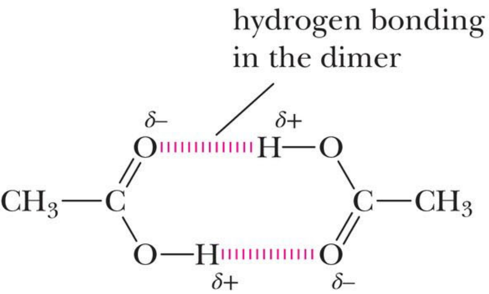
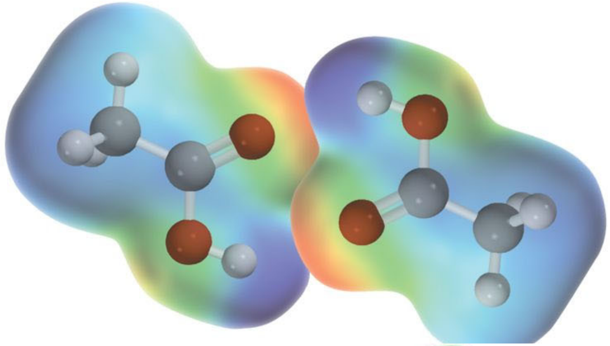
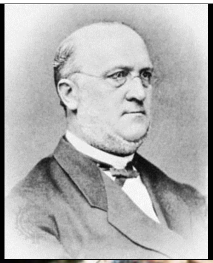
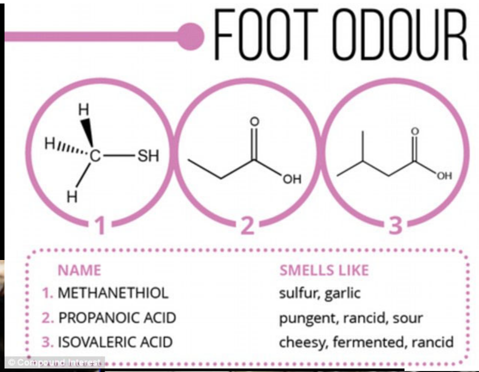
Chapter 13

Carboxylic Acids





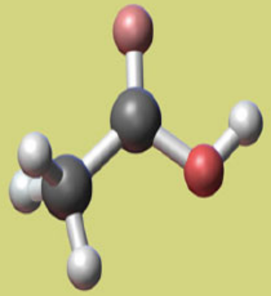




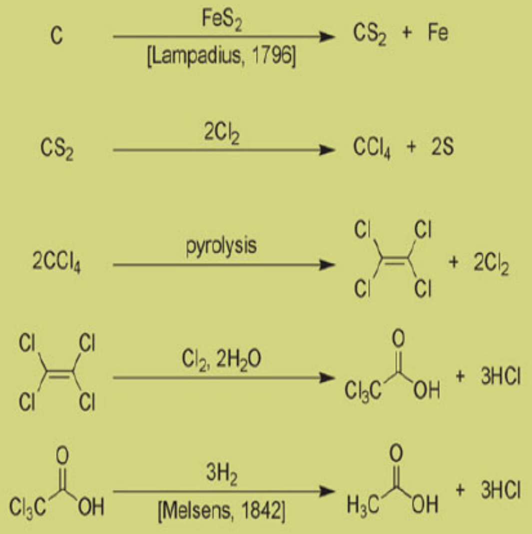
NAME	SMELLS LIKE
1. METHANETHIOL	sulfur, garlic
2. PROPANOIC ACID	pungent, rancid, sour
3. ISOVALERIC ACID	cheesy, fermented, rancid

Kolbe's synthesis of acetic acid

First Artificial Carbon-Carbon Bond Formation in 1845



Ball and stick model of the molecule of acetic acid



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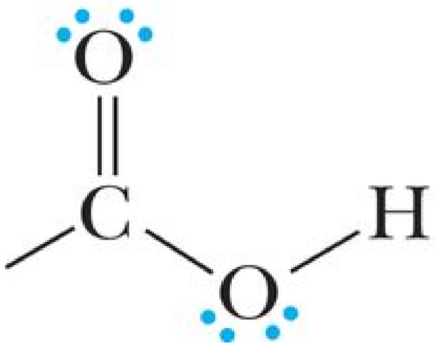
Structure

- The functional group of a carboxylic acid is a carboxyl group.

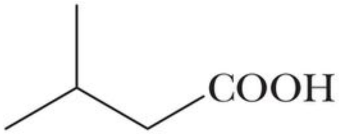


$-\mathrm{COOH}$ $-\mathrm{CO_2H}$

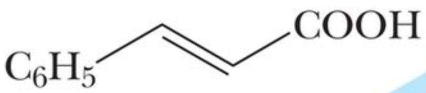
  - The general formula of an aliphatic carboxylic acid is RCOOH.
  - That of an aromatic carboxylic acid is ArCOOH.

Nomenclature

- IUPAC names: drop the **-e** from the parent alkane and add the suffix **-oic acid**.
  - If the compound contains a carbon-carbon double bond, change the infix **-an-** to **-en-**.



3-Methylbutanoic acid
(Isovaleric acid)

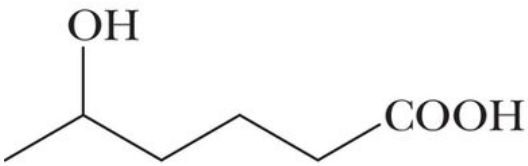


trans-3-Phenylpropenoic acid
(Cinnamic acid)

it is not necessary to indicate that the alkene occurs at position 2 because there is no other position where it can occur in this molecule

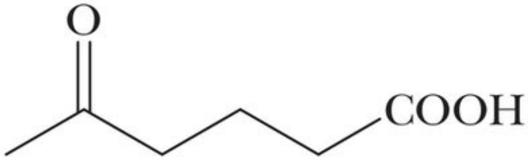
Nomenclature

- The carboxyl group takes precedence over most other functional groups.



5-Hydroxyhexanoic acid

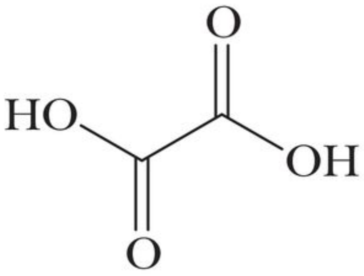
4-Aminobutanoic acid



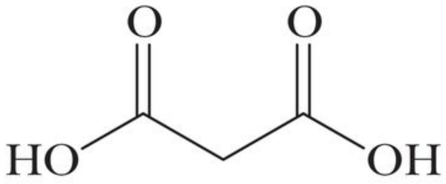
5-Oxohexanoic acid

Nomenclature

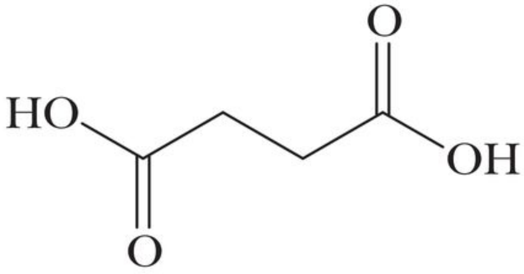
- Dicarboxylic acids: add **-dioic acid** to the name of the parent alkane containing both carboxyl groups.
- There is no need to use numbers to locate the carboxyl groups; they can only be on the ends of a chain.



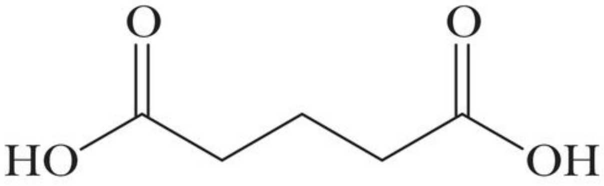
Ethanedioic acid
(Oxalic acid)



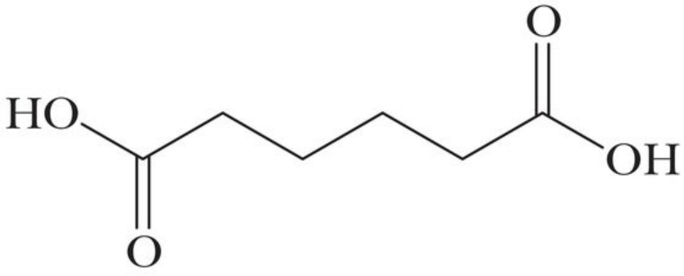
Propanedioic acid
(Malonic acid)



Butanedioic acid
(Succinic acid)



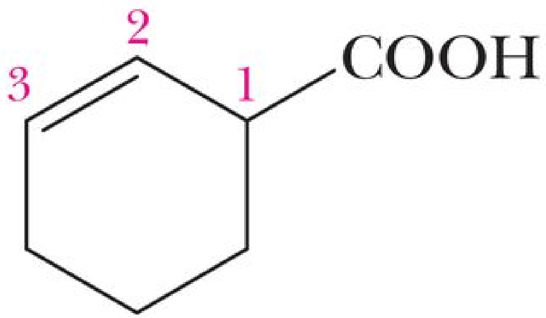
Pentanedioic acid
(Glutaric acid)



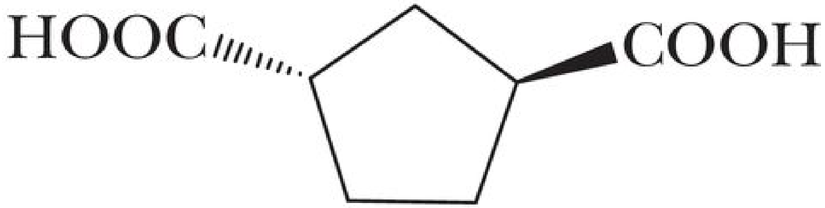
Hexanedioic acid
(Adipic acid)

Nomenclature

- If the carboxyl group is bonded to a ring, name the ring compound and add the suffix **-carboxylic acid**.



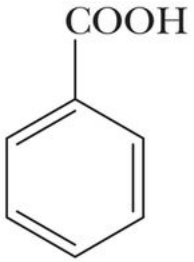
2-Cyclohexenecarboxylic acid



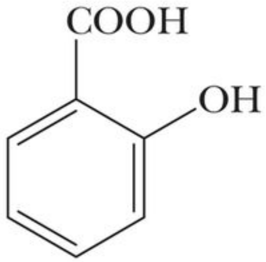
trans-1,3-Cyclopentane-dicarboxylic acid

Nomenclature

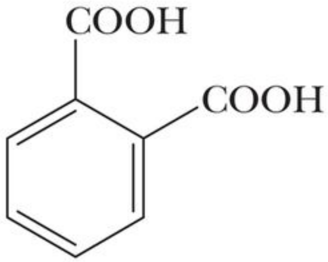
- Benzoic acid is the simplest aromatic carboxylic acid.
- Use numbers to show the location of substituents.



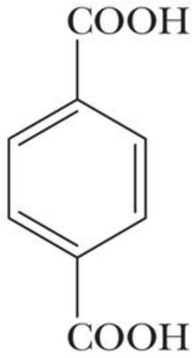
Benzoic acid



2-Hydroxybenzoic acid
(Salicylic acid)



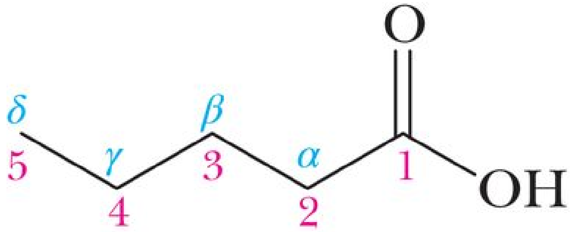
1,2-Benzenedicarboxylic acid
(Phthalic acid)

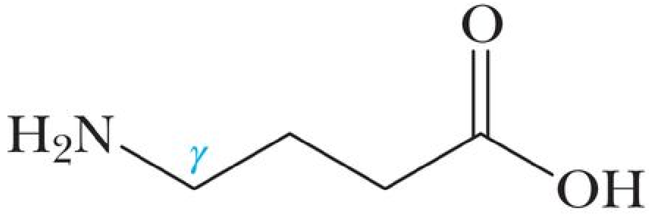


1,4-Benzenedicarboxylic acid
(Terephthalic acid)

Nomenclature

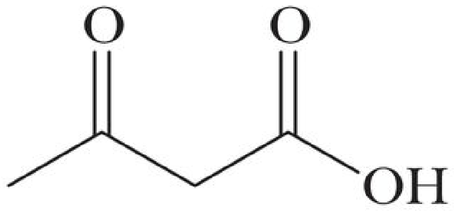
- When common names are used, the letters α, β, γ etc. are often used to locate substituents.



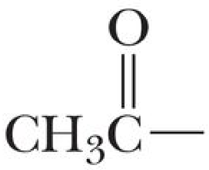


4-Aminobutanoic acid
(γ-Aminobutyric acid, GABA)

- In common nomenclature, keto indicates the presence of a ketone, and a CH_3CO— group is named an aceto group.



3-Oxobutanoic acid
(β-Ketobutyric acid;
Acetoacetic acid)



$CH_3\overset{O}{\overset{\|}{C}}—$

Acetyl group
(Aceto group)

Nomenclature

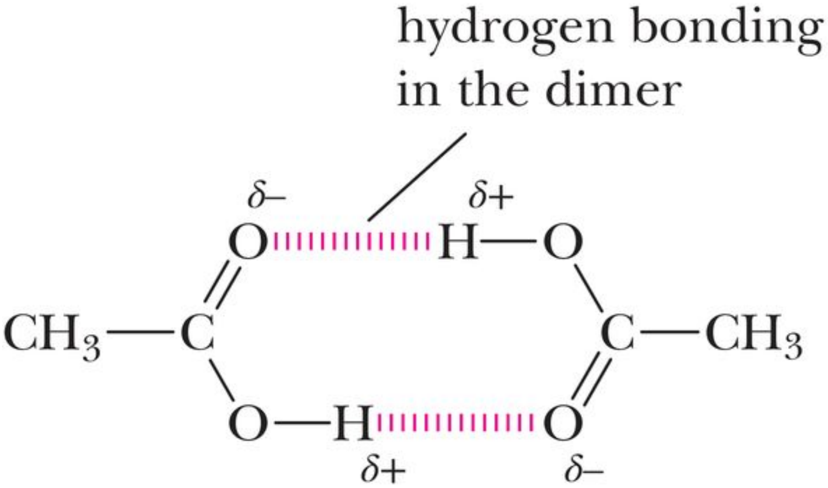
- **Problem**: In omega-3 fatty acids, the last carbon of the last double bond of a hydrocarbon chain ends three carbons from the methyl terminal of the chain. The last carbon of the chain is called the omega carbon, hence the designation omega-3. Eicosapentaenoic acid is a common polyunsaturated fatty acid found in cold water fatty fish and health food supplements.
- How many cis-trans isomers are possible for this polyunsaturated fatty acid?

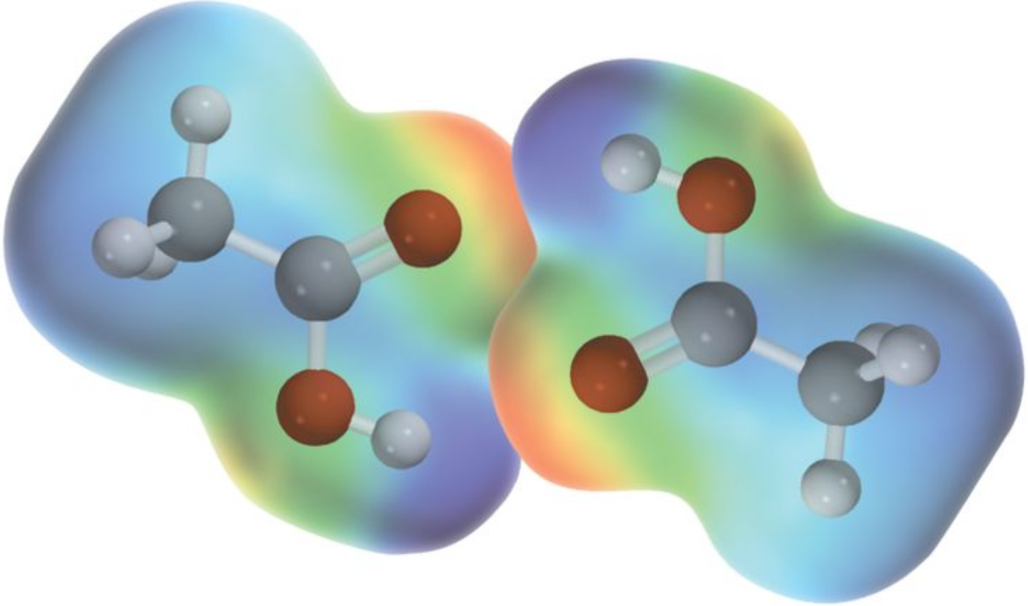
$CH_3(CH_2CH{=}CH)_5CH_2CH_2CH_2CO_2H$

Eicosapentaenoic acid
(an omega-3 fatty acid)

Physical Properties

- In the liquid and solid states, carboxylic acids are associated by hydrogen bonding into dimeric structures.





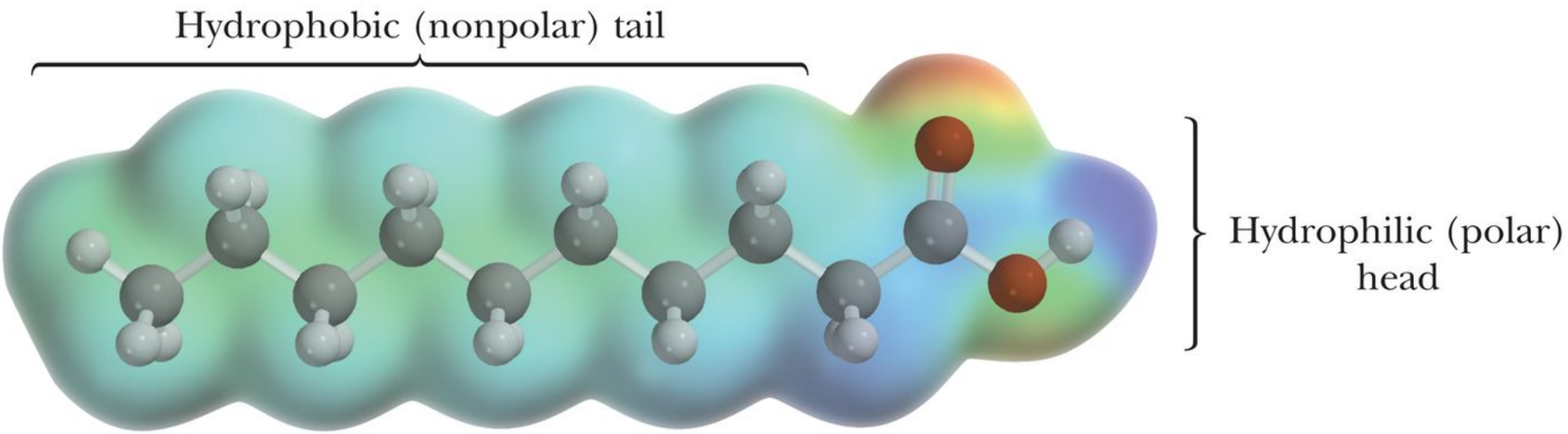
Physical Properties

- Carboxylic acids have significantly higher boiling points than other types of organic compounds with comparable molecular weight.
  - They are polar compounds and form very strong *intermolecular* hydrogen bonds.

- Carboxylic acids are more soluble in water than are alcohols, ethers, aldehydes, and ketones with comparable molecular weight.
  - They form *hydrogen bonds* with water molecules through their C=O and OH groups.

Physical Properties

- Water solubility decreases as the relative size of the hydrophobic portion of the molecule increases.



Decanoic acid
(0.2 g/100 mL H_2O)

Acidity

- Carboxylic acids are weak acids.
  - Values of pK_a for most aliphatic and aromatic carboxylic acids fall within the range 4 to 5.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.74 \times 10^{-5}$$

$$pK_a = 4.76$$

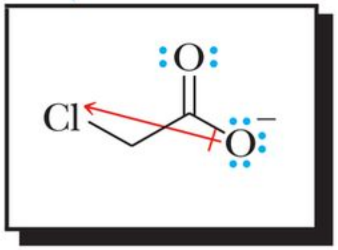
  - The greater acidity of carboxylic acids relative to alcohols, both of which contain an OH group, is due to resonance stabilization of the carboxylate anion.

Acidity

- *Electron-withdrawing substituents* near the carboxyl group increase acidity through their inductive effect.

Formula:	CH_3COOH	$ClCH_2COOH$	$Cl_2CHCOOH$	Cl_3CCOOH
Name:	Acetic acid	Chloroacetic acid	Dichloroacetic acid	Trichloroacetic acid
pK_a:	4.76	2.86	1.48	0.70

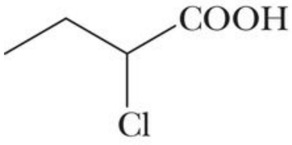
Increasing acid strength



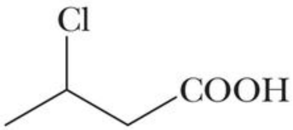
the inductive effect of an electronegative atom delocalizes the negative charge and stabilizes the carboxylate ion

Acidity

- The acid-strengthening effect of a halogen substituent falls off rapidly with *increasing distance* from the carboxyl group.



2-Chlorobutanoic acid (pK_a 2.83)



3-Chlorobutanoic acid (pK_a 3.98)

4-Chlorobutanoic acid (pK_a 4.52)

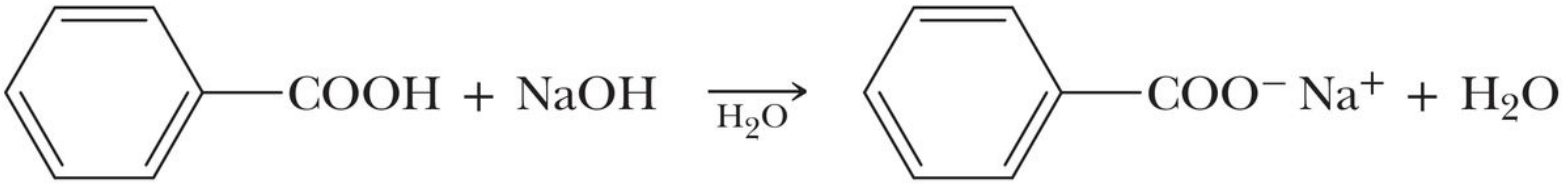
Butanoic acid (pK_a 4.82)

the further the halogen is from the carboxyl group, the lower is its effect on the acidity

Decreasing acid strength →

Reaction with Bases

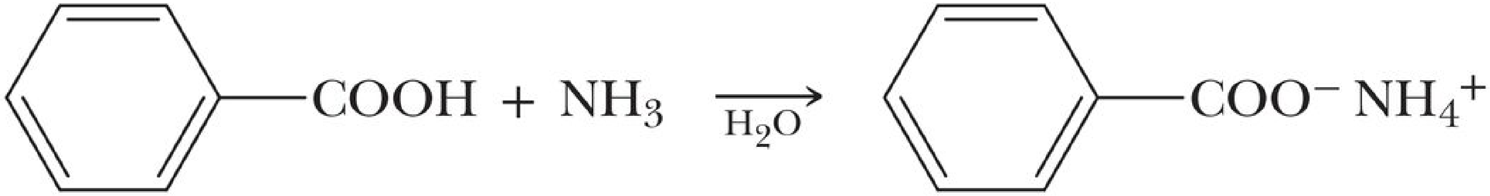
- Carboxylic acids, whether soluble or insoluble in water, react with NaOH, KOH, and other strong bases to give water-soluble salts.



Benzoic acid
(slightly soluble in water)

Sodium benzoate
(60 g/100 mL water)

- They also form water-soluble salts with ammonia and amines.



Benzoic acid
(slightly soluble in water)

Ammonium benzoate
(20 g/100 mL water)

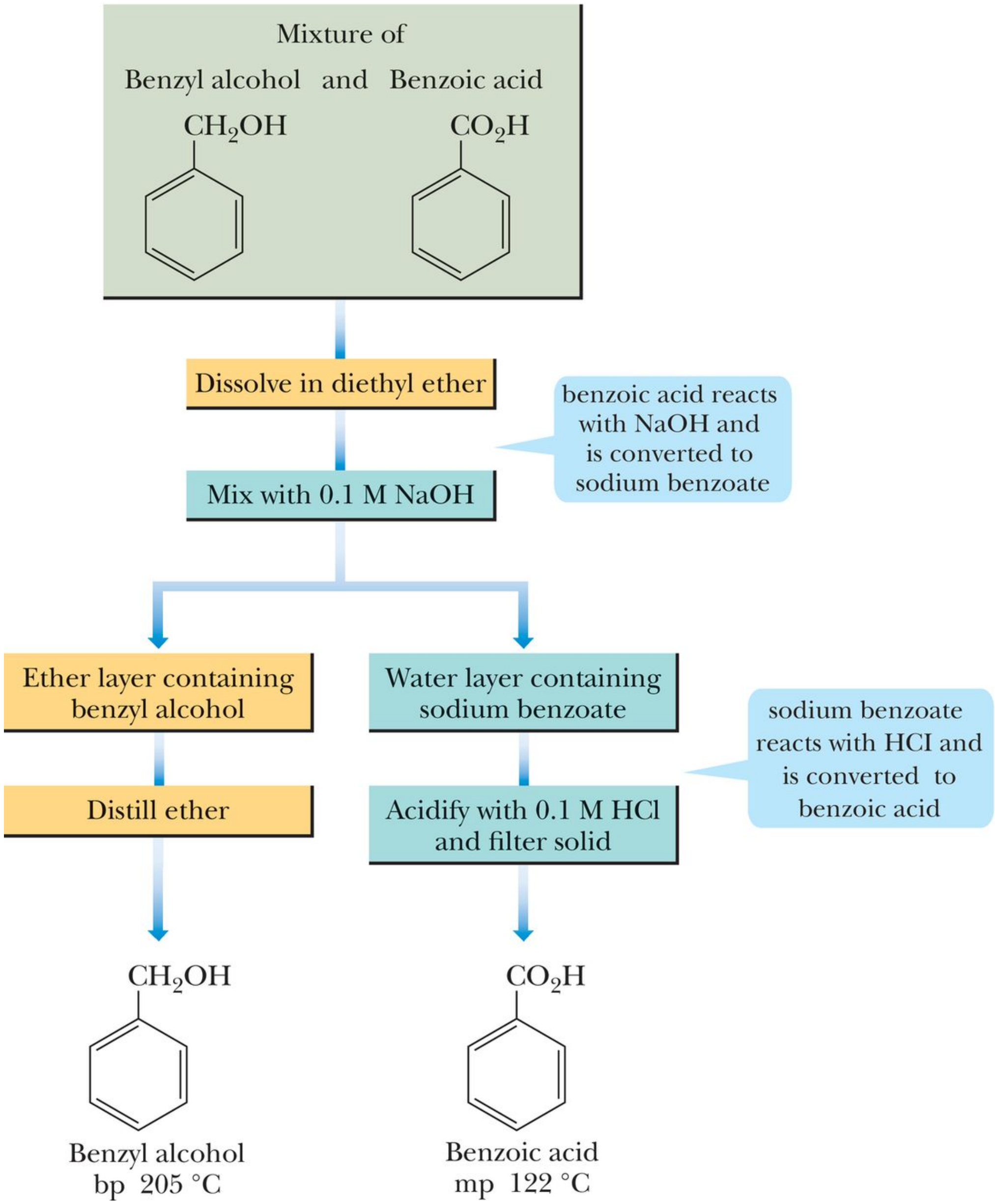
Reaction with Bases

- Carboxylic acids react with sodium bicarbonate and sodium carbonate to form water-soluble salts and carbonic acid.
  - Carbonic acid, in turn, breaks down to carbon dioxide and water.

$$\begin{array}{c}
CH_3COOH + Na^+HCO_3^- \xrightarrow{H_2O} CH_3COO^-Na^+ + H_2CO_3 \\
H_2CO_3 \longrightarrow CO_2 + H_2O \\
\hline
CH_3COOH + Na^+HCO_3^- \longrightarrow CH_3COO^-Na^+ + CO_2 + H_2O
\end{array}$$

Reaction with Bases

- **Figure 13.1** Flowchart for the separation of benzoic acid from benzyl alcohol.



Mixture of

Benzyl alcohol and Benzoic acid

CH_2OH CO_2H

Dissolve in diethyl ether

Mix with 0.1 M NaOH

benzoic acid reacts with NaOH and is converted to sodium benzoate

Ether layer containing benzyl alcohol

Distill ether

CH_2OH

Benzyl alcohol
bp 205 °C

Water layer containing sodium benzoate

Acidify with 0.1 M HCl and filter solid

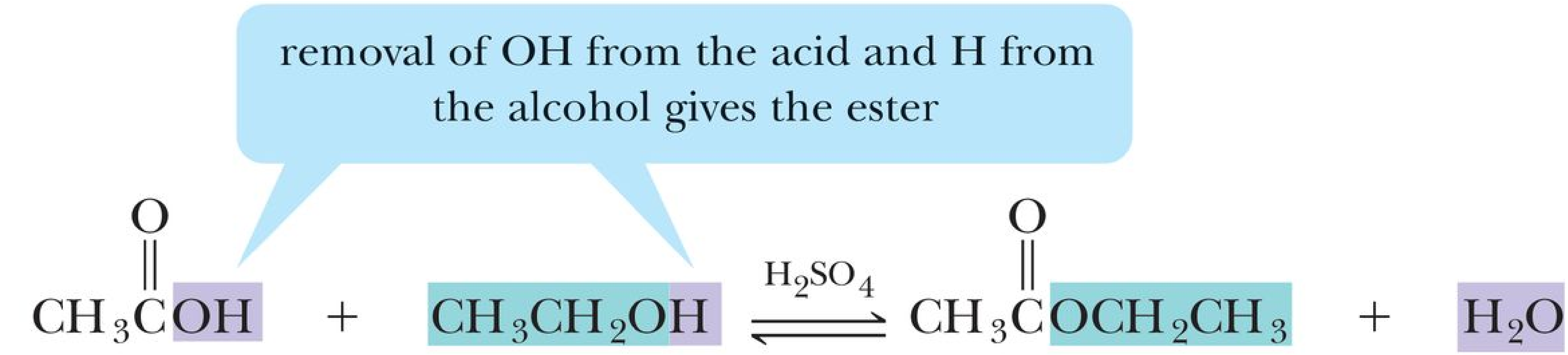
sodium benzoate reacts with HCl and is converted to benzoic acid

CO_2H

Benzoic acid
mp 122 °C

Fischer Esterification

- Esters can be prepared by treating a carboxylic acid with an alcohol in the presence of an acid catalyst, commonly H_2SO_4 or gaseous HCl.



removal of OH from the acid and H from the alcohol gives the ester

$$CH_3\overset{O}{\overset{\|}{C}}OH + CH_3CH_2OH \xrightleftharpoons{H_2SO_4} CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3 + H_2O$$

Ethanoic acid (Acetic acid)

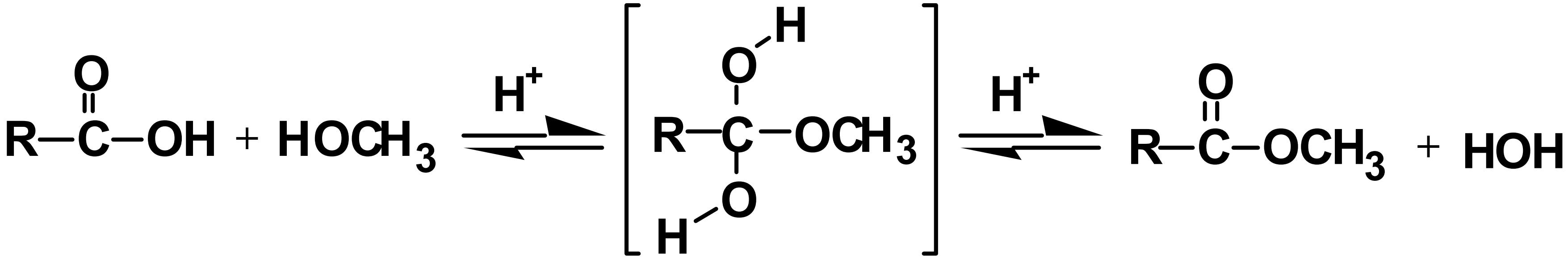
Ethanol (Ethyl alcohol)

Ethyl ethanoate (Ethyl acetate)

Fischer esterification is an equilibrium reaction. By careful control of experimental conditions, it is possible to prepare esters in high yield. If the alcohol is inexpensive relative to the carboxylic acid, it can be used in excess to drive the equilibrium to the right.

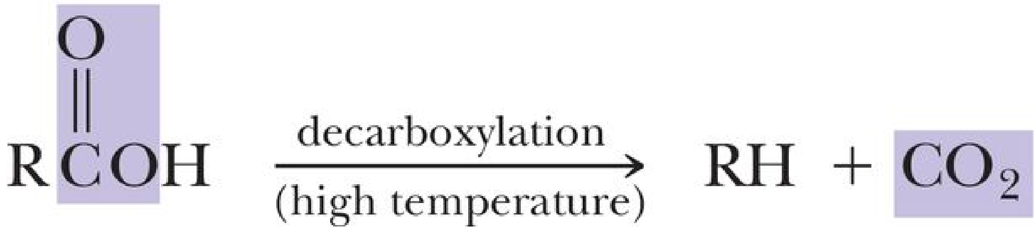
Fischer Esterification

- A key intermediate in Fischer esterification is a tetrahedral carbonyl addition intermediate formed by addition of an alcohol to the C=O group.



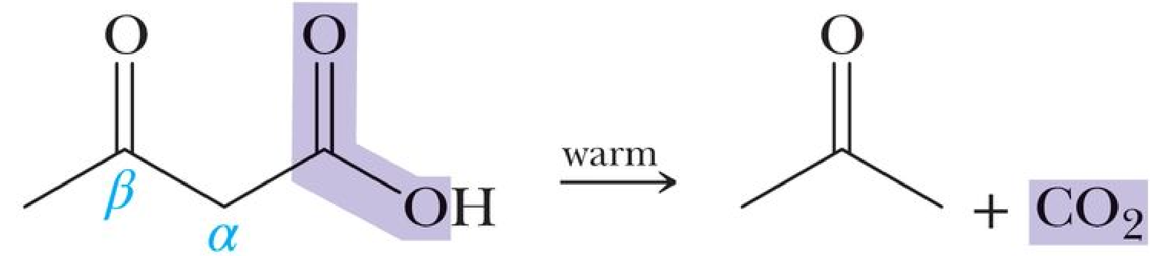
Decarboxylation

- **Decarboxylation**: loss of CO_2 from a carboxyl group.
  - Most carboxylic acids, if heated to a very high temperature, undergo thermal decarboxylation.



$$R\overset{O}{\overset{\|}{C}}OH \xrightarrow[\text{(high temperature)}]{\text{decarboxylation}} RH + CO_2$$

  - Most, however, are quite resistant to decarboxylation.
  - Exceptions are carboxylic acids that have a carbonyl group beta to the carboxyl group.
  - β-ketoacids undergo decarboxylation on mild heating.

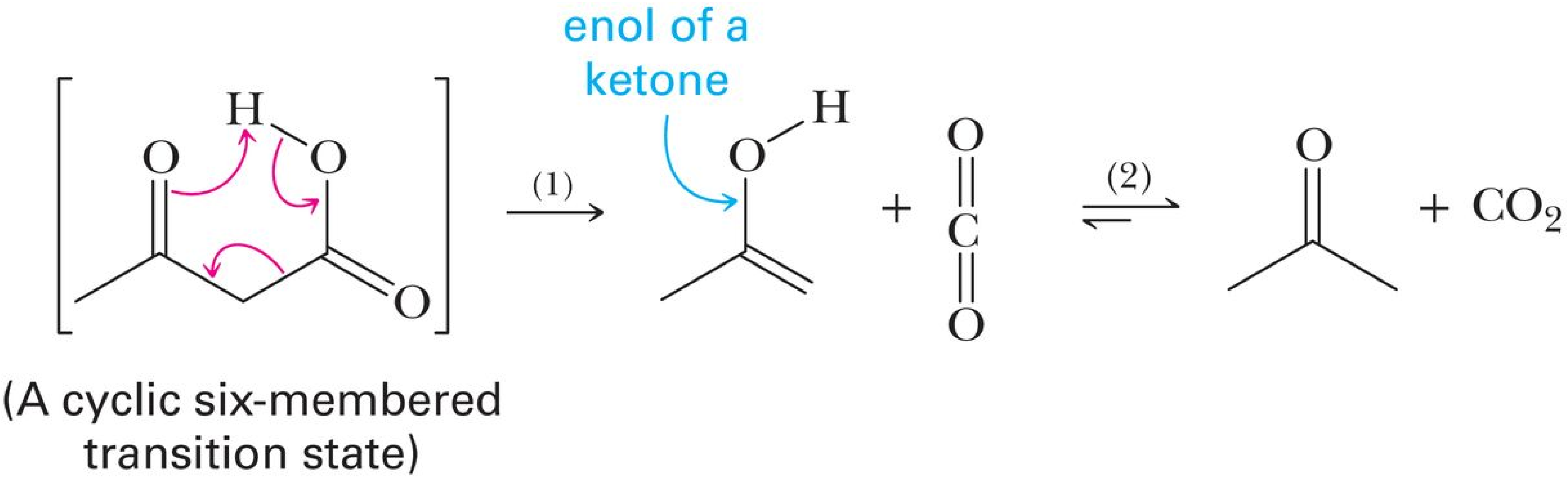


3-Oxobutanoic acid
(Acetoacetic acid)

Acetone

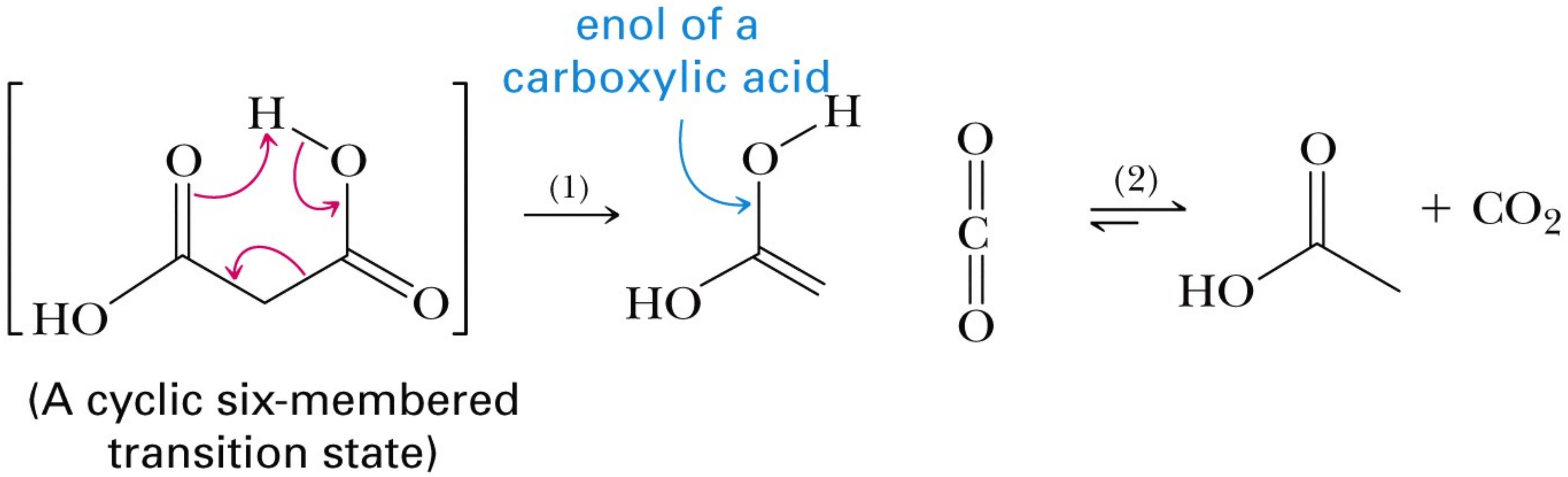
Decarboxylation

- Thermal decarboxylation of a β-ketoacid involves rearrangement of six electrons in a cyclic six-membered transition state.



Decarboxylation

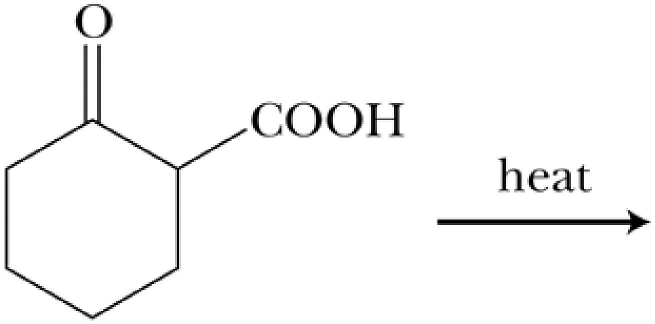
- Thermal decarboxylation of malonic acids also involves rearrangement of six electrons in a cyclic six-membered transition state.



(A cyclic six-membered transition state)

Decarboxylation

- **Problem**: Draw the product of decarboxylation.



- **Problem**: Draw the β-ketoacid that undergoes decarboxylation to give this ketone.