Functional derivatives of carboxylic acids

Closely related to the carboxylic acids and to each other are a number of chemical families known as functional derivatives of carboxylic acids: acid chlorides, anhydrides, amides, and esters. These derivatives are compounds in which the —OH of a carboxyl group has been replaced by —Cl, —OOCR, —NH₂, or —OR'.

They all contain acyl group (RCO-)

Nomenclature

The names of acid derivatives are taken in simple ways from either the common name or the IUPAC name of the corresponding carboxylic acid. For example:

Acyl compounds—carboxylic acids and their derivatives—typically undergo nucleophilic substitution in which —OH, —CI, —OOCR, —NH₂, or —OR' is replaced by some other basic group(Z)

$$R-C = -OH, -CI, -OOCR, -NH2, -OR'$$

ACID CHLORIDES

Acid chlorides are prepared from the corresponding acids by reaction with thionyl chloride ,PCl3,PCl5.

Mechanism with PC15

1- Conversion into acids Hydrolysis

Example:

$$\bigcirc$$
COCI + H₂O \longrightarrow \bigcirc COOH + HCI

Benzoyl chloride

Benzoic acid

2- Conversion into amides

$$RCOCI + 2NH_3 \longrightarrow RCONH_2 + NH_4CI$$
An amide

Mechanism

3- Conversion into esters

$$RCOCI + R'OH \longrightarrow RCOOR' + HCI$$
An ester

Example:

4. Formation of aldehydes by reduction.

5-formation of ketones, friedl-crafts acylation

Give the mechanism of the title reaction

6-formation of ketone with organocadmium compounds

$$R'MgX \xrightarrow{CdCl_2} R'_2Cd \longrightarrow R-C-R \text{ or } Ar-C-R' \xrightarrow{R' must be aryl or primary alkyl}$$

$$RCOCl \longrightarrow R-C-R \text{ or } Ar-C-R' \xrightarrow{R' must be aryl or primary alkyl}$$

$$RCOCl \longrightarrow R-C-R \text{ or } Ar-C-R' \xrightarrow{R' must be aryl or primary alkyl}$$

Preparation of acid anhydrides
$$CH_{3}COOH \xrightarrow{AIPO_{4} \atop 700^{\circ}} H_{2}O + CH_{2}=C=O \xrightarrow{CH_{3}COOH \atop Ketene} (CH_{3}CO)_{2}O \xrightarrow{Acetic anhydride}$$

$$H_{2}C \xrightarrow{OH} \xrightarrow{heat} H_{2}C \xrightarrow{C} OH \xrightarrow{H_{2}C} Water$$

$$Succinic anhydride$$

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Reactions of acid anhydrides

1-conversion into acid and acid derivatives

$$(RCO)_2O + HZ \longrightarrow RCOZ + RCOOH$$

(a) Conversion into acids. Hydrolysis

Example:

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$$

Acetic anhydride Acetic acid

(b) Conversion into amides. Ammonolysis

Examples:

$$(CH_3CO)_2O + 2NH_3 \longrightarrow CH_3CONH_2 + CH_3COO^-NH_4^+$$

Acetic anhydride Acetamide Ammonium acetate

(c) Conversion into esters. Alcoholysis

Examples:

Formation of ketones. Friedel-Crafts acylation.

$$(RCO)_2O + ArH \xrightarrow{AlCl_3} R-C-Ar + RCOOH$$

Lewis acid

O

A ketone

Phthalic anhydride

Preparation of amides

In the laboratory amides are prepared by the reaction of ammonia with acid chlorides or, when available, acid anhydrides In industry they are often made by heating the ammonium salts of carboxylic acids.

Reactions of amides Hydrolysis of amides

$$RCONH_2 + H_2O \longrightarrow RCOO + NH_3$$

Mechanism

Give the mechanism in alkaline medium

Hofmann degradation of amides

RCONH₂ or ArCONH₂
$$\xrightarrow{OBr^-}$$
 RNH₂ or ArNH₂ + CO₃⁻⁻
Amide 1° amine

Mechanism

Preparation of esters

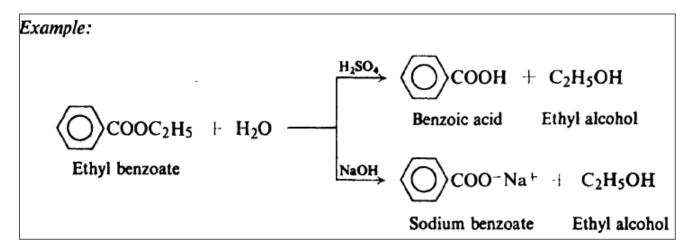
Esters are usually prepared by the reaction of alcohols or phenols with acids or acid derivatives.

From acid chlorides or anhydrides.

Write these mechanism

-reactions of esters

Conversion into acids and acid derivatives



Conversion into amides

$$RCOOR' + NH_3 \longrightarrow RCONH_2 + R'OH$$

$$Example:$$

$$CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$$

$$Ethyl acetate Acetamide Ethyl alcohol$$

Mechanism

Reaction with Grignard reagents.

mechanism

mechanism