UNIT 20

Carbonyl Compounds 2: Carboxylic Acids and Functional Derivatives

Learning Outcomes:

After Studying this unit Students will be able to:

- Describe Nomenclature, physical properties and structure of carboxylic acids.
- Discuss preparation of carboxylic acids by carbonation of Grignard's reagent, hydrolysis of nitriles, oxidation of primary alcohols, oxidation of aldehydes and oxidation of alkyl benzene.
- Discuss reactivity of carboxylic acids.
- Describe the chemistry of carboxylic acids by conversion to carboxylic acid i.e. acylhalides, acid anhydrides, esters, amides and reaction involving inter conversion of these.
- Describe reactions of carboxylic acid derivates.
- Describe isomerism in carboxylic acids.
- Identify carboxylic acid in the laboratory.

Introduction:

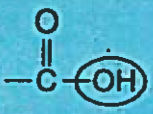
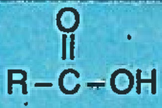
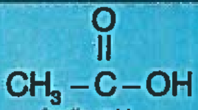
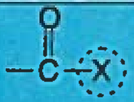
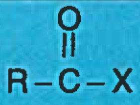
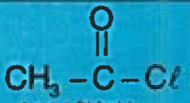
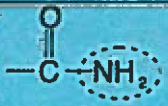
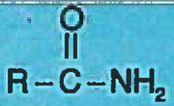
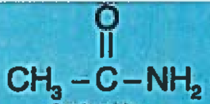
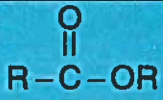
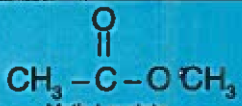
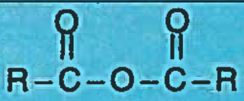
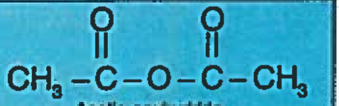
Carboxylic acids are organic acids containing the carboxyl group ($-\overset{O}{\overset{\|}{C}}-OH$ or $-COOH$) as a functional group. The carboxyl group itself consists of a carbonyl group $(>C=O)$ and a hydroxyl group $(-\dot{O}H)$ i.e. carb from carbonyl and oxyl from hydroxyl. Acids containing one such functional group are known as mono carboxylic acids, while those containing two carboxyl groups are called dicarboxylic acids. Carboxylic acids may be aliphatic or aromatic depending upon whether carboxyl group ($-\overset{O}{\overset{\|}{C}}-OH$) is attached to an alkyl group or an aryl group.

The general formula of an aliphatic carboxylic acid is RCOOH whereas that of aromatic carboxylic acid is ArCOOH.

Aliphatic carboxylic acids are also commonly called fatty acids because esters of several of their higher members are fats.

Carboxylic acids have many derivatives in which the –OH of an acid is replaced by other functional groups. This results in other classes of organic compounds. There derivatives alongwith their functional groups and general formulas are mentioned in the table 20.1 below;

Table: 20.1 Derivatives of Carboxylic acids:

Acid Derivatives	Functional Group	General Formula	Examples
Acid	 $-\overset{\overset{O}{\|}}{C}-\boxed{OH}$	 $R-\overset{\overset{O}{\|}}{C}-OH$	 $CH_3-\overset{\overset{O}{\|}}{C}-OH$ Acetic acid (Ethanoic acid)
Acid Halide or Acyl Halide	 $-\overset{\overset{O}{\|}}{C}-\boxed{X}$	 $R-\overset{\overset{O}{\|}}{C}-X$	 $CH_3-\overset{\overset{O}{\|}}{C}-Cl$ Acetyl Chloride (Ethanoyl chloride)
Acid amide	 $-\overset{\overset{O}{\|}}{C}-\boxed{NH_2}$	 $R-\overset{\overset{O}{\|}}{C}-NH_2$	 $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ Acetamide (Ethanamide)
Ester	 $-\overset{\overset{O}{\|}}{C}-\boxed{OR}$	 $R-\overset{\overset{O}{\|}}{C}-OR$	 $CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$ Methyl acetate (Methyl ethanoate)
Acid anhydrides	 $-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$	 $R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$	 $CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$ Acetic anhydride (Ethanoic anhydride)

20.1 Nomenclature:

Following two types of naming is employed in case of carboxylic acids.

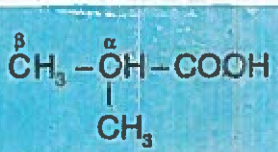
Common or Trivial Names:

Many of the acids have common names. These names usually come from some Latin or Greek words that indicate the original source of the acid. Following table 20.2 lists some common aliphatic carboxylic acids, with their common names.

Table: 20.2 Common Names of few Organic Acids:

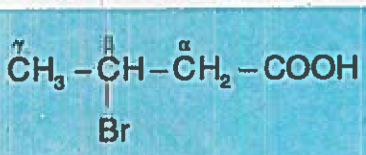
Carbon atoms	*Formula /common name*	*Sources*
1.	HCOOH Formic acid	From Latin word ‘Formica’ means ‘ant’
2.	CH_3COOH Acetic acid	From Latin word ‘ acetum means ‘vinegar’
3.	CH_3CH_2COOH Propionic acid	From Greek word ‘protos’ means ‘first’ and ‘pion’ means ‘fat’
4.	$CH_3CH_2CH_2COOH$ Butyric acid	From Latin word ‘butyrum’ means ‘butter’

In case of branched acids, the common name of the acid is used. Substituents are located with Greek letters α,β,γ etc. as given below.



$\overset{\beta}{C}H_3-\underset{CH_3}{\overset{\alpha}{C}H}-COOH$

$\alpha-$Methyl propionic acid
(Iso$-$Butyric acid)



$\overset{\gamma}{C}H_3-\underset{Br}{\overset{\beta}{C}H}-\overset{\alpha}{C}H_2-COOH$

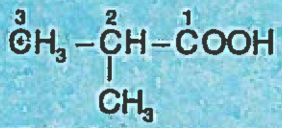
$\beta-$Bromobutyric acid

The IUPAC Nomenclature:

Aliphatic monocarboxylic acids are named as alkanoic acids. These are obtained by replacing the ending ‘e’ of the corresponding alkane with the suffix “oic acid”. e.g.

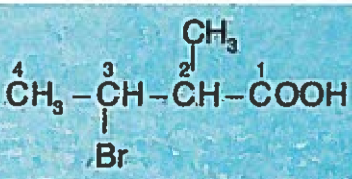
$HCOOH$	CH_3COOH	CH_3CH_2COOH	$CH_3CH_2CH_2COOH$
Methanoic acid	Ethanoic acid	Propanoic acid	Butanoic acid

In case of branched acids, the chain is numbered starting from the carboxyl carbon atom i.e. $(-\overset{\overset{O}{\|}}{{}^{1}C}-OH)$ and substituents are located in the usual way e.g.



$$\overset{3}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}OOH$$

2–Methyl propanoic acid



$$\overset{4}{C}H_3-\underset{\underset{Br}{|}}{\overset{3}{C}H}-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}OOH$$

3–Bromo–2–methyl butanoic acid

Similarly, the unsaturated carboxylic acids are named as alkenoic acid e.g.

$$\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}OOH$$

2–Propenoic acid

$$\overset{4}{C}H_3-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}OOH$$

2–Butynoic acid

Carboxylic acids containing two carboxyl groups are called dicarboxylic acids or dioic acids (IUPAC).

Table 20.3 Aliphatic dicarboxylic acids:

Formula	IUPAC Name
$HOOC-COOH$	Ethanedioic acid
$HOOC-CH_2-COOH$	Propanedioic acid
$HOOC(CH_2)_2\,COOH$	Butanedioic acid
$HOOC-(CH_2)_3-COOH$	Pentanedioic acid
$HOOC(CH_2)_4-COOH$	Hexanedioic acid

20.2 Physical Properties:

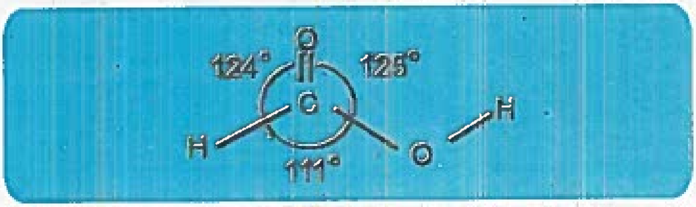
The lower members of the aliphatic acids $C_1 - C_{10}$ are liquids with distinctive penetrating odours. Acetic acid (ethanoic acid), which constitutes about 4 to 5 % of vinegar, has a characteristic smell which is recognizable in vinegar. Butyric acid (Butanoic acid) is the substance that can be smelled in rancid butter. Higher members of acid homologous series are wax-like solids. Anhydrous ethanoic acid (acetic acid) freezes at 17°C to form a solid which look like ice. It is, therefore, known as glacial acetic acid, (glacial means ice –like).

Carboxylic acids are more polar than alcohols. They form hydrogen bonds with themselves or with their own molecules. That is why they have high melting and boiling points.

Hydrogen bonding also explains the water solubility of lower –molecular weight carboxylic acids which form hydrogen bond with water molecule. Solubility of these acids in water decrease as their relative molecular mass increases.

20-3 Structure

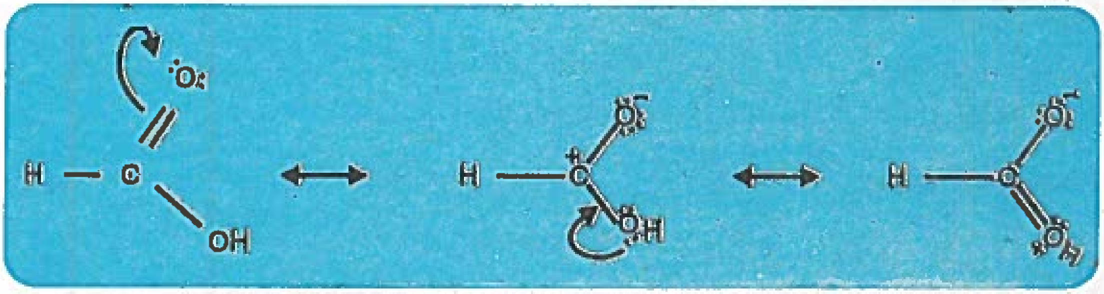
The Structural features of the carboxyl group are most apparent in formic acid. It is planar, with one of its carbon–oxygen bonds shorter than the other, and with bond angles at carbon close to 120°.



The bond lengths between C = O is 120 pm and C — O is 134 pm. Similarly, the bond angles of H – C = O is 124°, H – C = O is 111° and O – C = O is 125°.

This suggest sp^2 hybridization at carbon, and a carbon oxygen double bond similar to that of aldehydes and ketones.

Additionally, sp^2 hybridization of hydroxyl oxygen allows one of its unshared electron pair to be delocalized by orbital overlap with the π system of the carbonyl carbon i.e.

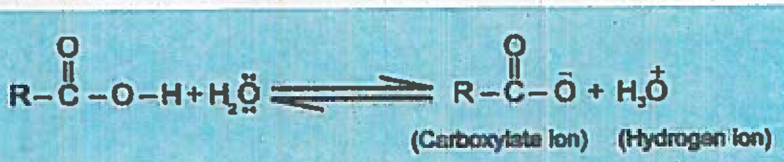


Lone –pair donation from hydroxyl oxygen makes the carbonyl group less electrophillic than that of aldehyde and ketones.

20.4 Acidity:

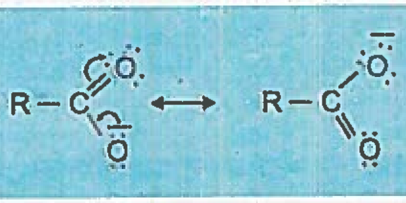
Carboxylic acids are the most acidic class of organic compounds. They are much stronger acids than water, alcohols and phenols but weaker than mineral acids.

Carboxylic acids dissociate in water, yielding carboxylate anion and a hydronium ion. The withdrawal of electrons away from the carboxyl hydrogen atom weakens the O–H bond. As a result the carboxyl group can lose a proton in aqueous medium. Mono carboxylic acids are thus monobasic acids. The following equilibrium is established.

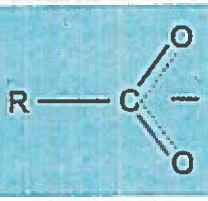


$$R-\overset{O}{\overset{\|}{C}}-O-H+H_2\ddot{O} \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-\bar{O}+H_3\overset{+}{O}$$

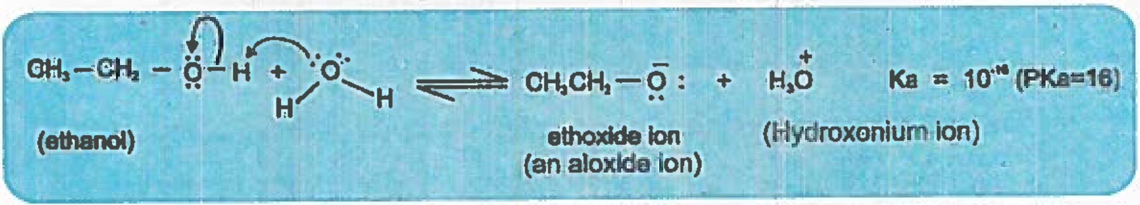
The carboxylate ion exists as a resonance hybrid of two canonical forms.



The resonance hybrid can be represented as

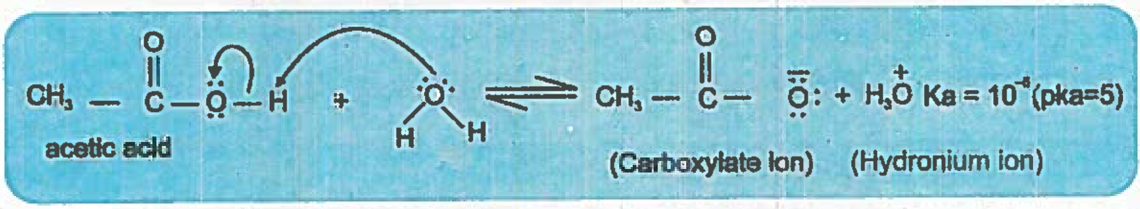


Carboxylic acids are much more acidic than alcohols and phenols as evident from their Ka values.



$$CH_3-CH_2-\ddot{O}-H+H_2\ddot{O} \rightleftharpoons CH_3CH_2-\ddot{O}:+H_3\overset{+}{O} \quad Ka = 10^{-16}\ (PKa=16)$$

Ionization of acetic acid (ethanoic acid).



$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}-H+H_2\ddot{O} \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}:+H_3\overset{+}{O} \quad Ka=10^{-5}\ (pka=5)$$

The ionization of ethanol yields an alkoxide (ethoxide) ion in which the negative charge is localized on oxygen. However, the carboxylate ion is stabilized by the delocalization of negative charge on two oxygen atoms.

The acidities of the carboxylic acids vary considerably with the nature of the substituents present in the molecule. Any electron withdrawing substituent (e.g. Cl, NO_2 etc.) will tend to stabilize the carboxylate ion by dispersing its negative charge and thus increase the acidity of acid. Whereas an electron donating substituent (e.g alkyl group) will tend to destabilize the carboxylate ion and thus decrease the acidity of the acid.

Table 20.4 Increasing order of acids strength and ionization constants of some acids.

Carboxylic acid	Formula	pka
Propanoic acid	CH_3CH_2-COOH	4.87
Ethanoic acid	CH_3-COOH	4.76
Methanoic acid	$H-COOH$	3.68
Chloroacetic acid	$CH_2C\ell COOH$	2.86
Dichloroacetic acid	$CHC\ell_2COOH$	1.29
Trichloro acetic acid	$CC\ell_3COOH$	0.65

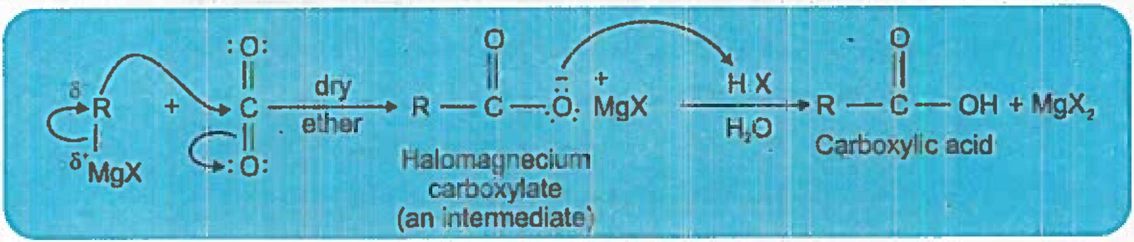
20.5 Preparations of carboxylic Acids:

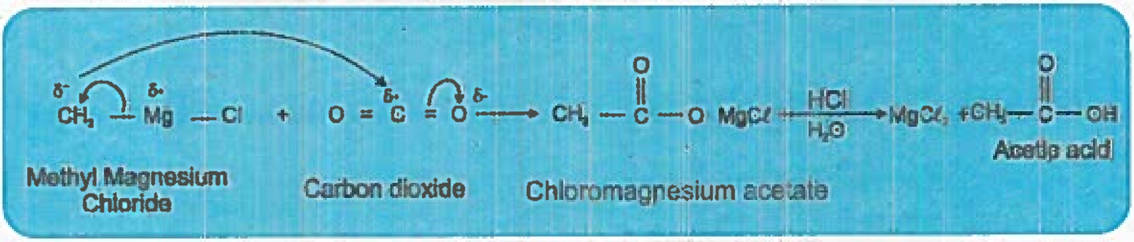
Following methods of preparations are used for carboxylic acids.

20. 5.1 Carbonation of Grignard Reagent:

Carboxylic acids can be prepared by the action of Grignard reagent (RMgX) with carbondioxide. This reaction is known as carbonation or carboxylation of Grignard reagent.

Grignard reagent reacts with carbon dioxide to give initially an intermediate magnesium salt of carboxylic acid which on hydrolysis in the presence of mineral acid ($HC\ell$) gives a carboxylic acid.

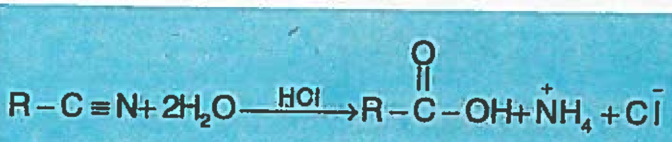




The acid obtained by the carboxylation of Grignard reagent has one more carbon atom than alkyl or aryl halide from which Grignard reagent is prepared, so the reaction provides a way to extend the length of a carbon chain.

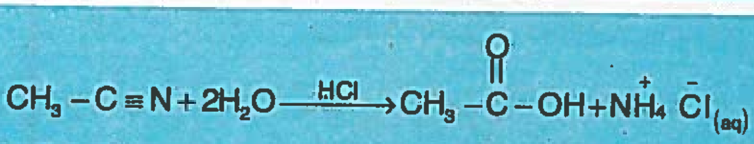
20.5.2 Hydrolysis of Nitriles:

Compounds having a cyanide $(-C\equiv N)$ group are called alkyl nitriles or alkyl cyanides. The carbon –nitrogen triple bond of alkyl nitriles can be hydrolyzed to a carboxylic acid in aqueous acid medium.



$$R-C\equiv N+2H_2O\xrightarrow{HCl}R-\overset{O}{\overset{\|}{C}}-OH+\overset{+}{N}H_4+\overset{-}{Cl}$$

Alkyle Nitrile an acid ammonium ion



$$CH_3-C\equiv N+2H_2O\xrightarrow{HCl}CH_3-\overset{O}{\overset{\|}{C}}-OH+\overset{+}{N}H_4\ \overset{-}{Cl}_{(aq)}$$

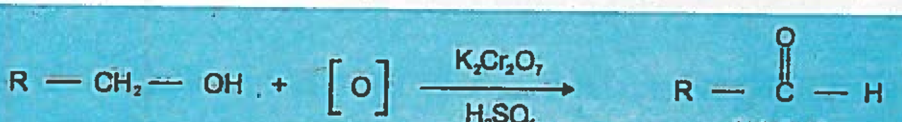
Methyl nitrile
(methyl cyanide)

acetic acid

20.5.3 Oxidation of Primary Alcohols:

Primary alcohols $(R-CH_2-OH)$ can be oxidized to carboxylic acids by oxidizing agents like acidified potassium permangnate or potassium dichromate etc.

Primary alcohol on oxidation, gives aldehyde which on further oxidation converts to carboxylic acid.

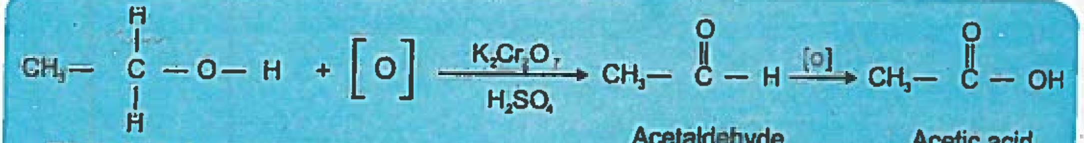


$$R-CH_2-OH+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}R-\overset{O}{\overset{\|}{C}}-H$$

Aldehyde

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

Carboxylic acid

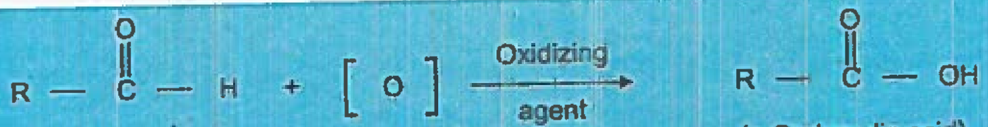


$$CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-O-H+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}CH_3-\overset{O}{\overset{\|}{C}}-H\xrightarrow{[O]}CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Ethyl alcohol Acetaldehyde Acetic acid

20.5.4 Oxidation of Aldehydes:

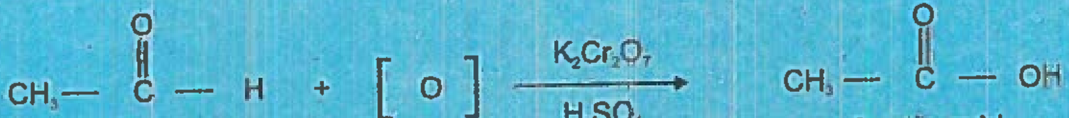
As mentioned earlier oxidation of aldehyde in the presence of oxidizing agents like acidified $KMnO_4$,$K_2Cr_2O_7$ or Ag_2O gives carboxylic acid with the same number of carbon atoms.



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

(an aldehyde)
An aldehyde

(a Carboxylic acid)
Carboxylic acid



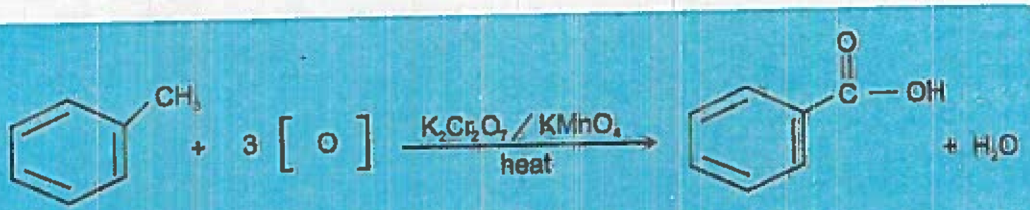
$$CH_3-\overset{\overset{O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Acetaldehyde

Acetic acid

20.5.5 Oxidation of Alkyl Benzene:

Aromatic carboxylic acids can be prepared by the oxidation of aliphatic side chain (alkyl group) present on the benzene ring, with oxidizing agent like $KMnO_4$, $K_2Cr_2O_7$. Any side chain is converted to carboxyl group.



Toluene
(Methyl benzene)

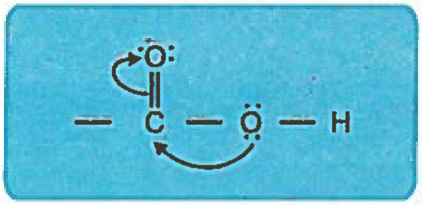
Benzoic acid
(Aromatic carboxylic acid)

The reaction illustrates the striking stability of aromatic rings towards oxidizing agents, it is methyl group, not the aromatic ring that is oxidized.

20.6 Reactivity:

The carboxylic group is so named because it contains a carboxyl group and a hydroxyl group. The two groups influence each other to such an extent that the reactivity of carboxylic acids shows little resemblance to those of carbonyl compounds (aldehydes and ketones) on one hand and alcohols on the other hand.

Although the carboxylic group contain the carbonyl group $(-\overset{\overset{\displaystyle O}{\|}}{C}-)$ carboxylic acids do not exhibit the characteristic reactions of aldehyde and ketones. For example, they do not undergo addition or condensation reactions. This is because the carbon atom of the carboxyl group is less positive than in the aldehyde or ketone. The carboxylic group is given below.



The polar $(>C=O)$ group attracts the electrons away from the $-O-H$ bond, and make it easier for the hydrogen atom to ionize than in the case in the $O-H$ bond in alcohols. Hence carboxylic acids show different chemical reactivity than alcohols. Similarly, the flow of the electrons from the $-O-H$ group towards, the carbonyl carbon reduces the partial positive charge on the carbonyl carbon of carboxylic group. As a result it is not attacked by nucleophiles as compared to aldehyde or ketones.

20.7 Reactions of Carboxylic Acids:

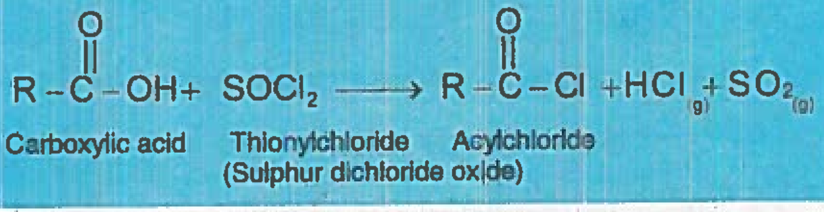
Following are some of the reactions of carboxylic acids that involve the conversion of the carboxylic acids to their derivatives as well as synthesis of some other compounds.

20.7.1 Conversion to Carboxylic Acid Derivatives

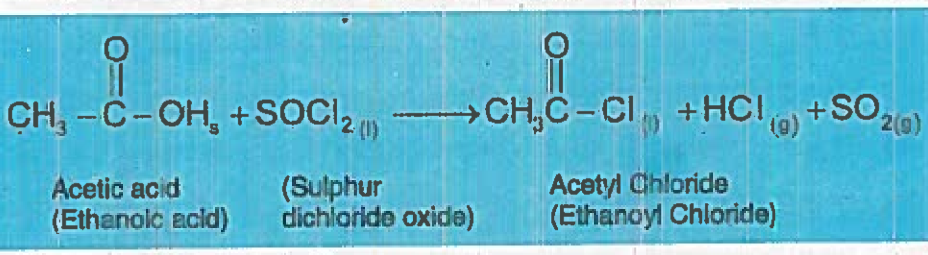
20.7.1.1 Acyl Halides / Acid Halides $(R-\overset{\overset{O}{\parallel}}{C}-X)$

Acyl halides or acid halides are the derivatives of carboxylic acids that are obtained by replacing the $-OH$ of carboxylic acid by halogen atoms $(X = F, Cl, Br, I)$.

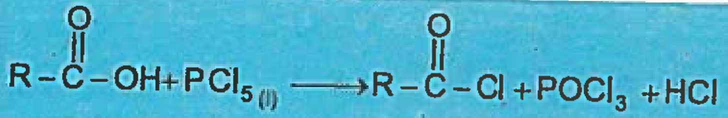
Acyl halides are the most reactive of carboxylic acid derivatives. Acyl chloride are more common and less expensive than bromides and iodides. They are usually prepared by the reaction of acids with thionyl chloride $(SOCl_2)$ or phosphorous pentachloride (PCl_5).



$$R-\overset{\overset{O}{\parallel}}{C}-OH + SOCl_2 \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-Cl + HCl_{(g)} + SO_{2(g)}$$



$$CH_3-\overset{\overset{O}{\parallel}}{C}-OH_s + SOCl_{2(l)} \longrightarrow CH_3\overset{\overset{O}{\parallel}}{C}-Cl_{(l)} + HCl_{(g)} + SO_{2(g)}$$



$$R-\overset{\overset{O}{\|}}{C}-OH+PCl_{5(l)} \longrightarrow R-\overset{\overset{O}{\|}}{C}-Cl+POCl_3+HCl$$

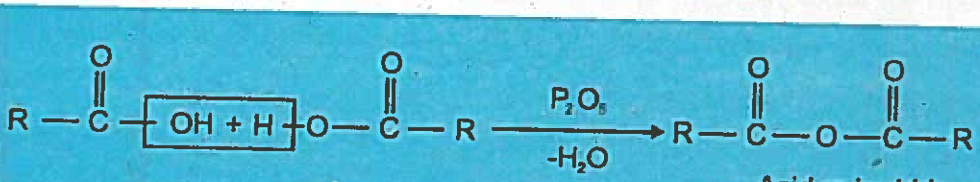
Acid
Phosphorous pentachloride
Acylchloride
Phosphorous oxychloride

$$CH_3COOH+PCl_{5(l)} \longrightarrow CH_3COCl_{(l)}+HCl_{(g)}+POCl_{3(l)}$$

Acetic acid
Acetychloride

20.7.1.2 Acid Anhydrides:

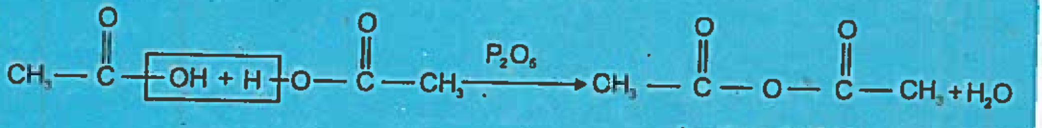
Acid anhydrides are derived from acids by removing water from two carboxylic acid molecules.



$$R-\overset{\overset{O}{\|}}{C}-\boxed{OH+H}-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow[-H_2O]{P_2O_5} R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$$

Acid anhydride

As the name indicates, these are anhydrous carboxylic acids. The name of anhydride is obtained by naming the acid from which it is derived and replacing the word acid with anhydride. The most important and commercially available anhydride is acetic anhydride or ethanoic anhydride. It is prepared by heating acetic acid at high temperature in the presence of dehydrating agent, phosphorous pentoxide (P_2O_5).

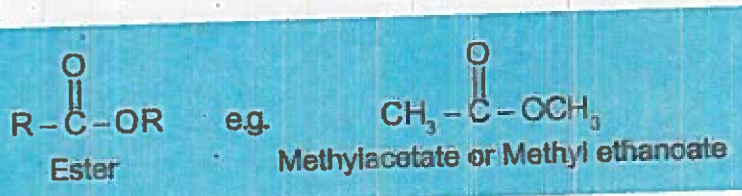


$$CH_3-\overset{\overset{O}{\|}}{C}-\boxed{OH+H}-O-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{P_2O_5} CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3+H_2O$$

Acetic anhydride

20.7.1.3 Esters $(R-\overset{\overset{O}{\|}}{C}-OR)$

Esters are a class of organic compounds that are derived from acids by replacing the –OH group by an alkoxy (-OR) group. While naming ester the R part of the –OR group is named first, followed by the name of the acid, whereby "-ic acid" is replaced by "ate."

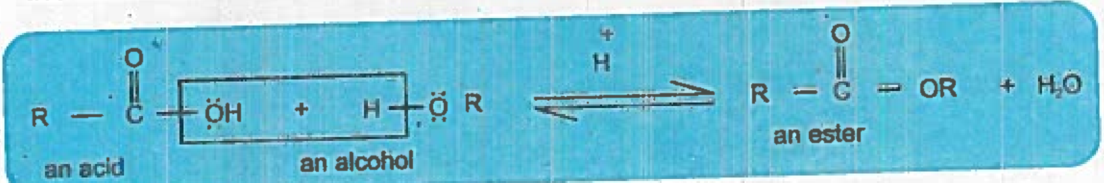


$R-\overset{\overset{O}{\|}}{C}-OR$ e.g. $CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$

Ester

Methylacetate or Methyl ethanoate

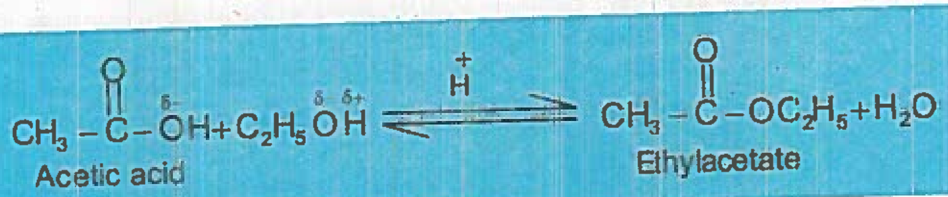
When a carboxylic acid and an alcohol are heated in the presence of an acid catalyst (usually H_2SO_4 or HCl) , an equilibrium is established with the formation of ester and water.



$R-\overset{\overset{O}{\|}}{C}-\boxed{\ddot{O}H \quad + \quad H}-\ddot{O}R \xrightleftharpoons{\overset{+}{H}} R-\overset{\overset{O}{\|}}{C}-OR + H_2O$

an acid an alcohol an ester

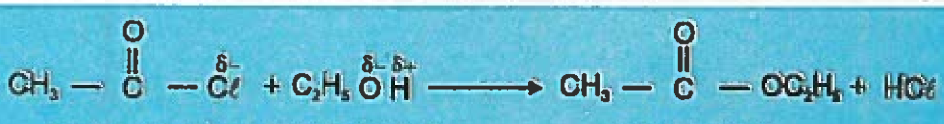
The process is called Fischer esterification after the name of Emil Fischer. Ethyl acetate is an important ester which can be prepared by this method by the reaction of acetic acid with ethanol.



$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\delta-}{O}H+C_2H_5\overset{\delta-\;\delta+}{O}H \xrightleftharpoons{\overset{+}{H}} CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5+H_2O$

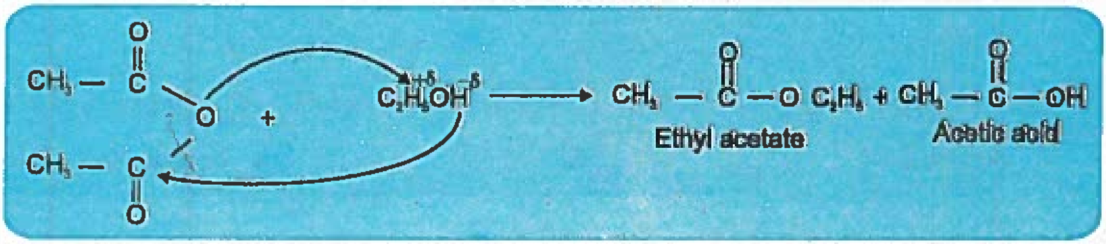
Acetic acid Ethylacetate

Esters can also be prepared by the reaction of an alcohol with acid halide or acid anhydride.



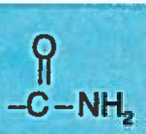
$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\delta-}{Cl}+C_2H_5\overset{\delta-}{O}\overset{\delta+}{H}\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5+HCl$$

Acetyl chloride Ethyl alcohol Ethyl acetate



20.7.1.4 Amides:

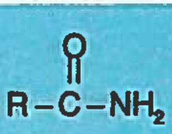
Amides are the least reactive of the derivatives of carboxylic acid derivatives. These are obtained by replacing –OH of the acid with $-NH_2$ group.



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

Amide functional group

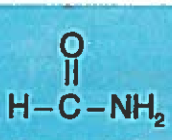
and



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

Amides general formula

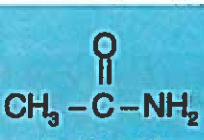
They are named by replacing "ic acid" or "Oic acid" of corresponding acid by word "amide".



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

Formamide
(Methanamide)

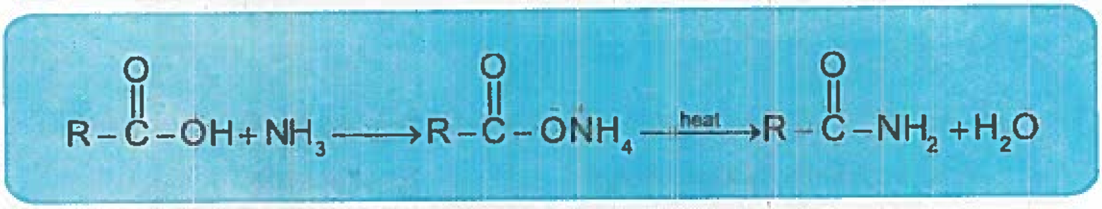
,



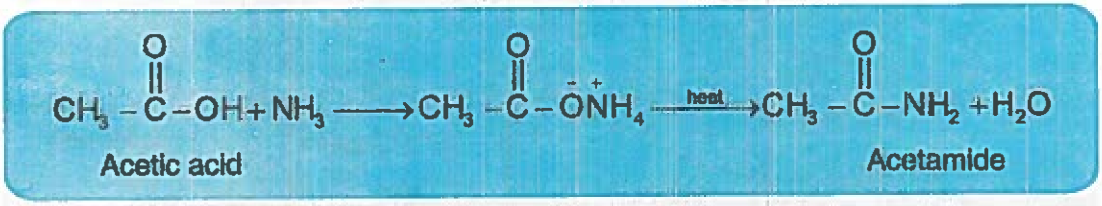
$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$$

Acetamide
(Ethanamide)

Amides can be prepared by the reaction of ammonia with carboxylic acid to form first ammonium salts which on heating produce acid amides.



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

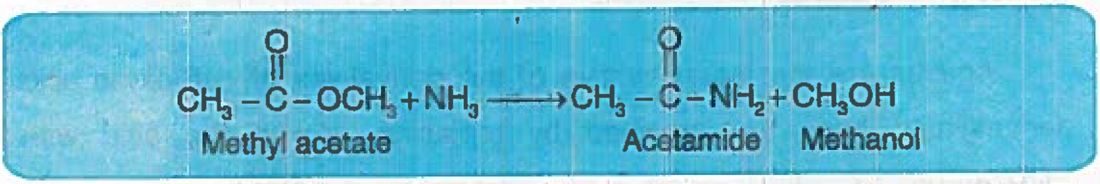


$$CH_3-\overset{O}{\overset{\|}{C}}-OH+NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{heat} CH_3-\overset{O}{\overset{\|}{C}}-NH_2+H_2O$$

Acetic acid

Acetamide

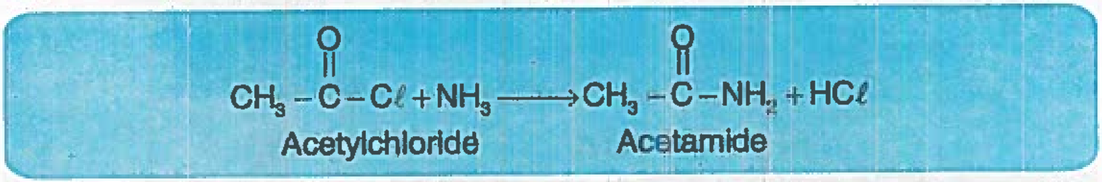
Amides can also be prepared by the reaction of ammonia with ester or acetyl chlorides.



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

Methyl acetate

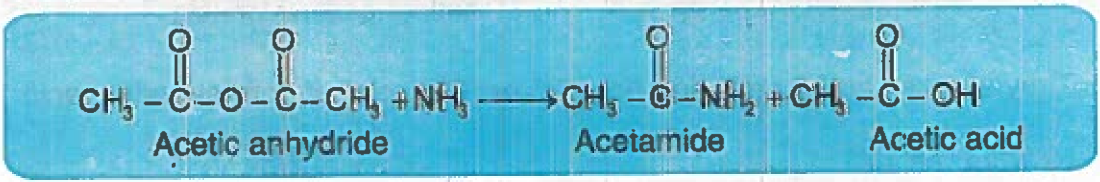
Acetamide Methanol



$$CH_3-\overset{O}{\overset{\|}{C}}-C\ell+NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2+HC\ell$$

Acetylchloride

Acetamide



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

Acetic anhydride

Acetamide

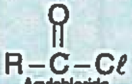
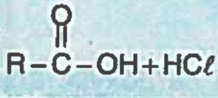
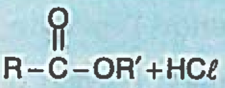
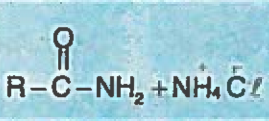
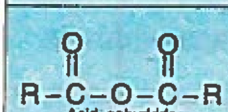
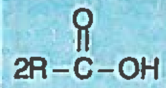
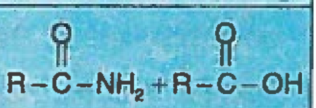
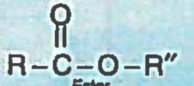
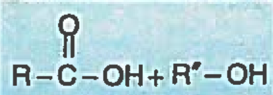
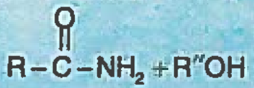
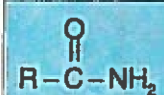
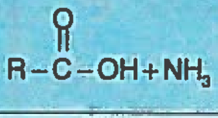
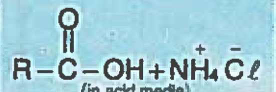
Acetic acid

20.7.2 Summary of the Reactions that Interconvert Carboxylic Acid Derivatives:

A summary of the reactions of different derivatives of carboxylic acids with certain nucleophiles, have been listed in table 20.5.

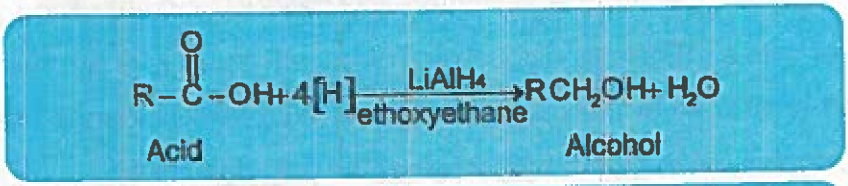
The different acids derivatives are listed at the left of the chart in order of decreasing reactivities towards nucleophiles. The common nucleophiles are listed across the top. In case of hydrolysis corresponding acid is obtained, we either start with an acyl halides, acid anhydride, ester, amide or nitrite. Similarly alcoholysis gives an ester and ammonolysis gives an amide. All of the reactions in table 20.5 take place via attack of the nucleophile on the carbonyl carbon of the acid derivative.

Table 20.5 Reactions of Acid Derivatives with Certain Derivatives Nucleophile:

Acid Derivatives	HOH (Hydrolysis)	R′OH (Alcoholysis)	NH_3 (Ammonolysis)
 $R-\overset{\overset{O}{\Vert}}{C}-C\ell$ Acylchloride	 $R-\overset{\overset{O}{\Vert}}{C}-OH+HC\ell$	 $R-\overset{\overset{O}{\Vert}}{C}-OR'+HC\ell$	 $R-\overset{\overset{O}{\Vert}}{C}-NH_2+\overset{+}{NH_4}\overset{-}{C\ell}$
 $R-\overset{\overset{O}{\Vert}}{C}-O-\overset{\overset{O}{\Vert}}{C}-R$ Acid anhydride	 $2R-\overset{\overset{O}{\Vert}}{C}-OH$	 $R-\overset{\overset{O}{\Vert}}{C}-OR'+R-\overset{\overset{O}{\Vert}}{C}-OH$	 $R-\overset{\overset{O}{\Vert}}{C}-NH_2+R-\overset{\overset{O}{\Vert}}{C}-OH$
 $R-\overset{\overset{O}{\Vert}}{C}-O-R''$ Ester	 $R-\overset{\overset{O}{\Vert}}{C}-OH+R''-OH$	–	 $R-\overset{\overset{O}{\Vert}}{C}-NH_2+R''OH$
 $R-\overset{\overset{O}{\Vert}}{C}-NH_2$ Amide	 $R-\overset{\overset{O}{\Vert}}{C}-OH+NH_3$	–	–
$R-C\equiv N$ Nitrite	 $R-\overset{\overset{O}{\Vert}}{C}-OH+\overset{+}{NH_4}\overset{-}{C\ell}$ (in acid media)	–	–
Main organic product	Carboxylic acid	Ester	Amide

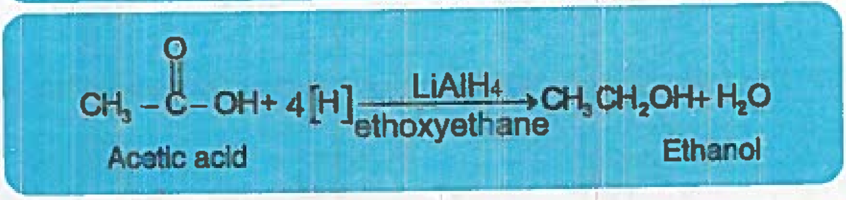
20.7.3 Reduction to Alcohols:

Carboxylic acids can be reduced to the corresponding alcohols using lithium aluminum hydride in dry ethoxy ethane.



$$R-\overset{\overset{O}{\|}}{C}-OH+4[H]\xrightarrow[\text{ethoxyethane}]{LiAlH_4}RCH_2OH+H_2O$$

Acid Alcohol

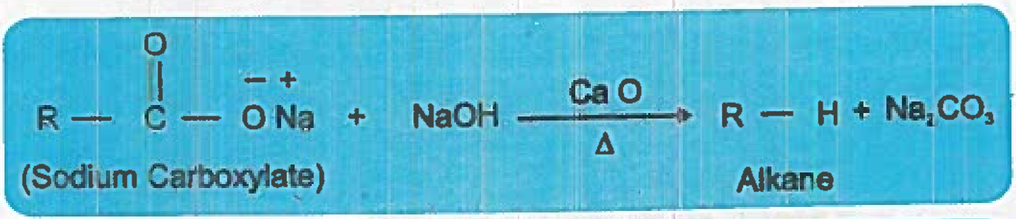


$$CH_3-\overset{\overset{O}{\|}}{C}-OH+4[H]\xrightarrow[\text{ethoxyethane}]{LiAlH_4}CH_3CH_2OH+H_2O$$

Acetic acid Ethanol

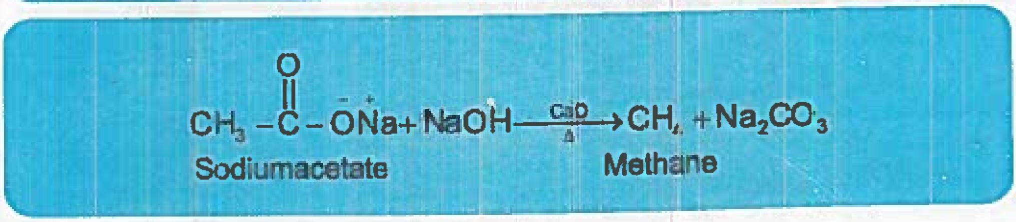
20.7.4 Decarboxylation Reactions:

The removal of carbon dioxide from a carboxylic acid is known as decarboxylation. Decarboxylation of carboxylic acid takes place when its sodium salt is heated with soda lime (dry mixture of caustic soda, NaOH and quick lime CaO) to form alkanes.



$$R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+NaOH\xrightarrow[\Delta]{CaO}R-H+Na_2CO_3$$

(Sodium Carboxylate) Alkane



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+NaOH\xrightarrow[\Delta]{CaO}CH_4+Na_2CO_3$$

Sodiumacetate Methane

Society, Technology and Science

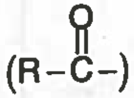
Ascorbic acid occur naturally in fruit, used as preservatives. It inhibits fungal growth but allow bacterial activity, hence it is useful for cheese. Benzoic acid and sodium benzoate have inhibitory effect on the growth of yeast, a major cause of food spoilage. You may have noticed the sharp sour taste of the lemonade. This tartness is a result of carboxylic acid. This is an organic acid found in variety of fruits including grapes, lemon, oranges (citric acid). This acid gives tangy taste. Acetic acid present in vinegar is responsible for giving its sour taste. Malic acid found in unripe fruit gives these fruit a sour or tart taste.

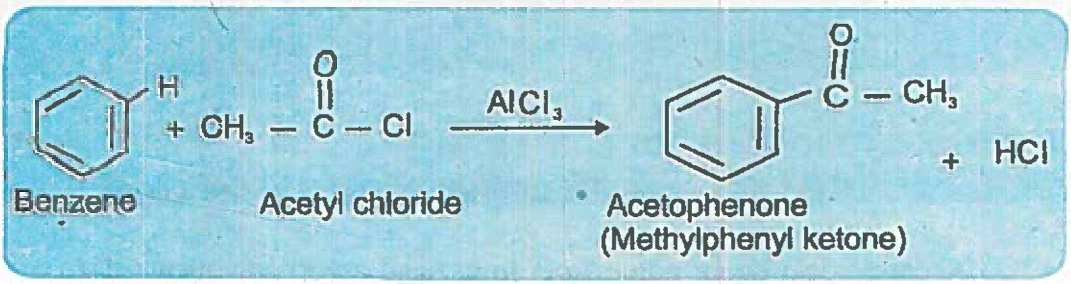
20.7.5 Reactions of Carboxylic Acid Derivatives:

20.7.5.1 Reactions of Acyl Halides:

Acid halides are the most reactive of all derivatives of carboxylic acid.

Friedel –Crafts Acylation Reaction:

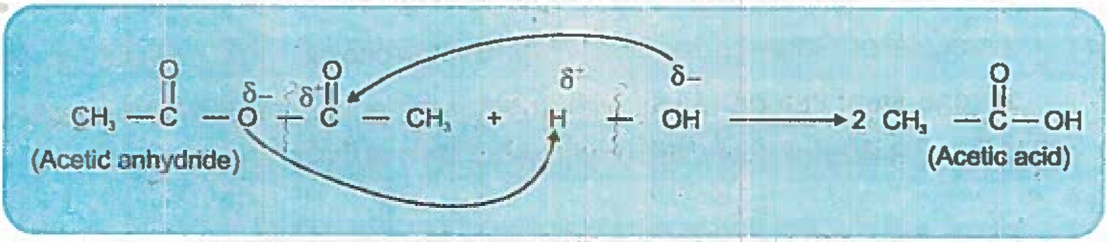
Acyl halides react with benzene in the presence of Lewis acid $AlC\ell_3$ to form aromatic ketones. The reaction involves the introduction of acyl group  $(R-\overset{\overset{O}{\parallel}}{C}-)$ to the ring and is known as Friedel-Crafts acylation reaction.



20.7.5.2 Reactions of Acid Anhydrides:

Acid Anhydrides are more reactive than esters, but less reactive than acid halides, toward nucleophiles.

i. Hydrolysis: On hydrolysis, anhydrides form corresponding carboxylic acids.



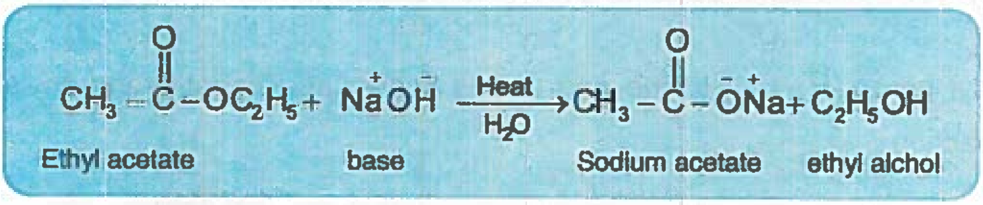
$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\delta-}{O}-\overset{\overset{O}{\|}}{\overset{\delta+}{C}}-CH_3 + \overset{\delta+}{H}-\overset{\delta-}{OH} \longrightarrow 2\ CH_3-\overset{\overset{O}{\|}}{C}-OH$$

20.7.5.3 Reactions of Esters:

Following are some of the important reactions of esters.

i. Hydrolysis: (Saponification of Esters)

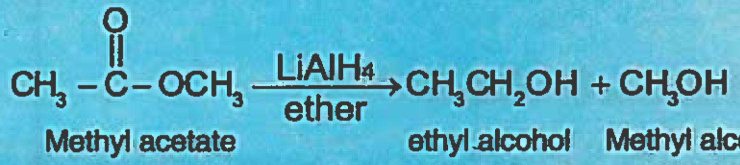
Esters are commonly hydrolyzed with bases. The reaction is called saponification (from the latin sapon, means soap) because this type of reaction is used to make soaps from fats. This reaction is given as;



$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + \overset{+}{Na}\overset{-}{OH} \xrightarrow[H_2O]{Heat} CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na} + C_2H_5OH$$

ii. Reduction of Esters:

Ester can be reduced to primary alcohols in the presence of reducing agent (lithium aluminum hydride) in ether which is used as solvent.

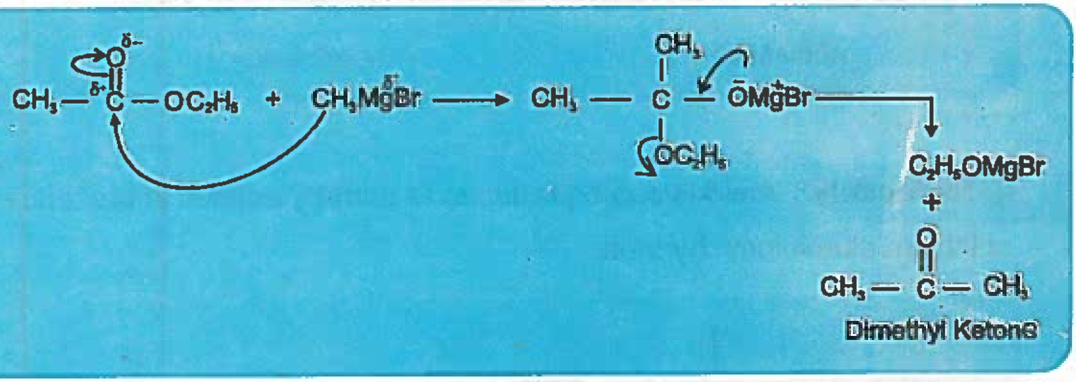


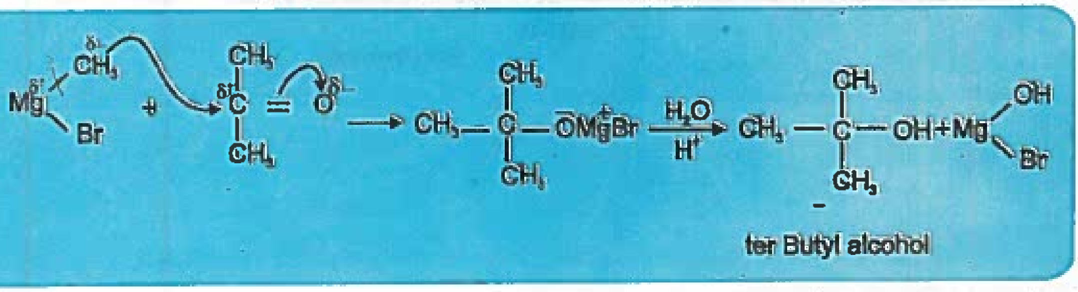
$$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2OH + CH_3OH$$

Methyl acetate ethyl alcohol Methyl alcohol

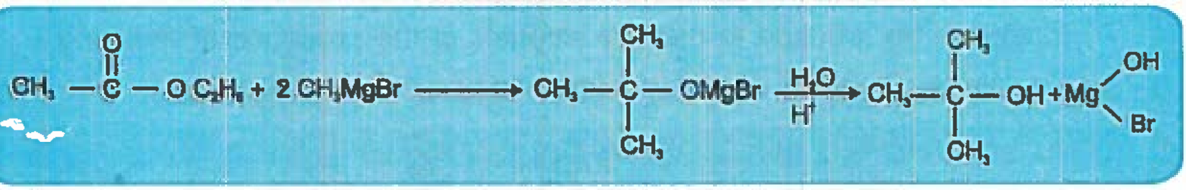
iii. Reaction of Ester with Grignard Reagent:

Esters react with two equivalents of Grignard reagent to give tertiary alcohols. This involves two steps. In first step ester reacts with a molecule of Grignard reagent to form intermediate product, ketone. In second step, ketone reacts with another molecules of Grignard reagent to form tertiary alcohol. The reaction mechanism is given below.





The overall reaction is given as;

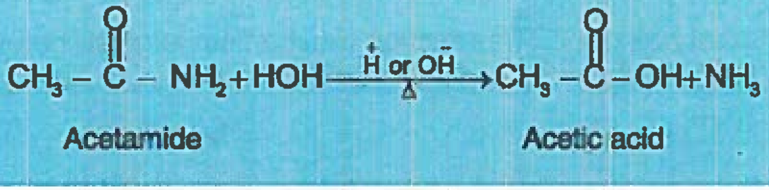


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + 2\,CH_3MgBr \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OMgBr \xrightarrow[H^+]{H_2O} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH + Mg\begin{matrix}OH\\Br\end{matrix}$$

20.7.5.4 Reactions of Amides:

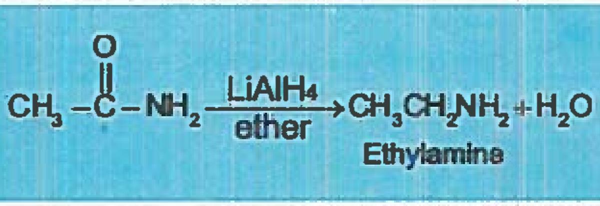
Amides are the least reactive of the common carboxylic acid derivatives. Like other acid derivatives, amides reacts with nucleophiles like water.

i. Hydrolysis: Amides on hydrolysis form the corresponding carboxylic acids. The reaction is slow and requires acid or base as catalyst.



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + HOH \xrightarrow[\Delta]{\overset{+}{H}\text{ or }\overset{-}{OH}} CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3$$

ii. Reduction: Amides can be reduced to primary amines in presence of lithium aluminium hydride.



$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2NH_2 + H_2O$$

20.7.5.5 Reactions of Nitriles:

Alkyl nitriles or simply nitriles $(R-CN)$ are also considered as derivatives of carboxylic acid because they can be obtained from carboxylic acids, though they do not contain acyl group. The following are some of the important reactions of nitriles.

I. Hydrolysis: On boiling with a dilute minerals acid or dilute alkali, nitriles are hydrolysed forming carboxylic acid.

$$CH_3-C\equiv N+2H_2O+HCl \longrightarrow CH_3COOH+\overset{+}{N}H_4\overset{-}{Cl}$$

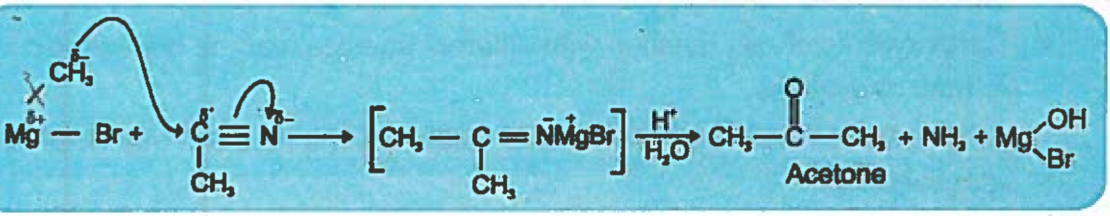
$$CH_3-C\equiv N+H_2O+NaOH \longrightarrow CH_3CO\overset{-}{O}\overset{+}{Na}+NH_3$$

II. Reduction: When treated with a reducing agent such as sodium and ethanol or lithium aluminium hydride (lithium tetra hydridoaluminate (III) in ethoxyethane, nitriles are reduced to primary amines.

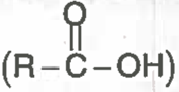
$$CH_3-C\equiv N \xrightarrow[\text{ether}]{\text{LiAlH}_4} CH_3CH_2NH_2$$

Methylcynide (methyl nitrile) ethylamine

III. Reaction with Grignard Reagent: Nitrites on reaction with Grignard reagent produce ketones.



Key Points:



- Carboxylic acids are organic acids having carboxyl group ($R-\overset{O}{\overset{\|}{C}}-OH$) as the functional group ("carb" from carbonyl and "oxyl" from hydroxyl).
- Acyl halides, acid anhydrides, esters, amides etc. are the derivatives of acids obtained by replacing the OH of carboxyl group ($-COOH$) by other functional groups.
- Some members of carboxylic acids have penetrating smells. They are water soluble and their solubility decreases with the increase in molecular mass.
- carboxylic acids, due to strong hydrogen bonds, have high boiling points than corresponding alcohols.
- The carbon atom of the carboxyl group is sp^2 hybridized.
- Carboxylic acids are the strongest organic acids, stronger than phenol, alcohols and water.
- Substituents in a carboxylic acid molecules strongly influence the strength of the acid due to the inductive effect of the substituent.
- Carboxylic acids can be prepared from Grignard reagent, by oxidation of alcohols and aldehydes and by hydrolysis of nitriles.
- Although the carboxylic group contains the carbonyl group, yet carboxylic acid do not exhibit some of the characteristic reactions of aldehydes and ketones.
- Carboxylic acids, on reaction with different species, can be converted to their derivatives.
- Among the derivatives of carboxylic acids, acyl halides are the most reactive.
- All of the acid derivatives can be converted back into the corresponding carboxylic acids on hydrolysis.

Exercise

Q.1 Multiple Choice question. Choose the correct answer from the given choices.

i. Which of the following represents the formula of an aromatic carboxylic acids?

a. HCOOH b. C_6H_5OH

c. C_6H_5COOH d. $C_6H_5CH_2OH$

ii. Which of the following acids is found in rancid butter?

a. $C_2H_4O_2$ b. $C_3H_6O_2$

c. $C_4H_8O_2$ d. $C_5H_{10}O_2$

iii. The compound with highest boiling point is.

a. Acetic acid b. Water

c. Ethyl alcohol d. Ether

iv. In which of the following compounds, the central atom does not show sp^2 hybridization?

a. Methanal b. Methanol

c. Methanoic acid d. Acetone

v. Which is the strongest acid?

a. Ethanol b. Acetic acid

c. chloroacetic acid d. Flouroacetic acid

vi. Acetic acid can be prepared by the hydrolysis of;

a. Methyl cyanide b. Methylmagnecium chloride

c. Ethanal d. Ethanol

vii. Esterification is the reaction between.

a. An acid and ester b. An acid and alcohol

c. An acid halide and ester d. An ester and Sodium hydroxide

viii. Acyl chloride can be prepared by the reaction of a carboxylic acid with.

a. Phosphorous pentoxide b. Soda lime

c. Hydrochloric acid d. Thionyl chloride

ix. The hydrolysis of an ester in presence of alkali (NaOH) is known as;

a. Saponification b. Decarboxylation

c. Esterification d. Transesterfication

x. All the acid derivatives can be converted back into the corresponding acid by one common reaction.

a. Ammonolysis b. Alcoholysis

c. Reduction d. Hydrolysis

Q.2 Explain Briefly.

i. Acetic acid is sometimes known as glacial acetic acid.

ii. Carboxylic acids have high boiling points than corresponding alcohols.

iii. Why carboxylic acids are stronger acids than phenol, alcohols and water but weaker than mineral acids?

iv. Methanoic acid is stronger acid than ethanoic acid.

v. Chloroacetic acid is stronger acid than acetic acid.

vi. Carboxylic acids can be obtained readily by the oxidation of primary alcohols.

vii. Carboxylic acids do not undergo addition reactions as compared to aldehydes.

viii. Acid halide are most reactive of all acid derivatives towards nucleophiles.

Q.3 Write Structural formula for each of the following.

i. 3 – methylpentanoic acid
ii. 2,2–dichlorobutanoic acid
iii. 2,2 –dimethyl -3 –butenoic acid
iv. Ethan,1, 2-dioic acid
v. Buta,1, 4-dioic acid
vi. Acetamide
vii. Methanamide
viii. Ethanoic anhydride
ix. Methyl Methanoate
x. Ethylnitrile

Q.4 Write IUPAC names of the following.

i. $HCOOH$
ii. CH_3COOH
iii. $CH_3CH(Cl)COOH$
iv. $HOOC\ CH_2COOH$
v. $CH_2 = CHCOOH$
vi. CH_3CF_2COOH
vii. $HC \equiv C\ CH_2\ CO_2H$
viii. $(CH_3)_3CCOOH$
xi. $CH_3 - (CH_2)_4 - COOH$
x. $HCONH_2$
xi. $HCOCl$
xii. $HCOOCH_3$

Q.5 Explain the acidity of carboxylic acids. How their acid strength is affected by substitution?

Q.6 How will you prepare propanoic acid by using.

a. an alkyl nitrile b. a Grignard reagent

c. an alcohol d. an aldehyde

Q.7 (a) Is there any method used for the preparation of formic acid? If yes explain with example.

(b) How benzoic acid can be prepared from toluene (methyl benzene)?

Q.8 Write an equation for.

a. Hydrolysis of acetyl chloride

b. Reaction of benzoyl chloride with methanol.

c. Esterification of But,1-ol with acetic anhydride.

d. Ammolysis of butanoyl chloride.

e. Fischer esterfication of pentanoic acid with ethanol.

f. Reaction of formic acid with ammonia.

g. Hydrolysis of ethanoic propanoic anhydride.

h. Reduction of ethyl cyanide.

Q. 9 Complete the following reactions.

i. $CH_3CH_2CH_2COOH + PCl_5 \longrightarrow$

ii. $CH_3CH_2COOH + SOCl_2 \longrightarrow$

iii. $CH_3CH_2CONH_2 + LiAlH_4 \longrightarrow$

iv. $2CH_3CH_2COOH + P_2O_5 \longrightarrow$

v. $CH_3CO\,OCOCH_3 + NH_3 \longrightarrow$

vi. $CH_3CH_2COOCH_3 + NaOH \xrightarrow{heat}$

vii. $CH_3CH_2COONa + NaOH \xrightarrow{CaO}$

viii. $CH_3CH_2\,COOC_2H_5 + Li\,Al\,H_4 \longrightarrow$

ix. $CH_3\,CH_2\,MgBr + CH_3CH_2CN \longrightarrow$

Q. 10 Starting from acetic acid, how will you prepare each of the following.

i. Ethanoyl chloride
ii. Ethanoic anhydride
iii. Ethanamide
iv. Ethyl ethanoate
v. Ethanol