

## 14.2 DERIVATIVES OF CARBOXYLIC ACIDS - CONTENTS

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### Learning outcomes

After the lesson, learners should be able to:

- Show the preparation of acid derivatives from carboxylic acids.
- Explain the comparative physical properties of acid derivatives.
- Explain the comparative chemical properties of acid derivatives (hydrolysis, ammonolysis, amines-RNH<sub>2</sub>), alcoholysis, and reduction only.
- Claisen condensation and Hofmann bromamide reaction.
- Describe the amphoteric nature of amide and relative reactivity of acid derivatives.

## Introduction

### 1. Acid Halides or Acyl Halides (R-COX)

These are the derivatives of carboxylic acids in which the -OH part of the carboxyl group is replaced by a halo- (-Cl, -Br or -I) group. The most reactive, most common and least expensive compounds among the acid halides are acid chlorides.

#### Nomenclature

The names of acid halides are derived from IUPAC or common names of the corresponding acids by replacing the suffix -ic acid with -yl halide. The secondary suffix for the acid chloride group is -**oyl chloride**. E.g.

| Formula                              | IUPAC names        | Common names       |
|--------------------------------------|--------------------|--------------------|
| HCOCl                                | Methanoyl chloride | Formyl chloride    |
| CH <sub>3</sub> COCl                 | Ethanoyl chloride  | Acetyl chloride    |
| CH <sub>3</sub> CH <sub>2</sub> COCl | Propanoyl chloride | Propionyl chloride |

### 2. Acid Amide or amide (-CONH<sub>2</sub>)

Acid amides can be regarded as derivatives of carboxylic acids in which the -OH part of the carboxylic group is replaced by the -NH<sub>2</sub> group.

#### Nomenclature

Acid amides are named by replacing the suffix -ic acid of the common name or -oic acid of the IUPAC name of the corresponding acid with the suffix 'amide'. Or the secondary suffix for the functional group amide is **-amide**. e.g.

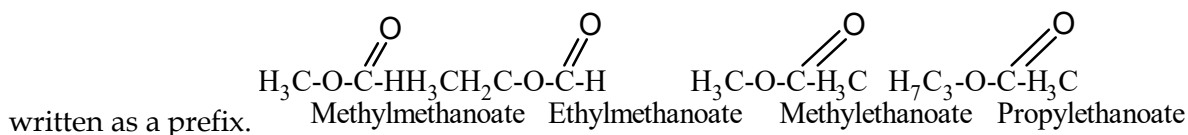
| Formula                                           | IUPAC names | Common names |
|---------------------------------------------------|-------------|--------------|
| HCONH <sub>2</sub>                                | Methanamide | Formamide    |
| CH <sub>3</sub> CONH <sub>2</sub>                 | Ethanamide  | Acetamide    |
| CH <sub>3</sub> CH <sub>2</sub> CONH <sub>2</sub> | Propanamide | Propionamide |

### 3. Ester (-COOR)

An ester is considered a derivative of a carboxylic acid whose -OH group is replaced by alkoxy group (-OR).

#### Nomenclature

While writing the IUPAC name of an ester secondary suffix **-oate** is used, and the alkyl group is

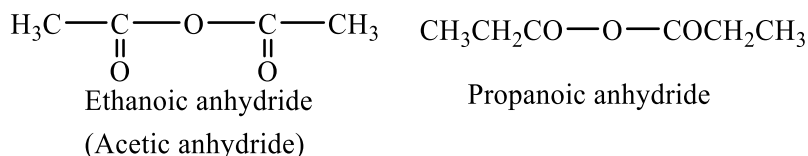


#### 4. Acid Anhydride ( -CO-O-CO- )

Acid anhydrides are considered to be derived from carboxylic acids formed by the removal of water from two molecules of the acid.

##### Nomenclature

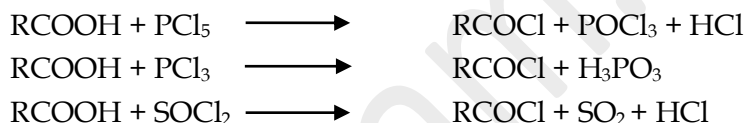
The acid anhydrides are named by replacing the suffix 'acid' of the IUPAC or common name of the carboxylic acids with 'anhydride'. Some examples are



### Preparation of derivatives from carboxylic acids

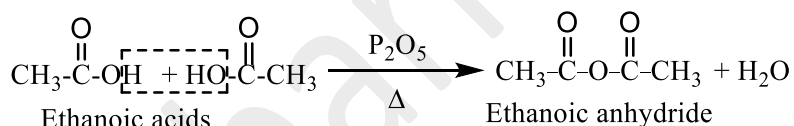
#### 1. Preparation of acid chloride (studied in carboxylic acids already)

Acyl chlorides can be prepared by the reaction of carboxylic acids with phosphorus pentachloride, phosphorus trichloride or thionyl chloride in the presence of pyridine.

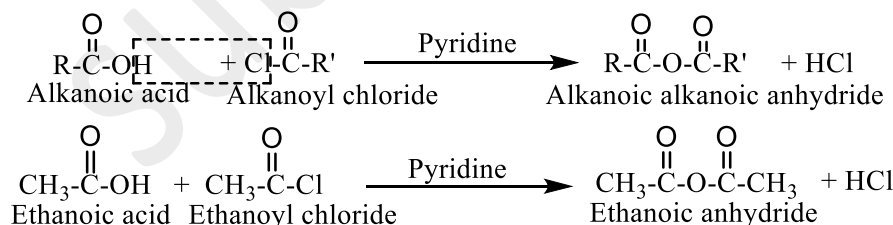


#### 2. Preparation of acid anhydride (studied in carboxylic acids already)

Acid anhydrides can be prepared by heating carboxylic acids in the presence of  $\text{P}_2\text{O}_5$ . e.g.

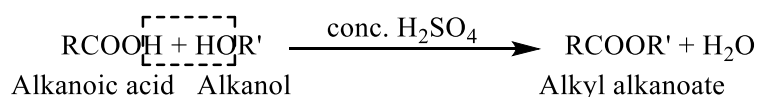


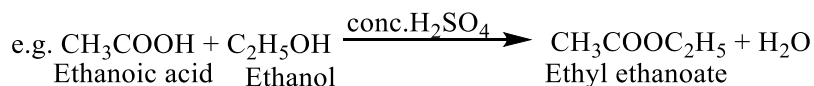
#### 3. By treatment of carboxylic acids with acid chlorides



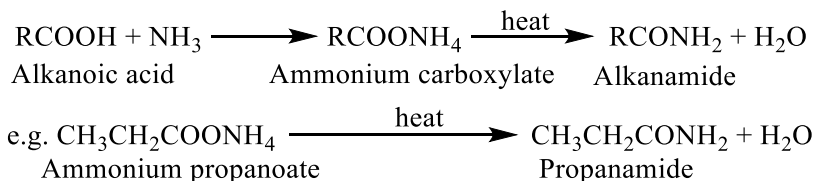
#### 4. Preparation of esters (studied in the [alcohols](#) chapter already)

Esters can be prepared by the reaction of carboxylic acids with alcohols in the presence of concentrated sulphuric acid. This is called the Esterification reaction.





## 5. Preparation of acid amide

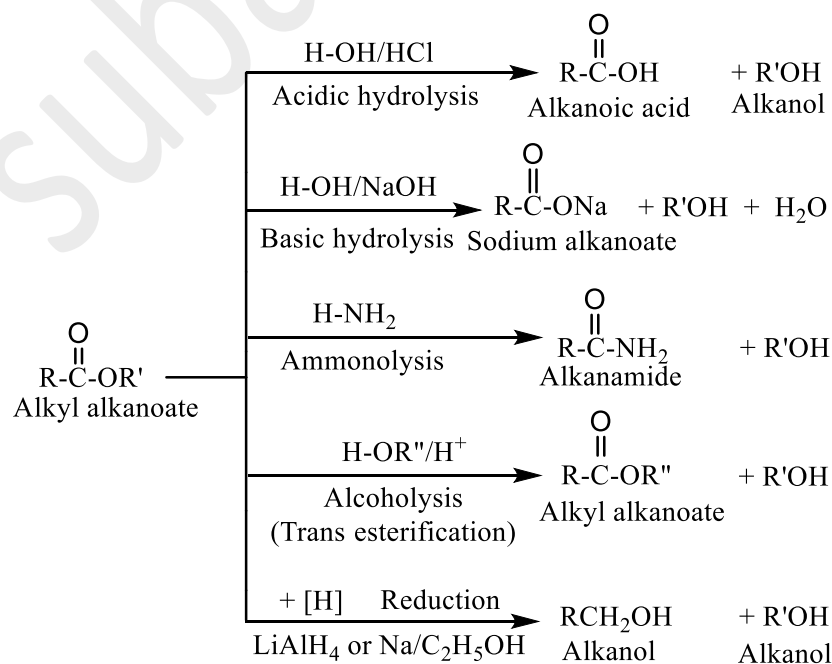
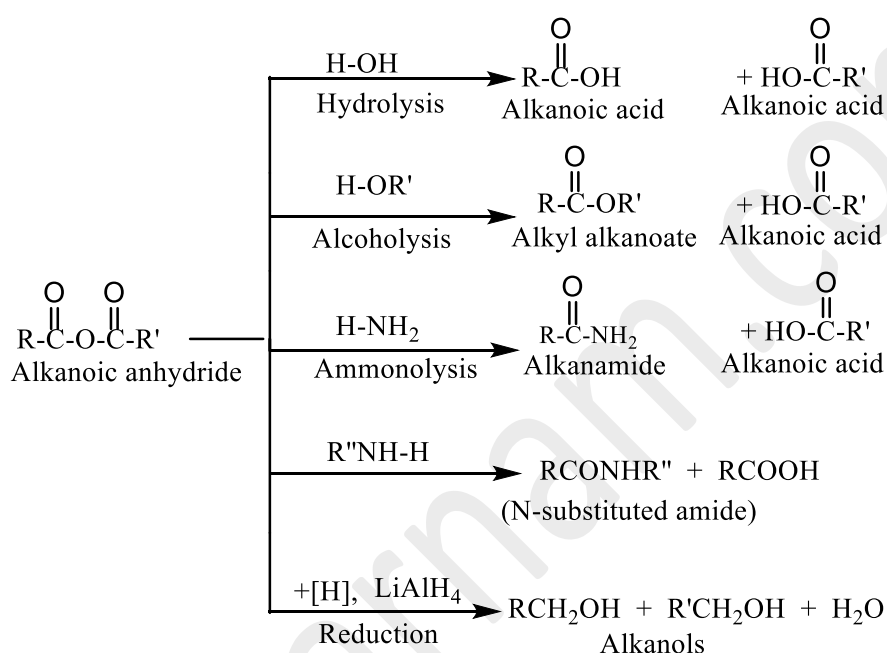
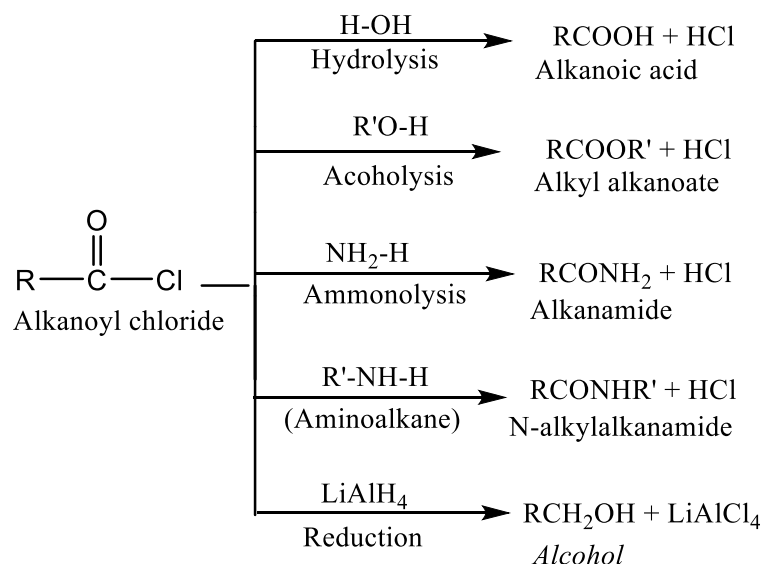


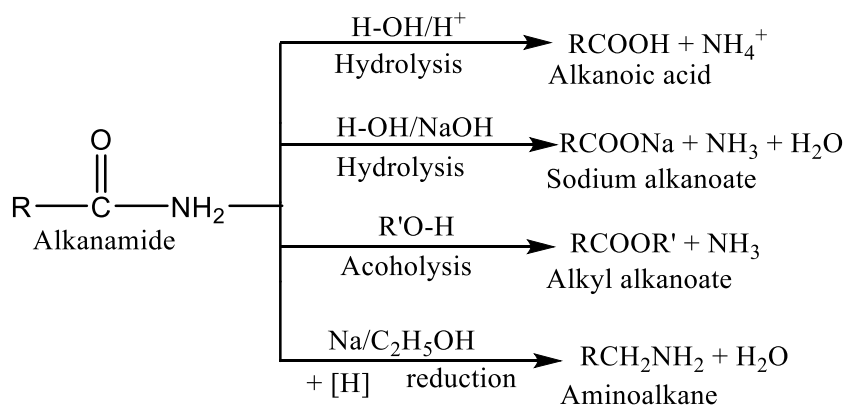
## Comparative physical properties of acid derivatives

|                 | State                                                                                                          | Boiling Point                                                                   | Solubility                                                                               |
|-----------------|----------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Acid chlorides  | Lower members - colourless liquids with pungent smell<br>Higher members - colourless solids                    | Less than that of parent acids due to absence of hydrogen bonding               | Soluble in organic solvents. Can't be used in water as they undergo hydrolysis.          |
| Acid anhydrides | Lower members - colourless liquids with pungent smell<br>Higher members - colourless solids                    | Higher than that of parent acid due to larger relative molecular mass.          | Soluble in organic solvents. Can't be used in water as they undergo hydrolysis.          |
| Esters          | Lower members - colourless liquids with pleasant fruity smell<br>Higher members - colourless, odourless solids | Lower than that of acid with comparable molecular wt. due to lack of H-bonding. | Soluble in organic solvents. Soluble in water as well.                                   |
| Amides          | First member- methanamide- liquid<br>All other colourless, odourless crystalline solids.                       | Higher than corresponding acid due to availability of 2 H atoms for H-bonding.  | Soluble in organic solvents. Lower members are soluble in water due to H-bond formation. |

## Comparative chemical properties of acid derivatives

Acid chlorides are the most reactive derivatives of carboxylic acids. These mainly give the following reactions.

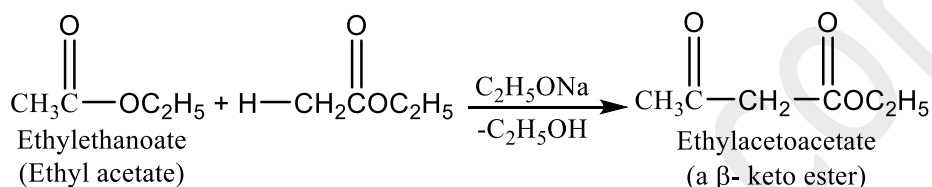




*Alcoholysis*

## Claisen condensation

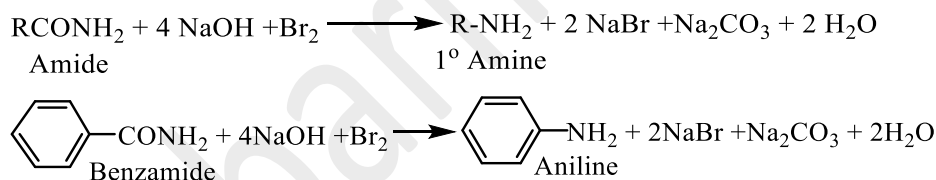
Esters containing an  $\alpha$ -hydrogen undergo self-condensation in the presence of a strong base such as sodium ethoxide to form  $\beta$ -keto esters; such a reaction is called Claisen condensation.



13) Write a chemical reaction for the Claisen condensation reaction. [1]

## Hofmann Bromamide degradation reaction

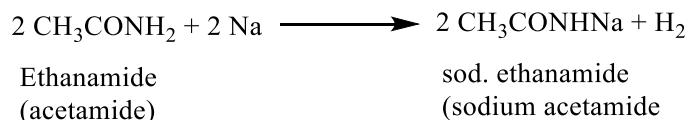
Amides react with bromine in the presence of alkali to form a primary amine carrying one carbon less than the parent amide. This is also called a degradation reaction.



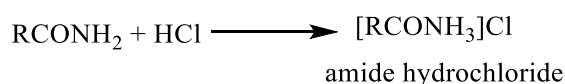
## Amphoteric nature of amide

Amides behave both as weak acids and weak bases, i.e., they are amphoteric in nature.

Amides react with reactive metals like Na, K, etc. to release hydrogen. Similarly, it also reacts with mercuric oxide, producing salt and water. These reactions show acidic nature.



Amides are Lewis bases as they have a lone pair of electrons on the N atom. But these are weaker bases than amines, as the electrons are delocalized due to resonance. These react with strong acids to form salts.



## Relative reactivity of acid derivatives

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The relative reactivity of acid derivatives is in the following order.

Acid chlorides > acid anhydrides > esters > amides

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