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# REVIEW IN CARBOXYLIC ACIDS AND ITS DERIVATIVES

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## ABSTRACT

Carboxylic acids are widespread in nature, often combined with other functional groups. Simple alkyl carboxylic acids, composed of four to ten carbon atoms, are liquids or low melting solids having very unpleasant odors. The fatty acids are important components of the bio molecules known as lipids, especially fats and oils. As shown in the following table, these long-chain carboxylic acids are usually referred to by their common names, which in most cases reflect their sources. They occur widely in nature and have many industrial and pharmaceutical applications like drugs

**KEYWORDS:** Carboxyl, Acid, Test, Acid Derivatives

## INTRODUCTION

Carboxylic acid is a class of organic compounds in which a carbon (C) atom is bonded to an oxygen (O) atom by a double bond and to a hydroxyl group (−OH) by a single bond. A fourth bond links the carbon atom to a hydrogen (H) atom or to some other univalent combining group. The carboxyl (COOH) group is so-named because of the carbonyl group (C=O) and hydroxyl group.

The IUPAC name of a carboxylic acid is derived from that of the longest carbon chain that contains the carboxyl group by dropping the final -e from the name of the parent alkane and adding the suffix -oic followed by the word "acid." The chain is numbered beginning with the carbon of the carboxyl group. Because the carboxyl carbon is understood to be carbon 1, there is no need to give it a number. For example, the compound CH3CH2COOH has three carbon atoms and is calledpropanoic acid, from propane, the name for a three-carbon chain, with -oic acid, the suffix for this class of compounds, appended.
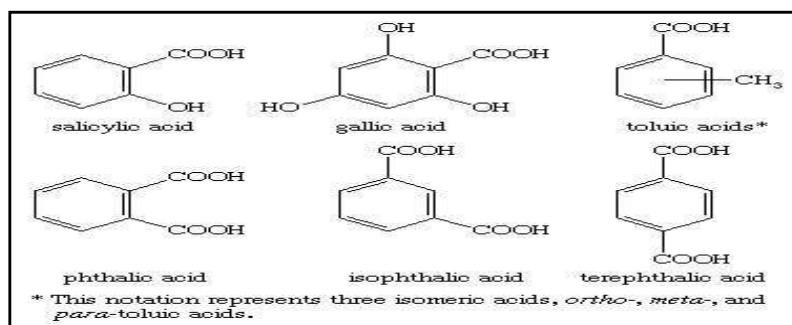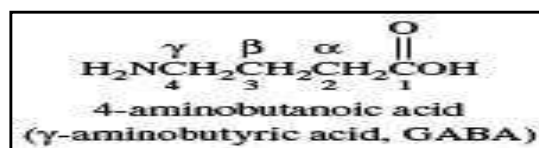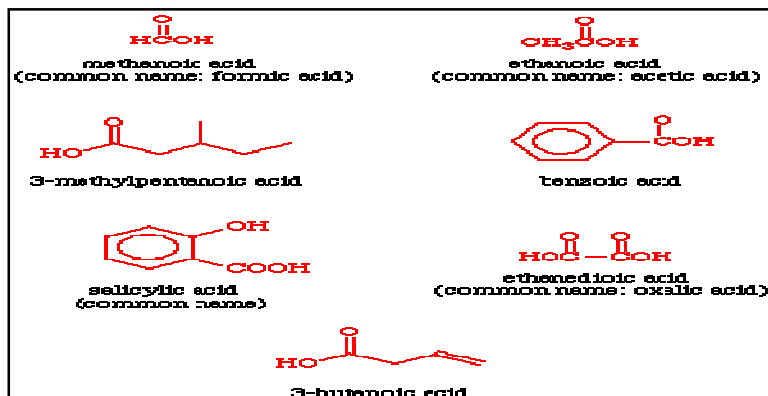
## Properties of Carboxylic Acids

The solubility of carboxylic acids in water is similar to that of alcohols, aldehydes, and ketones. Acids with fewer than about five carbons dissolve in water.

Carboxylic acids have much higher boiling points than hydrocarbons, alcohols, ethers, aldehydes, or ketones of similar molecular weight due to H- bonding.

## Acidity of Carboxylic Acidity (Inductive Effect)

In general, electron-withdrawing groups increase acidity by increasing the stability of the carboxylate ion. In contrast, electron-donating groups decrease acidity by destabilizing the carboxylate ion. For example, the methyl group, $-CH_3$, is generally regarded as electron-donating, and acetic acid, $CH_3 COOH$, is about 10 times weaker as an acid than formic acid, HCOOH. Similarly, chloroacetic acid, $ClCH_2 COOH$, in which the strongly electron-withdrawing chlorine replaces a hydrogen atom, is about 100 times stronger as an acid than acetic acid, and nitro acetic acid, $NO_2CH_2 COOH$, is even stronger. (The $NO_2$ group is a very strong electron-withdrawing group**.)**

## Preparation of Carboxylic Acids

There are many methods for preparation, like oxidation of Alkyl Chain, or oxidation of aldehyde, or oxidation of alcohols , or oxidation of alkene or alkyn
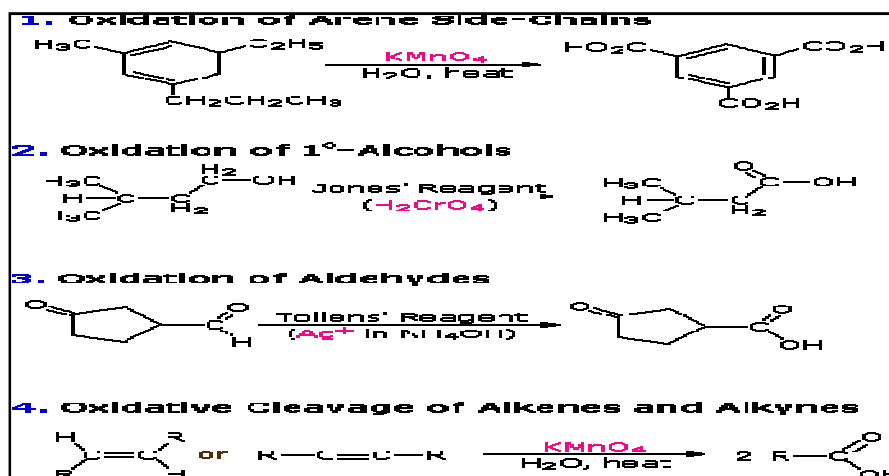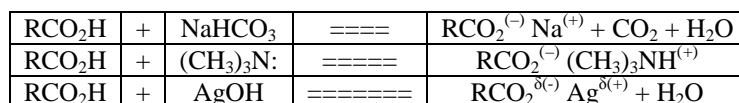


**And other Methods of Preparation:** By Hydrolysis of cyanide compounds or by gringard reagent
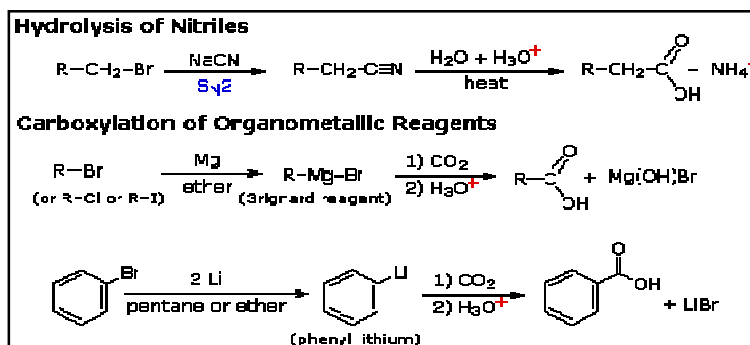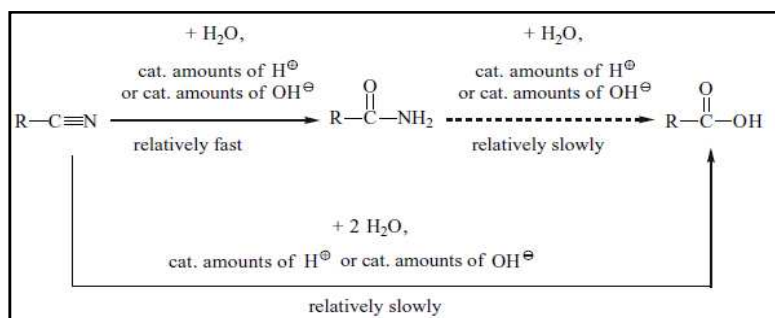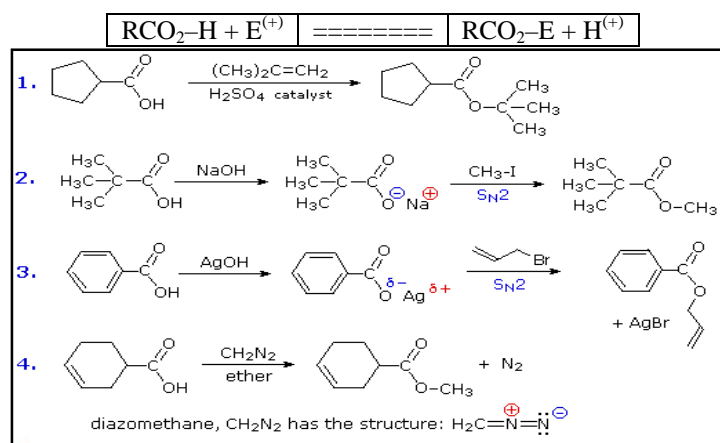
## Reactions of Carboxylic Acids

- **Carboxylic Salt Formation**

  Carboxylic acids react with bases to form ionic salts:

  | | | | |
  |---|---|---|---|
  | $RCO_2H$ | $+$ $NaHCO_3$ | $====$ | $RCO_2^{(-)} Na^{(+)} + CO_2 + H_2O$ |
  | $RCO_2H$ | $+$ $(CH_3)_3N:$ | $=====$ | $RCO_2^{(-)} (CH_3)_3NH^{(+)}$ |
  | $RCO_2H$ | $+$ $AgOH$ | $=======$ | $RCO_2^{\delta(-)} Ag^{\delta(+)} + H_2O$ |

- **Substitution of the Hydroxyl Hydrogen**

  Through electrophilic substitution at oxygen, If E is a strong electrophile:

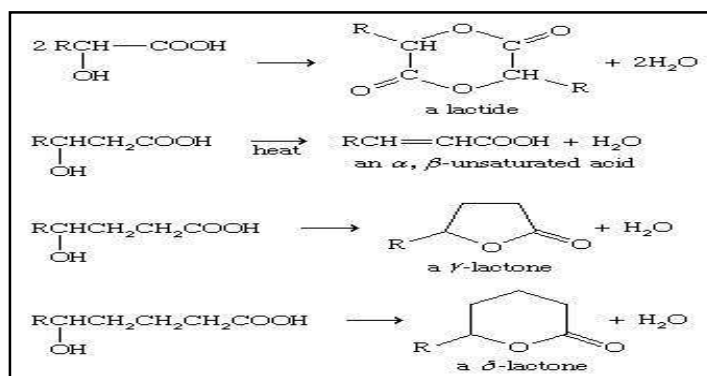  | $RCO_2-H + E^{(+)}$ | $========$ | $RCO_2-E + H^{(+)}$ |
  |---|---|---|



- **Substitution of the Hydroxyl Group**

       Reactions in which the hydroxyl group of a carboxylic acid is replaced by another nucleophilic group are important for preparing functional derivatives of carboxylic acids.
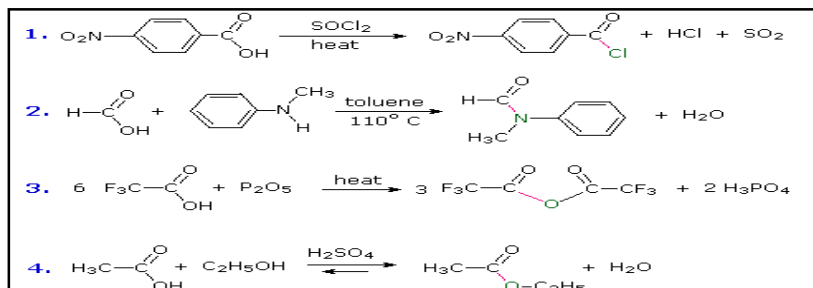
- **Ring Closure of Carboxylic Acid**

  Closing of carboxyl to formation lactone (cyclic ester)



**Identification Test of Carboxylic Acid**

- **Sodium Bicarbonate Test:**

  To a small portion of the organic compound taken in a test tube, a pinch of solid sodium bicarbonate is added. Evolution of carbon dioxide with brisk effervescence shows the presence of carboxylic acid. Alcohols do not give this test.
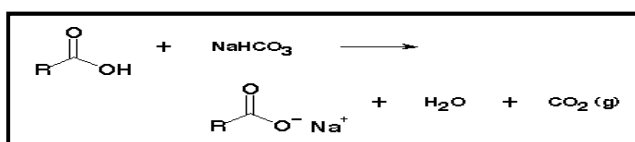


  A few drops or a few crystals of the unknown sample are dissolved in 1mL of methanol and slowly added to 1 mL of a saturated solution of sodium bicarbonate.

**Positive Test**

  Evolution of a carbon dioxide gas is a positive test for the presence of the carboxylic acid and certain phenols listed in the Complications section.

**Complications**

  Negatively substituted phenols such as nitro phenols, aldehyde , phenols, and poly halo phenols are sufficiently acidic to dissolve in 5% sodium bicarbonate.

- **Ester Test**

  In this test, the compound to be tested is warmed with small quantity of ethyl alcohol and 2-3 drops of concentrated sulphuric acid. The formation of sweet smelling vapours indicates the presences of some carboxylic acid. The
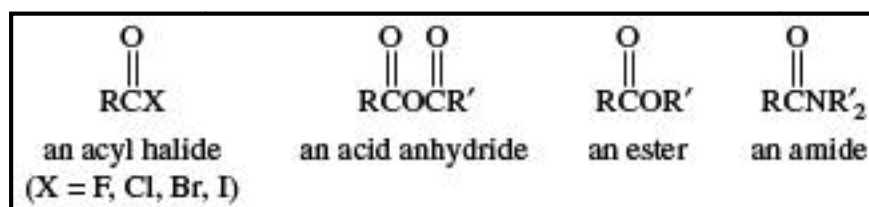
sweet smelling vapours are due to the formation of some ester by reaction between the acid and ethyl alcohol.

- **Litmus Test**

Carboxylic acids turn blue litmus red.

## Carboxylic Acid Derivatives

The most important of which are acyl halides, acid anhydrides, esters, and amides.





| class of compound | Z in R—C—Z (with =O) | add to root* prefix | add to root* suffix |
|---|---|---|---|
| Carboxylic acid | —OH | | -ic acid |
| Salt | —OM (metal) | metal | -ate |
| Acyl halide | —Cl, —Br, etc. | | -yl chloride (bromide, etc.) |
| Anhydride | —OCOR | | -ic anhydride |
| Carboxylic ester | —OR', OAr | alkyl, aryl | -ate |
| Amide | —NH₂ | | -amide |
| Amide | —NHR' | N-alkyl | -amide |
| Amide | —NR'₂ | N,N-dialkyl | -amide |
| Hydrazide | —NHNH₂ | | -hydrazide |
| Hydroxamic acid | —NHOH | | -ohydroxamic acid |
| Azide | —N₃ | | -yl azide |
| Peroxy acid | —OOH | per- or peroxy- | -ic acid |
| Nitrile | R—C≡N | | -onitrile |
| Amidine | R—C—NH₂ (with =NH) | | -amidine |
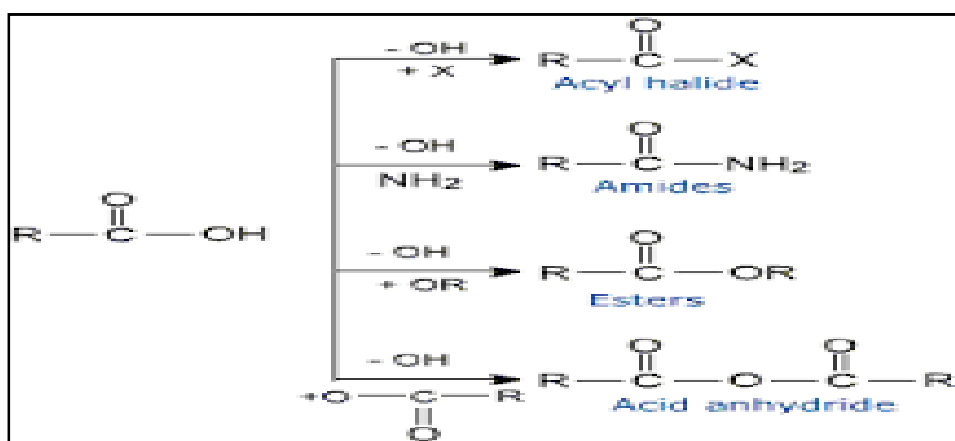


## Acyl Halide

The general formula for such an acyl halide can be written RCOX, where R may be, for example, an alkyl group, CO is the carbonyl group, and X represents the halide, such as chloride. Acyl chlorides are the most commonly encountered acyl halides
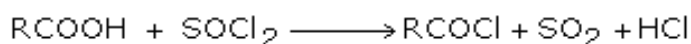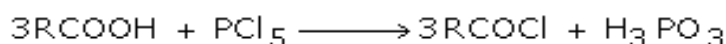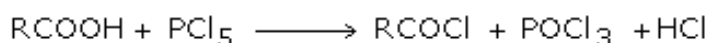
**Physical Properties of Acyl Halides:**

Acyl halides do not dissolve in water because they react (often violently) with it to produce carboxylic acids and hydrogen halides (e.g. HCl). it does not form hydrogen bonds. Its boiling point is therefore higher than analkane of similar size (which has no permanent dipoles) such as ethane., The most commonly performed reaction with acyl halides and the example reaction is known as nucleophilic acyl substitution**.**
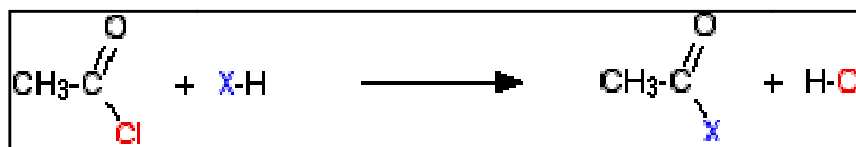


**Preparation of Acyl Halide**

The hydroxyl group of carboxylic acid like that of alcohols are easily replaced by chlorine atom on heating with $PCl_5$, $PCl_3$ or $SOCl_2$.

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$3RCOOH + PCl_5 \longrightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

Of the three, thionyl chloride is preferred because the other products are gaseous and excess from the reaction mixture, which makes the purification of the acyl chloride easier. Aqueous halogen acids are not used with carboxylic acids because the acyl chloride is easily hydrolyzed by water.
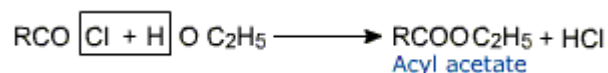
**Reactions of Acyl Halide**

- The reaction involving cleavage of a bond of amine compounds and formation other compounds like **amide**.
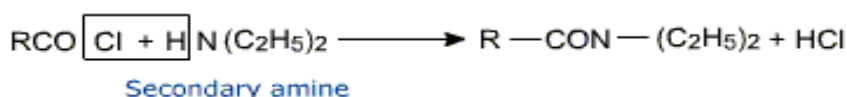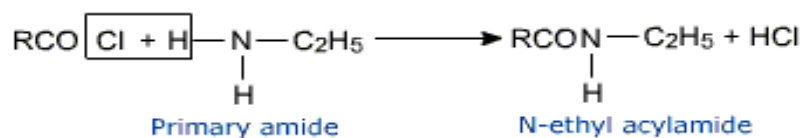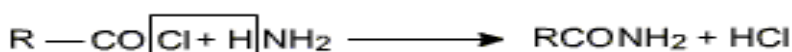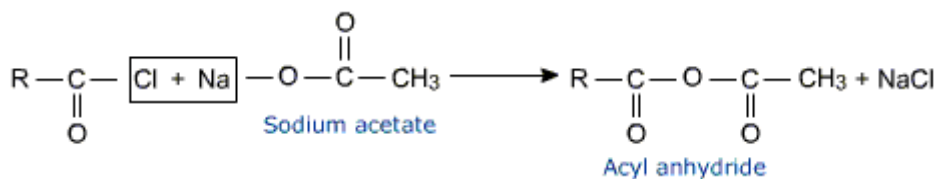


Tertiary amines do not react with acyl chlorides.

- Acyl chlorides react with alcohols and phenols to give esters.



- Acyl chlorides react with salts of carboxylic to form **anhydrides**.

**Note :** Aliphatic acyl chloride are very reactive acylating agents. Aromatic acyl chlorides like benzoyl chloride are less reactive.

- Acid chlorides acylate aromatic hydrocarbons in the presence of anhydrous in the presence of anhydrous aluminium chloride to yield aromatic **ketones**. This is called Friedel - Craft's acylation reaction.
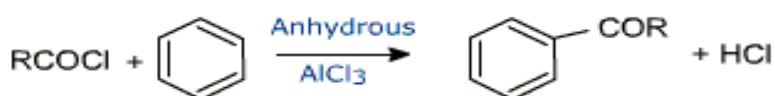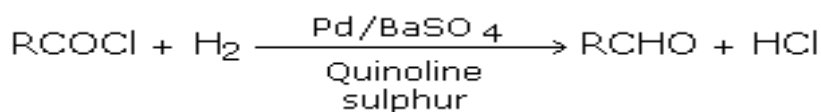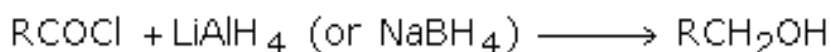


This is a good method for preparation of aromatic ketones. This reaction however fails when electron withdrawing group is present on the aromatic ring.
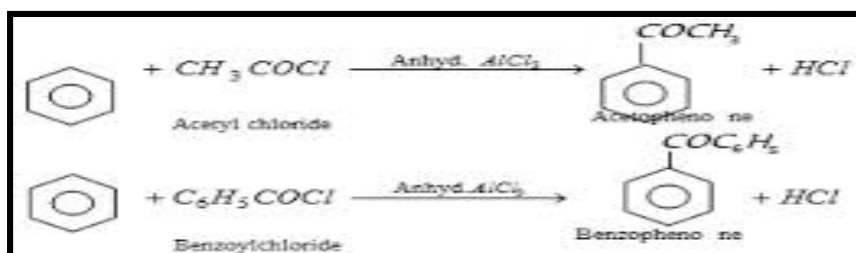


- Reduction of Acyl halides

  Acyl halides are reduced to primary alcohols with LiAlH$_4$ and NaBH$_4$.



**Acetyl Chloride Test**

**Identification Test of Acyl Halide**

By silver nitrate This reagent is useful for classifying compounds known to contain halogen. Add 1 drop or a couple of crystals of the unknown to 2 mL of the 2% ethanolic silver nitrate solution. If no reaction is observed after 5 min standing at room temperature, heat the solution to boiling and note if a precipitate is formed. If there is a precipitate, note its color. Add 2 drops of 5% nitric acid, and note if the precipitate dissolves. Silver halides are insoluble in dilute nitric acid; silver salts of organic acids are soluble. Positive Test alkyl halide - Production of solid silver halide salt is a positive test. acyl halide - Production of solid silver carboxylate salt is a positive test. This solid should re dissolve in dilute nitric acid.

**Alkyl Halide**

$$RX + AgNO_3 \longrightarrow AgX(s) + RONO_2$$

**Acyl Halide**
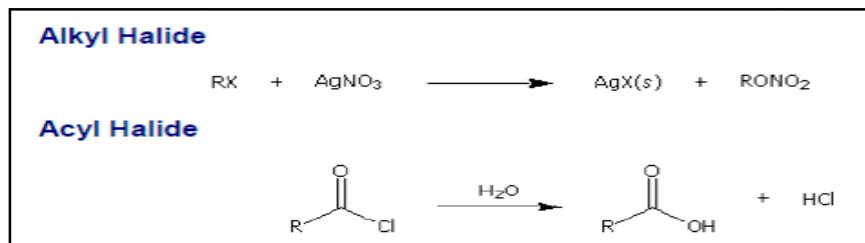


In hood: Add drop by drop 0.2 mL of acetyl chloride to 0.2 mL or 0.2 g of the unknown. Allow the mixture to stand for a minute or two and then pour it cautiously into 1 mL of water. Positive Test Evolution of heat and HCl gas or a precipitate is a positive test. Alcohols and phenols produce esters indicated by the formation of a top layer in the flask. Primary and secondary amines form amides which precipitate. Complications Moisture present in the unknown will give positive test.
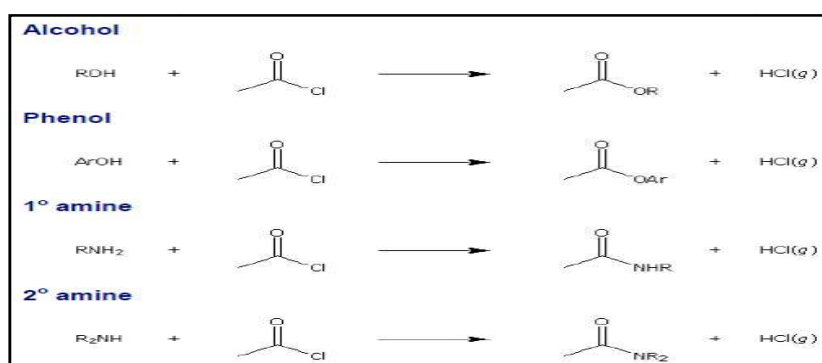


**Anhydrides**

Acid anhydrides are called symmetrical when the two acyl groups are identical when the two acyl groups are identical and if the two acyl groups are different it is said to be unsymmetrical.

Symmetrical anhydrides of unsubstituted carboxylic acids are derived from the names of the carboxylic acids by replacing the word acid with anhydride.



Common name: Acetic anhydride
IUPAC name: Ethanoic anhydride

Symmetrical anhydrides of substituted carboxylic acids are named by adding the prefix bis to the name to indicate that two identical acyl groups are present.



Common name - bis (Chloro acetic anhydride)
IUPAC name - bis (Chloro ethanoic anhydride)
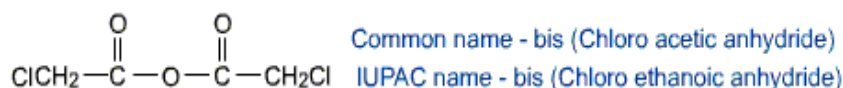
Unsymmetrical anhydrides are named by writing the names of the two acids alphabetically before the word anhydride.



Common name: Acetic benzoic anhydride
IUPAC name: Benzoic ethanoic anhydride

$$CH_3 \overset{O}{\overset{||}{C}} O \overset{O}{\overset{||}{C}} CH_3$$

**A c e t i c  a n h y d r i d e**

**B e n z o i c  a n h y d r i d e**

Succinic anhydride          M aleic anhydride          Phthalic anhydride
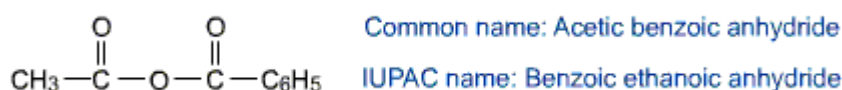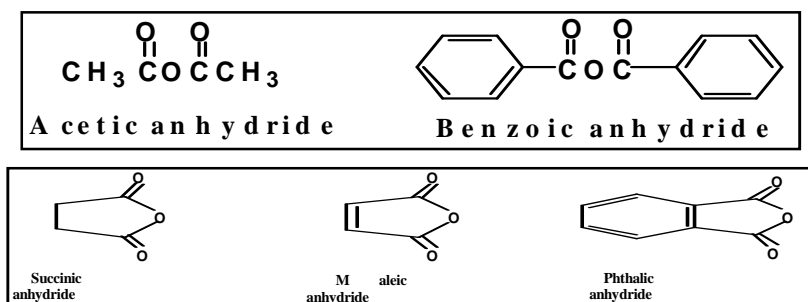
## Preparation of Anhydride

Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from two molecules of acid. So acid anhydrides can be prepared by heating carboxylic acid in the presence of $P_2O_5$ in dehydrating agent.
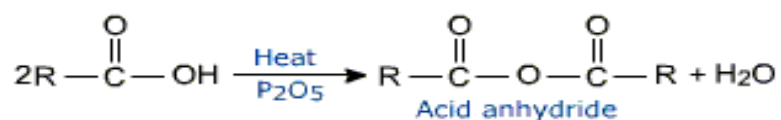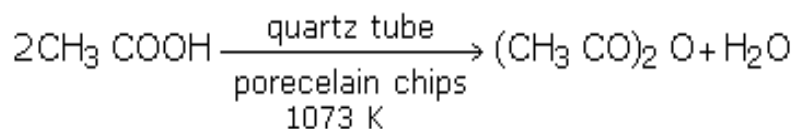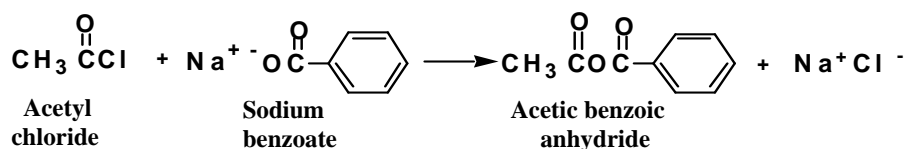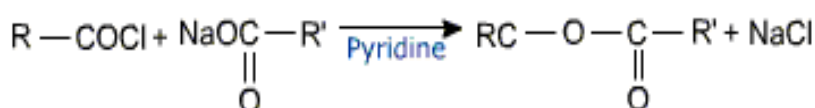
$$2R-\overset{O}{\overset{||}{C}}-OH \xrightarrow[P_2O_5]{Heat} R-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-R + H_2O$$

Acid anhydride

Industrially, acetic anhydride is prepared by heating acetic acid to 1073 K.

$$2CH_3 COOH \xrightarrow[\substack{porecelain\ chips \\ 1073\ K}]{quartz\ tube} (CH_3 CO)_2 O + H_2O$$

Acetic anhydride is a dehydrating agent

Symmetrical anhydrides are prepared from acids using a dehydrating agent like $P_2O_5$.

Asymmetrical and symmetrical anhydrides can be prepared by the reaction of acyl chlorides with sodium salts of carboxylic acids in the presence of pyridine.

$$R-COCl + NaO\overset{}{\underset{||}{\underset{O}{C}}}-R' \xrightarrow{Pyridine} RC-O-\overset{}{\underset{||}{\underset{O}{C}}}-R' + NaCl$$

$$CH_3 \overset{O}{\overset{||}{C}}Cl + Na^+ \ ^-O\overset{O}{\overset{||}{C}}\text{—}\bigcirc \longrightarrow CH_3 \overset{O}{\overset{||}{C}}O\overset{O}{\overset{||}{C}}\text{—}\bigcirc + Na^+Cl^-$$

**Acetyl chloride**          **Sodium benzoate**          **Acetic benzoic anhydride**

## Reactions of Anhydride

- They form esters with alcohols and phenols.

$$R-\overset{}{\underset{||}{\underset{O}{C}}}-O-\overset{}{\underset{||}{\underset{O}{C}}}-R \xrightarrow{R'OH} RCOOR' + RCOOH$$
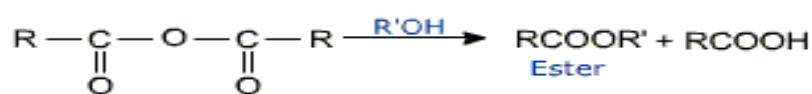
Ester

- They form amides with ammonia and amines.

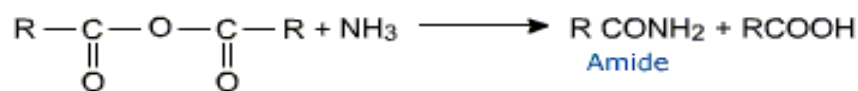$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R + R'NH_2 \longrightarrow RCONHR' + RCOOH$$
Substituted
amide

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R + NH_3 \longrightarrow R\,CONH_2 + RCOOH$$
Amide

- Friedel Craft's acylation reaction

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COR' + RCOOH$$
Ketone

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow[\underset{\text{Reduction}}{\text{(ii) }H_3O^+}]{\text{(i) LiAlH}_4} RCH_2OH$$
Alcohol
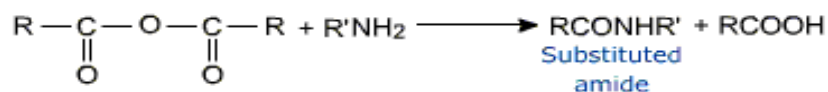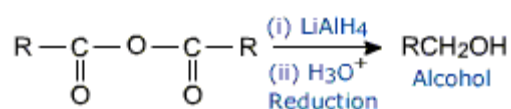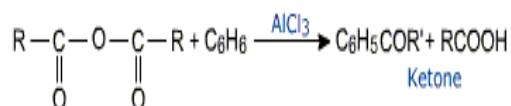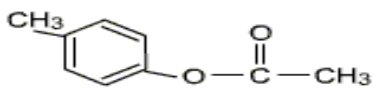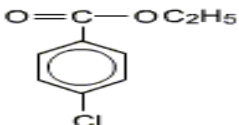
Anhydrides are on the whole less reactive than acyl chlorides.

**Esters**

RCOOR' are named after the corresponding carboxylic acids by replacing the ending -ic acid with -ate and preceding this with the name of the alkyl or aryl group attached to the oxygen atom.
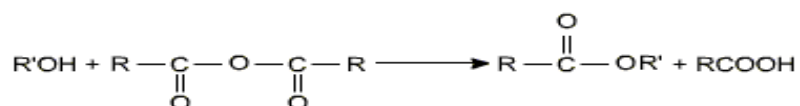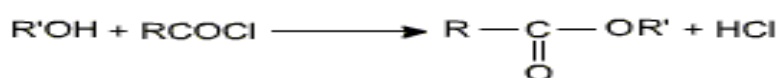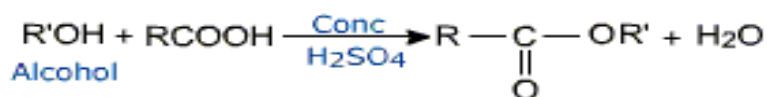
|  | Common name | IUPAC name |
|---|---|---|
| $H-\underset{\underset{O}{\|}}{C}-OC_2H_5$ | Ethyl formate | Ethyl methanoate |
| $CH_3-\underset{\underset{O}{\|}}{C}-OC_6H_5$ | Phenyl acetate | Phenyl ethanoate |

|  | Common name | IUPAC name |
|---|---|---|
| $CH_3-C_6H_4-O-\underset{\underset{O}{\|}}{C}-CH_3$ | P-tolyl acetate | 4-methyl phenyl ethanoate |
| $O=C-OC_2H_5$ (C_6H_4Cl) | - | Ethyl 4-chloro benzoate |

**Preparation of Ester**

Esters are prepared by the acylation of alcohols or phenols.

$$R'OH + RCOOH \xrightarrow{\underset{H_2SO_4}{Conc}} R-\underset{\underset{O}{\|}}{C}-OR' + H_2O$$
Alcohol

$$R'OH + RCOCl \longrightarrow R-\underset{\underset{O}{\|}}{C}-OR' + HCl$$

$$R'OH + R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-\underset{\underset{O}{\|}}{C}-OR' + RCOOH$$

The formation of esters is known as esterification.

Esterification of carboxylic acids with alcohols requires a mineral acid such as concentrated $H_2SO_4$ or HCl gas a catalyst.

(Fischer Esterification)

$$RCOOH + R'OH \rightleftharpoons \xrightarrow{H^+} RCOOR' + H_2O$$
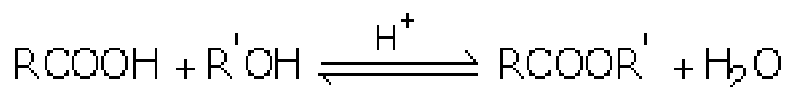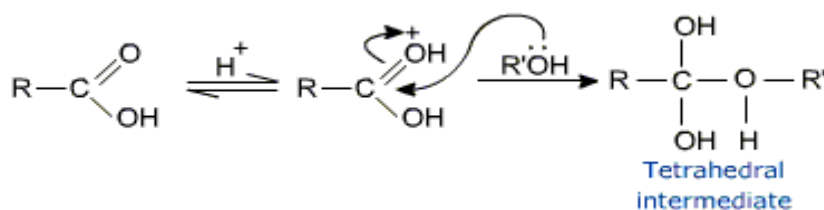
## Mechanism of Esterification of Carboxylic Acids

The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution.

The first step is the protonation of the carbonyl oxygen, which activates the carbonyl group towards nucleophilic addition of the alcohol.



Tetrahedral intermediate

The tetrahedral intermediate, which is formed transfers a proton converting the hydroxyl group into $-\overset{+}{O}H_2$ group. This species $-\overset{+}{O}H_2$ is a better leaving group and is eliminated at a neutral water molecule.



Proneted ester
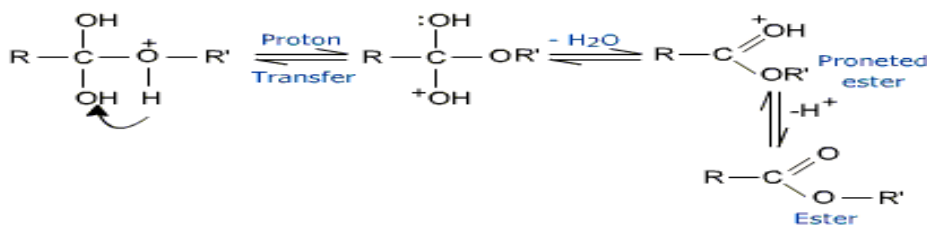
Ester

The protonated ester finally losses a proton to give the ester.

The above mechanism is supported by the using isotopically labeled methanol ($CH_3O^{18}H$) with acetic acid to give methyl acetate (having labeled oxygen) and water not containing any isotopic oxygen.
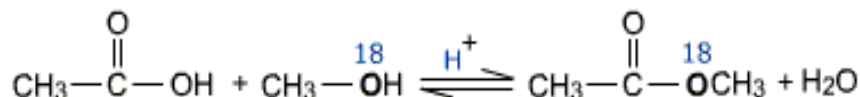


Esters of phenols are prepared by reversible acylation of phenols with acyl chloride or anhydrides rather than the reaction with carboxylic acid in which all the steps are reversible.

## Reactions of Esters

Esters undergo typical nucleophilic acyl substitution reactions but are less reactive than acyl chlorides and anhydrides.

- **Hydrolysis:**

Esters hydrolyzed by boiling water slowly to carboxylic acids and phenols. The hydrolysis is accelerated in the presence of mineral acid on alkali.
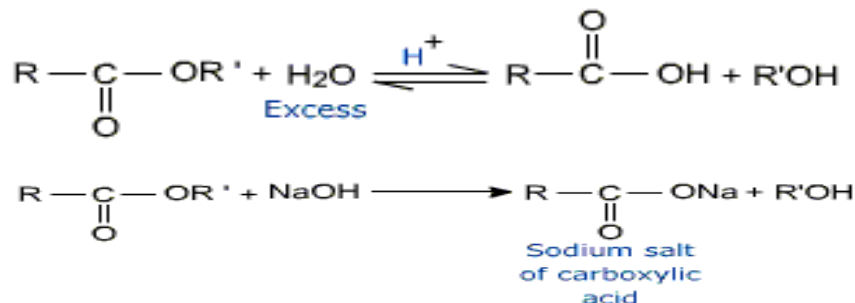


The alkaline hydrolysis is known as saponification. This is because esters with high molecular mass ($C_{12}$ - $C_{17}$) give soap on hydrolysis with a base. Soap on hydrolysis with a base. Soaps are sodium or potassium salts of Carboxylic acids with high molecular mass ($C_{12}$ - $C_{17}$). The carboxylic acid is obtained by acidification of the salt with mineral acid ($H_2SO_4$ or HCl).



- **Alcoholysis**

Esters react with alcohols in the presence of an acid catalyst to undergo exchange of alcohol resides i.e., alkoxy parts. The equilibrium mixture consists of the reactants and a new ester and a new alcohol. The reaction involves nucleophilic acyl substitution of the alkoxy group of the ester with the alkoxy group of the alcohol and is known as trans esterification.
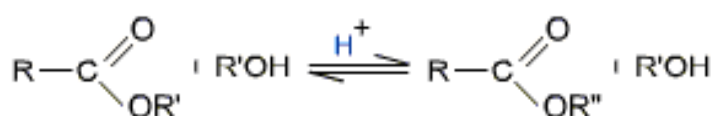


- **Esters React with Ammonia and Amines to Form Amides**
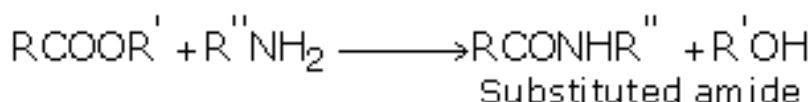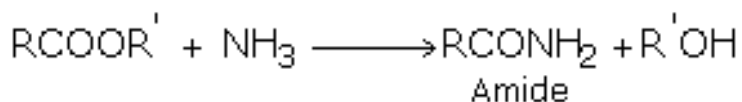


- **Reactions of Esters with Grignard's Reagent gives Tertiary Alcohols:**

First a ketone is formed which reacts further with Grignard reagent to give the tertiary alcohol.

- **The Acyl Group of the Ester is Reduced with LiAlH$_4$ (but not with NaBH$_4$) to a Primary Alcohol**



Catalytic hydrogenation of esters to alcohols is not easy unlike that of aldehydes and ketones. The reaction requires high temperature and pressure. The catalyst used is a mixture of oxides known as copper chromite. The alkoxy part of the ester gives the corresponding alcohol as by product.
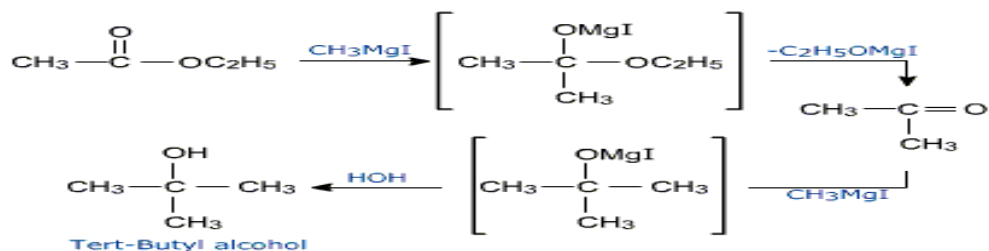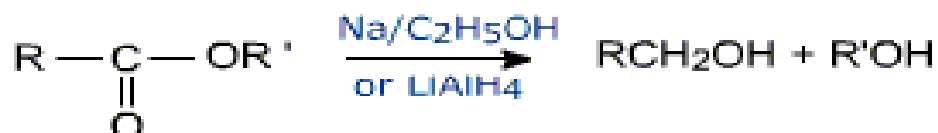
**Amides**

Acid amides may be regarded as the derivatives of carboxylic acids in which -OH part of the carboxylic group is replaced by the -NH$_2$ group.

Esters are derivatives of the carboxylic acids in which the -OH part of the carboxylic group has been replaced by -OR group where R may be alkyl or aryl group.

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

RCONH$_2$ are named in the trivial system by replacing the ending -ic acid from the name of the corresponding acid with - amide. The IUPAC names are derived by replacing the ending -oic acid with -amide or carboxylic acid with carboxamide. The position of the substituent at the nitrogen atom, if any, is indicated by the letter N.

**Examples**

|  | Common name | IUPAC name |
|---|---|---|
| H—C(=O)—NH$_2$ | Form amide | Methan amide |
| CH$_3$—C(=O)—N(CH$_3$)$_2$ | - | N,N-dimethyl acetamide |
| CH$_3$—CONH—CH$_3$ | - | N methyl ethanamide |

Amides are classified as primary, secondary and tertiary amides depending on whether none, one or two alkyl or aryl groups at attached to the nitrogen atom

RCONH$_2$ - Primary

RCONHR' - Secondary

RCONR'R'' – Tertiary



$$CH_3\overset{O}{\overset{\|}{C}}NH_2$$

**Acetamide**
**(a 1° amide)**

$$CH_3\overset{O}{\overset{\|}{C}}-N\overset{H}{\underset{CH_3}{\diagup}}$$

**N-Methylacetamide**
**(a 2° amide)**

$$H-\overset{O}{\overset{\|}{C}}-N\overset{CH_3}{\underset{CH_3}{\diagup}}$$

**N,N-Dimethyl-**
**formamide (DMF)**
**(a 3° amide)**

**Succinimide**

**Phthalimide**
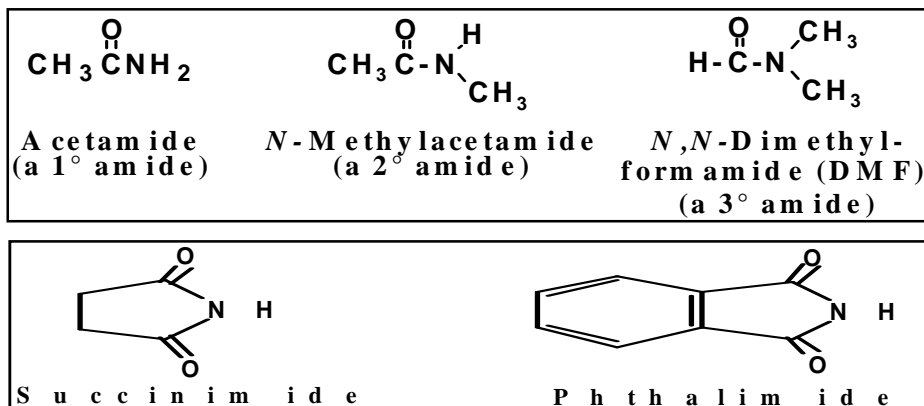
## Preparation of Amides

Amides are generally prepared by the reaction of acyl chlorides or anhydrides with ammonia or amines.

$$RCOCl + NH_3 \longrightarrow RCONH_2 + HCl$$
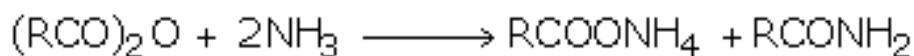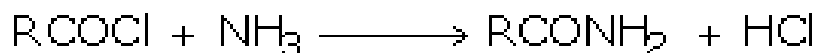
$$(RCO)_2O + 2NH_3 \longrightarrow RCOONH_4 + RCONH_2$$

Carboxylic amines give ammonium carboxylates, which need to heated to high temperatures gives amides. Thus this method is not useful for laboratory preparation of amides. It is however used in the industrial preparation of amides.

$$RCOOH + NH_3 \longrightarrow RCOO^- \ NH_4^+ \xrightarrow{\text{heat}} RCONH_2 + H_2O$$

## Reactions of Amides

- **Amphoteric Character**

Amides are feeble bases. The lone pair of electrons on the nitrogen atom is responsible for the basic character. This lone pair of electrons on nitrogen atom is involved in resonance with the carbonyl group (structure II). Thus the electron pair of nitrogen is not easily available for protonation. Consequently the basic character is considerably decreased.
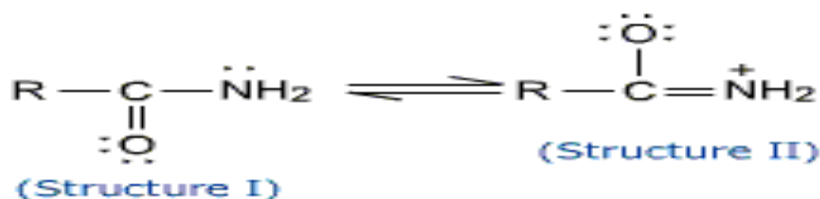


The basic character of the amide is illustrated in the following reaction with hydrochloric acid (an acid) to form a salt.

$$RCONH_2 + HCl \longrightarrow RCONH_2 \cdot HCl$$
$$\text{(Base)} \quad \text{(acid)} \qquad \text{Salt}$$
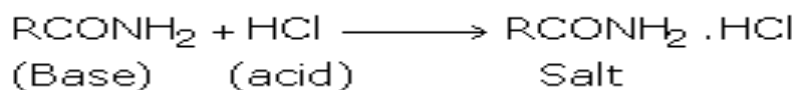
However, under suitable conditions, amides can also exhibit feeble acidic character. The amide (acting in the capacity of a acid) reacts with mercuric oxide (a base) to form mercury salt and water.

$$R\,CONH_2 + HgO \longrightarrow (R\,CONH)_2\,Hg + H_2O$$
$$\text{(acid)} \quad \text{Mercuric} \qquad \qquad \text{Salt} \qquad \text{Water}$$
$$\text{oxide}$$
$$\text{(base)}$$
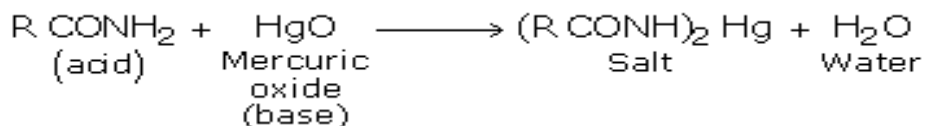
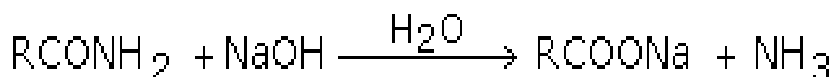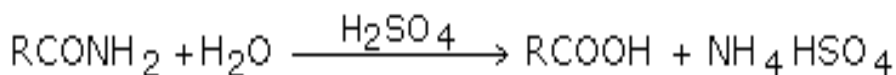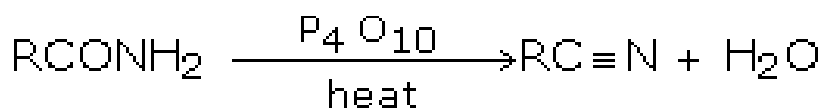Thus amides are said to be amphoteric in nature as they exhibit both acidic and basic character.

- **Amides are Hydrolyzed**: by aqueous solutions of mineral acids or alkalis to give carboxylic acids.

$$RCONH_2 + H_2O \xrightarrow{\ H_2SO_4\ } RCOOH + NH_4HSO_4$$

$$RCONH_2 + NaOH \xrightarrow{\ H_2O\ } RCOONa + NH_3$$

- **Primary Amides Get Dehydrated**: with phosphorous pentoxide to give nitriles.

$$RCONH_2 \xrightarrow[\text{heat}]{\ P_4O_{10}\ } RC\equiv N + H_2O$$

- **On Treatment with Nitrous Acid**: primary amides give carboxylic acid and nitrogen gas. The volume of nitrogen can be measured to determine the amide quantitatively.

$$RCONH_2 + HNO_2 \longrightarrow RCOOH + N_2 + H_2O$$
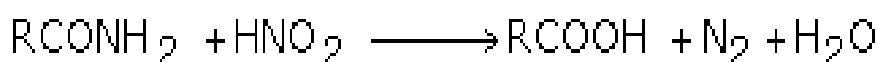
- **When Primary Amides are Treated with Bromine**: in the presence of an alkali, a primary amine containing one carbon less than the amide is formed.

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$
$$\text{primary amine}$$
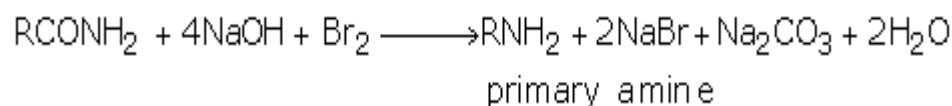
The reaction involves molecular management in which alkyl or aryl group migrates from the acyl carbon to nitrogen. This reaction is known as Hofmann Bromamide reaction and is useful for descending of series i.e., preparing a lower homologue from a higher one.

- **Amides are Reduced to Amines with LiAlH₄.**

$$RCONH_2 \xrightarrow[\text{(ii)}H_3O^+]{\text{(i) LiAlH}_4} RCH_2NH_2$$
$$\text{Amine}$$
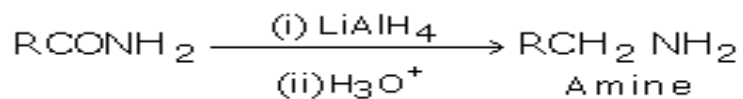
**Identification Test of Acid Derivatives**

Preliminary Test: Dissolve a drop or a few crystals of the compound to be tested in 1 mL of 95% ethanol and add 1 mL of 1 M hydrochloric acid. Note the color produced when 1 drop of 5% ferric chloride solution is added to the solution. If a definite orange, red, blue, or viole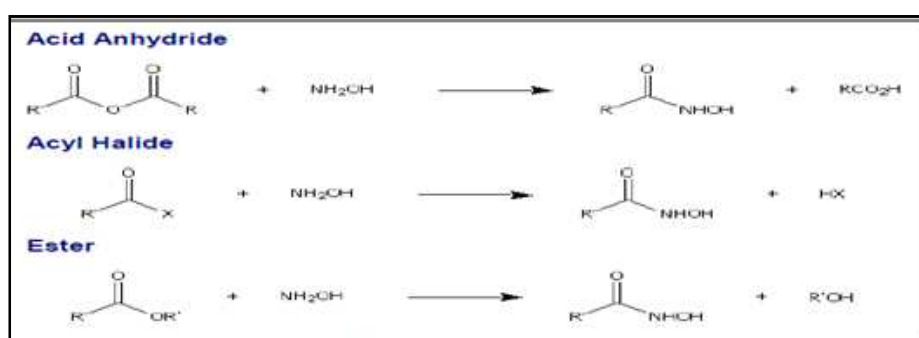t color is produced, the following test for the acyl group is not applicable and should be omitted. Too much hydrochloric acid prevents the development of colored complexes of many phenols and all enols.



Heat to boiling a mixture of 1 drop or about 40 mg of the compound, 1 mL of 0.5 M hydroxylamine hydrochloride in 95% ethanol, and 0.2 mL of 6 M sodium hydroxide. After the solution has cooled slightly, cautiously add 2 mL of 1 M hydrochloric acid. Anhydrides, acyl halides, and esters would have undergone the reaction with the hydroxylamine to form the hydroxamic acid, as indicated in the above equations. If the solution is cloudy, add 2 mL of 95% ethanol. Observe the color produced when one drop of 5% ferric chloride solution is added. If the color caused by the drop of ferric chloride solution does not persist, continue to add the ferric chloride solution drop wise until the observed color permeates the entire test solution. Compare the color with that produced in the preliminary test. Positive Test A distinct burgundy or magenta color of the ferric hydroxamate complex is a positive test. Compare the color of this solution with the yellow observed when the original compound is tested with ferric chloride in the presence of acid to assure the color is due to the formation of ferric hydroxamate complex. Complications Some acids will give a positive test. Primary and secondary nitro compounds, imides, some amides, most nitriles, -hydrogens give a positive test.$\alpha$and aldehydes (with no)

# CONCLUSIONS

**Structure of Functional Group in Carboxylic Acid Derivatives**

The structure of the functional groups in acyl halide, acid anhydride, ester and amide are similar to that of the carboxyl group. Due to the presence of lone pairs of electrons at the halogen, oxygen and nitrogen atoms, resonance is possible in these derivatives just like that in carboxylic acids.

$$[L = X \text{ (halogen)}, \text{O-COR}^{\cdot}, \text{OR}^{\cdot}, NH_2]$$
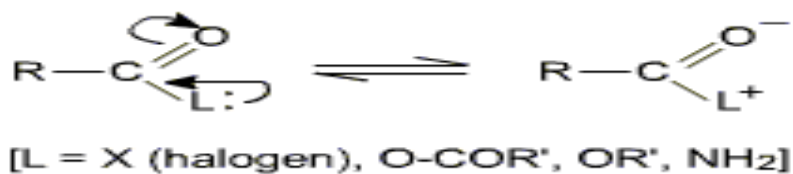
The nature of the L group determines the relative electrophilic nature of the carbonyl carbon and thus the relative reactivity of the acyl derivatives.

All acid derivatives are polar molecules.

**Physical Properties**

Being polar in nature, the acid derivatives have higher boiling points than hydrocarbons of comparable molecular masses.

Acid chlorides, anhydrides and esters have nearly the same boiling points as the aldehydes and ketones of comparable molecular masses. Their boiling points are lower than that of carboxylic acids of comparable molecular masses, due to the absence of hydrogen bonding in acid derivatives.

Primary amides have quite high melting points and boiling points because they form strong intermolecular hydrogen bonds.
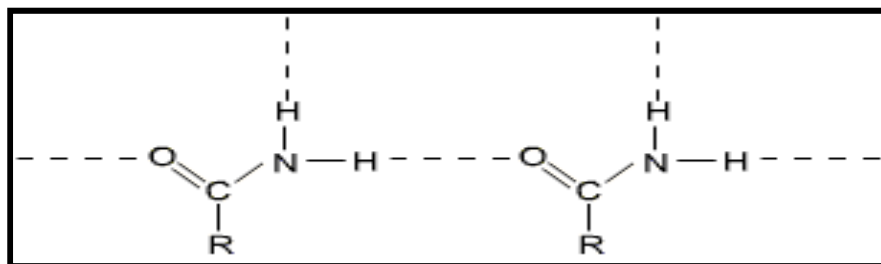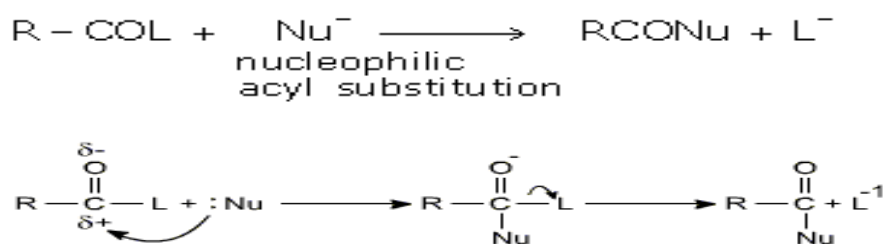


Esters and amides of low molecular masses are fairly soluble in water due to formation of hydrogen bonds with water. The solubility in water decreases with increasing molecular mass and is negligible for compounds containing more than six carbon atoms.

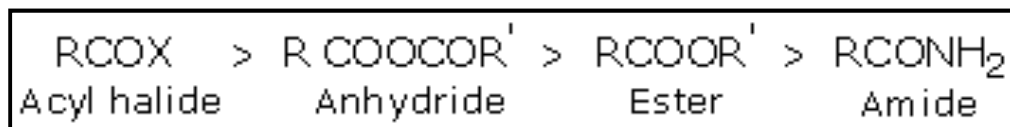All acid derivatives are soluble in usual organic solvents. Volatile esters have pleasant fruity smell. Acyl halides and anhydrides have sharp irritating odors and are lachrymatory (tear producing).

**Reactivity of Acid Derivatives**

The reactions of carboxylic acids and their derivatives involve substitution of the group L with nucleophiles and are known as nucleophilic acyl substitution reaction.

**Order of Reactivity of the Acid Derivatives is**

$$\boxed{\begin{array}{cccc} RCOX & > & R\,COOCOR' & > & RCOOR' & > & RCONH_2 \\ \text{Acyl halide} & & \text{Anhydride} & & \text{Ester} & & \text{Amide} \end{array}}$$

Carboxylic acids and their derivatives can be inter converted by nucleophilic acyl substitution reactions

**REFERENCES**

1. Smith, Michael B.; March, Jerry (2007), Advanced Organic Chemistry: Reactions, Mechanisms, and Structure (6th ed.), New York: Wiley-Inter science,

2. Chapter 19: Carboxylic Acids. Organic Chemistry 4e Carey. mhhe.com

3. Shirley, D. A. (1954). "The Synthesis of Ketones from Acid Halides and Organometallic Compounds of Magnesium, Zinc, and Cadmium". Org. React. **8**: 28–58.

4. Huryn, D. M. (1991). "Carbanions of Alkali and Alkaline Earth Cations: (ii) Selectivity of Carbonyl Addition Reactions". In Trost, B. M.; Fleming, I. Comprehensive Organic Synthesis, Volume 1: Additions to C—X $\pi$-Bonds, Part 1. Elsevier Science. pp. 49–75.

5. IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997).

6. Grignard, V.(1900)."Sur quelques nouvelles combinaisons organométaliques du magnésium et leur application à des synthèses d'alcools et d'hydrocabures". Compt. Rend. **130**: 1322–25.

7. Maruyama, K.; Katagiri, T. (1989). "Mechanism of the Grignard reaction".J. Phys. Org. Chem **2** (3): 205–213.

8. Garst, J. F.; Ungvary, F. "Mechanism of Grignard reagent formation". In Grignard Reagents; Richey, R. S., Ed.; John Wiley & Sons: New York, 2000; pp 185–275.

9. Advanced Organic chemistry Part B: Reactions and Synthesis F.A. Carey, R.J. Sundberg 2nd Ed. 1983

10. Rogers, H. R.; Hill, C. L.; Fujiwara, Y.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. (1980). "Mechanism of formation of Grignard reagents. Kinetics of reaction of alkyl halides in diethyl ether with magnesium". Journal of the American Chemical Society **102** (1): 217