Derivatives of carboxylic acids

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Derivatives of carboxylic acids

1. **substitutional derivatives**

   → substitution in the chain of an acid

   → no change in the carboxyl group

2. **functional derivatives**

   → functional carboxyl group is changed

Substitutional derivatives

- *substitution in the chain of an acid*

1.1. HALOGEN DERIVATIVES

R(X)—COOH *X = Cl, Br, I, F*

- **prefix: chloro-, bromo-, iodo-, fluoro-**

1.2. HYDROXY DERIVATIVES

R(OH)—COOH

- **prefix: hydroxy-**
- can be oxidized to oxo derivatives (= dehydrogenation)
- **trivial names!**

Important hydroxy derivatives

- **lactic acid**
  (= 2-hydroxypropanoic acid or α-hydroxypropionic acid)
- **β-hydroxybutyric acid**
  (= 3-hydroxybutanoic acid)
- **malic acid**
  (= 2-hydroxybutanedioic acid or α-hydroxysuccinic acid)
- **citric acid**
  (= 2-hydoxypropane-1,2,3-tricarboxylic acid)
- **salicylic acid**
  (= 2-hydroxybenzoic acid)

1.3. OXO DERIVATIVES

R—(C=O)—COOH

- **prefix: oxo- / keto-**
- can be reduced to hydroxy derivatives
- **trivial names!**

Important oxo derivatives:

- **pyruvic acid** (= 2-oxopropanoic acid)
- **acetoacetic acid** (= 3-oxobutanoic acid)
- **oxaloacetic acid** (= 2-oxobutanedioic acid)
- **α-ketoglutaric acid** (= 2-oxopentanedioic acid)

1.4. AMINO DERIVATIVES

$R(NH_2)$—COOH

- **<u>prefix</u>: amino-**
- α-L-amino acids are found in proteins
- **trivial names!**

examples:

- **glycine** (= 2-aminoethanoic acid)
- **alanine** (= 2-aminopropanoic acid)
- **phenylalanine** (= 2-amino-3-phenylpropanoic a.)

Functional derivatives

- *functional carboxyl group is changed*

2.1. SALTS $R—COO^- M^+$ (M^+ = metal cation)

= products of **neutralization** (acid + base → salt + water)

- **suffix**: **-ate** or **-oate**

  -ic acid → -ate / -oic acid → -oate

- $R—COO^-$ = carboxylate (anion of c.a.)
- **full name:** cation carboxylate

  (sodium acetate)

2.2. ESTERS $R_1—O—CO—R_2$

= products of **esterification** (acid + alcohol → ester + water)

- the opposite reaction = **ester hydrolysis**

- **<u>suffix</u>: -ate**
- **R1—O— = rest of alcohol**
- R1 = alkyl (from the alcohol name: „alkyl" alkohol)
- **<u>full name</u>**: alkyl carboxylate

(methyl acetate = methyl ethanoate)

Examples of esters

- ethyl formate = ethyl methanoate
- methyl benzoate
- methyl salicylate ≠ acetylsalicylic acid
- phenyl acetate = phenyl ethanoate
- CH_3-CH_2-CH_2-CO-O-CH_3 (apple)
- CH_3-CH_2-CH_2-CO-O-$(CH_2)_4$-CH_3 (apricot)
- CH_3-CO-O-$(CH_2)_4$-CH_3 (banana)
- CH_3-CH_2-CH_2-CO-O-CH_2-CH_3 (pineapple)
- H-CO-O-CH_2-CH_3 (rum)

Properties and reactions of esters

- lower boiling points than carboxylic acids and alcohols (~ absence of hydrogen bonds)
- less soluble in water than carboxylic acids
- esters have a fruity smell
- **reactions**:
  - **ester hydrolysis**
  - **saponification** = hydrolysis by a strong base
    → salt and alcohol
    → salts of long chain fatty acids are **SOAPS**
  - **polymerization** → polyesters (from difunctional monomers)

2.3. ANHYDRIDES $R_1—CO—O—CO—R_2$

- ***acid → anhydride***

  (acetic <u>acid</u> → acetic <u>anhydride</u>)

- **organic, organic-inorganic**

<u>examples</u>

- acetic formic anhydride
- phtalic anhydride
- „phosphoglycerate" (= phosphoric glyceric anhydride)

2.4. AMIDES $R—CO—NH_2$

- **suffix**: **-amide** *(ethanamide)*
- **-ic or –oic acid** → **-amide** *(acetamide)*
- substituted $-NH_2$ group: ***N-alkyl…amide***

- *substituted amide groups are found in proteins (the peptide bond = „amide bond")*
- nitrogen atom contains an unshared pair of electrons → delocalization ⇒ amides are not basic
- strong intermolecular **H-bonds**: amides are solids
- low MW amides are soluble in water

- carboxylic acid + ammonia (or amine) → amide + water

2.5. ACYLHALIDES *R—CO—X* *X = halogen*

- **acyl name + halide**
- *e.g.* *acetyl chloride (= ethanoyl chloride)*
  butyryl bromide (= butanoyl bromide)

2.6. NITRILES *R—C≡N*

- **hydrocarbon + suffix: -nitrile**
  or **alkyl cyanide**
- *e.g* *ethanenitrile or methyl cyanide*
  butanenitrile or propyl cyanide
- mostly toxic liquids

Exercise

- $H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$
- $CH_3\text{-}CO\text{-}CH_2\text{-}COOH$
- $CH_3\text{-}CH(OH)\text{-}CH_2\text{-}COOH$
- $CH_3\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}O\text{-}CH_3$
- $CH_3\text{-}CO\text{-}COOH$
- $CH_3\text{-}CH_2\text{-}O\text{-}CH_3$
- $CH_3\text{-}CO\text{-}CH_2\text{-}CH_3$
- $CH_3\text{-}(CH_2)_{14}\text{-}COOH$
- $CH_3\text{-}CH_2\text{-}CH_2\text{-}COONa$
- $(CH_3\text{-}CH_2\text{-}COO)_2Ca$
- $CH_3\text{-}CH_2\text{-}O\text{-}CO\text{-}H$

Exercise

- C_6H_5-CO-Cl
- H-CO-O-CH_2-CH_3
- CH_2=CH-CN

- H-CO-NH_2
- CH_3-CH_2-CO-NH-CH_2-CH_3