Chapter 20

Carbonyl Compounds 2: Carboxylic Acids and their Functional Derivatives

Major Concepts

- 20.1 Nomenclature
- 20.2 Physical Properties
- 20.3 Structure
- 20.4 Acidity
- 20.5 Preparations of Carboxylic Acids
- 20.6 Reactivity
- 20.7 Reactions of Carboxylic Acids

Learning Outcomes:

Students will be able to:

- Describe preparation of carboxylic acids by carbonation of Grignard's Reagent, hydrolysis of nitriles, oxidation of primary alcohols, oxidation of aldehydes and oxidation of alkyl benzenes. **(Applying)**
- Discuss reactivity of carboxylic acids. **(Applying)**
- Describe the chemistry of carboxylic acids by conversion to carboxylic acid derivatives: acyl halides, acid anhydrides, esters, amides and reactions involving inter conversion of these. **(Analyzing)**
- Describe reactions of carboxylic acid derivatives. **(Applying)**
- Describe isomerism in carboxylic acids. **(Understanding)**

Introduction

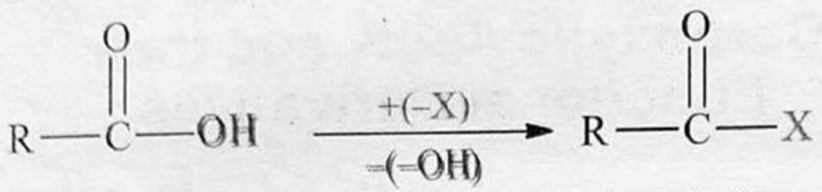
Carboxylic Acids

Carboxylic acids are organic compounds containing carboxyl group (—COOH) in their structures. Their general formula is R—COOH, where R stands for some aliphatic or aromatic group. The name carboxyl is obtained from **carb**onyl and hydr**oxyl** because these two groups are present in the carboxylic acids. The most important chemical property of carboxylic acids, as indicated by their names, is their acidity.

Carboxylic Acid Derivatives

Compounds that are obtained by replacing the hydroxyl group (—OH) of the carboxyl group (—COOH) by halogen (—X), alkoxy (—OR), amino (—NH_2) and carboxylate (—OCOR) are called carboxylic acid derivatives. There are four types of acid derivatives. These are acyl halides, esters, amides, and acid anhydrides.

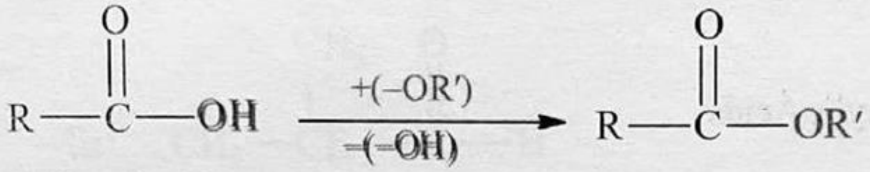
i) Acyl halides are obtained by replacing the hydroxyl group (—OH) of the carboxyl group by halogen (—X). They are also known as acid halides.



$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-(-OH)]{+(-X)} R-\overset{\overset{O}{\|}}{C}-X$$

Carboxylic acid Acyl Halide

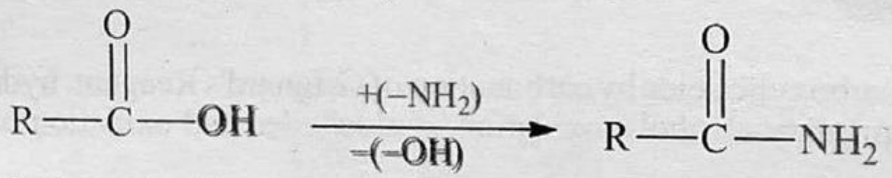
ii) Esters are obtained by replacing the hydroxyl group (—OH) of the carboxyl group by alkoxy (—OR).



$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-(-OH)]{+(-OR')} R-\overset{\overset{O}{\|}}{C}-OR'$$

Carboxylic acid Ester

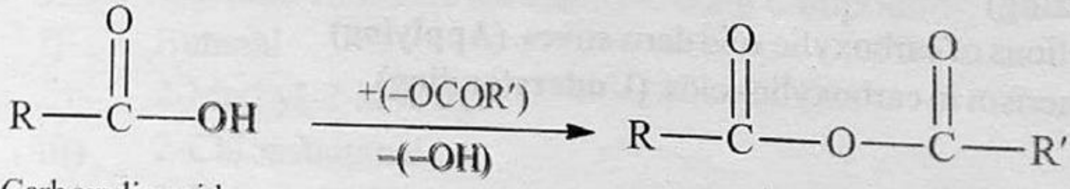
iii) Amides are obtained by replacing the hydroxyl group (—OH) of the carboxyl group by amino ($-NH_2$). They are also known as acid amides.



$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-(-OH)]{+(-NH_2)} R-\overset{\overset{O}{\|}}{C}-NH_2$$

Carboxylic acid Amide

iv) Acid anhydrides are obtained by replacing the hydroxyl group (—OH) of the carboxyl group by carboxylate (—OCOR).



$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-(-OH)]{+(-OCOR')} R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$$

Carboxylic acid Acid anhydride

Carboxylic acids and their functional derivatives are the important classes of organic compounds. They are the most abundant of all organic compounds.

20.1 Nomenclature of Carboxylic acids and Functional Group Derivatives

Both common and IUPAC names are used for carboxylic acids and their functional group derivatives.

20.1.1 Nomenclature of Carboxylic acids

20.1.1.1 Common System

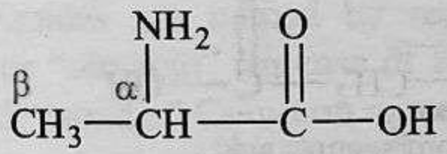
Carboxylic acids having six or less carbon atoms are often known by their common names. The common names of carboxylic acids usually derived from the

Latin or Greek word which indicates the original source of the acid. They do not follow any rule except that all common names of acids end in **—ic acid**.

Table 20.1: Common Names and Derivations of Some Carboxylic Acids

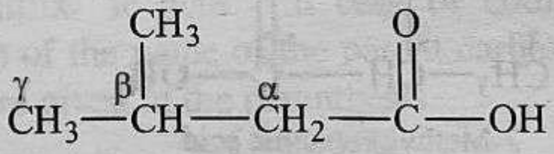
Structure	Common Name	Derivation
$HCOOH$	Formic acid	Latin: formica, ant
CH_3COOH	Acetic acid	Latin: acetum, vinegar
CH_3CH_2COOH	Propionic acid	Greek: propion, first fat
$CH_3(CH_2)_2COOH$	Butyric acid	Latin: butyrum, butter
$CH_3(CH_2)_3COOH$	Valeric acid	Latin: valeriana, a flowering plant
$CH_3(CH_2)_4COOH$	Caproic acid	Latin: caper, goat

Substituted carboxylic acids are named by indicating the group and the position where such group is bonded. The position of substituents on the chain is indicated by Greek letters α, β, γ, δ, etc. The α-carbon atom is one which is directly bonded to the carbon of carboxyl group. The common names of some substituted carboxylic acids are given below:



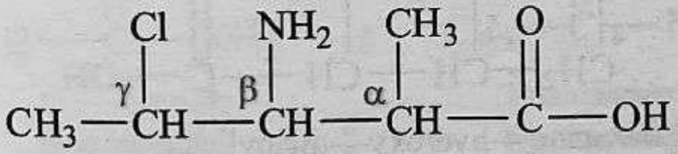
$$\overset{\beta}{CH_3}-\overset{\overset{NH_2}{|}}{\overset{\alpha}{CH}}-\overset{\overset{O}{\|}}{C}-OH$$

α-Aminopropionic acid



$$\overset{\gamma}{CH_3}-\overset{\overset{CH_3}{|}}{\overset{\beta}{CH}}-\overset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-OH$$

β-Methylbutyric acid



$$CH_3-\overset{\overset{Cl}{|}}{\overset{\gamma}{CH}}-\overset{\overset{NH_2}{|}}{\overset{\beta}{CH}}-\overset{\overset{CH_3}{|}}{\overset{\alpha}{CH}}-\overset{\overset{O}{\|}}{C}-OH$$

β-Amino-γ-chloro-α-methylvaleric acid

Keep in Mind

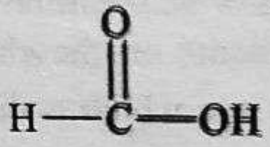
Formic acid is found in ants, bees, and other stinging insects.
Acetic acid is found in vinegar.
Propionic acid (***pro***, "the first" and ***pion***, "fat") shows some characteristic properties of larger fatty acids.
Butyric acid is found in rancid butter.
Valeric acid got its name from valerian, an herb that has been used as sedative since Roman times.
Caproic acid is found in goat's milk.

20.1.1.2 IUPAC System

Nomenclature of Monocarboxylic acids

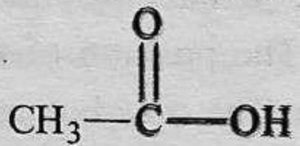
The IUPAC names of carboxylic acids are derived from the names of the corresponding alkanes by replacing the ending **–e** with ***–oic acid***. Hence, the carboxylic acids are named as ***'Alkanoic acids.'*** For example, if there is one carbon atom in the chain of carboxylic acid, it is derivative of methane and its name is methanoic acid. If there are two carbon atoms in the chain, then it is derivative of ethane and its name is ethanoic acid and so on. Since the carboxyl group lies at the end of the carbon chain, hence there is no need to indicate its position.

In case of substituted carboxylic acids, find the longest chain containing carboxyl group and number it in such a way that the carbon of carboxyl group is assigned position number one. There is no need to indicate the position of carboxyl group because it must always lie at the end of the carbon chain and it is given position number one. The carboxyl group takes priority over any of the other functional groups when naming them. The IUPAC names of some carboxylic acids are given below:



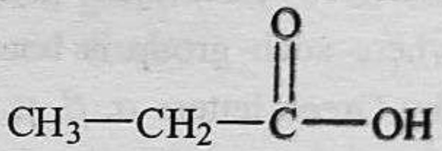
$H-\overset{\overset{O}{\|}}{C}-OH$

Methan**oic acid**



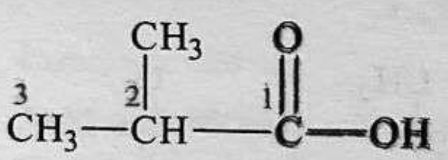
$CH_3-\overset{\overset{O}{\|}}{C}-OH$

Ethan**oic acid**



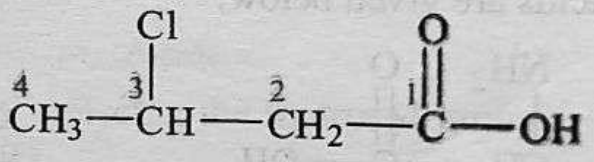
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

Propan**oic acid**



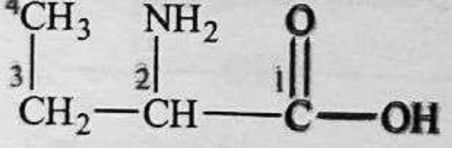
$\overset{3}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{\overset{O}{\|}}{\overset{1}{C}}-OH$

2-Methylpropan**oic acid**



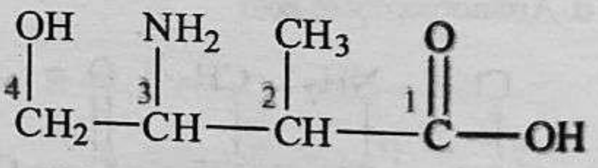
$\overset{4}{C}H_3-\overset{\overset{Cl}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{\overset{O}{\|}}{\overset{1}{C}}-OH$

3-Chlorobutan**oic acid**



$\overset{\overset{{}^4CH_3}{|}}{\overset{3}{C}H_2}-\overset{\overset{NH_2}{|}}{\overset{2}{C}H}-\overset{\overset{O}{\|}}{\overset{1}{C}}-OH$

2-Aminobutan**oic acid**



$\overset{\overset{OH}{|}}{\overset{4}{C}H_2}-\overset{\overset{NH_2}{|}}{\overset{3}{C}H}-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{\overset{O}{\|}}{\overset{1}{C}}-OH$

3-Amino-4-hydroxy-2-methylbutan**oic acid**

Nomenclature of Dicarboxylic acids

Dicarboxylic acids are also known as ***"diacids."*** They have two carboxyl groups in their structures. Dicarboxylic acids are named by adding the suffix –dioic acid to the name of parent alkane. There is no need to indicate the position of carboxyl groups because they lie at the ends of the parent chain.

$HOOC-COOH$

Ethane**dioic acid**

$HOOC-CH_2-COOH$

Propane**dioic acid**

$HOOC-CH_2-CH_2-COOH$

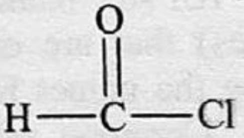
Butane**dioic acid**

The above three diacids are most frequently known by their common names that have accepted by IUPAC. The common names of ethanedioic acid, propanedioic acid and butanedioic acid are oxalic acid, malonic acid and succinic acid respectively.

20.1.2 Nomenclature of Carboxylic Acid Derivatives

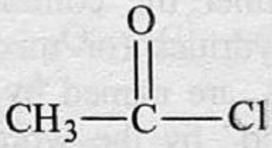
20.1.2.1 Nomenclature of Acyl halides

Acyl halides are named by replacing the suffix "ic acid" of the name of the parent carboxylic acid (either the common name or IUPAC name) with "yl halide." Common names of acyl halides are given in the parenthesis.



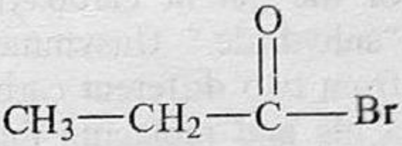
$H-\overset{\overset{O}{\|}}{C}-Cl$

Methanoyl chloride
(Formyl chloride)



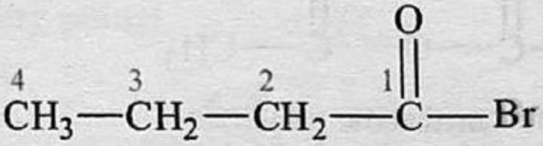
$CH_3-\overset{\overset{O}{\|}}{C}-Cl$

Ethanoyl chloride
(Acetyl chloride)



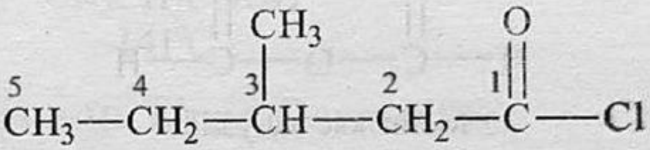
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-Br$

Propanoyl bromide
(Propionyl bromide)



$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{\overset{O}{\|}}{\overset{1}{C}}-Br$

Butanoyl bromide
(Butyryl bromide)

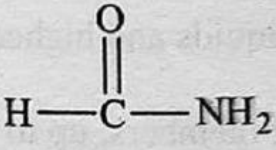


$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{\overset{CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{\overset{O}{\|}}{\overset{1}{C}}-Cl$

3-Methylpentanoyl chloride
(β-Methylvaleryl chloride)

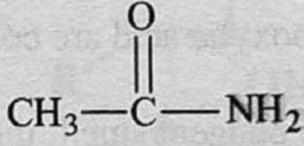
20.1.2.2 Nomenclature of Amides

Amides are named by replacing the suffix "ic acid" (in case of common names) or "oic acid" (in case of IUPAC names) of the name of the parent carboxylic acid with "amide." Common names of amides are given in the parenthesis.



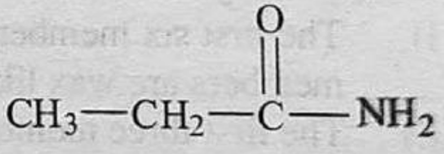
$H-\overset{\overset{O}{\|}}{C}-NH_2$

Methanamide
(Formamide)



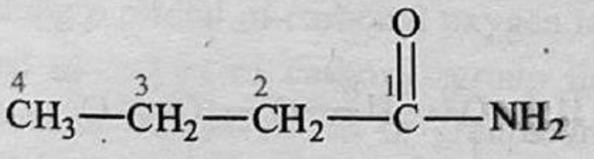
$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

Ethanamide
(Acetamide)



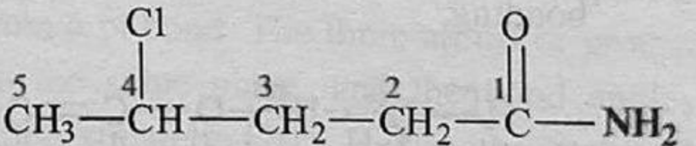
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2$

Propanamide
(Propionamide)



$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{\overset{O}{\|}}{\overset{1}{C}}-NH_2$

Butanamide
(Butyramide)

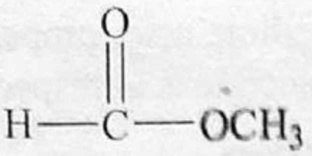


$\overset{5}{CH_3}-\overset{\overset{Cl}{|}}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{\overset{O}{\|}}{\overset{1}{C}}-NH_2$

4-Chloropentanamide
(γ-Chlorovaleramide)

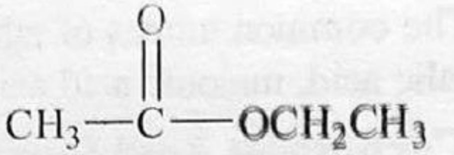
20.1.2.3 Nomenclature of Esters

Their names consist of two words. The first word is the name of the alkyl group bonded to oxygen atom. The second word is obtained by replacing the suffix "ic acid"of the name of the parent carboxylic acid (either the common name or IUPAC name) with "ate." Common names of esters are given in the parenthesis.



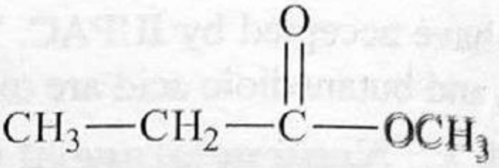
$H-\overset{\overset{O}{\|}}{C}-OCH_3$

Methyl methanoate
(Methyl Formate)



$CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_3$

Ethyl ethanoate
(Ethyl acetate)

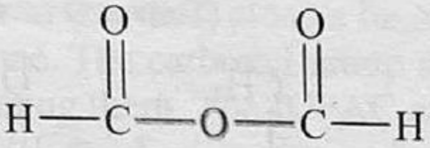


$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OCH_3$

Methyl Propanoate
(Methyl Propionate)

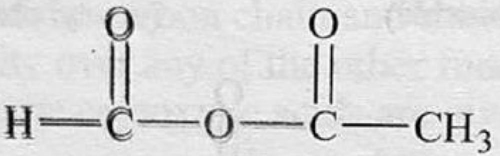
20.1.2.4 Nomenclature of Acid Anhydrides

Symmetrical Anhydrides are named by replacing the suffix"acid"of the name of the parent carboxylic acid (either the common name or IUPAC name) with "anhydride." Unsymmetrical Anhydrides (or mixed anhydrides) that are obtained from two different carboxylicacids, are named by alphabetizing the names for both acids and replacing the word "acid" by the word "anhydride."Common names of anhydrides are given in the parenthesis.



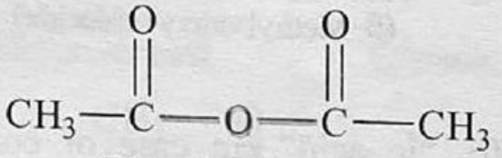
$H-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-H$

Methanoic anhydride
(Formic anydride)



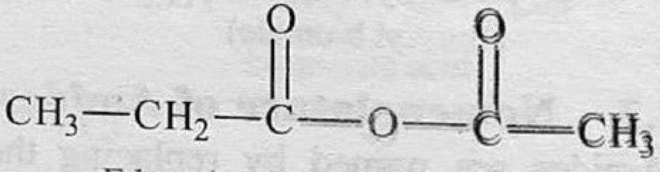
$H-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$

Ethanoicmethanoic anhydride
(aceticformic anydride)



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

Ethanoic anhydride
(Acetic anhydride)



$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$

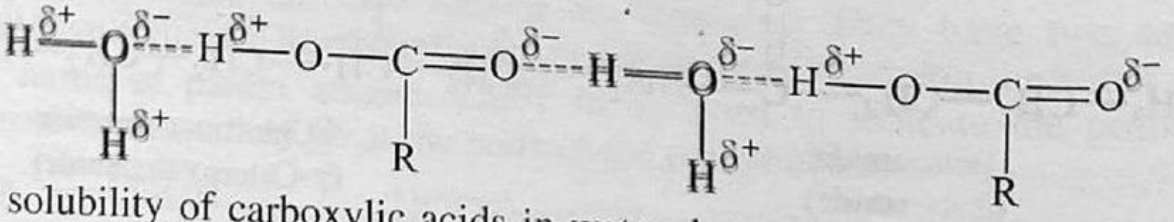
Ethanoicpropanoic anhydride
(Aceticpropionic anhydride)

20.2 Physical Characteristics of Carboxylic Acid

i) The first six members of carboxylic acid are colourless liquids and higher members are wax like solids.

ii) The first three members have pungent smell, the next six members, up to C_9, have a smell of rancid butter. The higher members have almost no smell.

iii) The first four members are completely soluble in water due to hydrogen bonding.



$H^{\delta+}-\underset{\underset{H^{\delta+}}{|}}{O^{\delta-}}\cdots H^{\delta+}-O-\underset{\underset{R}{|}}{C}=O^{\delta-}\cdots H-\underset{\underset{H^{\delta+}}{|}}{O^{\delta-}}\cdots H^{\delta+}-O-\underset{\underset{R}{|}}{C}=O^{\delta-}$

The solubility of carboxylic acids in water decrease when the length of carbon chain increases.

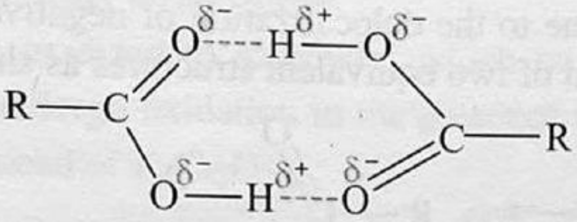
iv) Melting points of carboxylic acids increase irregularly with the increase in molecular masses. The acids with even member of carbon atoms have markedly higher melting points than odd members.

CH_3CH_2COOH,
(3-Carbons, mp = −21°C)

$CH_3CH_2CH_2COOH$,
(4-Carbons, mp = −7°C)

$CH_3CH_2CH_2CH_2COOH$
(5-Carbons, mp = −35°C)

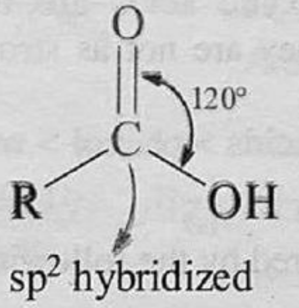
v) The boiling points of carboxylic acids are relatively high due to intermolecular hydrogen bonding. They exist in the form of cyclic dimers.



Formula:	HCOOH	CH_3COOH	CH_3CH_2COOH
Boiling point:	101°C	118°C	141°C

20.3 Structure of Carboxylic Acids and Their Derivatives

The carbon atom of carboxylic acid and carboxylic acid derivatives is sp^2 hybridized. The three sp^2 hybrid orbitals of carbon of carboxyl group forms three sigma bonds, one with carbonyl oxygen, one with oxygen of hydroxyl group and one with hydrogen atom or other group bonded to it.

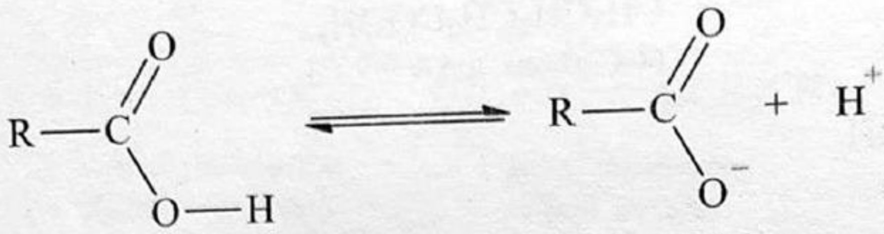


The remaining fourth unhybridized *p* orbital of carboxyl carbon overlaps the remaining *p* orbital of carbonyl oxygen to from a pi bond. The three atoms or groups bonded to carbon of carboxyl group lie in the same plane, and the bond angles between the bonded atoms or groups are approximately 120°. Hence, the carboxyl group shows trigonal planar geometry.

20.4 Acidity of carboxylic Acids

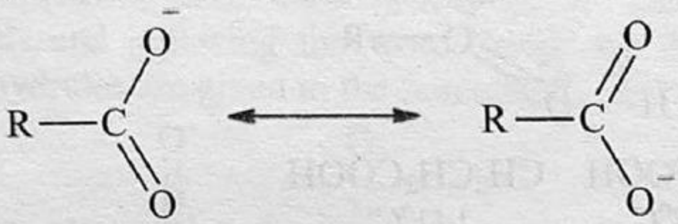
Carboxylic acids are the most acidic organic compounds. The acidic behaviour of carboxylic acid can be explained by the points given below:

i) The carboxylic acid has acidic behaviour because it has ability to give hydrogen ion in water. As a result of this, a conjugate base, carboxylate ion is produced.



Carboxylic acid Carboxylate ion

ii) The carboxylate ion is more stable in water than carboxylic acid. The stability of carboxylate ion is due to the delocalization of negative charge. Carboxylate ion is a resonance hybrid of two equivalent structures as shown below:



The conjugate base (carboxylate ion) of carboxylic acid most effectively resonance stabilized than alcohol and phenol. The greater the stability of resonance hybrid, the greater is the strength of acid.

iii) The strength of an acid can also be determined by pK_a values. The greater the value of pK_a, the weaker will be the acid. The pK_a values of HCl, H_2SO_4, CH_3COOH, C_6H_5OH, H_2O and C_2H_5OH are −7, −3, 4.75, 10, 14, and 16 respectively. Hence, carboxylic acids are much stronger acids than water, alcohols and phenols but they are not as strong as mineral acids (HCl, H_2SO_4 etc.).

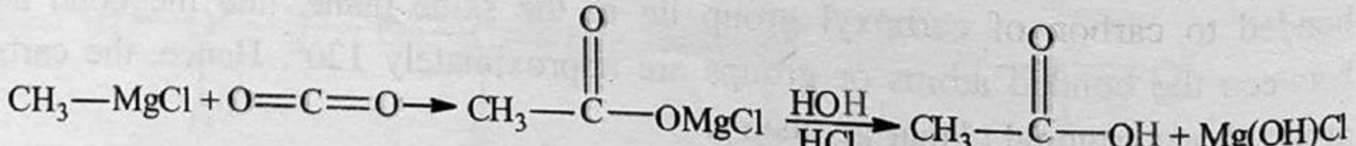
Mineral acids > carboxylic acids > phenol > water > alcohol

20.5 Preparations of Carboxylic Acids

Carboxylic acids are prepared by the following methods:

20.5.1 Carbonation of Grignard's reagent

Grignard's reagents reacts with CO_2 to give addition product which on acid hydrolysis gives carboxylic acids.



$$CH_3{-}MgCl + O{=}C{=}O \rightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}OMgCl \xrightarrow[HCl]{HOH} CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH + Mg(OH)Cl$$

The carbonation of Grignard's reagent is a convenient way to convert an alkyl or aryl halide to a carboxylic acid.

20.5.2 Hydrolysis of Nitriles

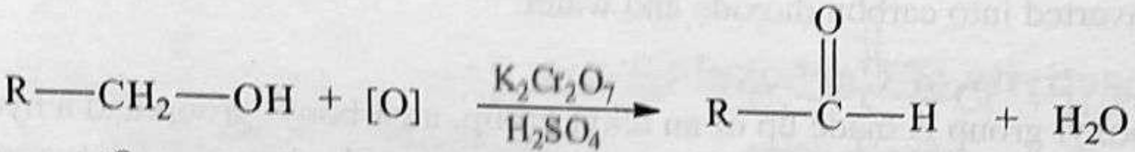
Alkyl nitriles (alkyl cyanides) react with hot aqueous solution of an acid (mineral acid) or alkali to produce carboxylic acids.

$$R-C\equiv N + 2\,HOH \xrightarrow{HCl} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3$$

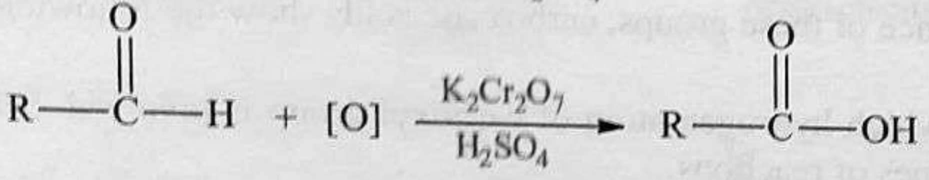
$$CH_3-C\equiv N + 2\,HOH \xrightarrow{HCl} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3$$

20.5.3 Oxidation of Primary Alcohols

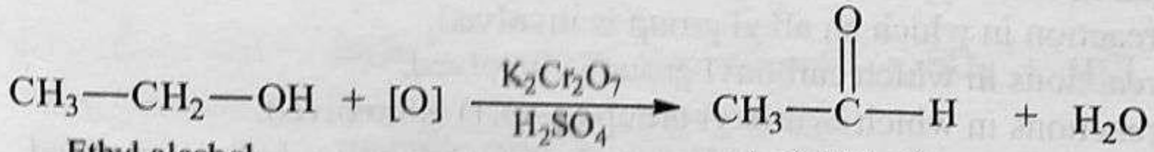
Primary alcohols are oxidized to aldehydes which on further oxidation give carboxylic acids. Alcohols undergo oxidation in the presence of $K_2Cr_2O_7$ and H_2SO_4. $KMnO_4$ can also be used instead of $K_2Cr_2O_7$.



$$R-CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O$$

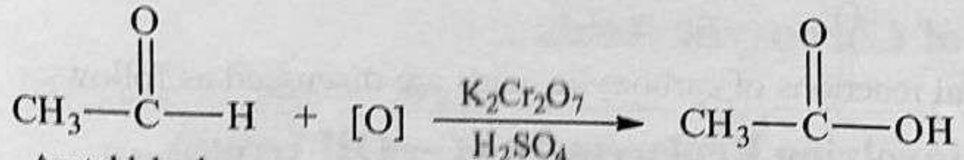


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$



$$CH_3-CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O$$

Ethyl alcohol **Acetaldehyde**

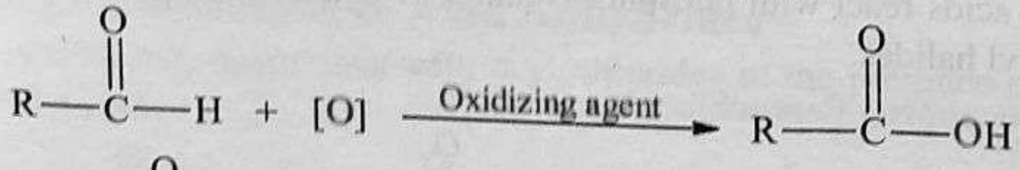


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

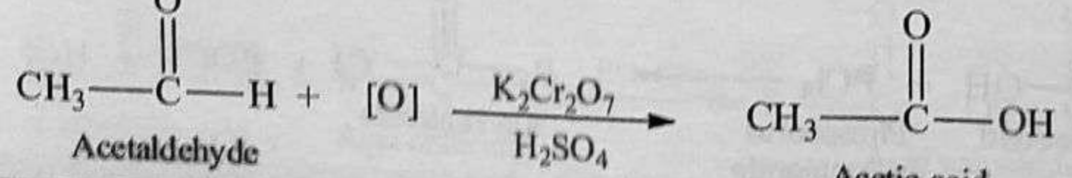
Acetaldehyde Acetic Acid

20.5.4 Oxidation of Aldehydes

Aldehydes can be oxidized by mild oxidizing agents such as silver oxide, Ag_2O. Aldehydes can also be oxidized by strong oxidizing agents such as potassium permanganate or potassium dichromate in acidic medium.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow{\text{Oxidizing agent}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

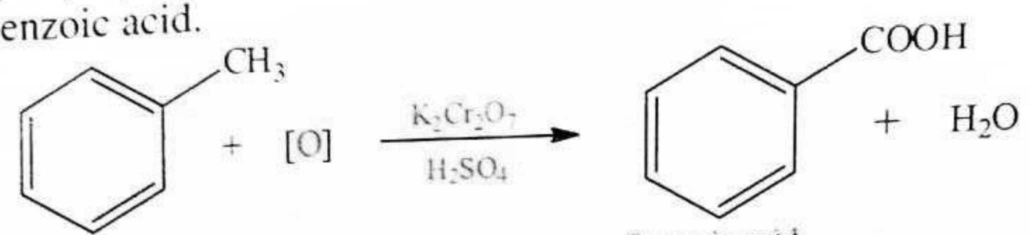


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Acetaldehyde **Acetic acid**

20.5.5 Oxidation of Alkyl Benzenes

Alkyl groups attached directly to the benzene ring are oxidized into carboxylic acid group by oxidizing agents. For example, toluene is oxidized by oxidizing agents into benzoic acid.



Toluene Benzoic acid

The alkyl benzenes will produce the same product (benzoic acid) whether the alkyl side chain is methyl, ethyl or any other alkyl group. The rest of the alkyl side chain is converted into carbon dioxide and water.

20.6 Reactivity of Carboxyl Group

Carboxyl group is made up of an alkyl group, a carbonyl group and a hydroxyl group. Due to the presence of these groups, carboxylic acids show the following types of reactions:

i) The reactions in which hydrogen atom of carboxyl group is involved. Salts are formed in these types of reactions.
ii) The reaction in which an alkyl group is involved.
iii) The reactions in which carbonyl group is involved.
iv) The reactions in which hydroxyl group (—OH) is involved.
v) The reactions in which carboxyl group (—COOH) as a whole is involved.

20.7 Reactions of Carboxylic Acids

The important chemical reactions of carboxylic acids are discussed as follows:

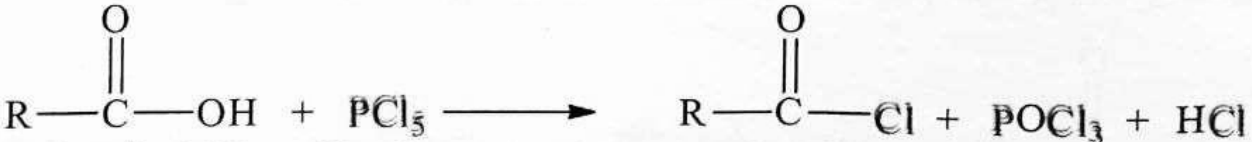
20.7.1 Reactions involving Replacement of —OH Group

Carboxylic acid derivatives are obtained by the replacement of hydroxyl group (—OH) of the carboxyl group (—COOH) by halogen (—X), alkoxy (—OR), amino (—NH_2) and carboxylate (—OCOR).

20.7.1.1 Conversion to Acyl Halides (Acid halides)

Carboxylic acids react with phosphorus halide (PCl_5, PCl_3) or thionyl chloride ($SOCl_2$) to give acyl halides.

Reaction with Phosphorus Pentachloride



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + PCl_5 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + POCl_3 + HCl$$

Carboxylic Acid Phosphorus pentachloride Acyl chloride

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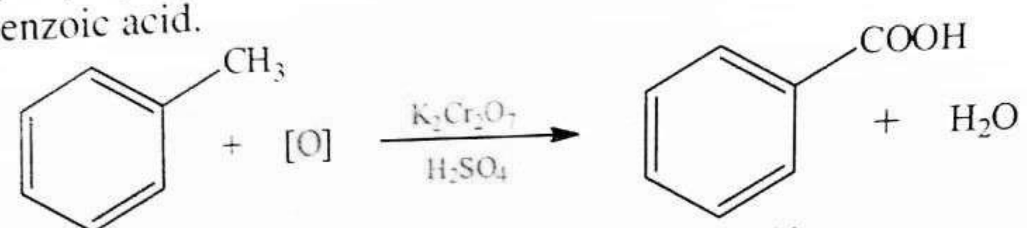

Toluene

Benzoic acid

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v) The reactions in which carboxyl group (—COOH) as a whole is involved.

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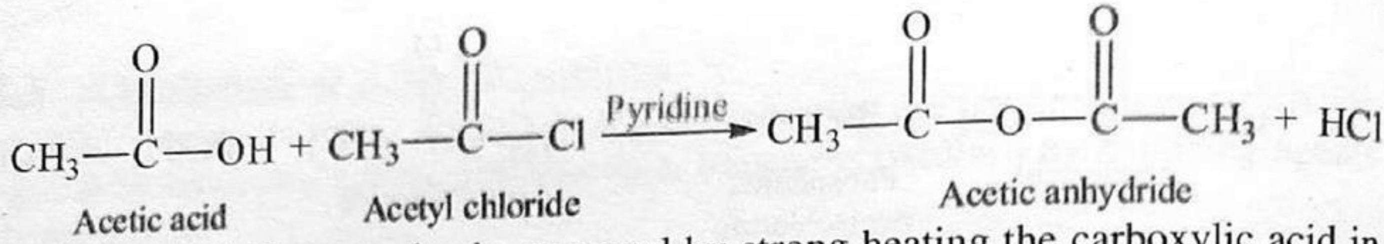
Reaction with Phosphorus Pentachloride

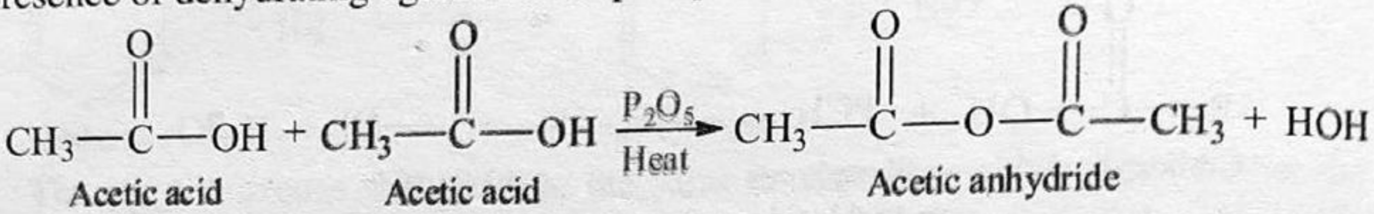
$$R—\overset{\overset{\displaystyle O}{\|}}{C}—OH + PCl_5 \longrightarrow R—\overset{\overset{\displaystyle O}{\|}}{C}—Cl + POCl_3 + HCl$$

Carboxylic Acid   Phosphorus pentachloride   Acyl chloride



$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} \xrightarrow{\text{Pyridine}} \underset{\text{Acetic anhydride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + HCl$$

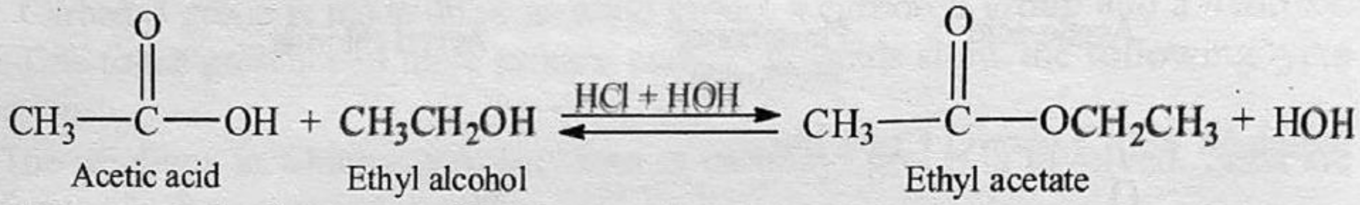
Acid anhydrides can also be prepared by strong heating the carboxylic acid in the presence of dehydrating agent such as phosphorus pentoxide.



$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Acetic anhydride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + HOH$$

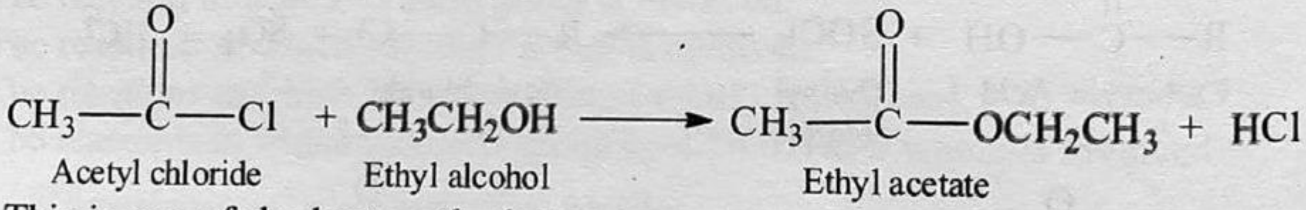
20.7.1.3 Conversion to Esters

Carboxylic acids react with alcohols in the presence of strong acid like H_2SO_4 or HCl to form esters. This reaction is reversible and is known as esterification.



$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightleftharpoons{HCl + HOH} \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_3} + HOH$$

Esters can also be prepared by the reaction of acyl chlorides with alcohols.



$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_3} + HCl$$

This is one of the best methods to prepare an ester and does not need an acid catalyst.

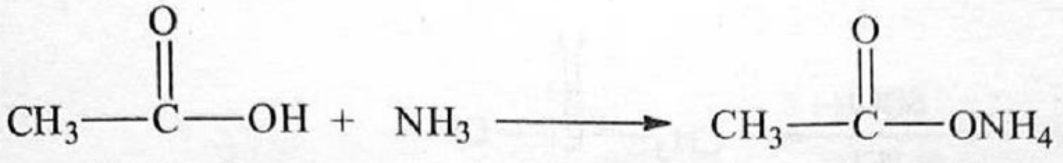
Esters have fruity smell and are used as artificial flavours.

Table 20.2: Esters and their Flavours

Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Ethyl butyrate	Pine apple
Benzyl acetate	Jasmine	Octyl acetate	Orange
Amyl butyrate	Apricot	Isoamylvalerate	Apple
Isobutyl formate	Raspberry		

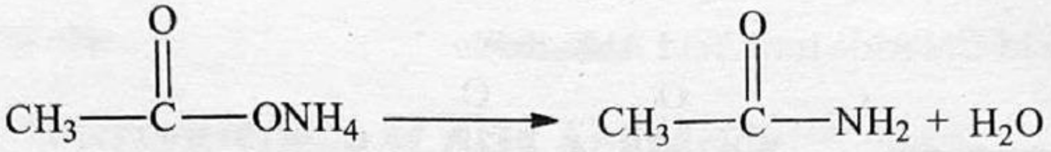
20.7.1.4 Conversion to Amides

Carboxylic acids react with aqueous ammonia to form ammonium salts of carboxylic acid, which on heating give amides. This is not a good method for the preparation of amides.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH + NH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONH_4$$

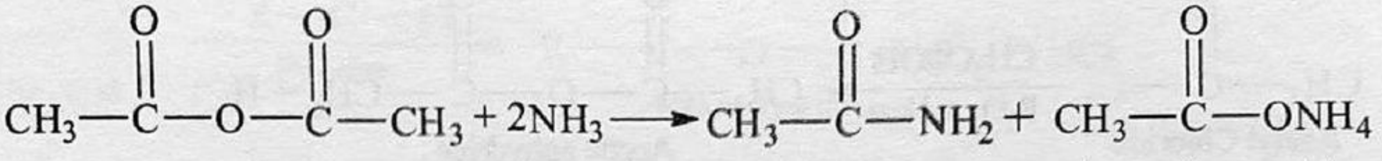
Acetic acid Ammonia Ammonium acetate



$$CH_3-\overset{\overset{O}{\|}}{C}-ONH_4 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$$

Acetamide

Amides can also be obtained by the reaction of acid anhydrides with ammonia (or amines).

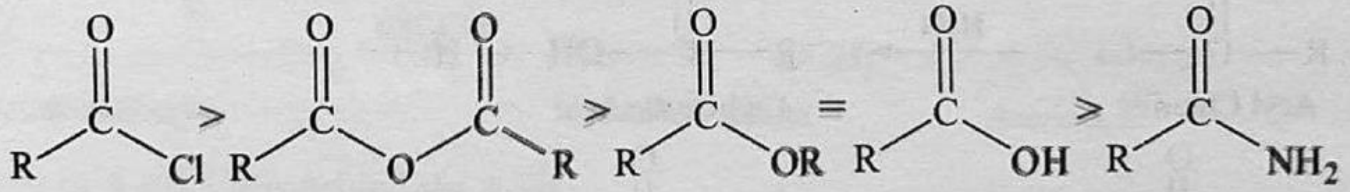


$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + 2NH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + CH_3-\overset{\overset{O}{\|}}{C}-ONH_4$$

Acetic anhydride Acetamide Ammonium acetate

20.7.2 Summary of Reactions that Interconvert Carboxylic Acids Derivatives

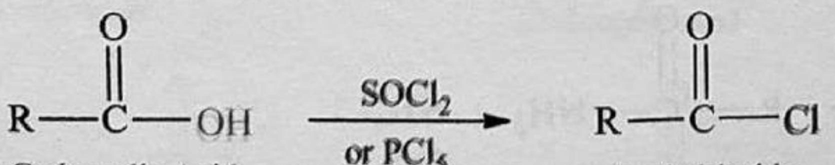
Carboxylic acid derivatives are compounds that can be converted to carboxylic acids through simple acidic or basic hydrolysis. The most important acid derivatives are esters, amides, acid halides and acid anhydrides. The carboxylic acid derivatives are a family of closely related functional groups. They all (carboxylic acid and their derivatives) contain carbonyl groups and many of these can be easily interconverted. All of the acid derivatives are converted to carboxylic acids. An acid derivative can be converted to a less reactive derivative and it cannot be converted to a more reactive derivative. For example, esters can be converted to amides, but not into acid halides or anhydrides. The order of reactivity for carboxylic acid and their derivatives is as:



Acyl chloride > Acid anhydride > Ester = Carboxylic acid > Amide

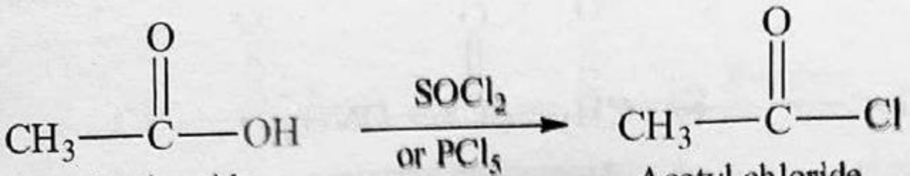
20.7.2.1 Interconversion of Acid Chloride

Conversion of Acid into Acid Chloride



$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\text{or } PCl_5]{SOCl_2} R-\overset{\overset{O}{\|}}{C}-Cl$$

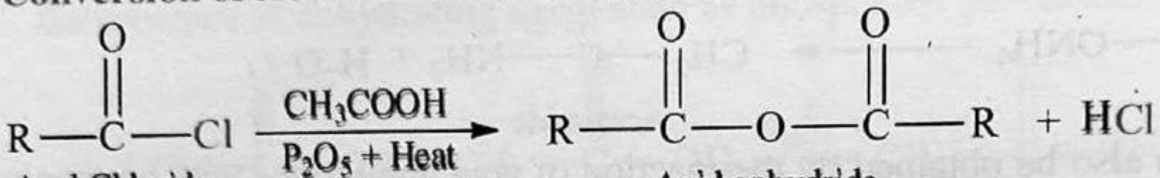
Carboxylic Acid Acyl chloride



$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{or } PCl_5]{SOCl_2} CH_3-\overset{O}{\overset{\|}{C}}-Cl$$

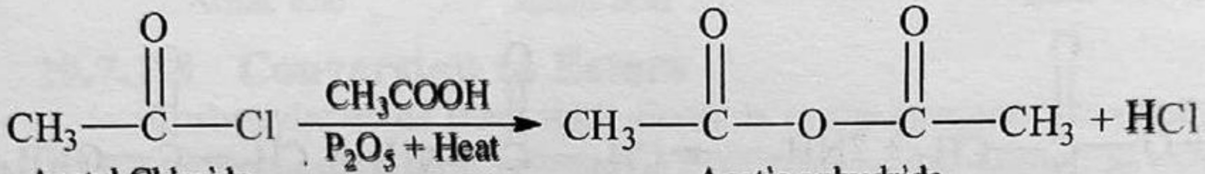
Acetic acid — Acetyl chloride

Conversion of Acid Chloride into Acid Anhydride



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[P_2O_5 + \text{Heat}]{CH_3COOH} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + HCl$$

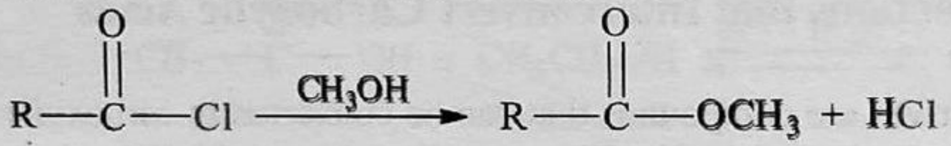
Acyl Chloride — Acid anhydride



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[P_2O_5 + \text{Heat}]{CH_3COOH} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$$

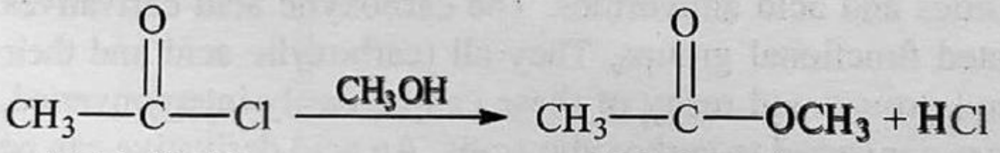
Acetyl Chloride — Acetic anhydride

Conversion of Acid Chloride into Ester



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{CH_3OH} R-\overset{O}{\overset{\|}{C}}-OCH_3 + HCl$$

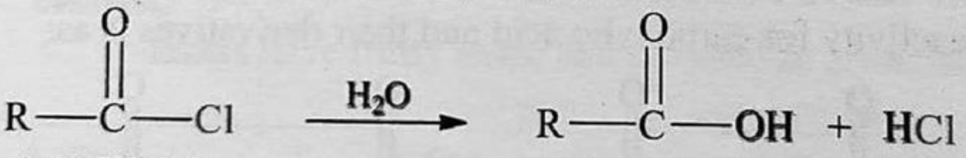
Acyl Chloride — Ester



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{CH_3OH} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + HCl$$

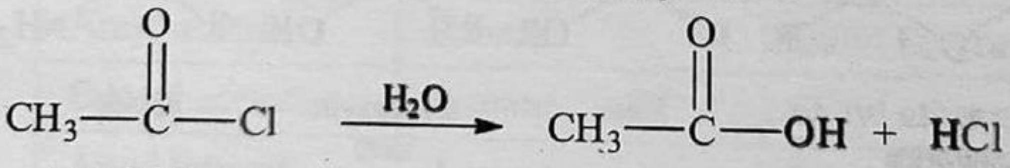
Acetyl chloride — Methyl acetate

Conversion of Acid Chloride into Acid



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + HCl$$

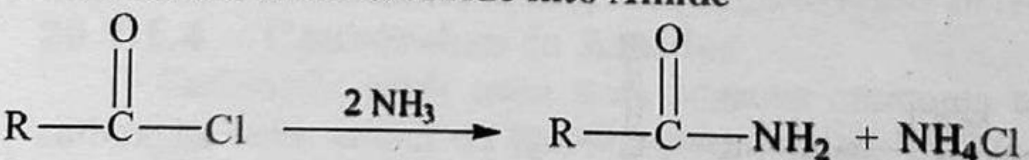
Acyl Chloride — Carboxylic Acid



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-OH + HCl$$

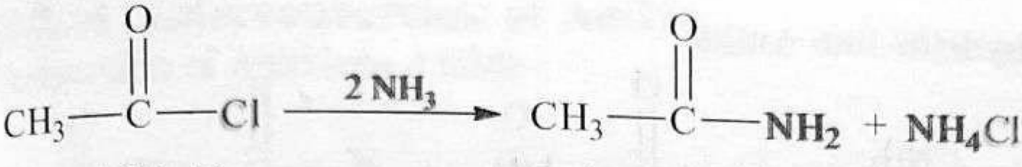
Acetyl Chloride — Acetic Acid

Conversion of Acid Chloride into Amide



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{2\,NH_3} R-\overset{O}{\overset{\|}{C}}-NH_2 + NH_4Cl$$

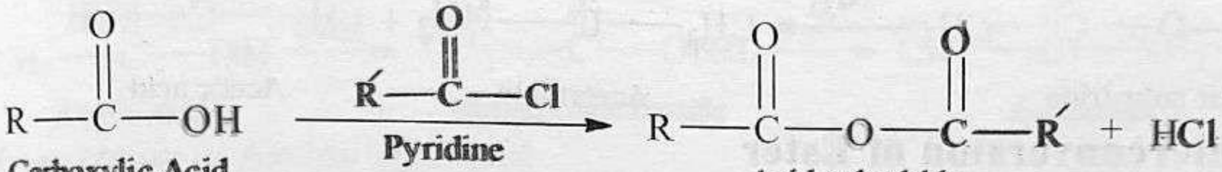
Acyl Chloride — Acyl Amide



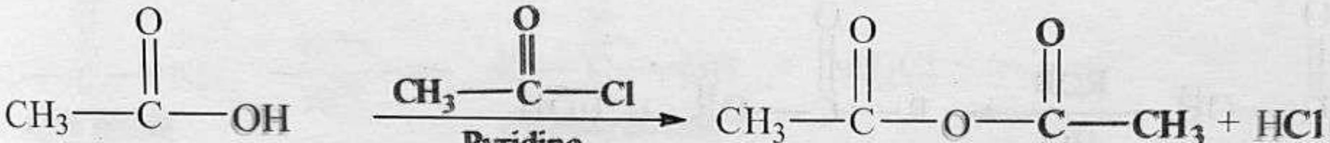
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{2\,NH_3} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + NH_4Cl$$

20.7.2.2 Interconversion of Acid Anhydride

Conversion of Acids into Acid Anhydride

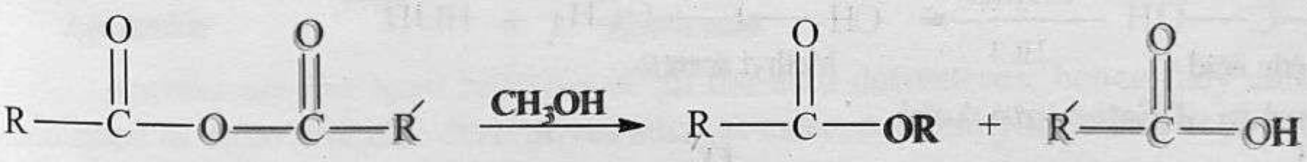


$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{Pyridine}]{R'-\overset{O}{\overset{\|}{C}}-Cl} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R' + HCl$$

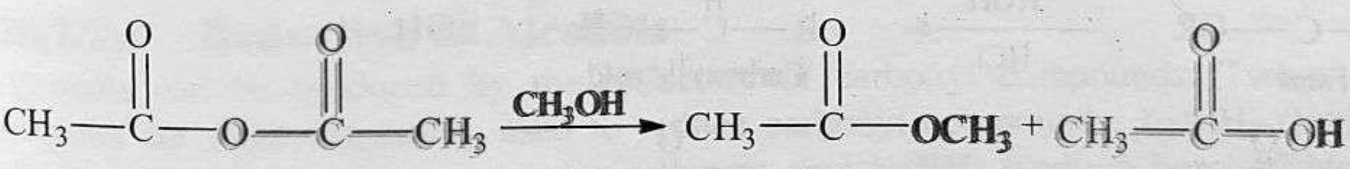


$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{Pyridine}]{CH_3-\overset{O}{\overset{\|}{C}}-Cl} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$$

Conversion of Acid Anhydride into Ester

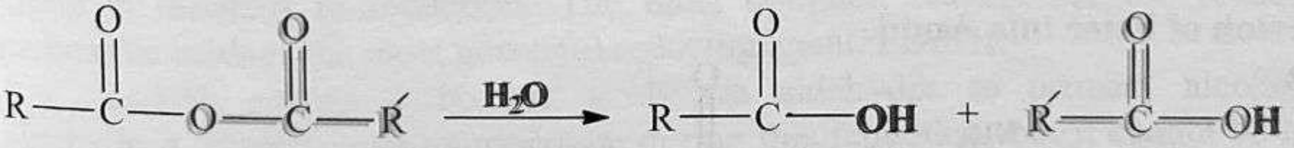


$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{CH_3OH} R-\overset{O}{\overset{\|}{C}}-OR + R'-\overset{O}{\overset{\|}{C}}-OH$$

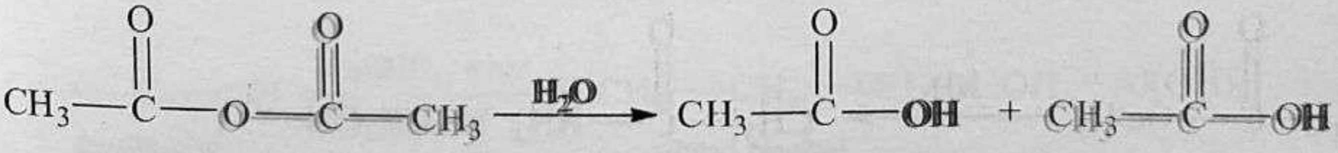


$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CH_3OH} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Conversion of Acid Anhydride into Acid

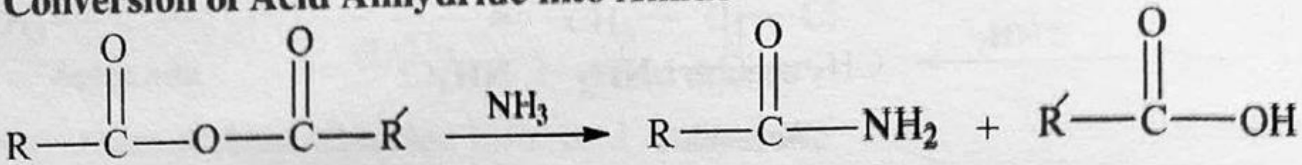


$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{O}{\overset{\|}{C}}-OH$$



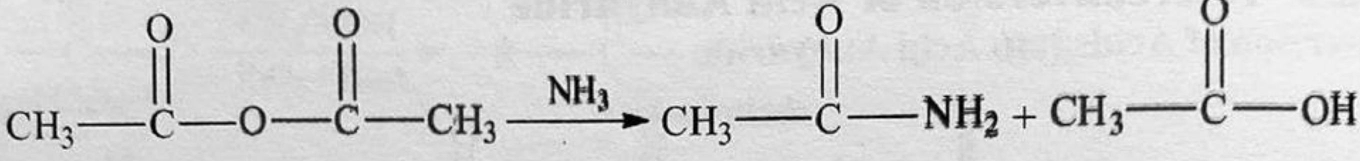
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Conversion of Acid Anhydride into Amide



$$\mathrm{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{NH_3} R-\overset{\overset{O}{\|}}{C}-NH_2 + R'-\overset{\overset{O}{\|}}{C}-OH}$$

Acid anhydride — Acid amide — Carboxylic acid

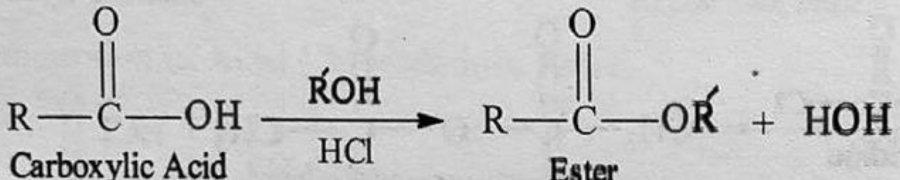


$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NH_3} CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

Acetic anhydride — Acetamide — Acetic acid

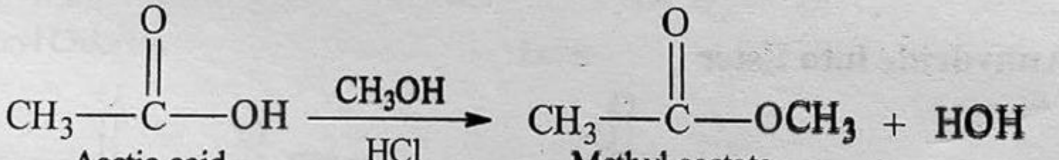
20.7.2.3 Interconversion of Ester

Conversion of Acid into Ester



$$\mathrm{R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[HCl]{R'OH} R-\overset{\overset{O}{\|}}{C}-OR' + HOH}$$

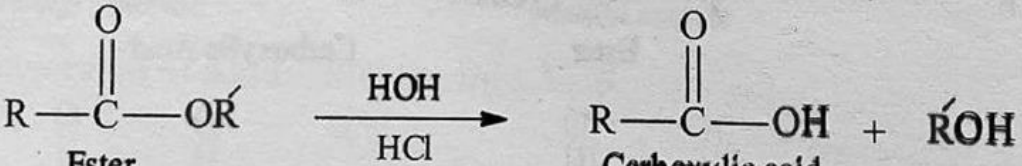
Carboxylic Acid — **Ester**



$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[HCl]{CH_3OH} CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 + HOH}$$

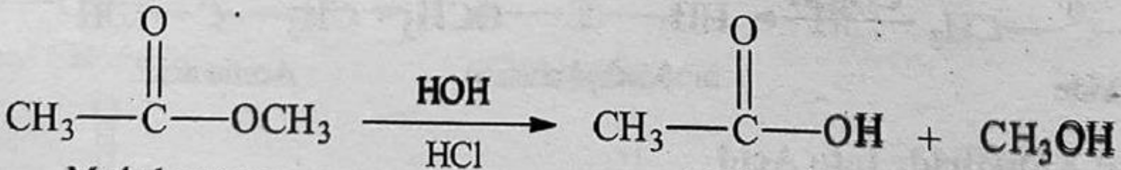
Acetic acid — **Methyl acetate**

Conversion of Ester into Acid



$$\mathrm{R-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow[HCl]{HOH} R-\overset{\overset{O}{\|}}{C}-OH + R'OH}$$

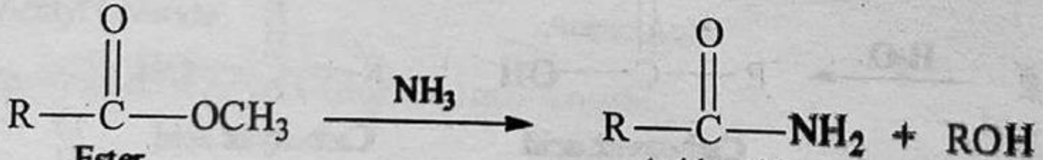
Ester — **Carboxylic acid**



$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 \xrightarrow[HCl]{HOH} CH_3-\overset{\overset{O}{\|}}{C}-OH + CH_3OH}$$

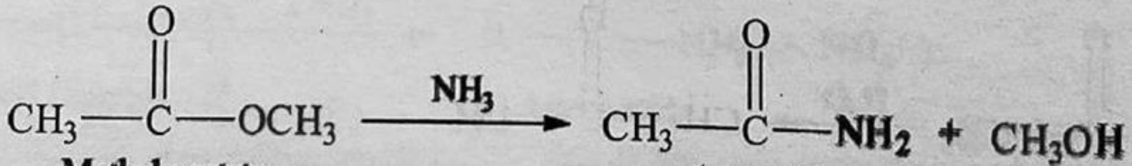
Methyl acetate — **Acetic acid**

Conversion of Ester into Amide



$$\mathrm{R-\overset{\overset{O}{\|}}{C}-OCH_3 \xrightarrow{NH_3} R-\overset{\overset{O}{\|}}{C}-NH_2 + ROH}$$

Ester — **Acid amide**

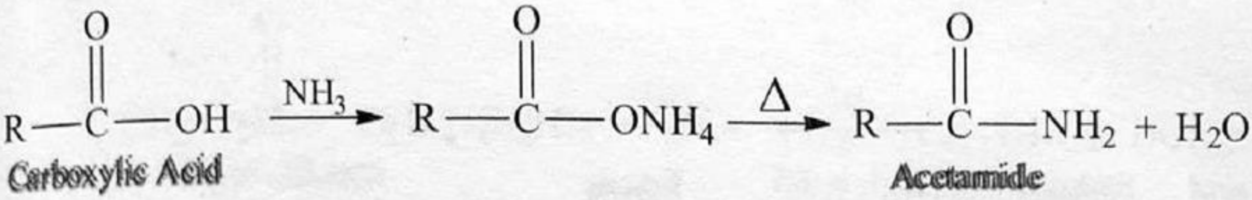


$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 \xrightarrow{NH_3} CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + CH_3OH}$$

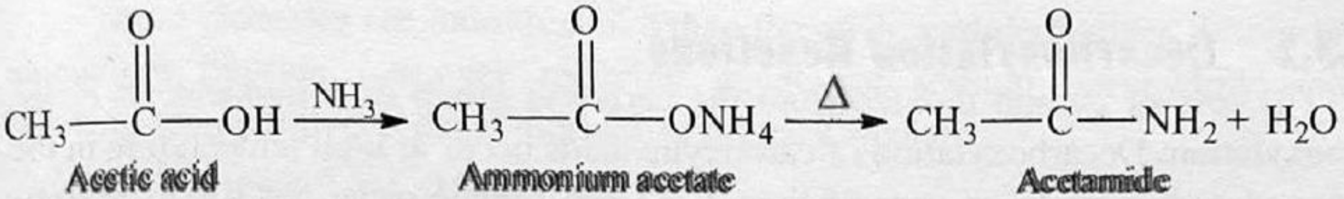
Methyl acetate — **Acetamide**

20.7.2.4 Interconversion of Amide

Conversion of Acid into Amide

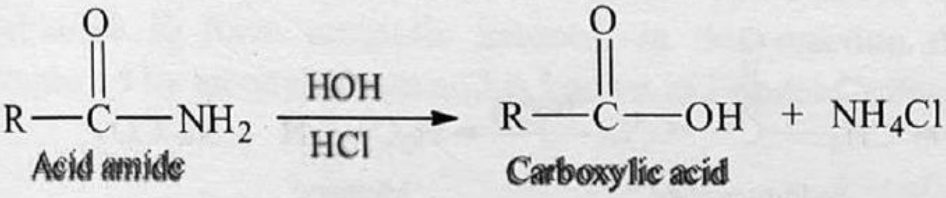


$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{NH_3} R-\overset{\overset{O}{\|}}{C}-ONH_4 \xrightarrow{\Delta} R-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$$

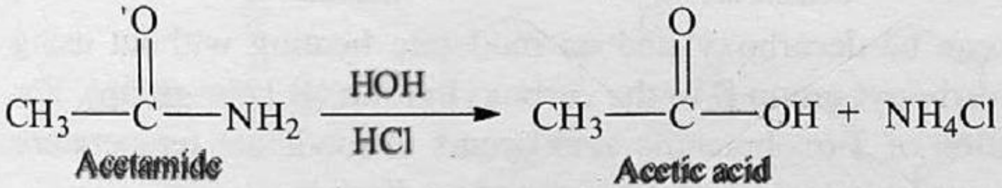


$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{NH_3} CH_3-\overset{\overset{O}{\|}}{C}-ONH_4 \xrightarrow{\Delta} CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$$

Conversion of Amide into Acid



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[HCl]{HOH} R-\overset{\overset{O}{\|}}{C}-OH + NH_4Cl$$



$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[HCl]{HOH} CH_3-\overset{\overset{O}{\|}}{C}-OH + NH_4Cl$$

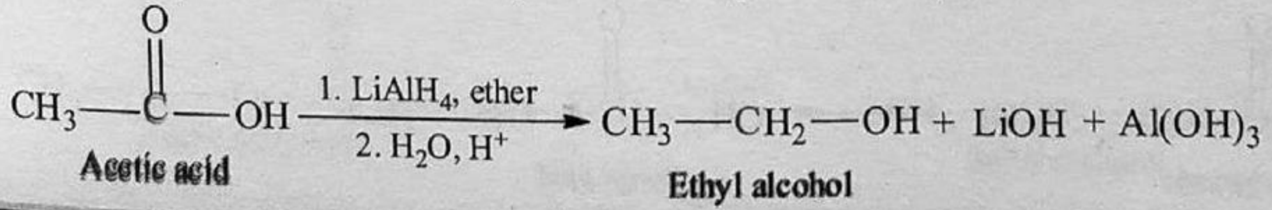
Amides are the least reactive of all the acid derivatives, hence they cannot be converted to more reactive derivatives such as ester, acid anhydride and acyl halides.

20.7.3 Reactions involving Carboxyl Group

20.7.3.1 Reduction to Alcohols

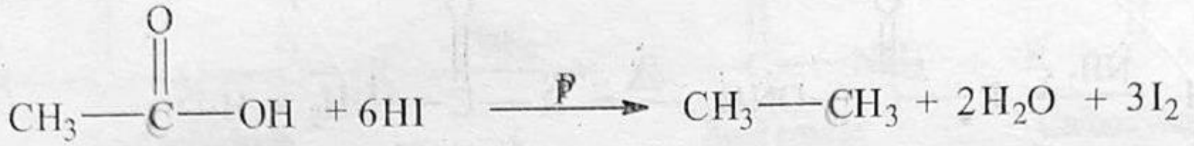
Alcohols can be produced by the reduction of carbonyl compounds. Two reagents are most commonly used to reduce carbonyl compounds, $LiAlH_4$ (lithium aluminum hydride), a stronger reducing agent, and $NaBH_4$ (sodium borohydride), a weaker reducing agent. $NaBH_4$ is used to reduce aldehydes, ketones, alkenes and alkynes but this reagent is not used to reduce carboxylic acids because the carboxyl group is resistant to reduction. The most common reagent for the reduction of carboxylic acids is the most powerful reducing agent, $LiAlH_4$.

$LiAlH_4$ reduce carboxylic acids via aldehydes to primary alcohols. An aldehyde is formed as an intermediate during this reduction, but it cannot be isolated because it is reduced more easily than the original carboxylic acid.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[2.\ H_2O,\ H^+]{1.\ LiAlH_4,\ ether} CH_3-CH_2-OH + LiOH + Al(OH)_3$$

Carboxylic acids on complete reduction with HI in the presence of red phosphorus give alkanes.

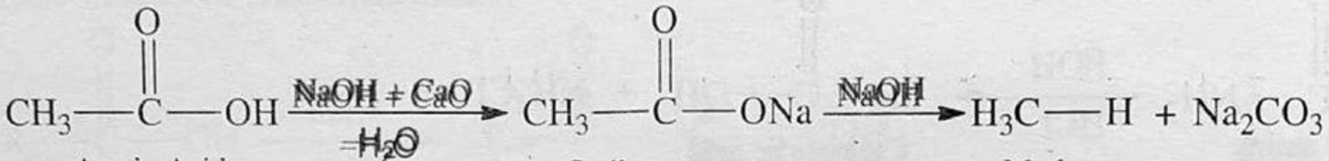


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 6HI \xrightarrow{P} CH_3-CH_3 + 2H_2O + 3I_2$$

Acetic acid Ethane

20.7.3.2 Decarboxylation Reactions

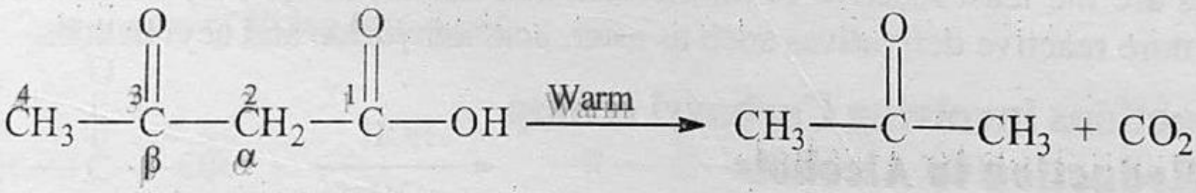
The loss of carbon dioxide from the carboxyl group of a molecule is called decarboxylation. Decarboxylation of carboxylic acids occur at high temperature in the presence of soda lime (a mixture of lime, CaO and caustic soda, NaOH) to produce alkanes.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[-H_2O]{NaOH + CaO} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa \xrightarrow{NaOH} H_3C-H + Na_2CO_3$$

Acetic Acid Sodium acetate Methane

A carboxylic acid can be decarboxylated on moderate heating without using soda lime if it contains a carbonyl group β to the carboxyl group (β keto group). For example, the decarboxylation of 3-oxobutanoic acid occurs at moderate temperature in the absence of soda lime and produces acetone and carbon dioxide.



$$\overset{4}{C}H_3-\underset{\beta}{\overset{\overset{\displaystyle O}{\|}}{\overset{3}{C}}}-\underset{\alpha}{\overset{2}{C}H_2}-\overset{\overset{\displaystyle O}{\|}}{\overset{1}{C}}-OH \xrightarrow{Warm} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CO_2$$

3-Oxobutanoic acid
(Acetoacetic acid)

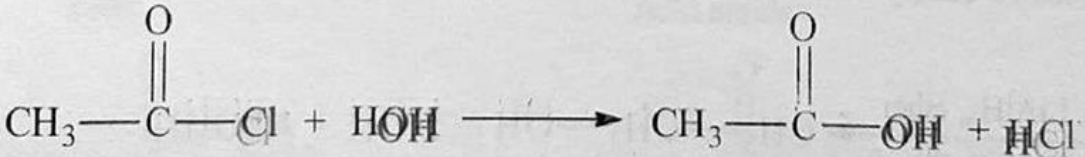
Acetone

20.7.4 Reactions of Carboxylic Acid Derivatives

20.7.4.1 Reactions of Acyl Halides

Hydrolysis (Reaction with Water)

Acyl halides react spontaneously with water to produce carboxylic acids and HCl. The reaction of low molecular mass acid halides with water is fast and that of high molecular mass acid halides is slow. This is because the higher molecular mass acid halides are less soluble in water.

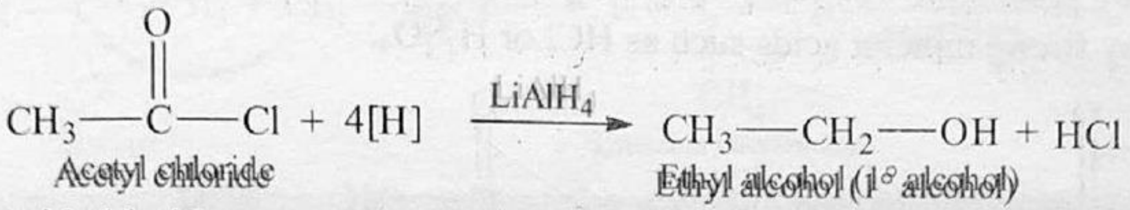


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + HOH \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HCl$$

Acetyl chloride Acetic acid

Reduction

Acyl chlorides are reduced to produce primary alcohols when treated with $LiAlH_4$.



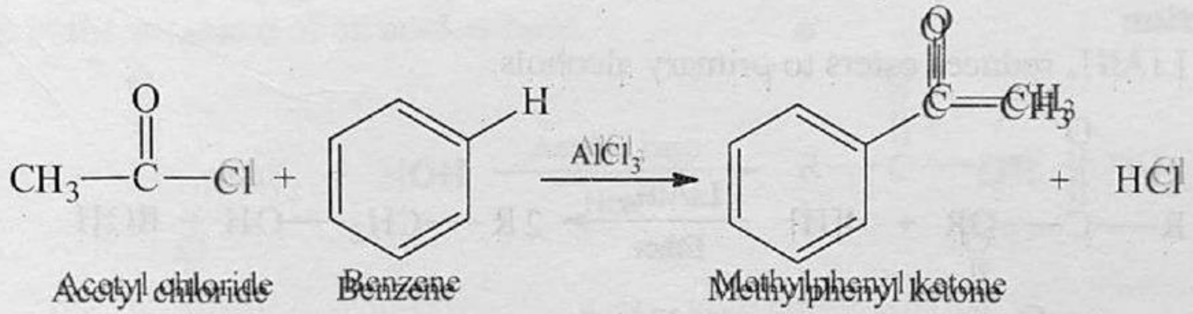
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + 4[H] \xrightarrow{LiAlH_4} CH_3-CH_2-OH + HCl$$

Acetyl chloride; Ethyl alcohol (1° alcohol)

Acid chlorides are more reactive than the other acid derivatives. Either lithium aluminium hydride (stronger reducing agent) or sodium borohydride (weaker reducing agent) converts acid chlorides to primary alcohols.

Friedel-Crafts Acylation

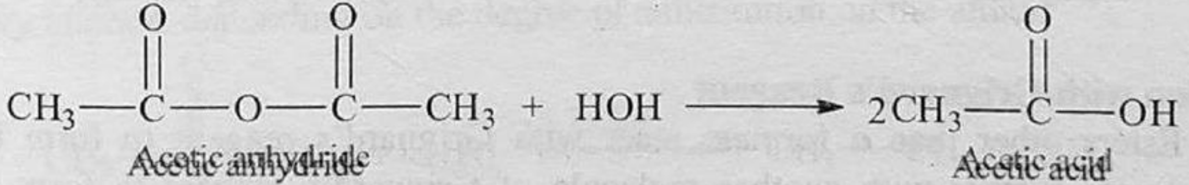
Acid halides react with aromatic hydrocarbons in the presence of aluminum chloride to form aromatic ketones. In this reaction the hydrogen of benzene is replaced by an acyl group and is known as Friedel-Crafts Acylation.



20.7.4.2 Reactions of Acid Anhydrides

Hydrolysis

Acid anhydrides react with water to produce carboxylic acids.

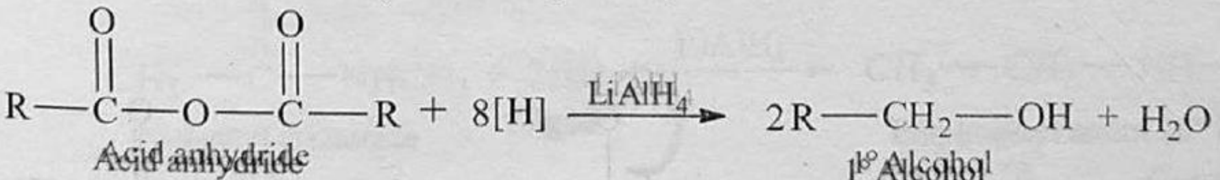


$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + HOH \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Acetic anhydride; Acetic acid

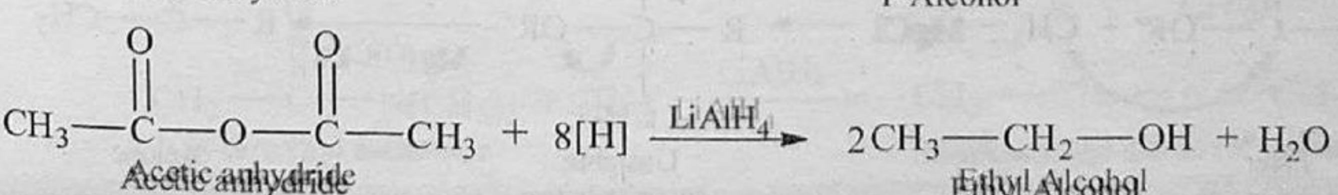
Reduction

$LiAlH_4$ reduces anhydrides to primary alcohols.



$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + 8[H] \xrightarrow{LiAlH_4} 2R-CH_2-OH + H_2O$$

Acid anhydride; 1° Alcohol



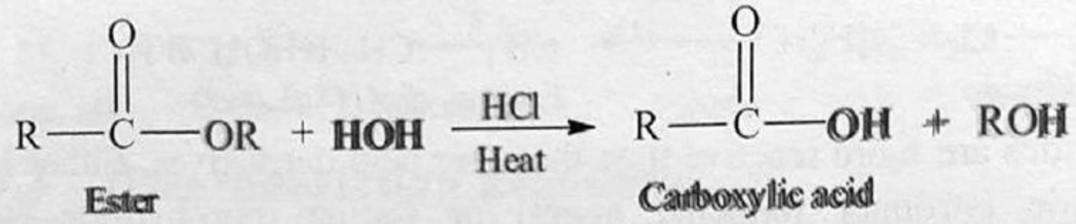
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + 8[H] \xrightarrow{LiAlH_4} 2CH_3-CH_2-OH + H_2O$$

Acetic anhydride; Ethyl Alcohol

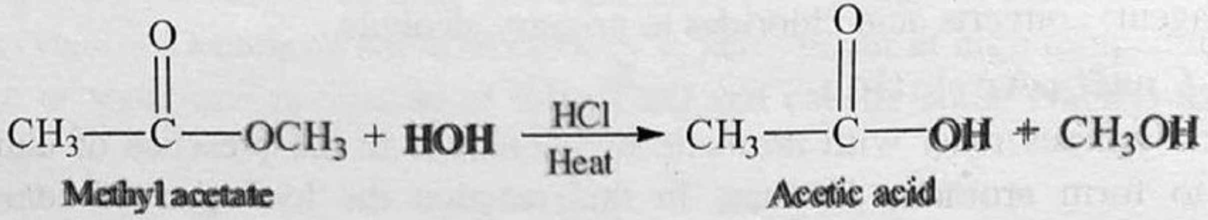
20.7.4.3 Reactions of Esters

Hydrolysis

Esters react with water to produce carboxylic acids and water. This reaction is catalyzed by strong mineral acids such as HCl or H_2SO_4.



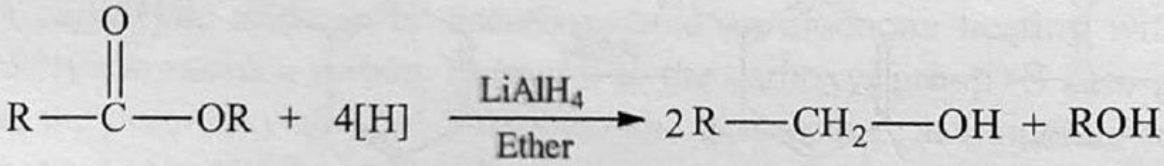
$$\underset{\textbf{Ester}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OR} + \mathbf{HOH} \xrightarrow[\text{Heat}]{\text{HCl}} \underset{\textbf{Carboxylic acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-\mathbf{OH}} + \mathbf{ROH}$$



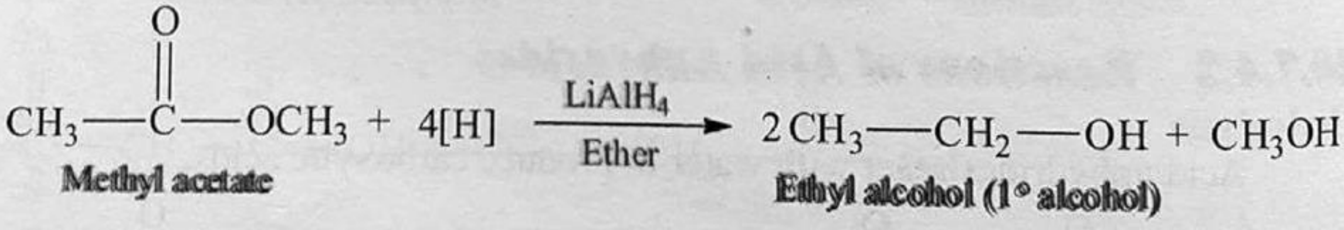
$$\underset{\textbf{Methyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3} + \mathbf{HOH} \xrightarrow[\text{Heat}]{\text{HCl}} \underset{\textbf{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\mathbf{OH}} + \mathbf{CH_3OH}$$

Reduction

$LiAlH_4$ reduces esters to primary alcohols.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} 2\,R-CH_2-OH + ROH$$

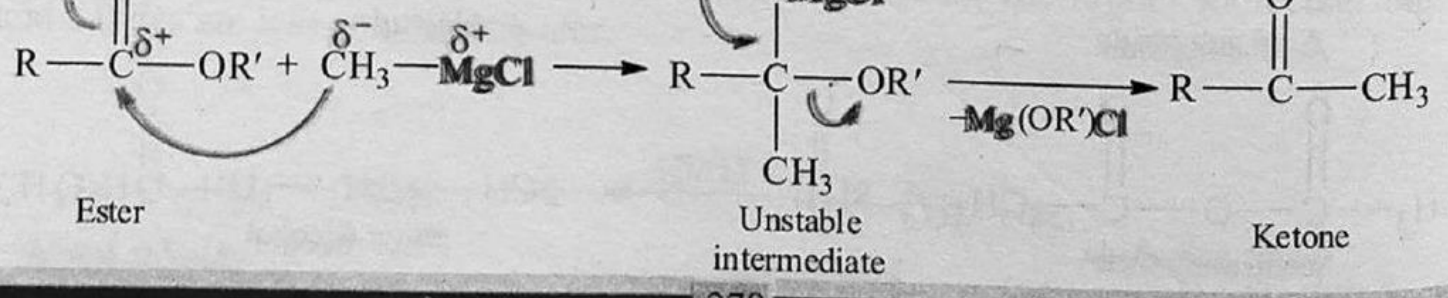


$$\underset{\textbf{Methyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3} + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\textbf{Ethyl alcohol (1° alcohol)}}{2\,CH_3-CH_2-OH} + CH_3OH$$

Reaction with Grignard's Reagent

Esters other than a formate react with Grignard's reagent to form ketones which reacts further with another molecule of Grignard's reagent to form tertiary alcohol as a final product.

Step 1:



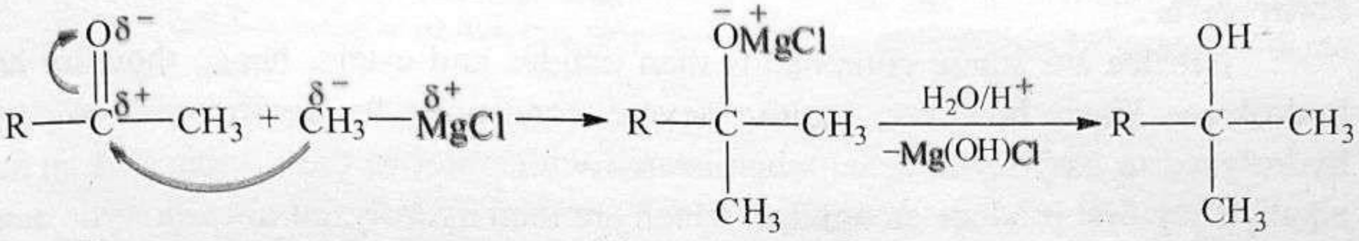
$$R-\overset{\overset{\displaystyle O^{\delta-}}{\|}}{C^{\delta+}}-OR' + \overset{\delta-}{CH_3}-\overset{\delta+}{\mathbf{MgCl}} \longrightarrow R-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle \overset{-}{O}\overset{+}{\mathbf{MgCl}}}{|}}{C}}-OR' \xrightarrow[-\mathbf{Mg}(OR')\mathbf{Cl}]{} R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Ester

Unstable intermediate

Ketone

Step 2:



$$R-\overset{O^{\delta-}}{\overset{\|}{C}}{}^{\delta+}-CH_3 + \overset{\delta-}{C}H_3-\overset{\delta+}{MgCl} \longrightarrow R-\overset{\overset{-\ +}{OMgCl}}{\underset{CH_3}{C}}-CH_3 \xrightarrow[-Mg(OH)Cl]{H_2O/H^+} R-\overset{OH}{\underset{CH_3}{C}}-CH_3$$

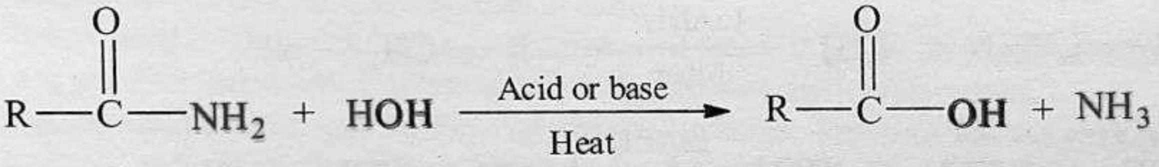
Ketone Unstable intermediate Tertiary alcohol

Keep in Mind

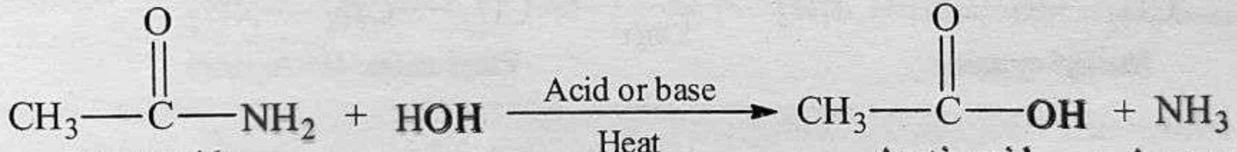
The esters namely formates react in the same way with an excess of Grignard's reagents to form secondary alcohols.

20.7.4.4 Reactions of Amides

Hydrolysis: Amides are the most stable of acid derivatives, and considerably more vigorous conditions are needed for their hydrolysis. Amides do not react with water at normal conditions. Amides do, however, react with water if the reaction mixture is heated in the presence of an acid or base.



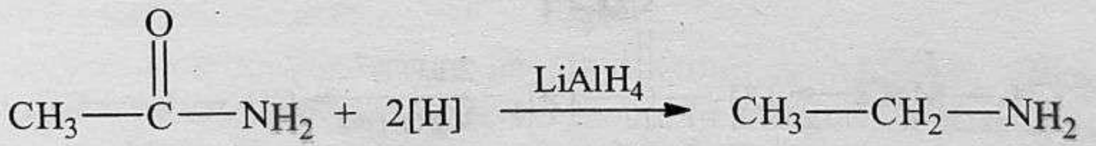
$$R-\overset{O}{\overset{\|}{C}}-NH_2 + \mathbf{HOH} \xrightarrow[\text{Heat}]{\text{Acid or base}} R-\overset{O}{\overset{\|}{C}}-\mathbf{OH} + NH_3$$



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + \mathbf{HOH} \xrightarrow[\text{Heat}]{\text{Acid or base}} CH_3-\overset{O}{\overset{\|}{C}}-\mathbf{OH} + NH_3$$

Acetamide **Acetic acid** **Ammonia**

Reduction: Lithium aluminum hydride reduces amides to primary, secondary or tertiary amines, depending on the degree of substitution on the amide.



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + 2[H] \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2$$

Acetamide **Ethyl amine (1° Amine)**

$$CH_3-\overset{O}{\overset{\|}{C}}-NHCH_3 + 2[H] \xrightarrow{LiAlH_4} CH_3-CH_2-NH-CH_3$$

N-methyl acetamide **Ethylmethyl amine (2° Amine)**

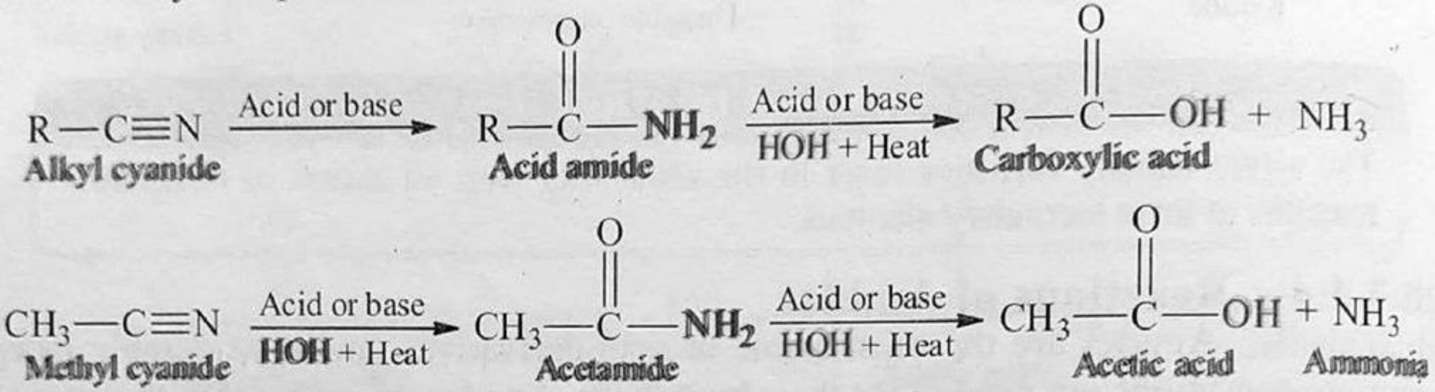
$$CH_3-\overset{O}{\overset{\|}{C}}-N(CH_3)_2 + 2[H] \xrightarrow{LiAlH_4} CH_3-CH_2-\overset{CH_3}{\overset{|}{N}}-CH_3$$

N,N-dimethyl acetamide **Ethyldimethyl amine (3° Amine)**

20.7.4.5 Reactions of Nitriles

Hydrolysis

Nitriles are stable compounds than amides and esters, hence they are hard to hydrolyze. They, however, require severe conditions for hydrolysis. Nitriles are hydrolyzed to carboxylic acids when heated with water in the presence of an acid or alkali. They first produce an amides, which are then hydrolyzed to carboxylic acids.



$$\underset{\textbf{Alkyl cyanide}}{R-C\equiv N} \xrightarrow{\text{Acid or base}} \underset{\textbf{Acid amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[\text{HOH + Heat}]{\text{Acid or base}} \underset{\textbf{Carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + NH_3$$

$$\underset{\textbf{Methyl cyanide}}{CH_3-C\equiv N} \xrightarrow[\text{HOH + Heat}]{\text{Acid or base}} \underset{\textbf{Acetamide}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[\text{HOH + Heat}]{\text{Acid or base}} \underset{\textbf{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\textbf{Ammonia}}{NH_3}$$

Reduction

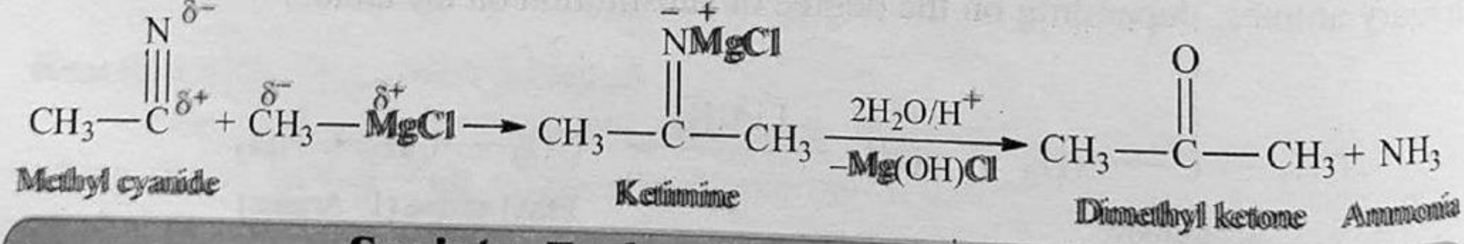
Lithium aluminum hydride reduces nitriles to primary amines.

$$R-C\equiv N + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} R-CH_2-NH_2$$

$$\underset{\textbf{Methyl cyanide}}{CH_3-C\equiv N} + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\textbf{Ethyl amine (1° Amine)}}{CH_3-CH_2-NH_2}$$

Reaction with Grignard's Reagent

Nitriles react with Grignard's reagent to form ketimines, which on acid hydrolysis gives ketones.



$$\underset{\textbf{Methyl cyanide}}{CH_3-\overset{\overset{N^{\delta-}}{|||}}{C^{\delta+}}} + \overset{\delta-}{C}H_3-\overset{\delta+}{MgCl} \longrightarrow \underset{\textbf{Ketimine}}{CH_3-\overset{\overset{\overset{-}{N}\overset{+}{MgCl}}{\|}}{C}-CH_3} \xrightarrow[-Mg(OH)Cl]{2H_2O/H^+} \underset{\textbf{Dimethyl ketone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\textbf{Ammonia}}{NH_3}$$

Society, Technology and Science

Sources and Uses of Carboxylic Acids

Most of the simpler saturated carboxylic acids are found in fruits, vegetables and other natural products that give them a distinct flavour or a tinge. Carboxylic acids are primarily used as antibacterial and antifungal preservatives and as flavouring agents in foods and pharmaceutical products. If the acids are not present in foods their taste may bland.

i) **Formic acid** is found in insect stings and nettles. It is used in food preservation.

ii) **Acetic acid** is found in vinegar. It is used in food preservation. It is used in pickles to preserve fruits and vegetables. It stops the growth of bacteria.

iii) **Butyric acid** is found in butter. It is responsible for the smell of rancid butter and to the odour of sweat.

iv) **Palmitic acid** is found in palm oil.

v) **Stearic acid** is found in chocolate, waxes, soaps, animal fats and oils.

vi) **Oxalic acid** is found in spinach and some other plant foods including rhubarb. It is used as a cleaning agent for rust stains on fabric and porcelain.

vii) **Citric acid** is found in citrus fruits such as lemons, limes, oranges, grape fruits as well as pineapple and tomatoes. It is also found in tea, cocoa and pepper. It is used as preservative and flavouring agent in both foods and soft drinks.

viii) **Malic acid** is found in many unripe fruits such as green apples and pears. It is also found in plums, currants, etc.

ix) **Tartaric acid** is found in grapes, bananas, potatoes and tamarinds. It is also found in wine and molasses. The tartaric acid in the wine contributes to the tartness of the wine, along with malic acid.

x) **Lactic acid** is found in sour milk such as laban, yougurt, kefir and koumiss. Lactic acid is used as preservative to prevent microbial growth.

xi) **Benzoic acid** is found in berries, plums, prunes, etc.

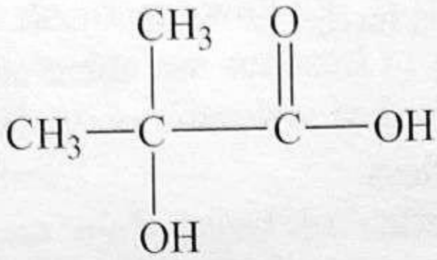
xii) **Adipic acid** is found in beets and sugar cane.

xiii) **Tannic acid** is found in the bark of number of trees. It has been used for tanning. It is now used for the staining of wood and is also used when dyeing cotton.

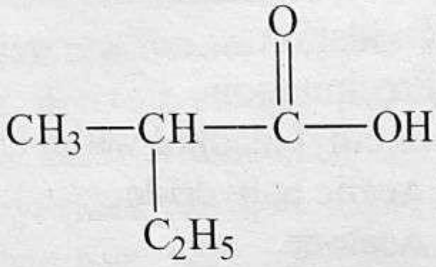
xiv) **Amino acids** are the special form of carboxylic acids. Amino acids are very important because groupings of amino acids make up the proteins. The skin, hair and muscle is composed of protein.

Summary of Facts and Concepts

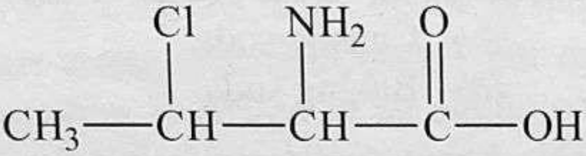
- Carboxylic acids are organic compounds having carboxyl group (—COOH) as functional group. They are of two types: (i) aliphatic carboxylic acids and (ii) aromatic carboxylic acids.
- In aliphatic carboxylic acids, an alkyl group or hydrogen atom is directly attached with the carbon of carboxyl group. In aromatic carboxylic acids, an aryl group is directly attached with the carbon of carboxyl group.
- Carboxylic acids are prepared by oxidation aldehydes, alcohols and alkyl benzenes. They can also be prepared by hydrolysis of nitriles.
- They have higher boiling points than their corresponding alcohols. Boiling point increases with increase in the molecular mass.
- The reaction of a carboxylic acid with excess alcohol and an acid catalyst is called a Fischer esterification.
- The derivatives of carboxylic acids are: (i) acid halides (ii) acid amides (iii)esters (iv) acid anhydrides.
- Lower members of carboxylic acids are water soluble and have pungent smell.

iii) 

$CH_3-C(CH_3)(OH)-C(=O)-OH$

iv) 

$CH_3-CH(C_2H_5)-C(=O)-OH$

v) 

$CH_3-CH(Cl)-CH(NH_2)-C(=O)-OH$

Q.5. Write structural formulas for the following compounds:
- i) Propionic acid
- ii) Valeric acid
- iii) Lactic acid
- iv) Phenylacetic acid
- v) 2-Chloro-3-phenylpentanoic acid

Q.6. Describe structure, acidity, and reactivity of carboxylic acids.

Q.7. Write down five physical properties of carboxylic acids.

Q.8. Write down five different methods for preparing carboxylic acids.

Q.9. Write short note on the conversion of carboxylic acids to carboxylic acid derivatives (acyl halides, acid anhydrides, esters and amides).