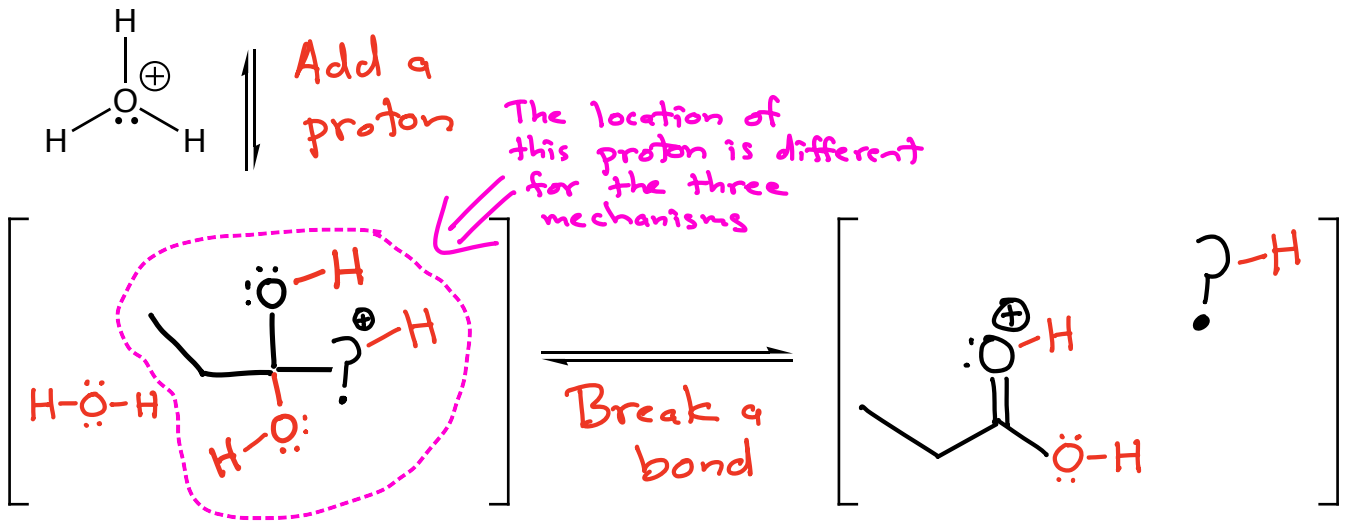
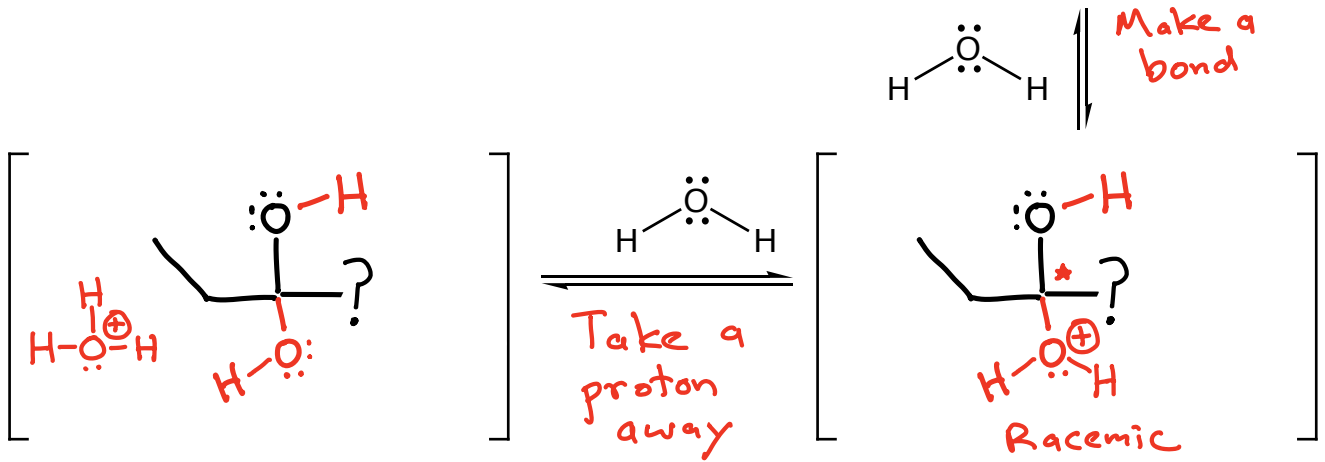
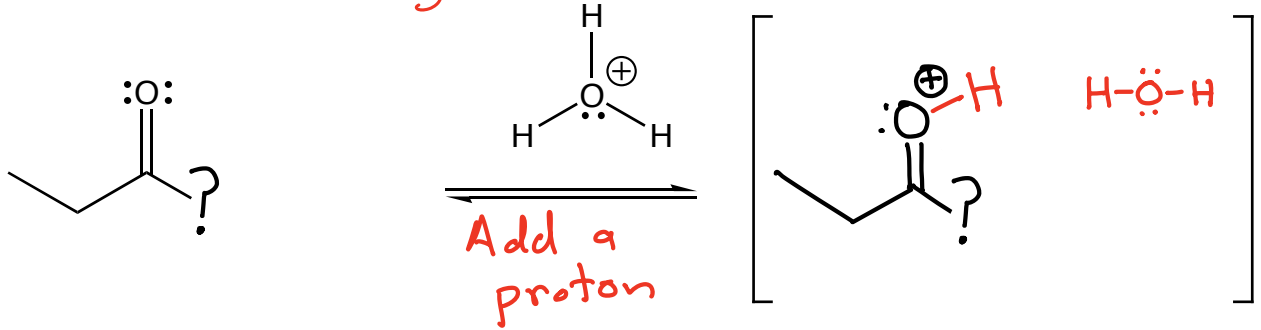
Acid Promoted Amide Hydrolysis

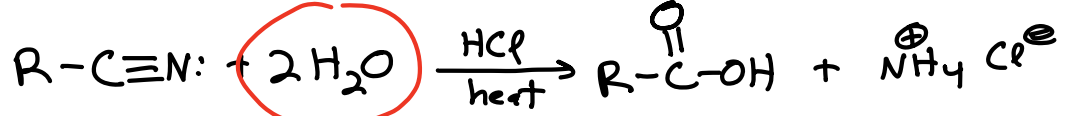


Take a proton away

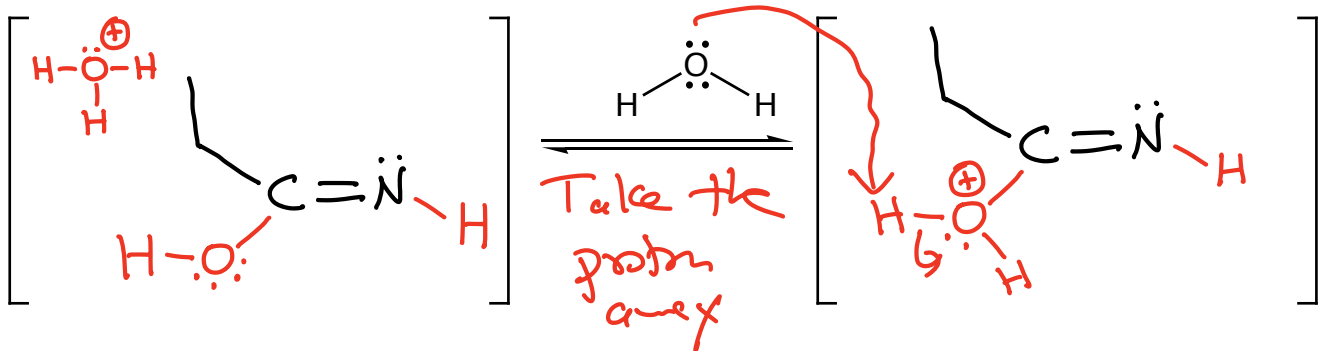
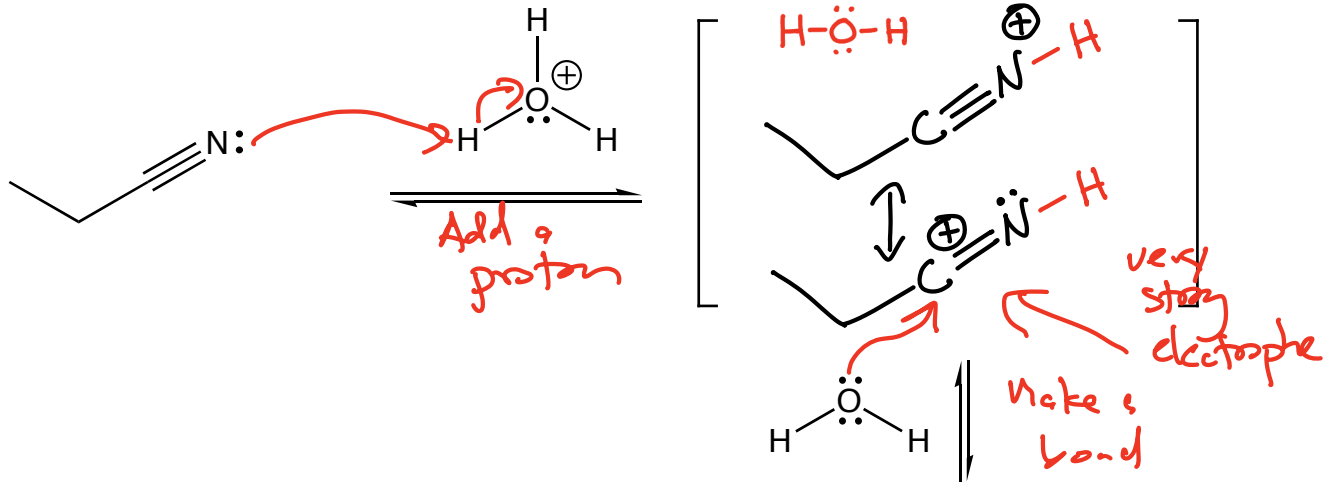
This is NOT H_3O^+ , this reaction is NOT catalytic in acid

The following mechanism applies to which reaction we have seen? Trick Question → it applies to three reactions → Anhydride, ester and amide hydrolysis in acid! "Same song different verse!"

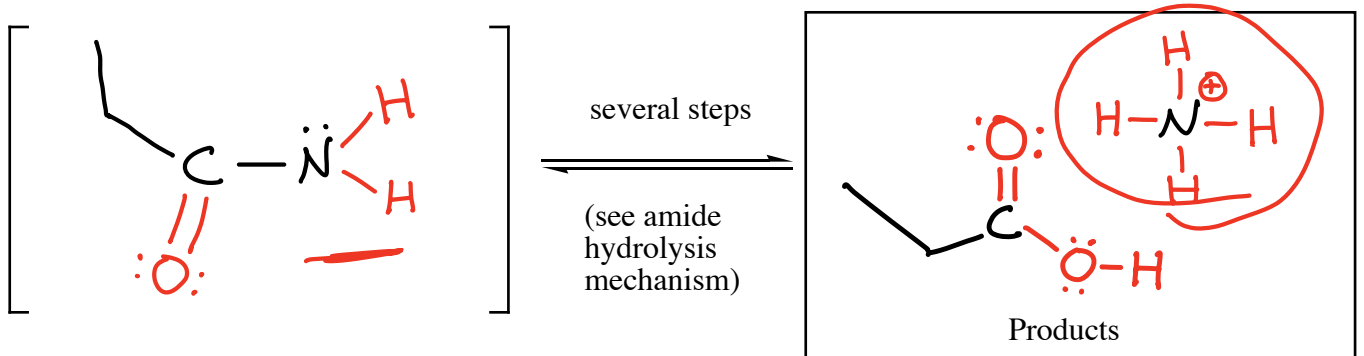


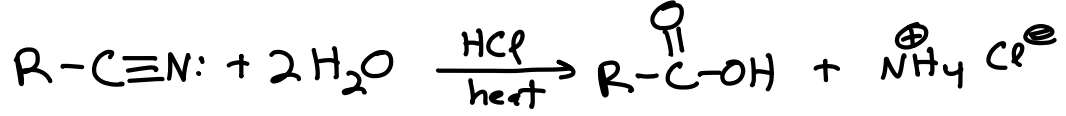


Acid Promoted Nitrile Hydrolysis

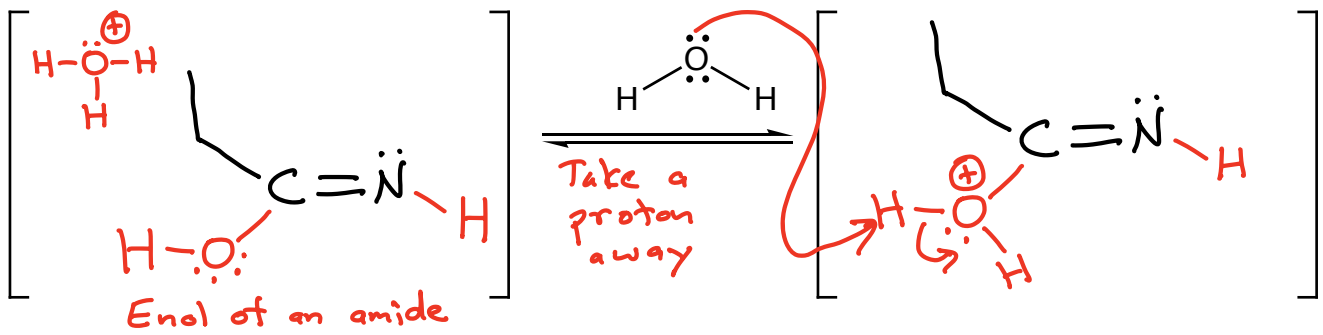
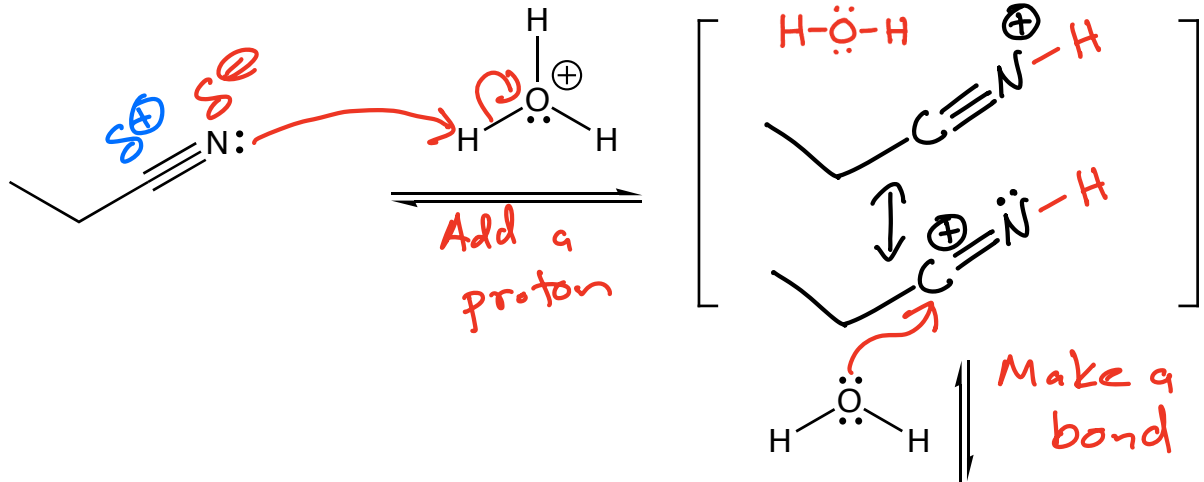


tautomerization \rightleftharpoons

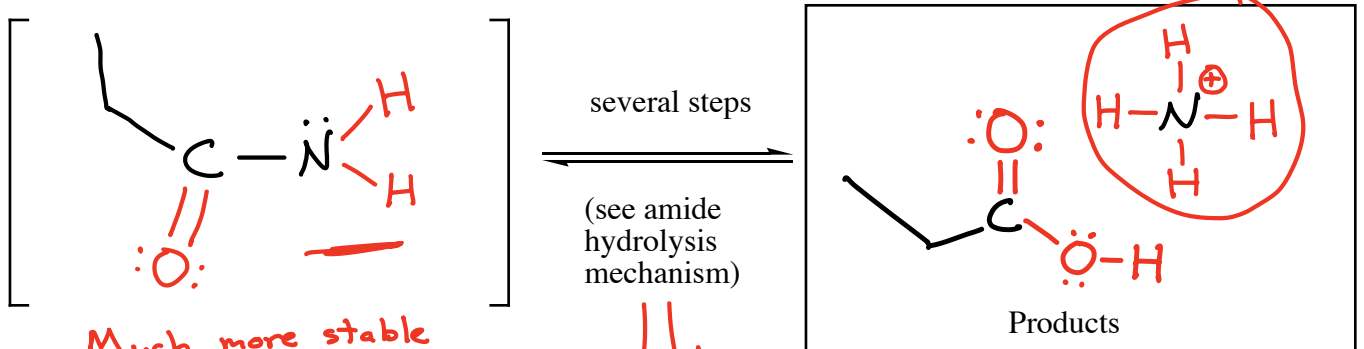




Acid Promoted Nitrile Hydrolysis

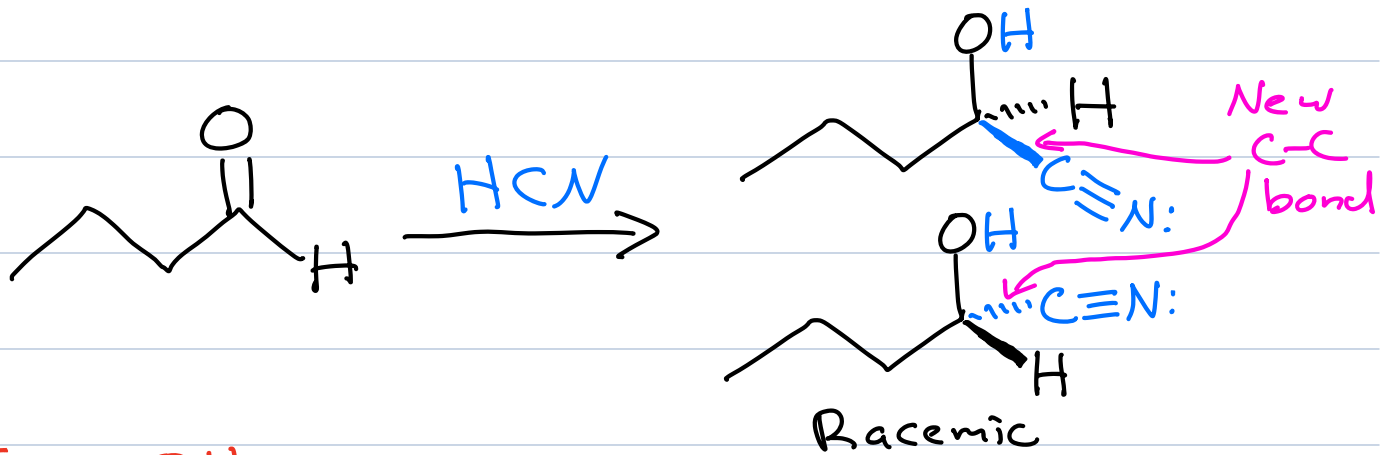
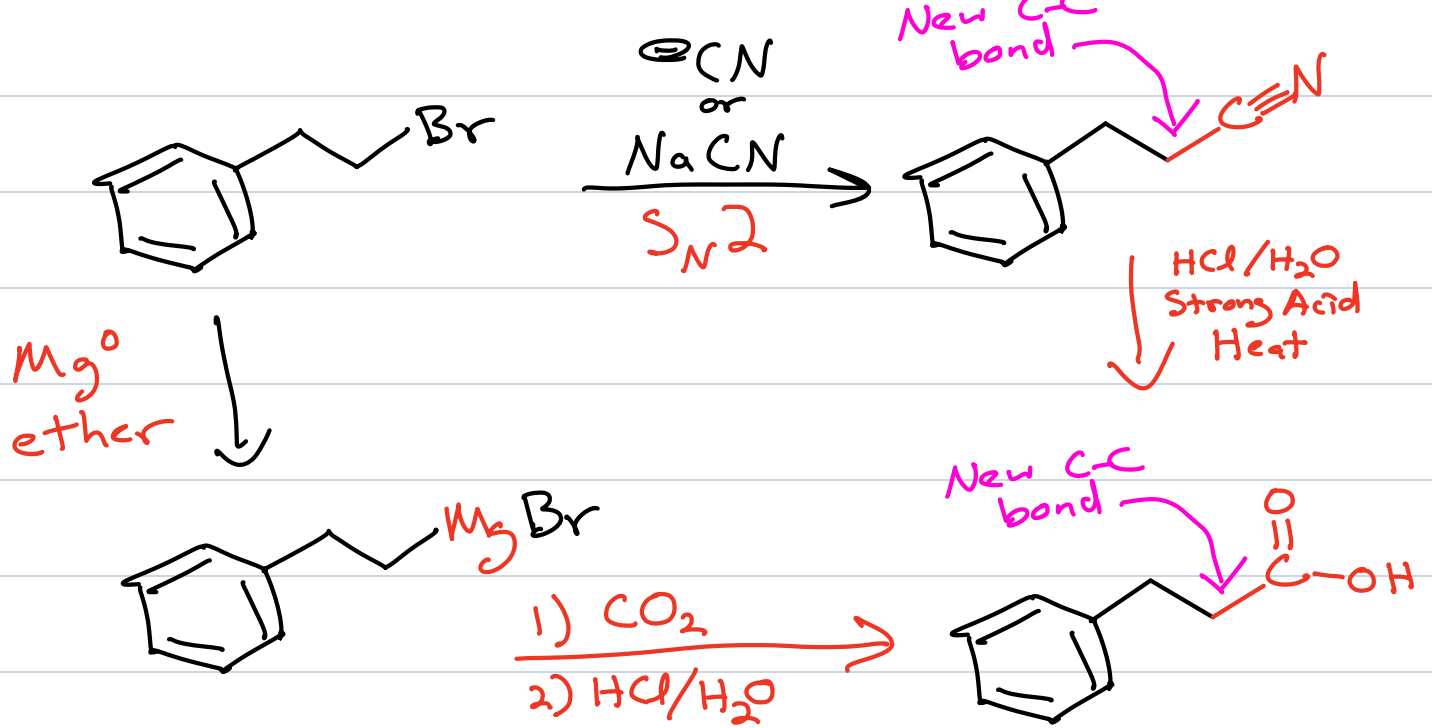


tautomerization



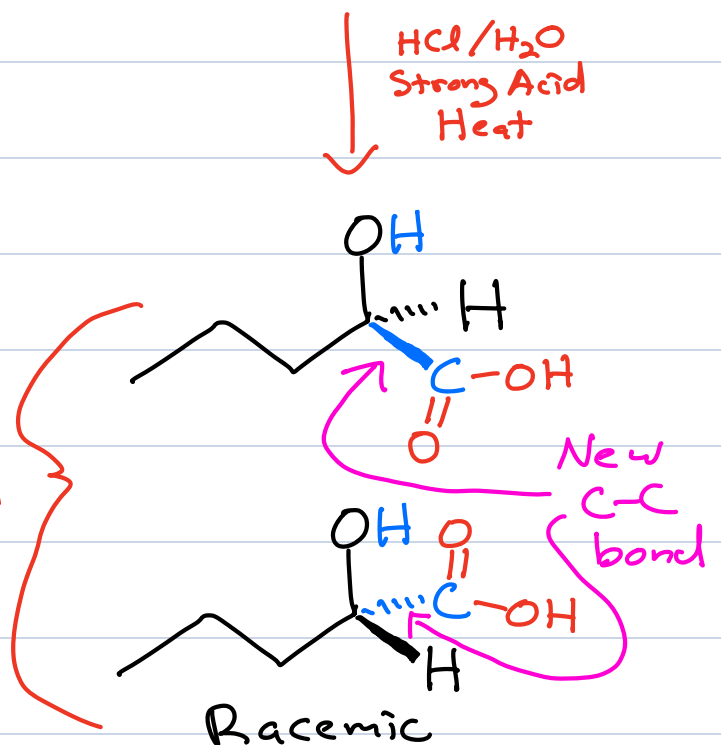
Much more stable keto form of an amide

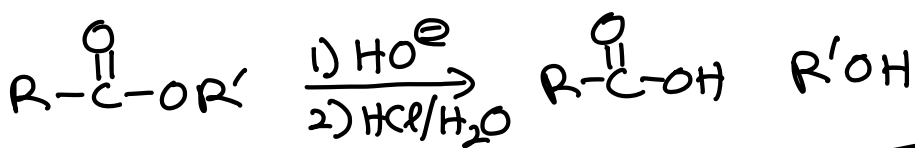
These conditions are strong enough to hydrolyze amides according to the mechanism we saw as "Acid Promoted Hydrolysis of an Amide"



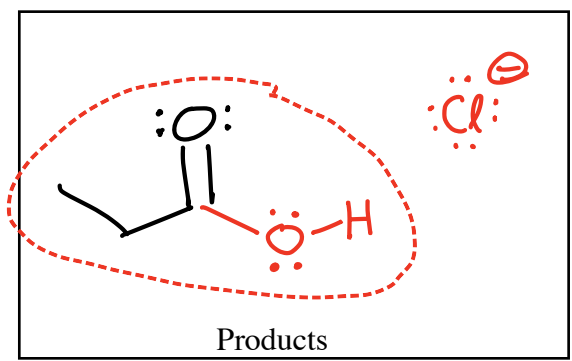
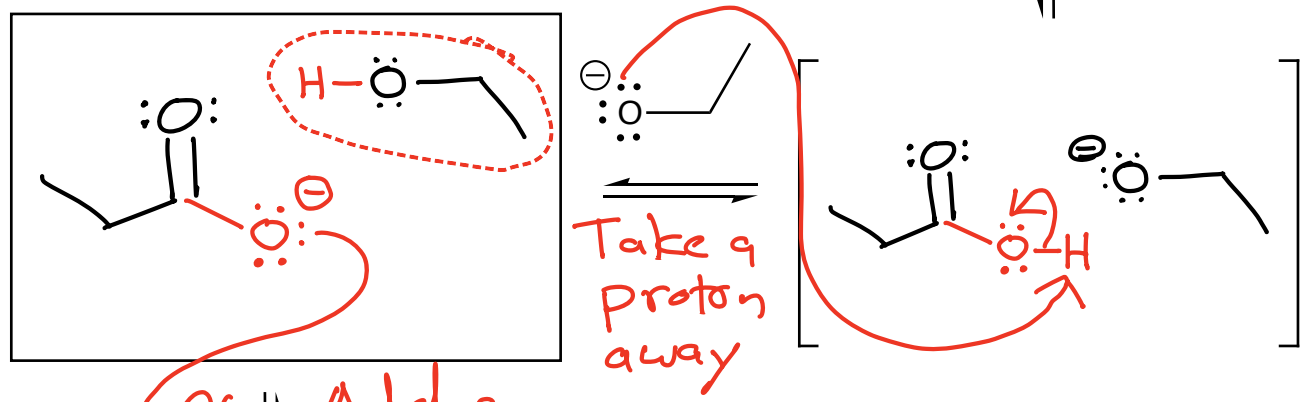
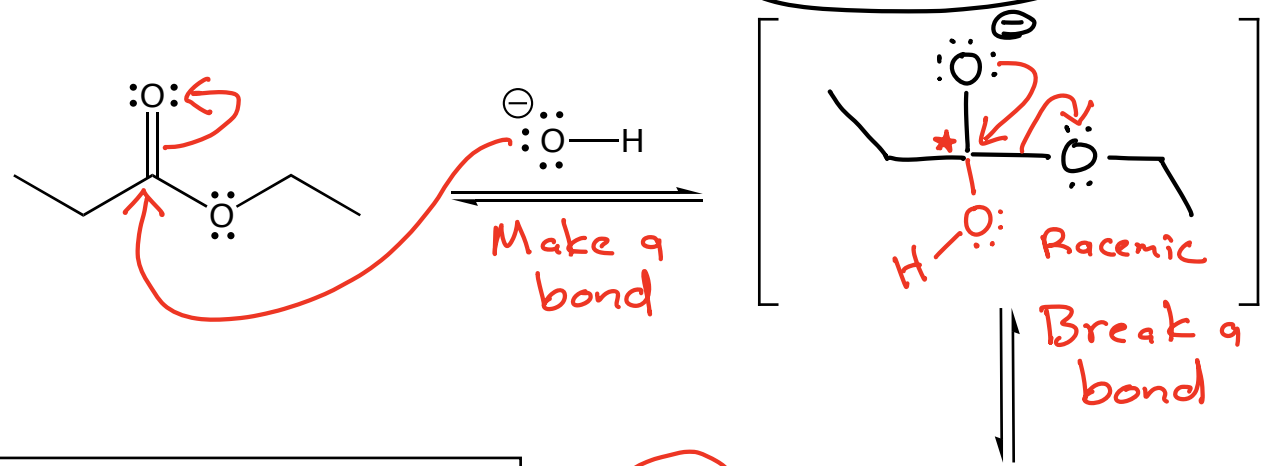
KRE \rightarrow OH group on
 an α (alpha) carbon
 of a carboxylic acid
 \rightarrow New C-C bond
 adding 1 carbon atom

α -hydroxy acid





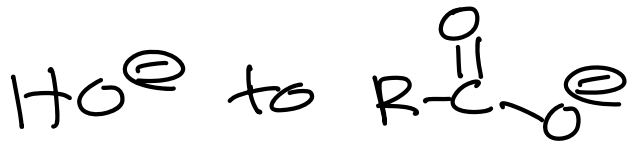
Base-Promoted Ester Hydrolysis - Saponification



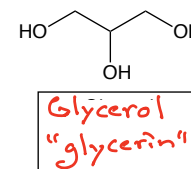
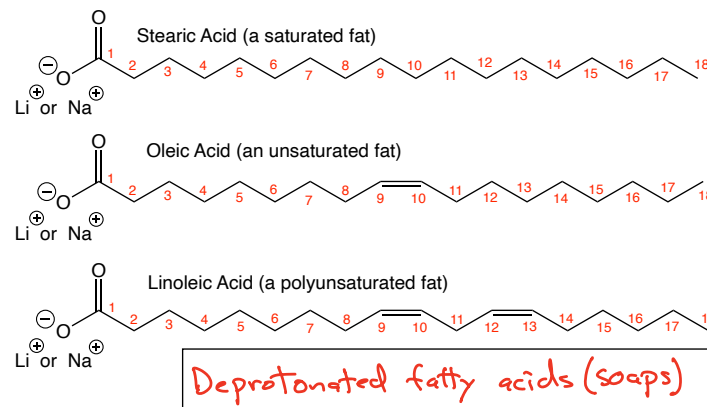
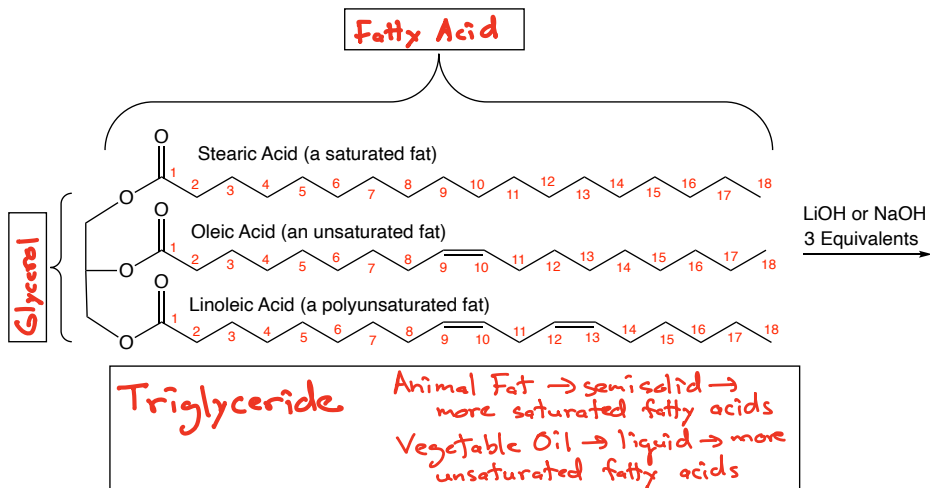
NOT catalytic
in base

Mechanism B

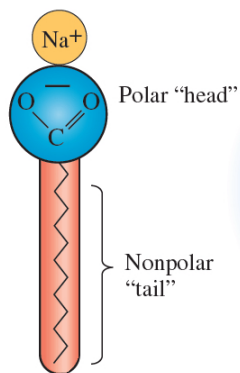
Driving force \rightarrow converts



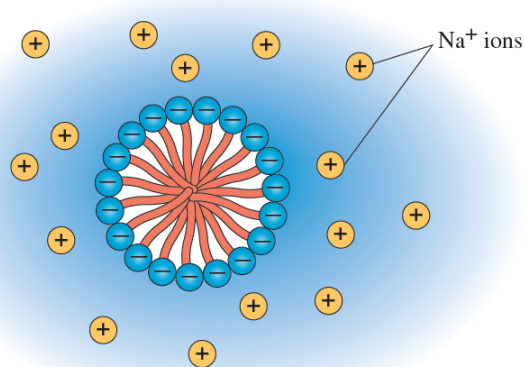
More stable anion
 \rightarrow favored \rightarrow MOTIVE



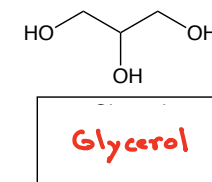
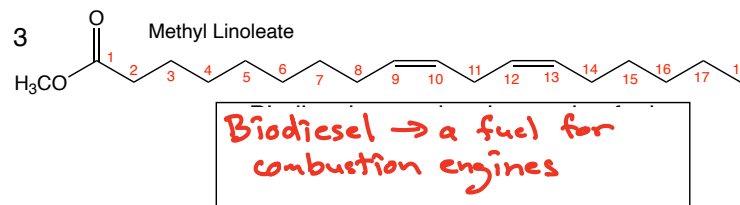
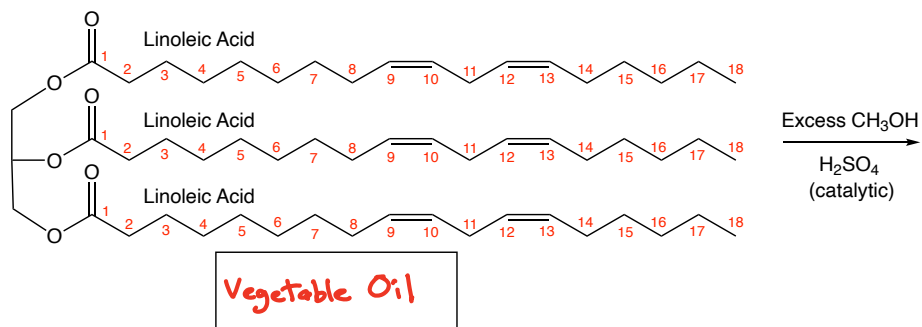
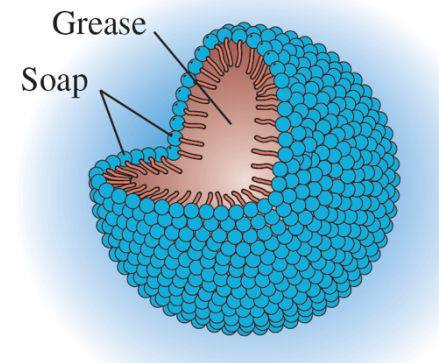
(a) A soap

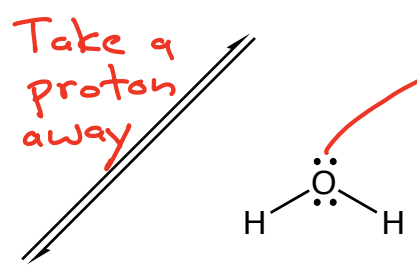
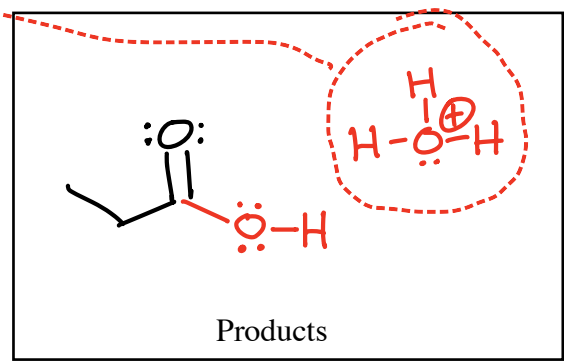
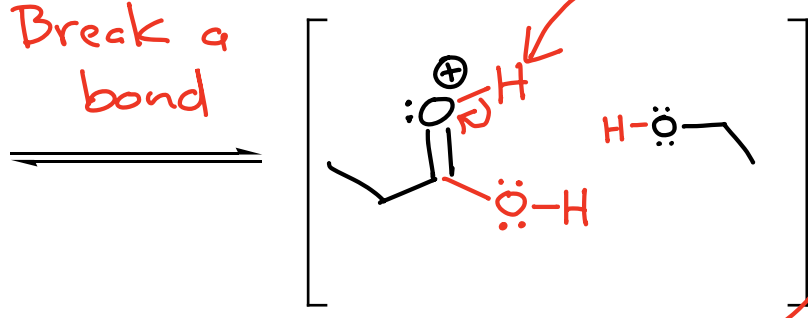
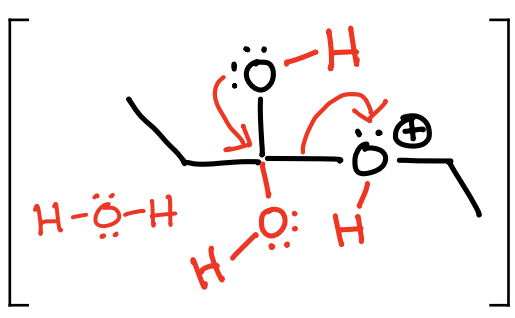
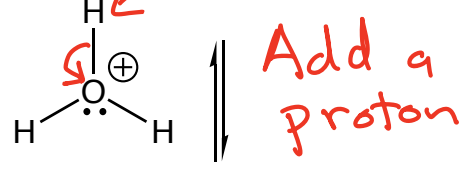
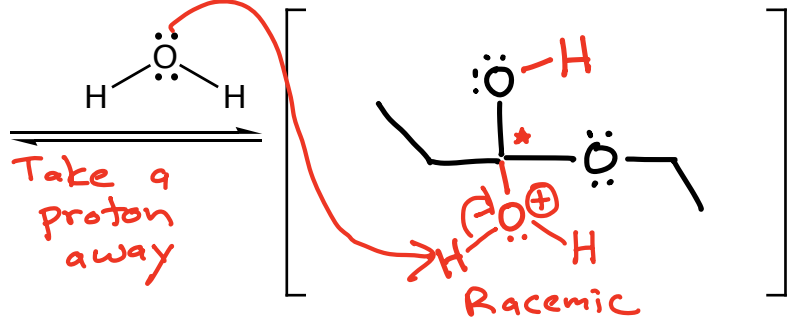
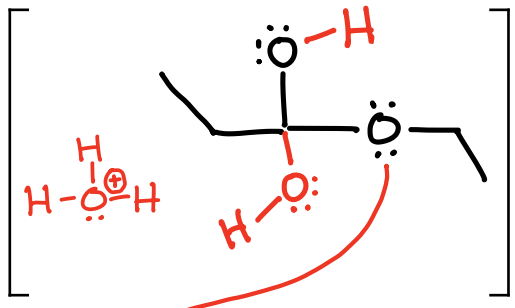
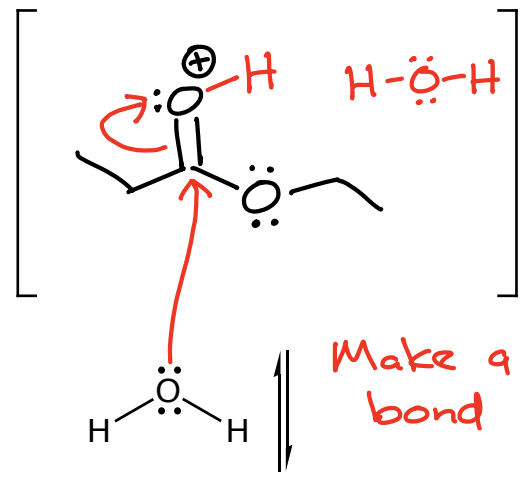
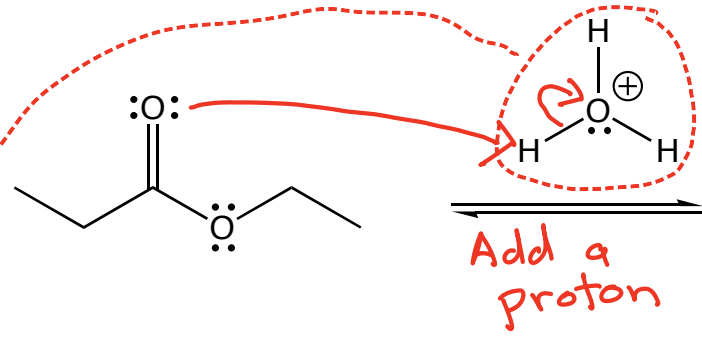
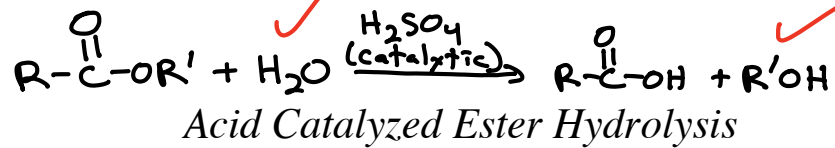


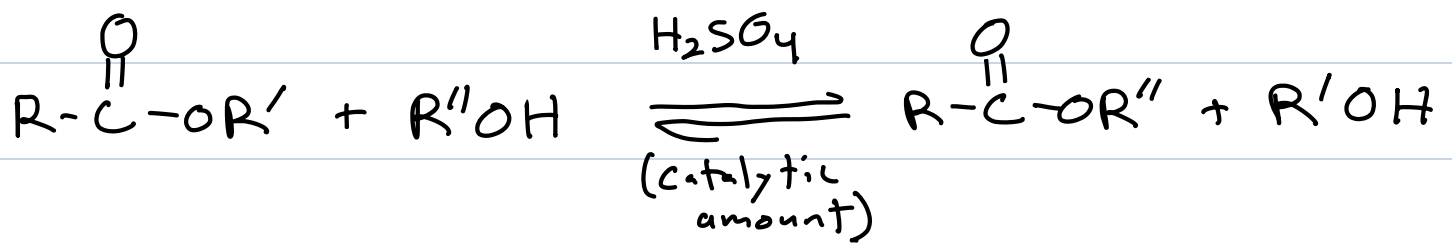
(b) Cross section of a soap micelle in water



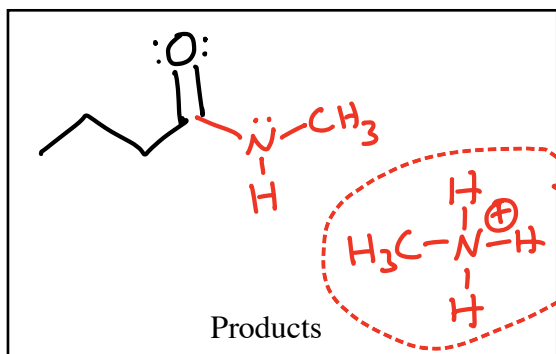
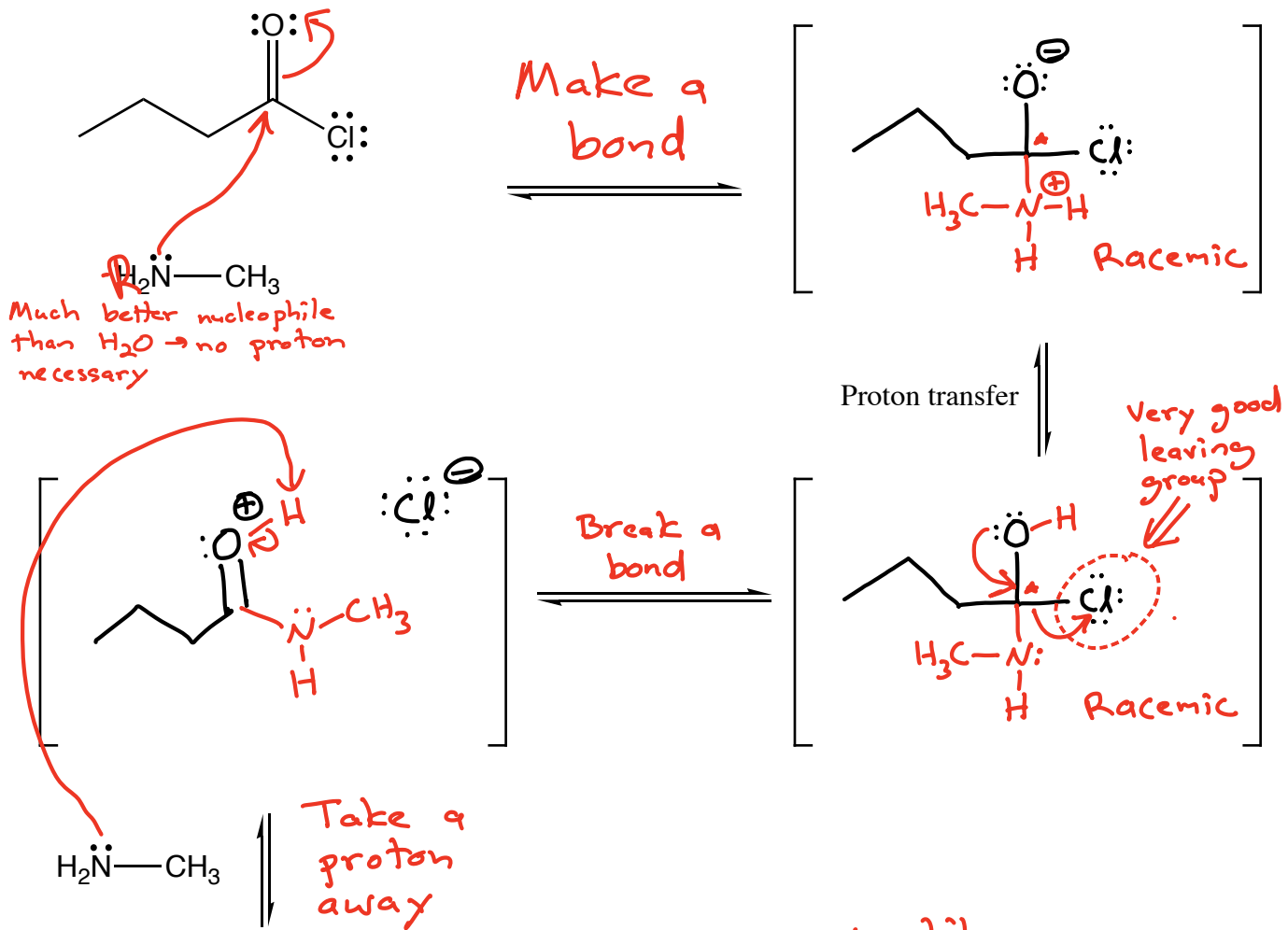
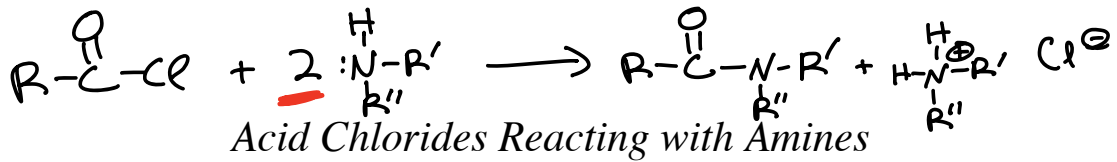
Soap micelle with "dissolved" grease







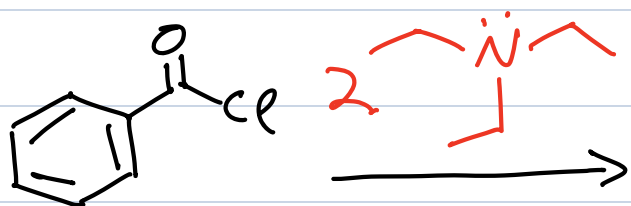
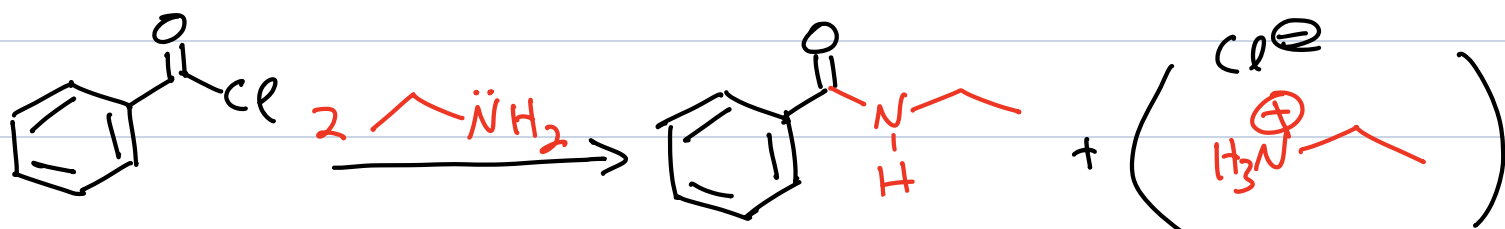
Transesterification → the chemistry behind biodiesel production
(see handout)



NOT a nucleophile so we need 2 equivalents of amine for this reaction

Remember — you need two equivalents of the amine!

Examples



No Reaction \rightarrow
the amine must
have at least one
H atom so that a
stable amide can be
made.