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Functional derivativies of carboxylic acids

Closely related to carboxylic acids and to each other are a number of chemical families known as fucntional derivatives of carboxylic acids: Acid halide, anhydride, amide and esters. These derivatives are compounds in which the OH of the carboxylic acid has been replaced by X(Cl, Br, I), OOCR, NH₂ or OR.

The all contain the group

$$R-C$$

1. Esters

They have a general formula

$$R-C$$
 OR

Examples

HCO₂CH₃ Methylmethanoate CH₃COOCH₂CH₃ Ethylethanoate CH₃CH₂COOCH₂CH₃ Ethylpropanoate

Physical properties

- (i) Insoluble in water but soluble in organic solvent
- (ii) They are neutral liquids with pleasant smell
- (iii) They have low boiling points compared to carboxylic acids of comparable molecular mass.

Preparation

(a) By reacting carboxylic acids with alcohol in the presence of mineral acids

RCOOH +R'OH
$$\xrightarrow{H^+}$$
 R-C OR'

Example

$$CH_3COOH + CH_3OH \xrightarrow{H^+} CH_3 - C$$

OCH₃

Methylethanoate

Mechanism

$$CH_{3} - C - OH$$

$$CH_{3} - C - OH$$

$$HOCH_{3}$$

$$CH_{3} - C - OH$$

$$HOCH_{3}$$

$$CH_{3} - C - OH$$

$$OCH_{3} - C - OH$$

$$OCH_{3} - C - OH$$

$$OCH_{3} - C - OH$$

(b) reaction of alcohols with acid halides

$$R - C$$
 X
 $+ R'OH$
 $R - C$
 OR'
where X = Cl, Br, or I

Example

$$CH_3COCl + CH_3OH \longrightarrow CH_3 \longrightarrow CH_3$$

CH₃

OCH₃

Methylethanoate

Mechanism

$$CH_{3} \xrightarrow{C} C$$

$$CH_{3} \xrightarrow{C} CI$$

$$CH_{3} \xrightarrow{C} CI$$

$$CH_{3} \xrightarrow{C} CI$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3}$$

$$CH_{3} \xrightarrow{C} CI$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3}$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3}$$

(c) By reacting silver salts of carboxylic acid with alkyl halide

$$R - C + R'X \longrightarrow R - C$$

$$O^{-}Ag^{+}$$

$$OR^{-}$$

Chemical properties

1. Hydrolysis

Esters are hydrolyzed by mineral acids or alkalis Example

$$CH_3$$
— C
 $H^+ \text{ or } \overline{}^-OH$
 $CH_3COCl + CH_3OH$

Mechanism (acid catalyzed)

$$CH_{3} - C \longrightarrow CH_{3} \longrightarrow CH_{3}$$

(ii) base catalyzed

$$CH_{3} \longrightarrow CH_{3}O^{-} \longrightarrow CH_{3}OH + OH^{-}$$

$$CH_{3} \longrightarrow CH_{3}OH \longrightarrow CH_{3}COOH \longrightarrow CH_{3}COO^{-} + HOH$$

$$CH_{3} \longrightarrow CH_{3}COOH \longrightarrow CH_{3}COO^{-} + HOH$$

2. Esters are reduced by LiAlH₄ in presence of dry ether to alcohols Examples

$$CH_{3} - C - \frac{\text{LiAlH}_{4}}{\text{dry ether}} - CH_{2}CH_{2}OH + CH_{3}OH$$

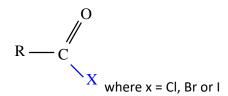
3. Esters react with ammonia to form acid amide

Uses of esters

In formation of perfumes

Acid halides

These have a general formula



Examples

C₆H₅COCl Benzoylchloride

CH₃COBr Ethanoylbromide

CH₃CH₂COI Propanoyliodide

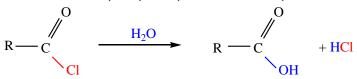
Preparation

By reacting carboxylic acid with phosphorus halide or thionylchloride

Examples

Chemical properties

1. Acid halides are hydrolyzed by water to carboxylic acids



Example

$$CH_3$$
 CH_3 CH_3

Mechanism

$$CH_{3} \xrightarrow{C} C$$

$$CH_{3} \xrightarrow{C} CI$$

$$+ OH_{2}$$

When ethanoyl chloride is exposed to moist air white fumes are seen due to the production of HCl.

Acid halides react with ammonia and amines to produce amides Example

$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3

Mechanism

$$CH_{3} \xrightarrow{C} CI \xrightarrow{CH_{3}} CH_{3} \xrightarrow{C} CI \xrightarrow{-HCl} CH_{3} \xrightarrow{C} CI \xrightarrow{NH_{2}} CH_{3} \xrightarrow{C} CI$$

 Acid halide react with alcohols to form esters Example

$$CH_3 - C \xrightarrow{C} CH_3OH CH_3 - C \xrightarrow{O} OCH_3$$

Mechanism

$$CH_{3} \xrightarrow{C} C$$

$$CH_{3} \xrightarrow{C} C$$

$$CH_{3} \xrightarrow{C} C$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{4} \xrightarrow{C} CH_{$$

4. Acid halides react with anhydrous sodium salt of carboxylic acid to form acid anhydride Example

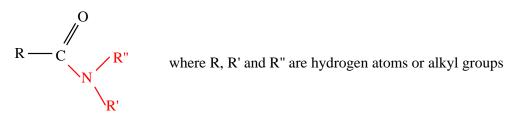
Mechanism

$$CH_{3} \xrightarrow{C} C$$

$$CH_{3} \xrightarrow{C} CI$$

Acid amide

These have a general formula



Examples

CH₃CONH₂ Ethanamide

CH₃CH₂CONH₂ Propanamide

Physical properties

- They are white crystalline salts except methanamide

 Lower members are soluble in water but the solubility decreases with increasing molecular mass.

- They have relatively high boiling points due to formation of intermolecular hydrogen bonds

Preparation

1. By reaction of ammonia with ester, acid anhydride or acid halides Examples

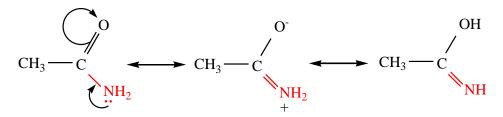
$$CH_3$$
 CH_3 CH_3

2. Dehydration of carboxylic acids with ammonium carbonate

$$CH_3COOH + (NH_4)_2CO_3$$
 \longrightarrow $CH_3CONH_2 + H_2O + CO_2$

Chemical properties

1. They are weaker bases compared to amines and are neutral to litmus. The do not form salts with acids as amines do because their lone pair of electron on the nitrogen atom is delocalized.



2. Amides form nitriles when distilled over phosphorus pentoxide, P₄O₁₀.

$$CH_{3} \longrightarrow C$$

$$CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3}$$

$$-H_{2}O$$

3. Amides react with hot alkaline bromine solution to give amines

$$CH_3$$
 \longrightarrow CH_3 \longrightarrow

4. Like amines, amides react with nitrous acid liberating nitrogen

$$CH_3$$
 \longrightarrow $CH_3COOH + N_2 + H_2O$

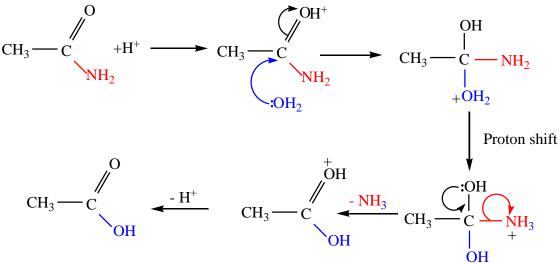
5. Amides are hydrolyzed with mineral acid or alkais Example

$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 $COOH + NH_4^+$

$$CH_3$$
 CH_3 $CH_3COO^- + NH_3$

Mechanism

(a) Acid catalyzed



Dr. Bbosa Science