Carboxylic Acid Derivatives and Their Reactions.
Carboxylic Acid Esters

Synthesized from a carboxylic acid and an alcohol:

\[ R\text{-}C\text{-}OH + HO\text{-}R' \rightarrow R\text{-}C\text{-}O\text{-}R' + H_2O \]

condensation

hydrolysis

Nomenclature base on parent alcohol and carboxylic acid:

\[ \text{propanoic acid} + \text{methanol} \rightarrow \text{methyl propanoate} + H_2O \]
A Diester Synthesis

terephthalic acid + excess methyl alcohol

\[ \text{dimethyl terephthalate} + 2 \text{H}_2\text{O} \]
A Polyester Synthesis

\[
\text{HO-C-} \quad \text{O} \quad \text{C-} \quad \text{OH} \quad + \quad \text{excess} \quad \text{HO-CH}_2\text{CH}_2-\text{OH}
\]

terephthalic acid

\[
\text{H}^+ \quad \text{ethyleneglycol}
\]

ethanediol

A polyester
Hydrolysis Reaction of Esters

Hydrolysis of Esters Under Acidic Conditions

\[ \text{ester} \xrightleftharpoons{\text{H}^+} \text{carboxylic acid} + \text{alcohol or phenol} \]

Notice that this is the reverse of the condensation reaction used to synthesize an ester !!
Hydrolysis Reaction of Esters

Hydrolysis of Esters Under Basic Conditions

$$\text{R-C-O} - \text{H}_2\text{O} \rightarrow \text{R-C-OH} + \text{NaOH}$$

The carboxylic acid is an intermediate but reacts with the basic NaOH!!
Hydrolysis Worksheet
HCl, H₂O

ethyl-2,4-difluoro benzoate

NaOH, H₂O

phenyl-3-methyl butanoate
2-methylpropyl benzoate

isobutyl benzoate
Soaps are produced by a process called “saponification” (technically, “basic hydrolysis of fats”)

\[
\text{Hot aq NaOH}
\]
Soaps are the sodium or potassium salts of long-chain fatty acids.
Synthetic Detergents

- Sodium Dodecyl Sulfate (SDS)
- Sodium Alkyl Benzene Sulfonate (ABS)
- Sodium Dodecyl Benzene Sulfonate (LAS)
Synthetic Detergents

Chemical structures of synthetic detergents.
Amides - Synthesis and Nomenclature

Acetic acid + methylamine $\xrightarrow{\text{condensation}}$ N-methylacetamide

acetic acid methylamine N-methylacetamide
Amides - Basic Hydrolysis

R-C\(\text{N}-\text{R'}\) \(\text{H}_2\text{O}, \text{NaOH}\) \(\text{Two Products}\)
Example

\[
\text{N,N-diethylbenzamide} + \text{Na}^+ \text{OH}^- \xrightarrow{\text{H}_2\text{O}}
\]
Amides - Acid Hydrolysis

\[ \text{R-C-N-R}' \xrightarrow{H_2O, H_3O^+} \text{R-C-OH} \]

\[ \text{H-N-R}' \xrightarrow{H_3O^+} [\text{H-N-R}'] \]

\[ \text{H-N-R}' \xrightarrow{H_3O^+} [\text{H-N-R}'] \]

\[ \text{R-C-OH} \xrightarrow{H_2O} \text{R-C-N-R}' \]
Hydrolysis Worksheet
**Amides - Acid Hydrolysis**

**Example**

\[
\text{N,N-diethylbenzamide} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} \]

N,N-diethylbenzamide
HCl, H₂O
sodium 2-nitro-benzoate
A Polyester Synthesis

\[ \text{terephthalic acid} + \text{excess ethylene glycol} \rightarrow \text{A polyester} \]
Amides - Condensation Polymers

adipic acid

H₂N-CH₂CH₂CH₂CH₂CH₂CH₂-NH₂

hexamethylene diamine

mix at room temperature

H₃N-CH₂CH₂CH₂CH₂CH₂CH₂CH₂NH₃

hexamethylene diammonium adipate

heat

H₂O

polyhexamethylenediamine adipate

Nylon 6,6
Carboxylic Acids and Their Derivatives

- acetic acid
- acetyl chloride
- methyl acetate
- acetic anhydride
Carboxylic Acid Anhydrides and Halides

Synthesis from a carboxylic acid:

\[
\text{R-COOH} + \text{HO-CR} \xrightarrow{\text{H}^+} \text{R-CO} \cdot \text{O-CR} + \text{H}_2\text{O}
\]

Very unstable; very “reactive”
Low boiling points and melting points
“Lachrymators”
Generate the starting acids upon hydrolysis
Carboxylic Acid Anhydrides and Halides

Used to Synthesize Esters

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{ClC—CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{O—C—CH}_3
\]

\text{ethyl alcohol} \quad \text{acetyl chloride} \quad \text{ethyl acetate}

\[
\text{OH} \quad \text{O} \quad \text{OH}
\]

\[
\text{CH}_3\text{—C—O—C—CH}_3
\]

\text{salicylic acid} \quad \text{acetic anhydride} \quad \text{acetyl salicylic acid} \quad \text{aspirin}

\[
\text{H} \quad \text{C} \quad \text{CH}_3
\]
These highly reactive compounds are used to transfer the acetyl group to an alcohol group.

Summary of reactivity of carboxylic acid related functional groups:
Similar Derivatives of Inorganic Acids

- **Acetic acid**: \( \text{CH}_3\text{C} = \text{O}\text{H} \)
- **Sulfuric acid**: \( \text{HO-S-OH} \)
- **Phosphoric acid**: \( \text{HO-P-OH} \)
- **Methyl acetate**: \( \text{CH}_3\text{C} = \text{OCH}_3 \)
- **Dimethyl sulfate**: \( \text{CH}_3\text{O-S-OCH}_3 \)
- **Trimethyl phosphate**: \( \text{CH}_3\text{O-P-OCH}_3 \)
- **Acetic anhydride**: \( \text{CH}_3\text{C}=\text{O-C}=\text{OCH}_3 \)
- **Pyrosulfuric acid**: \( \text{HO-S-O-S-OH} \)
- **Pyrophosphoric acid**: \( \text{HO-P-O-P-OH} \)
Similar Derivatives of Inorganic Acids

- Acetic anhydride
- Pyrosulfuric acid
- Pyrophosphoric acid

Anhydride Linkages

“Reactive Linkages”

“High Energy Bonds”
What is ATP??