Alcohol aldehydes
cetones and
carboxylic acids
# Classes of organic compounds

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<th>Structure</th>
<th>Examples</th>
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<td>Alkane</td>
<td>-C-</td>
<td>contains only C=C and C-H bonds</td>
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<tr>
<td>Alkene</td>
<td>C=C</td>
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<tr>
<td>Alkyne</td>
<td>C≡C</td>
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<td>Nitrile</td>
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<tr>
<td>Alkyl halide</td>
<td>R-X</td>
<td>X = F, Cl, Br, or I</td>
</tr>
<tr>
<td>Ether</td>
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<tr>
<td>Alcohol</td>
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<td>Phenol</td>
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<td>Aldehyde</td>
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<td>Amides</td>
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<td>Amine (primary)</td>
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<td>Amine (secondary)</td>
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<tr>
<td>Amine (tertiary)</td>
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</tbody>
</table>
Alcohols

Alcohols are organic compounds containing hydroxyl (-OH) group attached to C atom. In an alcohol, -OH group replaces a hydrogen atom in an alkane. In a phenol, -OH group is attached to a benzene ring.
Classification of alcohols (1)

- Alcohols are classified as primary, secondary, or tertiary.
- Classification is determined by the number of alkyl groups attached to the carbon bonded to the hydroxyl.

**Primary (1°)**
- 1 group
- \( \text{H} \)
- \( \text{CH}_3 - \text{C} - \text{OH} \)

**Secondary (2°)**
- 2 groups
- \( \text{CH}_3 \)
- \( \text{CH}_3 - \text{C} - \text{OH} \)

**Tertiary (3°)**
- 3 groups
- \( \text{CH}_3 \)
- \( \text{CH}_3 - \text{C} - \text{OH} \)
Classification of alcohols (2)

- According to the number of -OH groups, there are monohydroxylic, dihydroxylic and trihydroxylic alcohols.

  - Ethanol (monohydroxylic alcohol)
  - 1,2-ethanediol (dihydroxylic alcohol)
  - 1,2,3-propanetriol (trihydroxylic alcohol)
  - Glycerol

- According to the saturation of C atom chain, alcohols fall into saturated and unsaturated aliphatic, cyclic and aromatic.

  - 1-propanol (aliphatic alcohol)
  - Cyclohexanol (cyclic alcohol)
  - Phenylmethanol (aromatic alcohol)
Naming alcohols (1)

- The IUPAC system replaces the -e in the name of the alkane main chain with -ol.
- Common names for simple alcohols use the alkyl name followed by alcohol.

\[
\text{CH}_4 \quad \text{methane} \quad \text{CH}_3\text{OH} \quad \text{methanol} \\
\text{CH}_3\text{CH}_3 \quad \text{ethane} \quad \text{CH}_3\text{CH}_2\text{OH} \quad \text{ethanol} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad \text{1-propanol} \\
\text{CH}_3\text{CH}-(\text{CH}_3)\text{CH}_2\text{CH}_3 \quad \text{2-butanol} \\
\text{CH}_3\text{CH}-(\text{CH}_3)\text{CH}_2\text{CH}-(\text{CH}_3) \quad 4\text{-methyl-2-pentanol}
\]

In the IUPAC names for longer chains, the chain is numbered from the end nearest the -OH group.
Naming alcohols (2)

- Dihydroxylic alcohols are called **glycols**, or according to IUPAC: -**diols**; trihydroxylic alcohols: -**triols**.

![Chemical structures](image)

- Ethylene Glycol
- (1,2-Ethanediol) (1,2-Propanediol)
- (1,2,3-Propanetriol)
Chemical properties of alcohols (1)

**Acidic-basic properties:** although OH group is polar, alcohols are very weak acids.

The acidic properties of **di-** and **trihydroxylic** alcohols are stronger than those of **monohydroxylic** alcohols. They react with bases producing salts: diols form glycolates, triols - glycerates.

The reaction for identification of \(-\text{CHOH-CHOH-}\) fragment in various compounds:

\[
CH_2-OH \quad CH_2-OH + \text{Cu(OH)}_2 + 2\text{KOH} \rightarrow \left[ \begin{array}{c} \text{H}_2\text{C-O-Cu-O-CH}_2 \\ \text{H}_2\text{C-O-Cu-O-CH}_2 \end{array} \right]^{2-} + 2\text{K}^+ + 4\text{H}_2\text{O}
\]

- blue colour precipitate
- water soluble blue complex compound
Chemical properties of alcohols (2)

**Oxidation** of primary alcohols results in formation of aldehydes, and then aldehydes undergo further oxidation to carboxylic acids.

$$\text{R-CH}_2\text{-OH} \xrightarrow{[O]} \text{R-CH} = \text{O} \xrightarrow{[O]} \text{R-C} = \text{O}$$

Under oxidation of secondary alcohols, ketones are produced. Ketones are more resistant to oxidation.

$$\text{R-CH-R}_{1} \xrightarrow{[O]} \text{R-C-R}_{1}$$
Chemical properties of alcohols (3)

Formation of ethers:

\[ \text{R}_1\text{CH}_2\text{OH} + \text{R}_2\text{CH}_2\text{OH} \rightarrow \text{R}_1\text{CH}_2\text{O}\text{CH}_2\text{R}_2 \]

Formation of esters with both mineral and organic acids.

\[ \text{R}_1\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4 \rightarrow \text{R}_1\text{CH}_2\text{O}\text{SO}_3^- \]

\[ \text{R}_1\text{CH}_2\text{OH} + \text{R}-\text{COOH} \rightarrow \text{R}-\text{C}-\text{O}\text{CH}_2\text{R}_1 \]

Esters of glycerol and organic acids are triacylglycerols (fats).
Ethers

- Ethers contain an -O- between two carbon groups.
- Simple ethers are named by listing the alkyl names in alphabetical order followed by *ether*.

\[
\begin{align*}
\text{CH}_3\text{OCH}_3 & \quad \text{dimethyl ether} \\
\text{CH}_3\text{OCH}_2\text{CH}_3 & \quad \text{ethyl methyl ether} \\
\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 & \quad \text{diethyl ether}
\end{align*}
\]

- In the IUPAC system, the shorter alkyl group and the oxygen are named as an *alkoxy* group attached to the longer alkane.

\[
\begin{align*}
\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{methoxy propane}
\end{align*}
\]

- Numbering the longer alkane gives *1-methoxypropane*.
Physical properties of alcohols

- Alcohols contain a strongly electronegative O in the OH groups.
- Thus, hydrogen bonds form between alcohol molecules.
- Hydrogen bonds contribute to higher boiling points for alcohols compared to alkanes and ethers of similar mass.

- Alcohols and ethers are more soluble in water than alkanes because the oxygen atom can hydrogen bond with water.
- Alcohols with 1-4 C atoms are soluble, but alcohols with 5 or more C atoms are not.
Aromatic alcohols

ea benzyl group
Oxidation of aromatic alcohols

1-phenylethanol $\xrightarrow{\text{MnO}_2 \Delta} $ acetophenone

phenylmethanol $\xrightarrow{\text{MnO}_2 \Delta} $ benzaldehyde

benzyl alcohol $\xrightarrow{\text{MnO}_2 \Delta} $ benzaldehyde
Phenols(1)

- A phenol is a benzene ring with a hydroxyl group.
- For two substituents, assign C-1 to the carbon attached to the –OH.
- Number the ring to give the lowest numbers.
- The prefixes o, m, and p are used for common names.

Phenol is soluble in water because the hydroxyl group ionizes slightly as a weak acid.
Phenols(2)

Phenol

catechol
resorcinol
hydroquinone

1,2,5-benzenetriol
Chemical properties of phenols (1)

Phenols are stronger acids than aliphatic and aromatic alcohols.

**Form salts:**

\[
\text{phenol} + \text{NaOH} \rightarrow \text{sodium phenolate}
\]

**Form ethers:**

\[
\text{phenol} + \text{CH}_3\text{OH} \rightarrow \text{methyl phenyl ether (anisol)}
\]

**Form esters:**

\[
\text{phenol} + \text{CH}_3\text{COCl} \rightarrow \text{phenylethanoate}
\]
Chemical properties of phenols (2)

- Phenols are characterized with one specific reaction. They can form coloured compounds reacting with ferric trichloride. In such reaction phenols form coloured coordination compounds - ferric phenolates:

\[
\text{FeCl}_3 + 6\text{C}_6\text{H}_5\text{OH} = [\text{Fe(OC}_6\text{H}_5)_6]^3^- + 6\text{H}^+ + 3\text{Cl}^- 
\]
Phenols: examples

- Physiologically active aromatic alcohols:

  - adrenaline
  - noradrenaline

Many phenols are used as antiseptics and disinfectants.

- Phenol
- Resorcinol (antiseptic)
- 4-Hexylresorcinol (antiseptic)
Alcohol in the body

- Enzymes in the liver oxidize ethanol.
- The aldehyde produced impairs coordination.
- A blood alcohol level over 0.4% can be fatal.

\[ \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH} \rightarrow 2\text{CO}_2 + \text{H}_2\text{O} \]

Ethyl alcohol  →  acetaldehyde
Carbonyl compounds: Aldehydes and ketones

- The carbonyl group is found in aldehydes and ketones.
- In an aldehyde, an H atom is attached to a carbonyl group.
- In a ketone, two carbon groups are attached to a carbonyl group.
The polar carbonyl group

The carbonyl group (C=O):

- Consists of a sigma and pi bond.
- Has a partially negative O and a partially positive C.
- Has polarity that influences the properties of aldehydes and ketones.
Groups of carbonyl compounds

Aldehydes

\[ \text{ethanal} \]

\[ \text{benzaldehyde} \]

Ketones

\[ \text{propanone (acetone)} \]

\[ \text{Benzophenone} \]
Naming aldehydes

**systematic name:**

methanal
formaldehyde

ethanal
acetaldehyde

2-bromopropanal
$\alpha$-bromopropionaldehyde

**systematic name:**

trans-2-methylcyclohexanecarbaldehyde

benzenecarbaldehyde

benzaldehyde
Naming ketones

- **Propanone (systematic name):** Acetone (common name), Dimethyl ketone (derived name)
- **3-hexanone:** Ethyl propyl ketone
- **6-methyl-2-heptanone:** Isohexyl methyl ketone

- **Cyclohexanone:**
- **Butanedione:**
- **2,4-pentanedione (acetylacetone):**
- **4-hexen-2-one:**

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Physical properties of carbonyl compounds (1)

Aldehydes and ketones with up to 4 C atoms in molecules are volatile liquids of specific odour. They are soluble in water and in organic solvents.

Solubility in water decreases with an increase of a number of C atoms in a chain.

Aldehydes containing 8-10 C atoms in a chain have odour of flowers and are used in perfumery.
Physical properties of carbonyl compounds (2)

- The polar carbonyl group provides dipole-dipole interactions.

\[ \delta^+ \delta^- \quad \delta^+ \delta^- \]

\[ C=O \quad C=O \]

- The electronegative O atom of the carbonyl group of aldehydes and ketones forms hydrogen bonds with water.
Chemical properties of carbonyl compounds

**Reduction** producing alcohols (both aldehydes and ketones).

\[ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \rightarrow \text{H}_3\text{C}-\text{C}-\text{CH}_3 \]

propanone (acetone)

**Oxidation** producing acids (only aldehydes).

\[ \text{H}_3\text{C}-\text{C}-\text{H} \rightarrow [\text{O}] \rightarrow \text{H}_3\text{C}-\text{C}-\text{OH} \]

Acetaldehyde Acetic acid
Tollens’ test

- Tollens’ reagent, which contains Ag⁺, oxidizes aldehydes, but not ketones.
- Ag⁺ is reduced to metallic Ag, which appears as a “mirror” in the test tube.

\[
\text{Ag}^+ + 1\text{e}^- \rightarrow \text{Ag} \ (s)
\]

Example:

\[
\text{H}_3\text{C}-\text{C}=\text{H} + 2\text{Ag}^+ \xrightarrow{[O]} 2\text{Ag} (s) + \text{H}_3\text{C}-\text{C}=\text{OH}
\]

Acetaldehyde + Tollens reagent \rightarrow Silver mirror + Acetic acid
Benedict’s test

- Benedict’s reagent, which contains Cu\(^{2+}\), reacts with aldehydes that have an adjacent OH group.
- When an aldehyde is oxidized to a carboxylic acid, Cu\(^{2+}\) is reduced to give Cu\(_2\)O(s).

Example:

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{C} \quad \text{H} \quad + \quad \text{Cu}^{2+} \quad \rightarrow \quad \text{Cu}_2\text{O}(s) \quad + \quad \text{H}_3\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{OH}
\]

2-Hydroxypropanal  Benedict's reagent  Brick-red solid  2-Hydroxypropanoic acid
Carboxylic acids

The carboxyl group:
- Is a carbonyl group (C=O) attached to a hydroxyl group (OH).
- Is found on carbon 1 in carboxylic acids.
- Is written in different ways.

\[
\begin{align*}
\text{O} \\
\text{CH}_3\text{C} \text{OH} & \quad \text{CH}_3\text{COOH} & \quad \text{CH}_3\text{CO}_2\text{H}
\end{align*}
\]
Preparation of carboxylic acids

- Carboxylic acid can be prepared by oxidizing primary alcohols or aldehydes.
- The oxidation of ethanol produces ethanoic acid (acetic acid).

\[
\begin{align*}
\text{Ethanol} & \quad \text{ethanal} & \quad \text{ethanoic acid} \\
\text{Ethyl alcohol} & \quad \text{acetaldehyde} & \quad \text{acetic acid}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{[O]}} \text{CH}_3\text{C}=:\text{H} & \xrightarrow{\text{[O]}} \text{CH}_3\text{C}=:\text{OH} \\
& \text{Ethanol} & \text{ethanal} & \text{ethanoic acid}
\end{align*}
\]
Naturally occurring carboxylic acids

- Pyruvic acid
- (S)-(+)-lactic acid
- Oxalic acid
- Succinic acid
- Citric acid
- (S)-(−)-malic acid
- Prostaglandin A$_2$
- Prostaglandin F$_{2\alpha}$
Naming carboxylic acids

The IUPAC names of carboxylic acids:

- Replace the -e in the alkane name with -oic acid.
  
  \[
  \begin{align*}
    \text{CH}_4 & \quad \text{methane} \\
    \text{HCOOH} & \quad \text{methanoic acid} \\
    \text{CH}_3—\text{CH}_3 & \quad \text{ethane} \\
    \text{CH}_3—\text{COOH} & \quad \text{ethanoic acid}
  \end{align*}
  \]

- Number substituents from the carboxyl carbon 1.

\[
\begin{align*}
  \text{CH}_3 & \\
  \text{CH}_3—\text{CH}—\text{CH}_2—\text{COOH} & \quad 3\text{-methylbutanoic acid}
\end{align*}
\]

The common names of simple carboxylic acids:

- Use formic acid (1C), acetic acid (2C), propionic acid (3C), and butyric acid (4C).
  
  \[
  \begin{align*}
    \text{HCOOH} & \quad \text{formic acid} \\
    \text{CH}_3—\text{COOH} & \quad \text{acetic acid}
  \end{align*}
  \]

- Locate substituents by assigning \( \alpha, \beta, \_ \) to the carbon atoms adjacent to the carboxyl carbon.
  
  \[
  \begin{align*}
    \text{CH}_3 & \\
    \_ & \quad \beta | \quad \alpha \\
    \text{CH}_3—\text{CH}—\text{CH}_2—\text{COOH} & \quad \beta\text{-methylbutyric acid}
  \end{align*}
  \]
### Some common names of carboxylic acids

<table>
<thead>
<tr>
<th>Common</th>
<th>IUPAC</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic</td>
<td>methanoic</td>
<td>HCOOH</td>
</tr>
<tr>
<td>Acetic</td>
<td>ethanoic</td>
<td>CH₃COOH</td>
</tr>
<tr>
<td>Propionic</td>
<td>propanoic</td>
<td>CH₃CH₂COOH</td>
</tr>
<tr>
<td>Butyric</td>
<td>butanoic</td>
<td>CH₃(CH₂)₂COOH</td>
</tr>
<tr>
<td>Capric</td>
<td>decanoic</td>
<td>CH₃(CH₂)₈COOH</td>
</tr>
<tr>
<td>Lauric</td>
<td>dodecanoic</td>
<td>CH₃(CH₂)₁₀COOH</td>
</tr>
<tr>
<td>Stearic</td>
<td>octadecanoic</td>
<td>CH₃(CH₂)₁₆COOH</td>
</tr>
</tbody>
</table>
Aromatic carboxylic acids

Benzoic acid:

- Is the aromatic carboxylic acid.
- Locates substituents by assigning 1 to the carbon attached to the carboxyl group.
- Has common names that assign prefixes ortho, meta, and para for 2 substituents.

  ortho 1, 2 location
  meta 1, 3 location
  para 1, 4 location

Benzoic acid 3-Chlorobenzoic acid 4-Aminobenzoic acid
Polar functional groups in carboxylic acids

Carboxylic acids are among the most polar organic compounds because the functional carboxyl group consists of two polar groups: a hydroxyl (-OH) group and a carbonyl (C=O) group.

\[
\begin{align*}
\text{H}_2\text{C} & \text{O} \quad \delta^- \\
\text{O} & \quad \delta^+ \\
\text{H} & \quad \delta^+ \\
\text{C} & \quad \delta^- \\
\text{O} & \quad \delta^- \\
\end{align*}
\]
Physical properties of carboxylic acids

Carboxylic acids:
- Have higher boiling points than alcohols, ketones, and aldehydes of similar mass.
- Form dimers in which hydrogen bonds form between two carboxyl groups.

\[
\begin{align*}
\text{CH}_3cC & \quad \text{C--CH}_3 \\
\text{O--H} & \quad \parallel \\
\text{O--H} & \quad \parallel \\
\text{O} & \quad \text{H--O}
\end{align*}
\]

A dimer of acetic acid

Carboxylic acids:
- With 1-4 carbon atoms are very soluble in water.
- Form hydrogen bonds with many water molecules.
The acidity of carboxylic acids

- Are weak acids.
  \[ CH_3\text{--COOH} + H_2O \rightleftharpoons CH_3\text{--COO}^- + H_3O^+ \]
- Exist mostly as molecules and a few ions in aqueous solutions.
- Have small $K_a$ values.

The equilibrium concentrations of the **carboxylic acid** R-COOH and the **carboxylate ion** R-COO$^-$ depend upon pH:
- At low pH the acid form predominates, at pH 7.4 the carboxylate ion predominates.

Carboxylic acids react with bases to produce carboxylate salts and water.
The carboxylic acid salts are solids at room temperature. Because they are ionic compounds, carboxylic acid salts of the alkali metals (Li\(^+\), Na\(^+\), and K\(^+\)) and NH\(_4^+\) are usually soluble in water.
Soap formation

\[
\begin{align*}
\text{a fat or an oil} & \quad \text{NaOH} \\
\text{glycerol} & \quad \text{sodium salts of fatty acids}
\end{align*}
\]
Cleaning action of soap

One of the problems of using soaps is that the carboxylate end reacts with ions in water such as Ca$^{2+}$ and Mg$^{2+}$ and forms insoluble substances.

$$2\text{CH}_3(\text{CH}_2)_{16}\text{COO}^- + \text{Mg}^{2+} \rightarrow [\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-]_2\text{Mg}^{2+}$$

Stearate ion

Magnesium stearate (insoluble)
Esterification

Carboxylic acids, acid chlorides and acid anhydrides react with alcohols to produce esters. Esters can also be formed when inorganic acids (e.g., phosphoric acid) react with alcohols.

An ester is produced by the reaction of a carboxylic acid and alcohol in the presence of an acid catalyst.

\[
\begin{align*}
\text{CH}_3\text{C}--\text{OH} + \text{HO}--\text{CH}_2--\text{CH}_3 & \rightarrow \\
\text{CH}_3\text{C}--\text{O}--\text{CH}_2--\text{CH}_3 + \text{H}_2\text{O}
\end{align*}
\]
Esters

- In an ester, the H in the carboxyl group is replaced by an alkyl group.

\[ \begin{align*}
    &CH_3-C\equiv O-CH_3 \\
    \text{ester group}
\end{align*} \]

Esters are named with the alkyl name of the alcohol followed by the carboxylate name from the acid.

- Ethanoate (Acetate)
  - from acid: \( CH_3-C\equiv O-CH_3 \)
  - from alcohol: methyl

- methyl ethanoate (IUPAC)
- methyl acetate (common)
Examples of esters

from 1-propanol

\[
\text{CH}_3\text{C}O\text{O-CH}_2\text{CH}_2\text{CH}_3
\]

Propyl ethanoate (IUPAC)
Propyl acetate (common)

\[
\text{CH}_3\text{C}O\text{O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

Butyl acetate

\[
\text{CH}_3\text{C}O\text{O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

Ethyl propionate
Reactions of esters - hydrolysis

In hydrolysis:
- An ester reacts with water to produce a carboxylic acid and an alcohol.
- An acid catalyst is required.

\[
\text{H-C-O-CH}_2\text{-CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{H-C-OH} + \text{HO-CH}_2\text{-CH}_3
\]

In base hydrolysis or saponification, an ester reacts with a strong base to produce the salt of the carboxylic acid and an alcohol.

\[
\text{CH}_3\text{-C-O-CH}_2\text{-CH}_3 + \text{NaOH} \xrightarrow{} \text{CH}_3\text{-C-O-}^{\text{Na}^+} + \text{HO-CH}_2\text{-CH}_3
\]

salt of carboxylic acid  alcohol
Esters in medicine

Aspirin:
- Is used to relieve pain and reduce inflammation.
- Is an ester of salicylic acid and acetic acid.

Oil of wintergreen:
- Is used to soothe sore muscles.
- Is an ester of salicylic acid and methanol.

Acetylsalicylic acid (Aspirin)

Methyl salicylate (Oil of wintergreen)
Acid anhydrides

They form from the combination of two carboxylic acids and the loss of water.

\[
2 \text{H}_3\text{C} - \text{C} - \text{OH} \xrightarrow{\text{H}^+, \text{heat}} \text{H}_3\text{C} - \text{C} - \text{O} - \text{C} - \text{CH}_3 + \text{H}_2\text{O}
\]

ethanoic acid  \hspace{1cm} \text{ethanoic anhydride}

Examples:

\[
\text{H}_3\text{C} - \text{CH}_2 - \text{C} - \text{O} - \text{C} - \text{CH}_2 - \text{CH}_3
\]

propanoic anhydride

[Chemical structure of propanoic anhydride]

\[
\text{C} - \text{O} - \text{C} - \text{C} - \text{H}_2 - \text{C} - \text{H}_3
\]

benzoic anhydride

[Chemical structure of benzoic anhydride]
Reactions of acid anhydrides

\[
\text{RCO}_2\text{OCR} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{RCO}_2\text{CH}_2\text{CH}_3 + \text{RCOOH}
\]

\[
\text{RCO}_2\text{OCR} + \text{H}_2\text{O} \rightarrow 2 \text{RCOOH}
\]