Chapter 20
Carboxylic Acids

Chapter Objectives

- Describe the physical and spectroscopic properties of carboxylic acids based on their structure and bonding.
- Explain why carboxylic acids are more acidic than other organic functional groups
- Describe the major reactions of carboxylic acids
- Predict the products of reactions of carboxylic acids
- Draw curved arrow mechanisms for the core reactions of carboxylic acids
- Design multistep syntheses that start from carboxylic acids

Roadmap

- **20.1-20.5:** Properties of carboxylic acids (supplemental videos)
- **20.6**: Synthesis of carboxylic acids
- **20.7-20.11**: Reactions of carboxylic acids

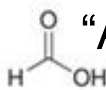
- Carboxylic acids combine the electrophilic chemistry of ketones with the leaving group ability of alcohols and bonus acidity

- Skip: 20.9B, 20.11B

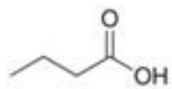
20.1: Nomenclature of carboxylic acids

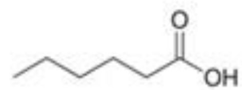
- See Panopto video

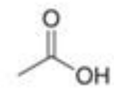
Formic = ant, formic acid makes fire ant bites burn

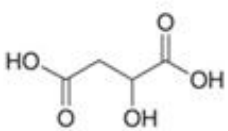


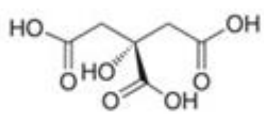
“Ant-acid”









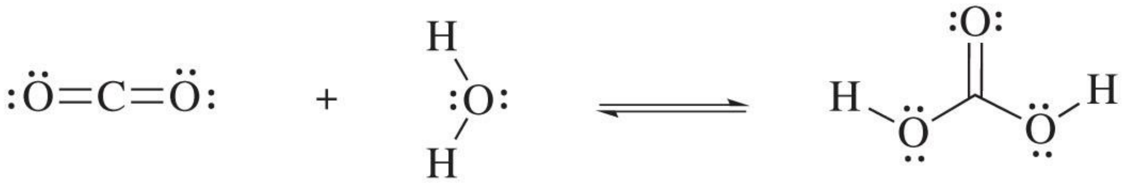


Malic acid (Latin for apples), found in apples

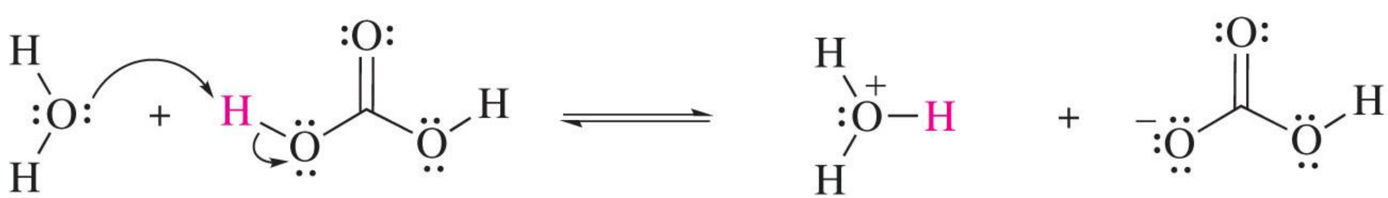
Citric acid, found in citrus fruits

Carbonic acid

- In equilibrium with CO_2, water



- Carbonic acid roughly as acidic as most carboxylic acids
  - pKa = 3.6 based on "pure" liquid carbonic acid
  - pKa = 6.4 taking into account how little CO_2 actually turns into carbonic acid



Blood buffers

- For humans, normal blood is between pH 7.35-7.45
- pH maintained with bicarbonate/carbonic acid/CO_2 buffer
- pH controlled by breathing and kidneys
- Holding breath → higher [CO_2] → more acidic blood

20.5: Fatty Acids and Soaps

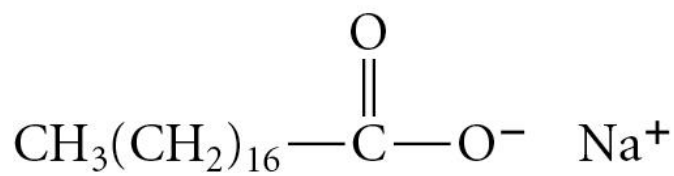
- Fatty acid – long chain carboxylic acid, nonpolar

$CH_3(CH_2)_{14}CO_2H$ or $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CO_2H$

or 

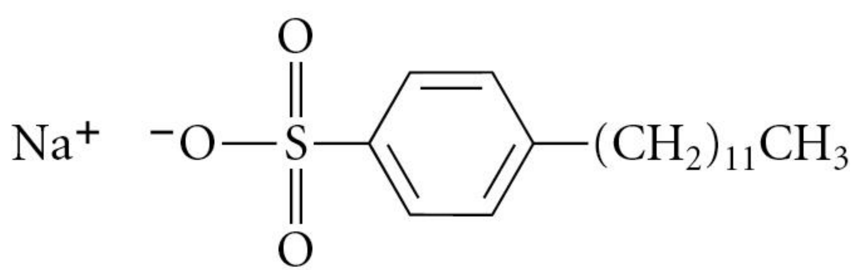
palmitic acid
(from palm oil)

- Soap – alkali salt of fatty acid



sodium stearate
(a soap)

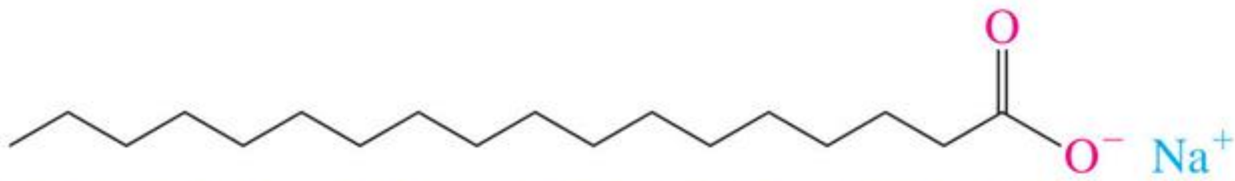
- Detergent – similar to soap, but doesn’t have to be a carboxylate

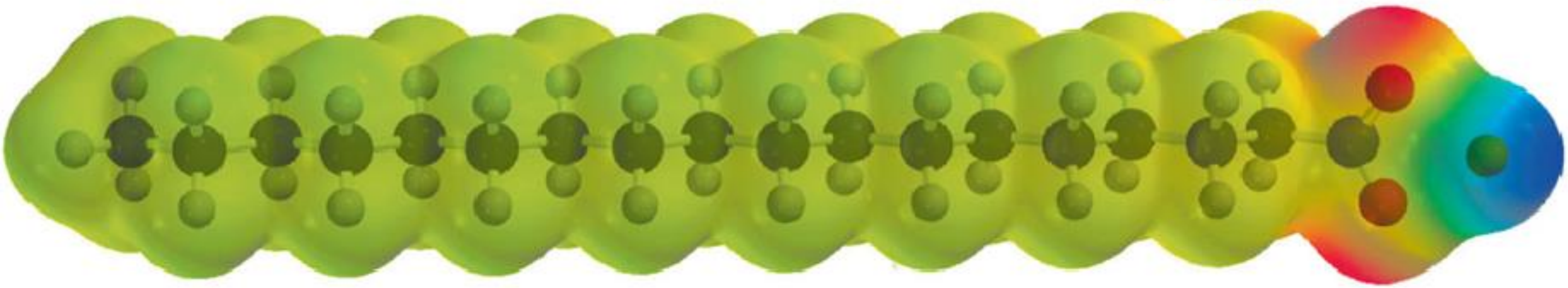


sodium 4-dodecyl-1-benzenesulfonate
(a synthetic detergent)

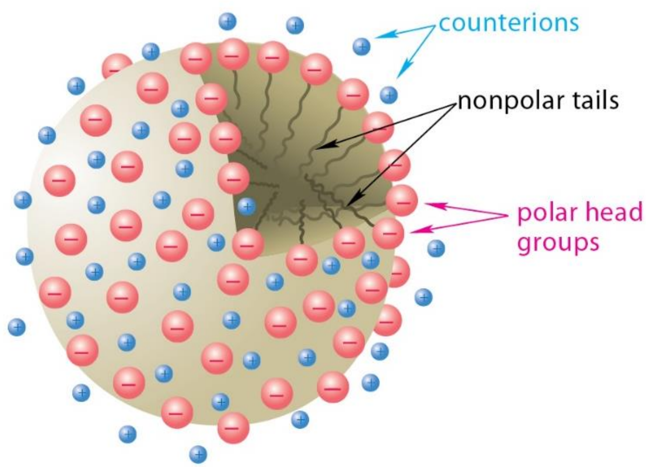
Micelles

- Large carboxylic acids have polar and nonpolar portions





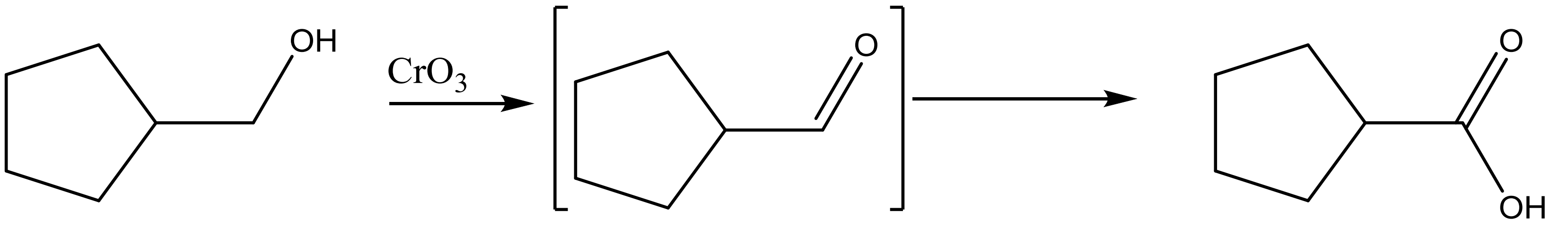
- Bubbles form to "protect" the nonpolar (hydrophobic) portions from the polar water



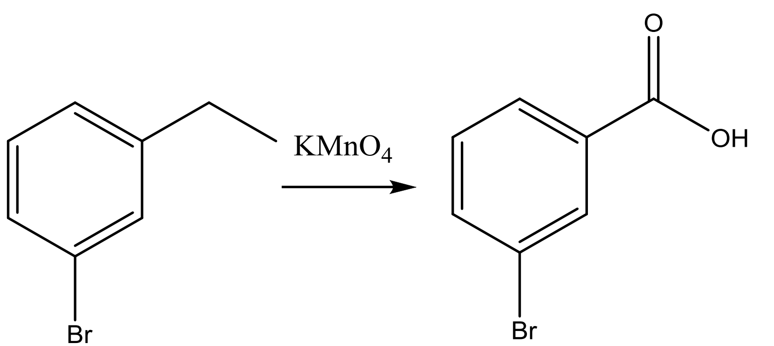
- Similar chemistry in cell membrane lipid bilayers

20.6: Synthesis of carboxylic acids

- Oxidation of 1^{o} alcohols (**10.7**) and aldehydes (**19.14**)

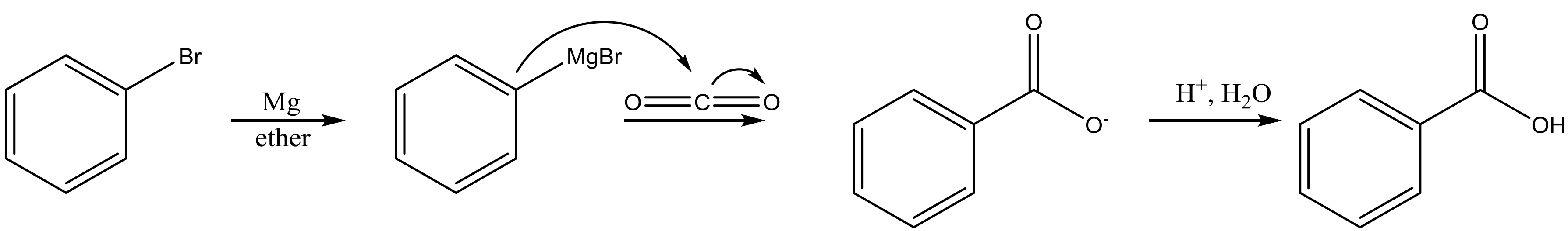


- Oxidation of alkyl benzenes (**17.5**)



R-MgX or R-Li with carbon dioxide

- Grignard + CO_2 → Carboxylic acid (no side chain leaving group)
- Initially makes carboxylate, acidic workup gives neutral carboxylic acid

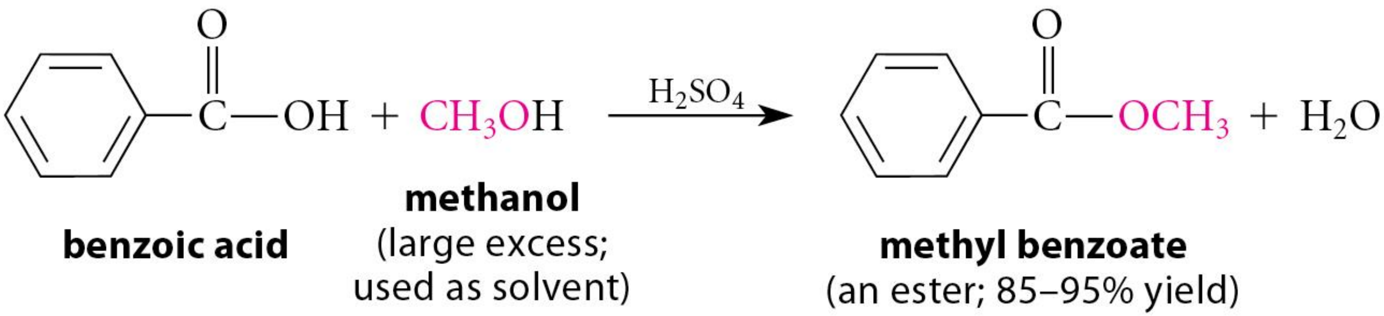


- Chem 241

20.7-8: Reactions of carboxylic acids

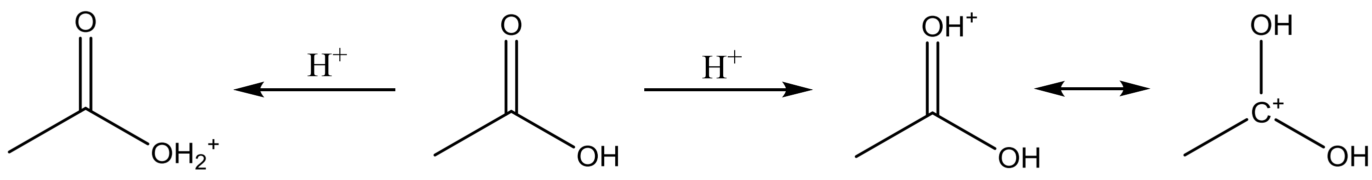
- Nucleophile attacks C=O carbon
- Electrophile attacked by O- ion
- Decarboxylation

Fischer Ester Synthesis



- Reaction is reversible, equilibrium favors both ester and carboxylic acid roughly evenly

Carboxylic acids as **bases**

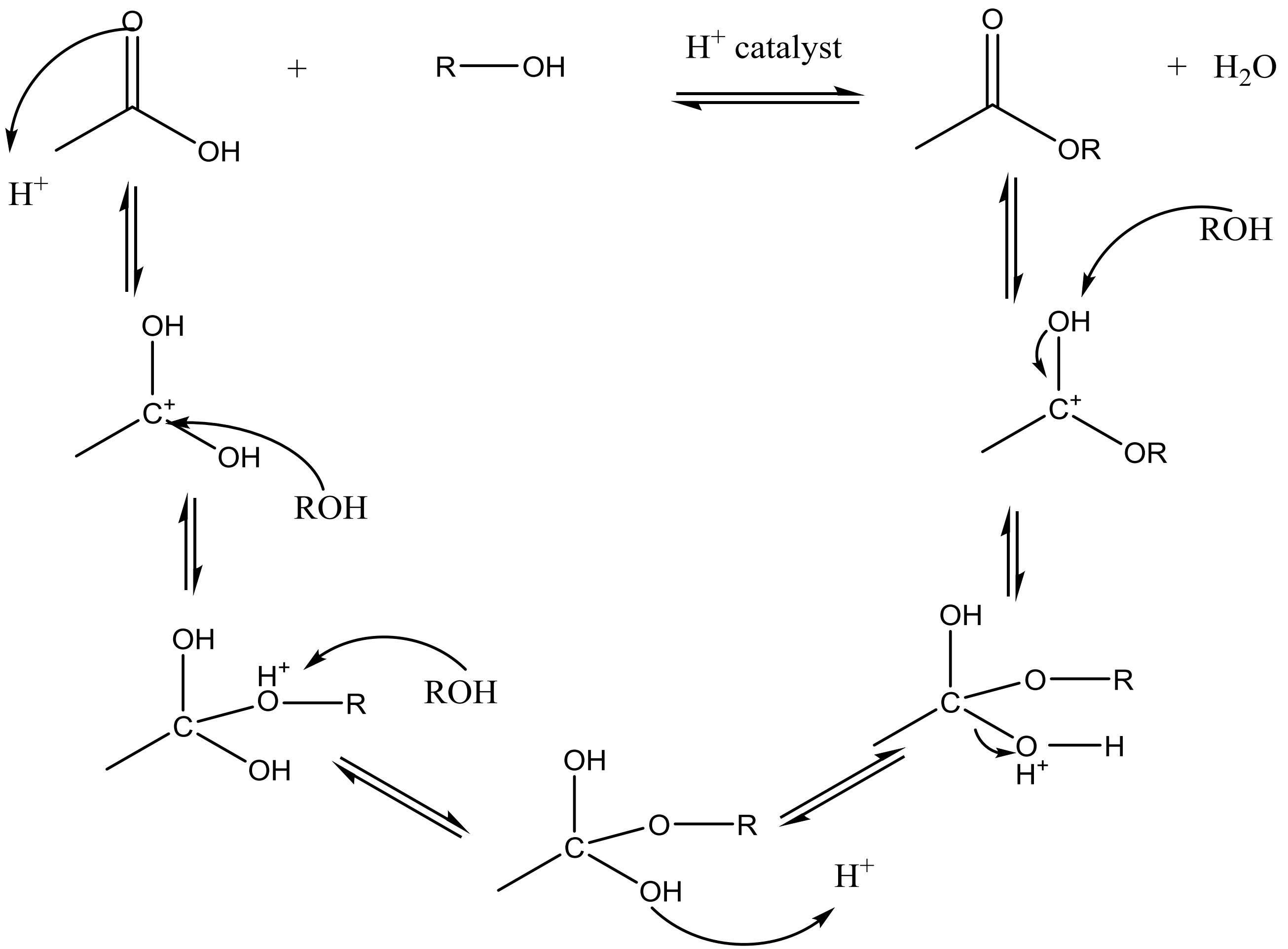


No resonance
Less stable

Resonance
More stable

- Carboxylic acids are very weak bases
- Requires very strong acid – sulfuric acid
- Same logic as protonating ketones/aldehydes to activate them (chapter **17**)

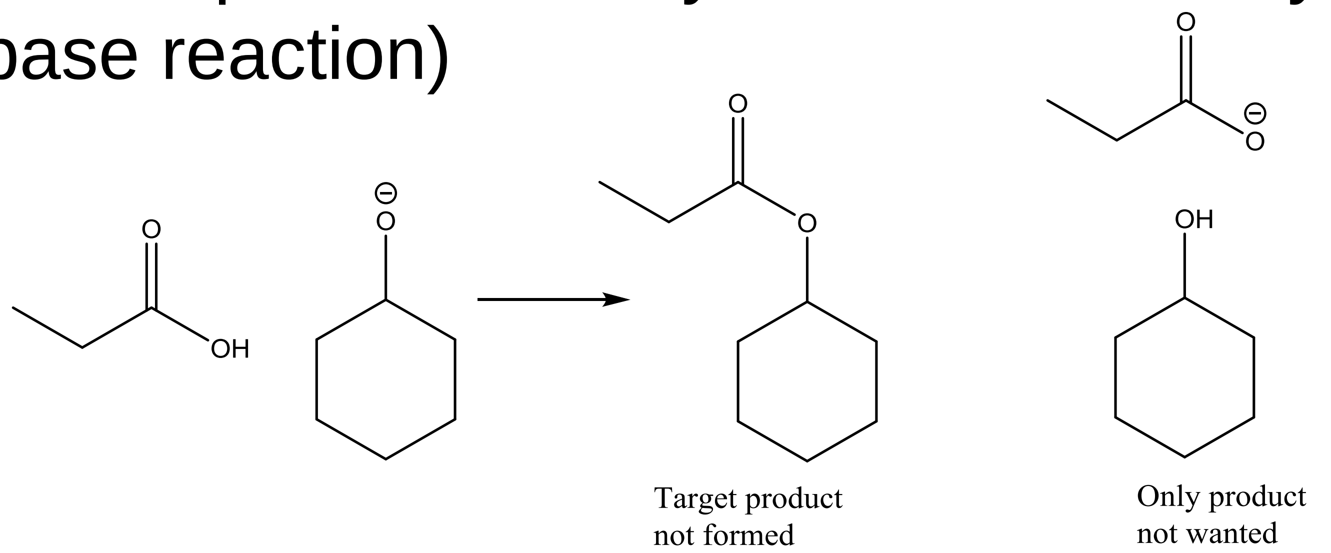
Mechanism for esterification (both directions)



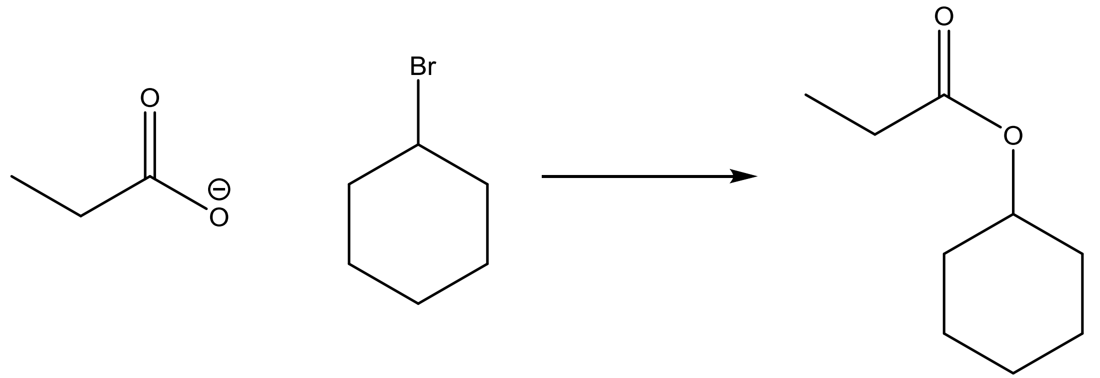
Like a Hemiacetal!

Esterification under basic conditions

- Basic nucleophile + carboxylic acid → carboxylate (acid-base reaction)



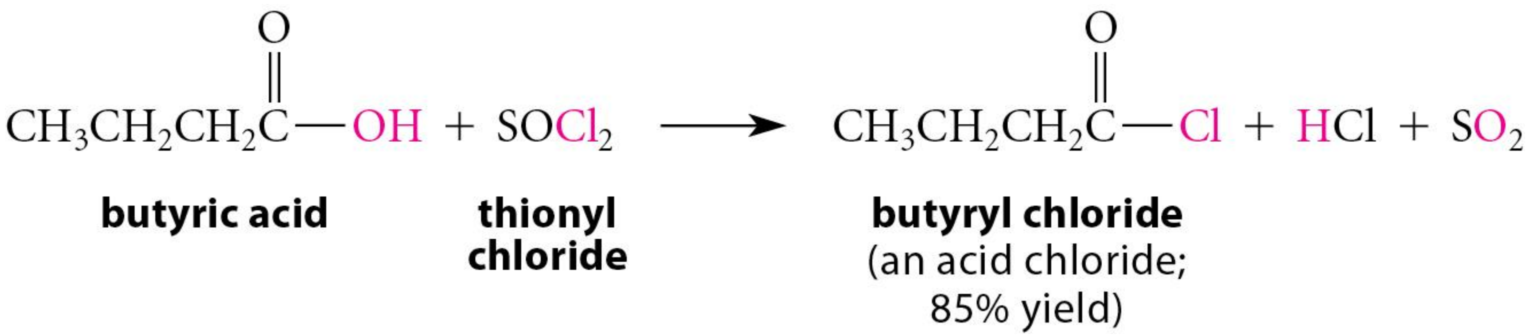
- Instead, make carboxylic acid the **nucleophile**



- Weak base, E2 doesn't compete

20.9: Synthesis of Acid Chlorides

- Carboxylic acid + $SOCl_2$ → Acid chloride

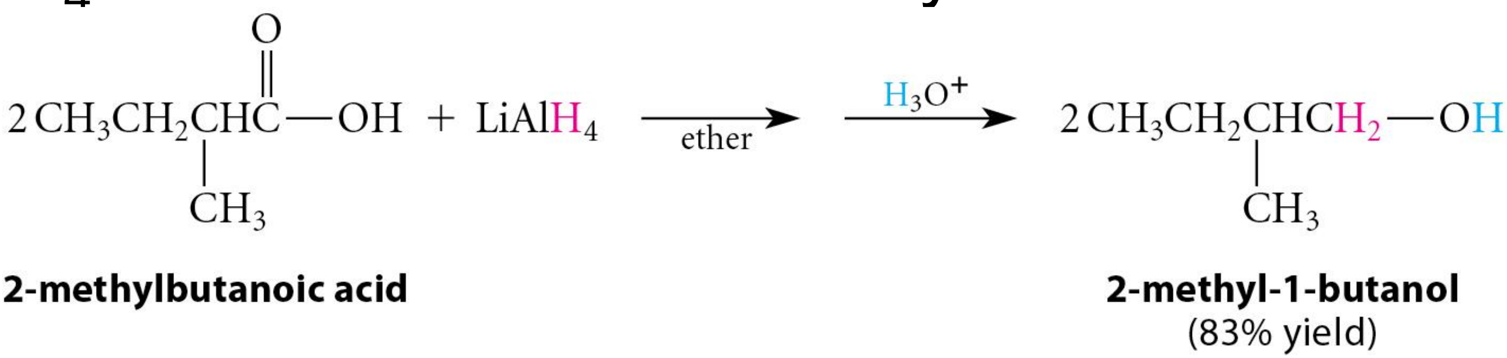


- Compare alcohol + $SOCl_2$ → alkyl chloride (**10.4D**)

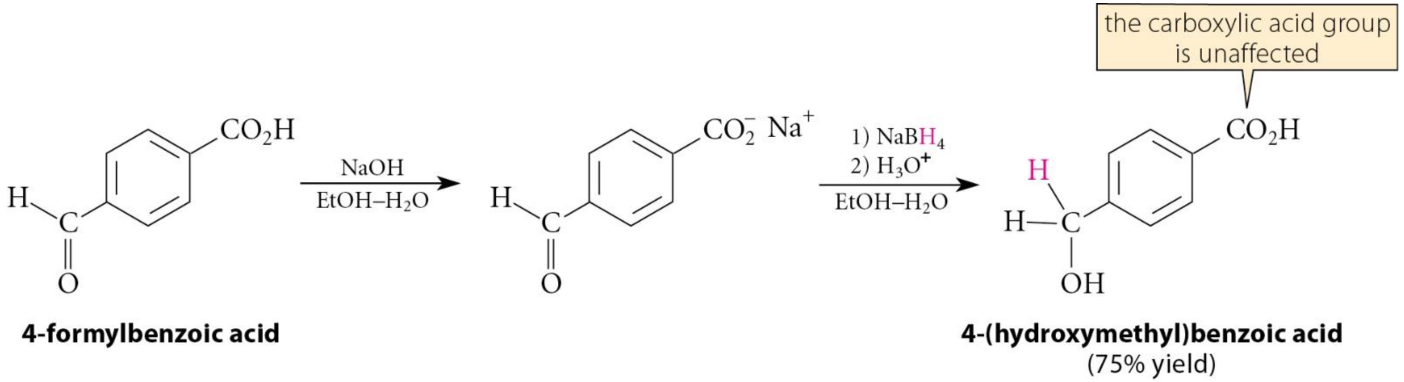
- Best way to make anhydrides is from acid chlorides (**21.8**) – skip **20.9B**

20.10: Reduction of carboxylic acids

- $LiAlH_4$ “double” reduces carboxylic acids to alcohols

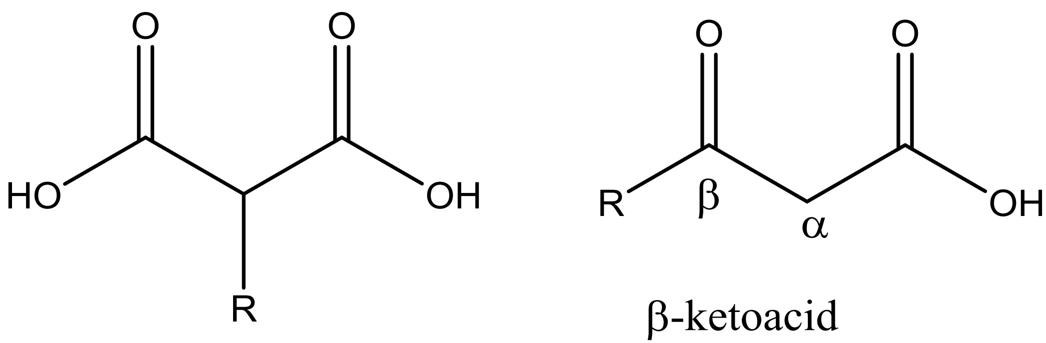


- An aldehyde is a key mechanistic intermediate
- $NaBH_4$ is not reactive enough



20.11 Decarboxylation of malonic acids and β-ketoacids

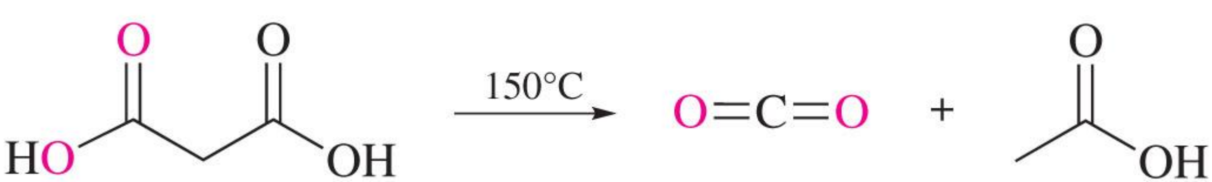
- Malonic acids and β-ketoacids show the normal reactions of carboxylic acids



Substituted malonic acid

β-ketoacid

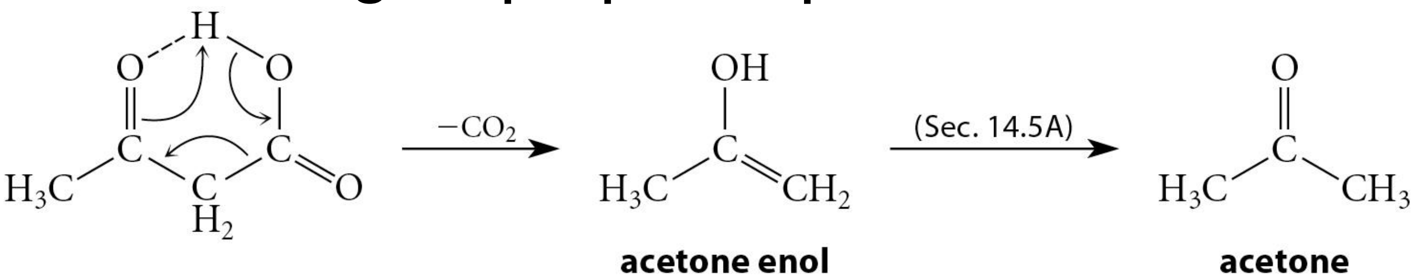
- In addition, they can also decarboxylate (lose CO_2)



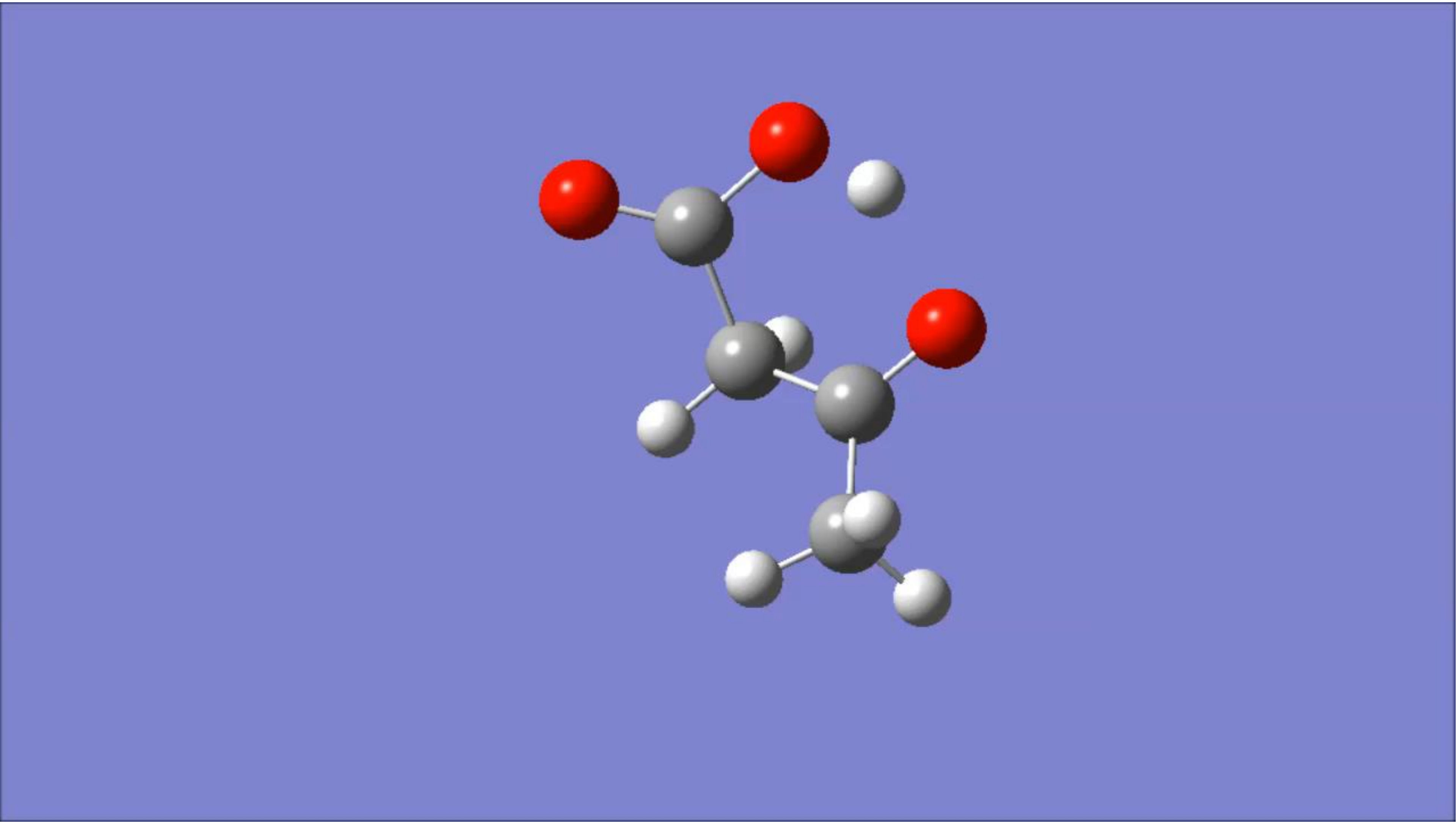
- We will return to these reactions in Chapter 22

Mechanism of decarboxylation

- Concerted mechanism
- Both C=O groups participate

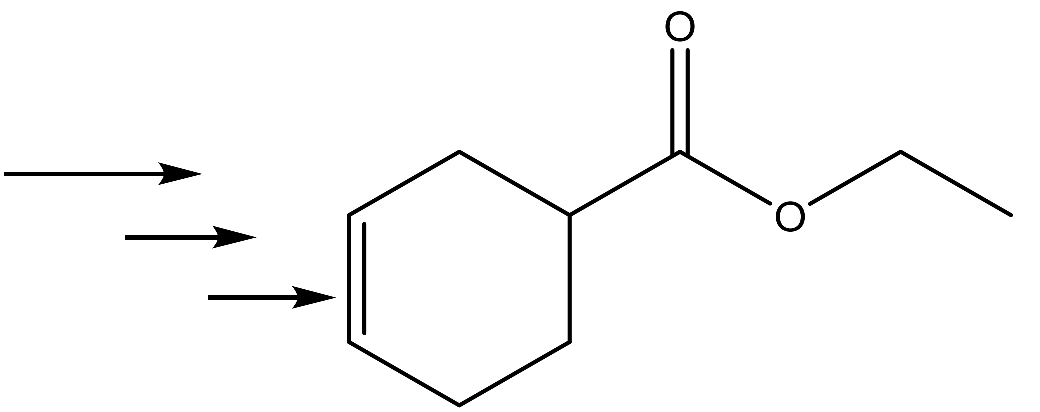


- We saw enols during alkyne hydration (**14.5**)



Synthesis question

Hydrocarbons, alkyl halides
or alcohols with 4 or fewer C atoms



Summary of Chapter 20

- Carboxylic acids have 2 major reactions
  - Acidity
  - Acyl substitution (incl. reduction)
- We can understand acidity trends based on induction and resonance
- We can understand acyl substitution based on ketone chemistry

- Acyl substitution will be important to other carboxylic acid derivatives (Chapter 21)

What questions do you have about Chapter 20?

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