

<b>CHAPTER</b>	<b>8</b>
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# CARBOXYLIC ACIDS AND FUNCTIONAL DERIVATIVES

Organic compounds which contain the carboxyl functional group ( $-\text{COOH}$ ) are called the carboxylic acids. Their general formula is:



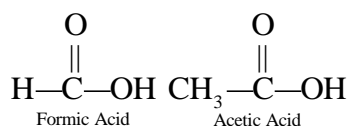
where R is an alkyl group or aryl group. Genral formula of carboxylic acid is  $\text{C}_n\text{H}_{2n+1}\text{COOH}$  or  $\text{C}_n\text{H}_{2n+2}\text{COO}$  or  $\text{C}_n\text{H}_{2n+2}\text{CO}_2$ .

The carboxyl group consist of carbonyl and hydroxyl group, i.e. “carb” from carbonyl ( $\text{C}=\text{O}$ ) and “oxyl” from hydroxyl.

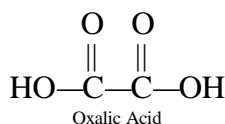
In the carboxyl group the carbonyl and hydroxyl groups are directly bonded to each other. The properties of the carboxyl group are not simply those of carbonyl and hydroxyl groups combined; the two groups interact to give carboxylic acids their own distinctive properties.

Carboxylic acids are further classified as monocarboxylic acids, dicarboxylic acids, tricarboxylic acids, etc., according as the number of  $-\text{COOH}$  groups present in the molecule.

- Monocarboxylic acids:** The carboxylic acids which consist of single  $-\text{COOH}$  group are called monocarboxylic acids. Like formic acid, acetic acid etc.



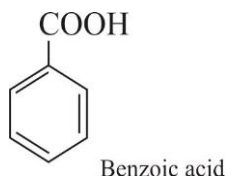
- Dicarboxylic acids:** The carboxylic acids which consist of two  $-\text{COOH}$  groups are called dicarboxylic acids. Like oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid etc etc.



**3. Polycarboxylic acids:** The carboxylic acids which consist of many  $-\text{COOH}$  groups are called polycarboxylic acids.

**Fatty acids:** The long-chain monocarboxylic acids are commonly called fatty acids because many of them are obtained by the hydrolysis of animal fats or vegetable oils.

**Aromatic carboxylic acids:** The carboxylic acids in which the carboxyl group is attached to aryl group are called aromatic carboxylic acids. Their general formula is  $\text{Ar-COOH}$ . Examples are benzoic acid, salicylic acid, phthalic acid, terephthalic acid etc.



**Derivatives of carboxylic acids:** Carboxylic acids has many derivatives in which the  $-\text{OH}$  group of an acid is replaced by other functional groups. Acid halides, acid amides, esters, acid anhydrides etc. are the derivatives of carboxylic acids.

Acid Derivatives	Functional Group	General Formula	Examples	Names
Acid	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{OH} \end{array}$	Acetic Acid
Acid Halide Or Acyl Halide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{X} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{X} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{Cl} \end{array}$	Acetyl Chloride
Acid Amide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{NH}_2 \end{array}$	Acetamide
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{OCH}_3 \end{array}$	Methyl Acetate
Acid Anhydride	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}- \end{array}$	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{array}$	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{CH}_3-\text{C}-\text{O}-\text{C}-\text{CH}_3 \end{array}$	Acetic Anhydride

### Nomenclature

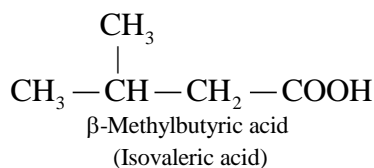
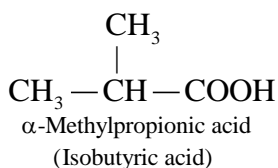
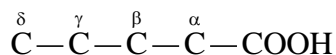
There are three ways of naming carboxylic acids:

(1) **Common System:** The simple carboxylic acids are better known by their common names. The common names are usually derived from the Latin or Greek word that indicates the original source of the acid. They do not follow any rule except

that all common names of acids end in *-ic acid*. For example,

HCOOH	Formic acid	From “Formica” means “Ant”.
CH <sub>3</sub> COOH	Acetic acid	From “Acetum” means “Vinegar”.
CH <sub>3</sub> CH <sub>2</sub> COOH	Propionic acid	From “Protos pion” means “First fat”.
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Butyric acid	From “Butyrum” means “Butter”
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Valeric acid	

In the common system, Greek letters ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , etc.) are used to indicate the position of substituents. The carbon atom adjacent to the carboxyl carbon is assigned the letter  $\alpha$ , the next carbon on the chain  $\beta$ , the next one  $\gamma$ , and so on. For example,



**(2) Derived System:** Some carboxylic acids may be named as substituted acetic acids. In this system the C-COOH part of the compound is named as acetic acid and the alky group to which it is attached is considered as substituent. The substituent is named first followed by the word acetic acid. For example,

CH <sub>3</sub> CH <sub>2</sub> COOH	Methylacetic acid
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Ethylacetic acid
(CH <sub>3</sub> ) <sub>3</sub> CCOOH	Trimethylacetic acid
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COOH	Phenylacetic acid

**(3) IUPAC System:** In the IUPAC system, the carboxylic acids are named as Alkanoic acids (Alkane – e + oic acid). The systematic name of the individual acid is obtained by replacing the ending ‘e’ of the corresponding alkane by *-oic acid*. For example,

HCOOH	Mathanoic acid ( <i>Methane – e + oic acid</i> )
CH <sub>3</sub> COOH	Ethanoic acid
CH <sub>3</sub> CH <sub>2</sub> COOH	Propanoic acid
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Butanoic acid

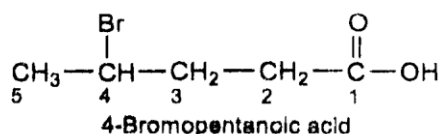
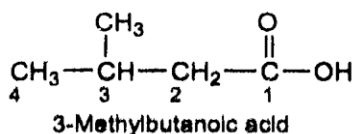
For naming higher members, the longest continuous chain containing the carboxyl group (–COOH) is selected. The number of carbon atoms in this chain gives the name of the parent alkane. The position of substituents is indicated by numbers. The carboxyl carbon is always given number 1, the carbon adjacent to it is given the number 2, and so on. Following rules are used:

**Rule 1.** Select the longest continuous carbon chain containing the carboxyl group.

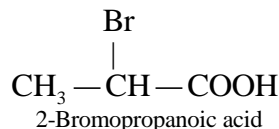
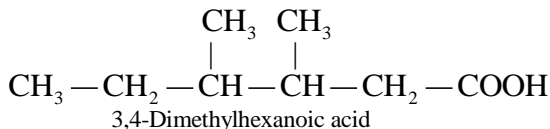
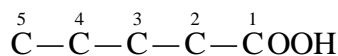
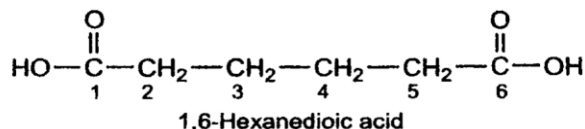
**Rule 2.** Name the longest chain. The name is obtained by dropping the final *-e* from the name of the corresponding alkane, and adding the ending *-oic acid*.

**Rule 3.** Number the chain starting with carboxyl carbon as number 1. The number 1 is not used to indicate the position of the carboxyl carbon, since it is always located at the end of the chain.

**Rule 4.** Other substituents are numbered, named, and placed as prefixes in alphabetical order. For example,



**Rule 5.** When there are two carboxyl groups in a molecule, it is named as alkanedioic acid. Notice that *-e* of the corresponding alkane name is retained.



Formula	Common Name	IUPAC Name
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC-CH <sub>2</sub> -COOH	Malonic acid	Propanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>2</sub> -COOH	Succinic acid	Butanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>3</sub> -COOH	Glutaric acid	Pentanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>4</sub> -COOH	Adipic acid	Hexanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>5</sub> -COOH	Pimelic acid	Heptanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>6</sub> -COOH	Suberic acid	Octanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>7</sub> -COOH	Azelaic acid	Nonanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>8</sub> -COOH	Sebacic acid	Decanedioic acid

### Nomenclature of carboxylic acid derivatives

Carboxylic acid derivatives are compounds in which the hydroxyl part of the carboxyl group is replaced by various other groups.

(a) **Acid Chlorides:** Acid chlorides are derived from acids by replacing *OH* group by

Cl atom. These are named by changing the ending *-ic acid* of the corresponding carboxylic acid to *-yl chloride*.

Formula	Common Name	IUPAC Name
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{Cl} \end{array}$	Acetyl chloride	Ethanoyl chloride
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{Cl} \end{array}$	Propionyl chloride	Propanoyl chloride

(b) **Esters:** Esters are derived from acids by replacing the *OH* group by *OR* group. Their names consist of two words. The first word is the name of the alkyl group attached to the oxygen atom. The second word is derived from the carboxylic acid name with *-ic acid* changed to *-ate*.

Formula	Common Name	IUPAC Name
$\begin{array}{c} \text{O} \\ \parallel \\ \text{H} - \text{C} - \text{OCH}_3 \end{array}$	Methyl formate	Methyl methanoate
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{OC}_2\text{H}_5 \end{array}$	Ethyl acetate	Ethyl ethanoate

(c) **Anhydrides:** Anhydrides are derived from acids by replacing *OH* by *OCOR*. These are named by changing the suffix *acid* of the parent acid to *anhydride*.

Formula	Common Name	IUPAC Name
$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{CH}_3 - \text{C} - \text{O} - \text{C} - \text{CH}_3 \end{array}$	Acetic anhydride	Ethanoic anhydride
$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{C}_2\text{H}_5 - \text{C} - \text{O} - \text{C} - \text{C}_2\text{H}_5 \end{array}$	Propionic anhydride	Propanoic anhydride

(d) **Amides:** Amides are derived from acids by replacing *OH* by *NH<sub>2</sub>*. These are named by replacing the ending *-oic acid* (of the IUPAC name) or *-ic acid* (of the common name) of the corresponding carboxylic acid with the ending *-amide*.

Formula	Common Name	IUPAC Name
$\begin{array}{c} \text{O} \\ \parallel \\ \text{H} - \text{C} - \text{NH}_2 \end{array}$	Formamide	Methanamide
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{NH}_2 \end{array}$	Acetamide	Ethanamide

## Physical Properties

- (1) Lower carboxylic acids (up to C<sub>10</sub>) are liquids with sharp or disagreeable odours. Higher members are wax-like solids and almost odourless. Acetic acid which constitutes about 5% of vinegar has a characteristic smell. Butyric acid (butanoic acid) can be smelled in rancid butter as it is present in butter.
- (2) Acetic acid has freezing point 17°C. it form a solid which look like ice, it is

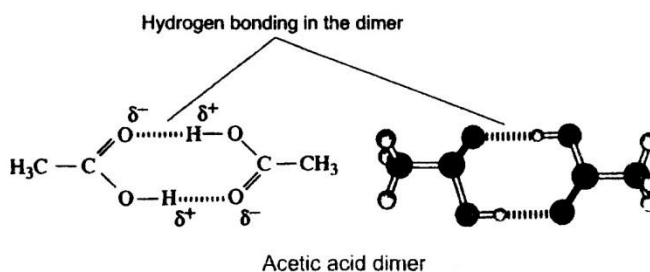
therefore known as glacial acetic acid (glacial = ice like).

- (3) Boiling points of carboxylic acids increase regularly with increase in molecular weight.
- (4) Melting points of carboxylic acids increase irregularly with increase of molecular weight. The 'even' members have markedly higher melting points than 'odd' members.

### Melting and Boiling Points of Some Carboxylic Acids

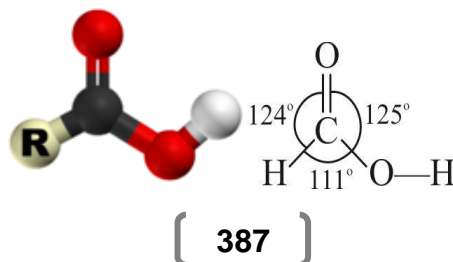
Name	Formula	mp°C	bp°C
Formic acid	HCOOH	8	101
Acetic acid	CH <sub>3</sub> CH <sub>2</sub> COOH	16	118
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> COOH	-21	141
Butyric acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	-7	164
Valeric acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	-35	186

- (5) Boiling points of carboxylic acids are higher than those of alcohols of same molecular weight. This is attributed to hydrogen-bonding between acid molecules.
- (6) First four members are completely soluble in water. This is due to the ability of the carboxyl group to form hydrogen bonds with water molecules. *As the hydrocarbon chain in the acid lengthens, the solubility of the acid in water falls off rapidly.* Carboxylic acids are readily soluble in ethanol, ether, and benzene.

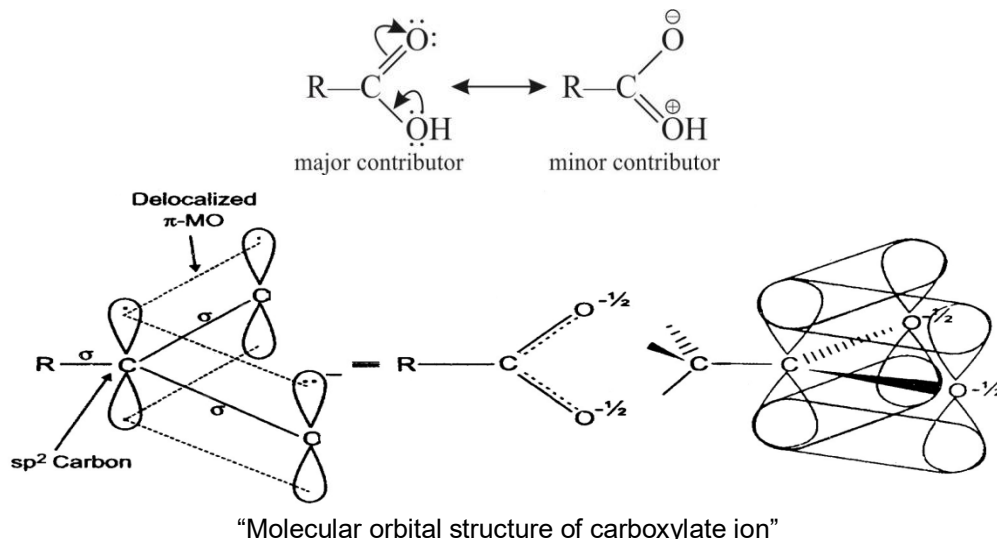


### Structure

The carbon and oxygen of the carbonyl group both are sp<sup>2</sup> hybridized due to which it has a basic trigonal shape with bond angles close to 120°. The bond lengths between C = O is 120pm and C – O is 134pm, similarly the bond angles H – C = O is 124° while H – C – O is 111° and O – C = O is 125°.



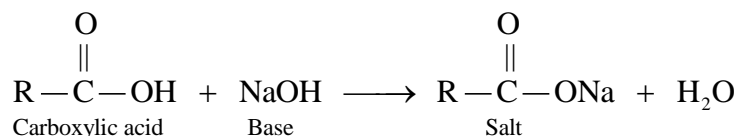
The hydroxyl oxygen is  $sp^3$  hybridized which allow one of the lone pair electrons to conjugate with pi system of the carbonyl group which make the carbonyl structure planer and can be represented by following resonating structures.



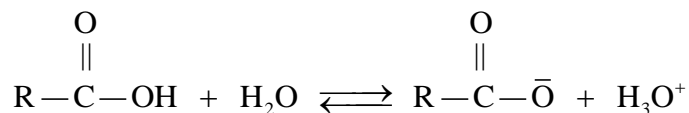
The lone pair donation from hydroxyl group make the carbonyl group less electrophilic than that of the aldehydes and ketones.

### Acidity of Carboxylic Acids

Carboxylic acids are acidic in nature. These are more acidic than water, alcohols and phenols but less than mineral acids. These are the most acidic class of organic compounds. These can donate a proton and form salts with bases.

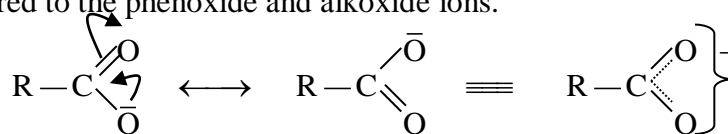


Carboxylic acids are only partially ionizable in aqueous solution and an equilibrium exists between the ionized and un-ionized forms.



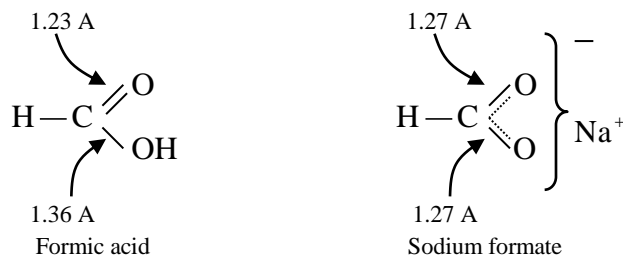
Carboxylic acids are more acidic than alcohols and phenols (due to the presence of CO group which is electron withdrawing) and lose a proton readily because the carboxylate ion formed by ionization or reaction with a base is more stabilized by

resonance compared to the phenoxide and alkoxide ions.



Resonance forms of carboxylate ion Resonance hybrid

X-Ray studies support the fact that carboxylate ion exists as a resonance hybrid. For example, in formic acid the carbon-oxygen bonds have different lengths, whereas in sodium formate the two carbon-oxygen bond lengths are identical and intermediate in length between those of normal double and single carbon-oxygen bonds.



The stability of carboxylate ion can also be explained on the basis of its molecular orbital structure. The carbon atom of carboxylate ion is  $sp^2$ -hybridized. It is bound to each oxygen atom by a  $\sigma$  bond. The unused carbon  $p$  orbital overlaps with  $p$  orbitals of both oxygen atoms to form stable delocalized molecular orbital. Notice that the four electrons are bound to three atoms (1 carbon + 2 oxygens). This delocalization of  $\pi$  electrons is responsible for the extra-stability of the carboxylate ion.

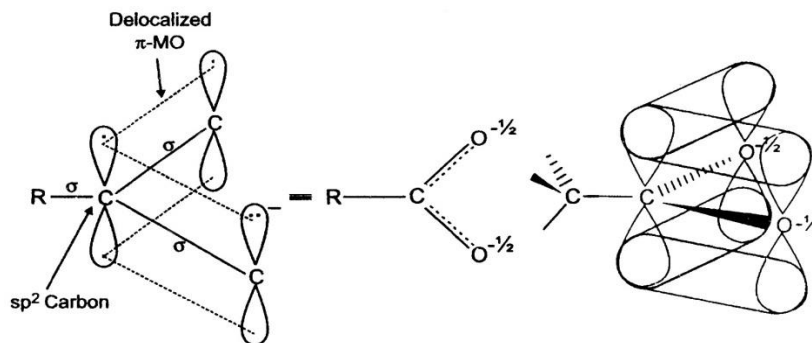


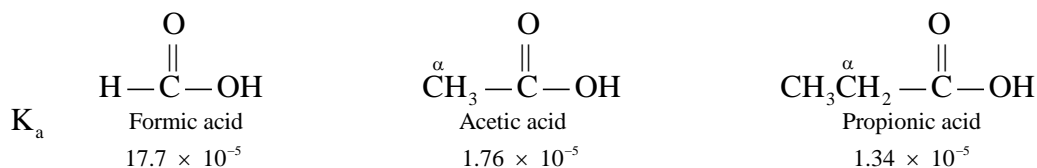
Fig. 12.1. Orbital structure of carboxylate ion.

**Effect of Substituents on Acidity:** The most important factor affecting the acidity is the *Inductive Effect* of substituents on the  $\alpha$ -carbon atom.

**(1) Electron-releasing alkyl groups decrease the acidity:** This is because the electron-releasing groups increase the negative charge on the carboxylate ion and

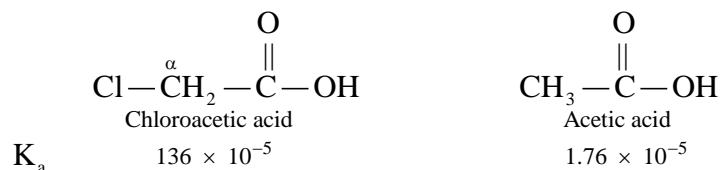


destabilize it. The loss of proton becomes more difficult. Also, as the size of the alkyl group increases, acidity decreases. For example,

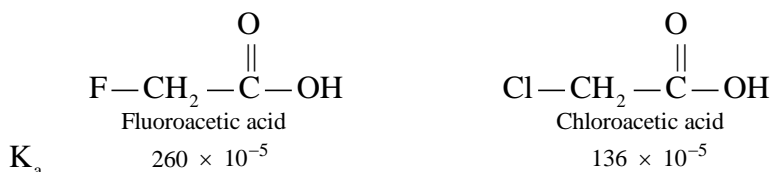


**(2) Electron-withdrawing substituents (Cl, Br, F, OH, CN) increase the acidity:**

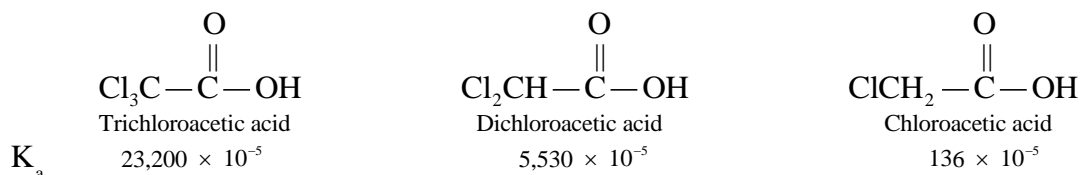
This is because the electron-withdrawing substituents decrease the negative charge on the carboxylate ion and stabilize it. The loss of proton becomes relatively easy. For example, chloroacetic acid is about 100 times stronger than acetic acid.



Fluoroacetic acid is stronger than chloroacetic acid since F is more electronegative than Cl.



As the number of electron-withdrawing substituents increases, acidity also increases. For example,



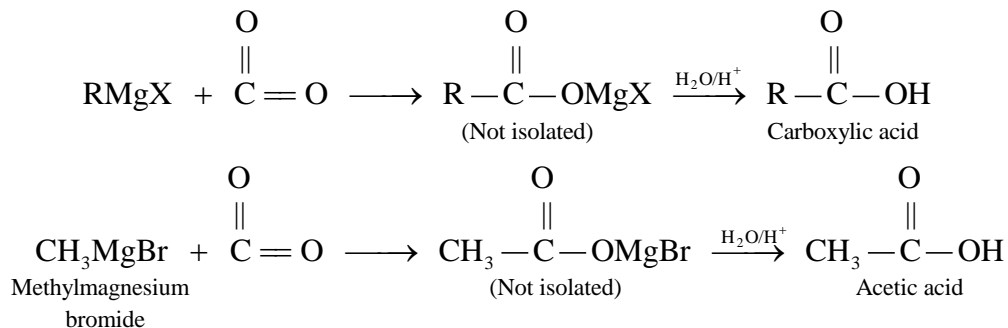
This has been summarized in the following table.

Carboxylic acid	Formula	pka
Propanoic acid	CH <sub>3</sub> CH <sub>2</sub> -COOH	4.87
Ethanoic acid	CH <sub>3</sub> -COOH	4.76
Methanoic acid	H-COOH	3.68
Chloroacetic acid	CH <sub>2</sub> ClCOOH	2.86
Dichloroacetic acid	CHCl <sub>2</sub> COOH	1.29
Trichloro acetic acid	CCl <sub>3</sub> COOH	0.65

## Methods of Preparation

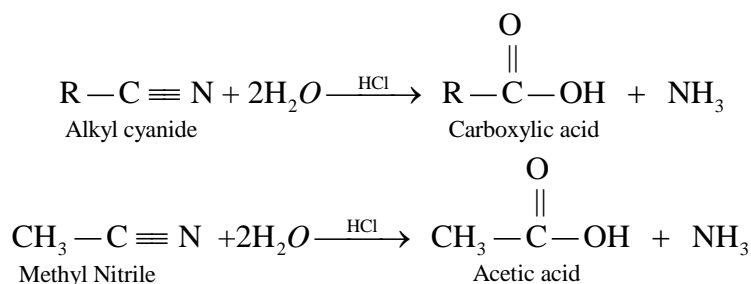
Carboxylic acids are prepared by the following methods:

**(1) Reaction of Grignard Reagents with CO<sub>2</sub>:** Grignard reagents (RMgX) react with carbon dioxide to form addition products that can be hydrolyzed to carboxylic acids. This reaction is called carbonation of Grignard reagent.



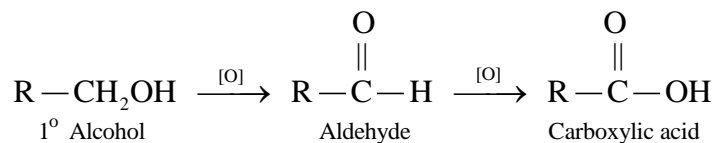
Notice that the acid formed by this method contains one more carbon than the original Grignard reagent.

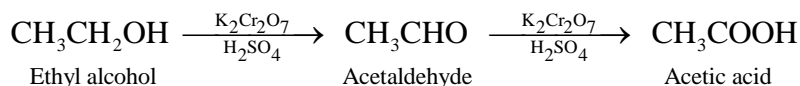
**(2) Hydrolysis of Nitriles (Alkyl Cyanides):** Nitriles or alkyl cyanides are compounds with the general formula R—C≡N. The nitriles on acid-hydrolysis form carboxylic acids.



Notice that the acid produced by this method contains one more carbon atom than the original alkyl cyanides.

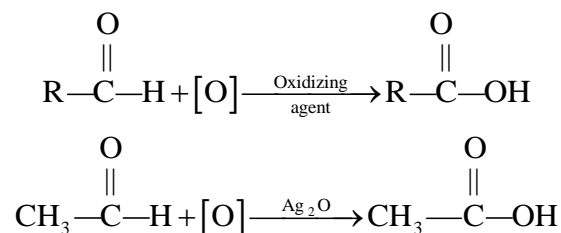
**(3) Oxidation of Primary Alcohols or Aldehydes:** Primary alcohols or aldehydes undergo oxidation with a mixture of potassium dichromate and sulphuric acid to form carboxylic acids. The alcohol is first oxidized to an aldehyde, and then to a carboxylic acid.



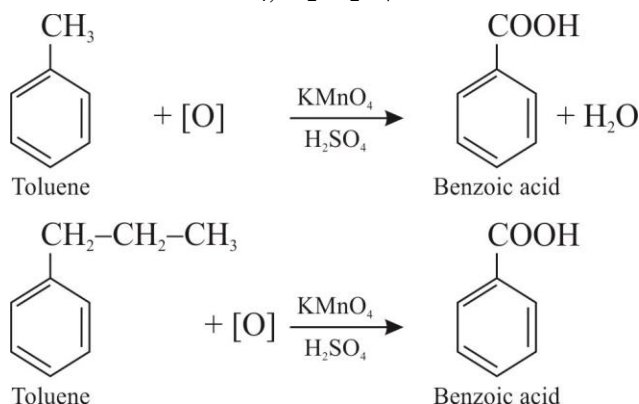


Potassium permanganate can also be used in place of potassium dichromate.

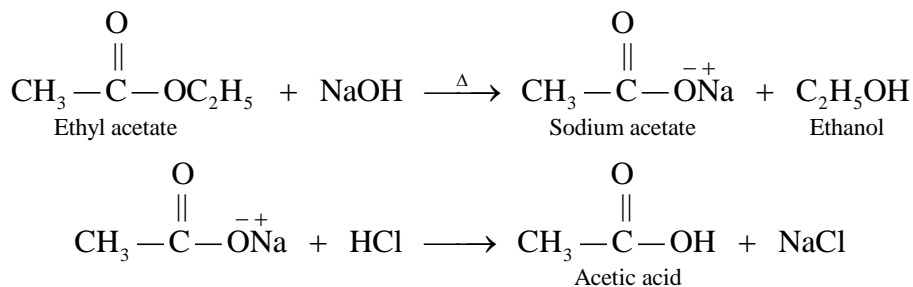
**(4) Oxidation of Aldehydes:** Aldehydes can easily be oxidized even with mild oxidizing agent such as acidified  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{Ag}_2\text{O}$  to give carboxylic acid with the same number of carbon atoms.



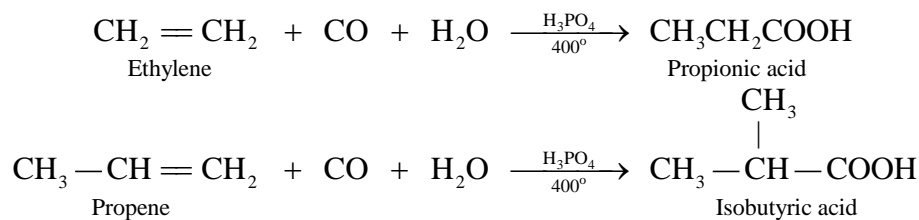
**(5) Oxidation of Alkyl Benzene:** This is one of the best method used to prepare aromatic carboxylic acids by the oxidation of side chain of benzene ring with oxidizing agents like acidified  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ .



**(6) Hydrolysis of Esters:** When an ester is boiled with concentrated aqueous  $\text{NaOH}$ , sodium salt of the acid is formed. This on treatment with dilute  $\text{HCl}$  gives the corresponding carboxylic acid. For example,



(7) **Carboxylation of Alkenes:** When an alkene is heated with carbon monoxide and steam under pressure with phosphoric acid ( $\text{H}_3\text{PO}_4$ ) at  $400^\circ\text{C}$ , carboxylic acids are formed. This is a recent industrial method of making carboxylic acids and is called **Koch Reaction**.



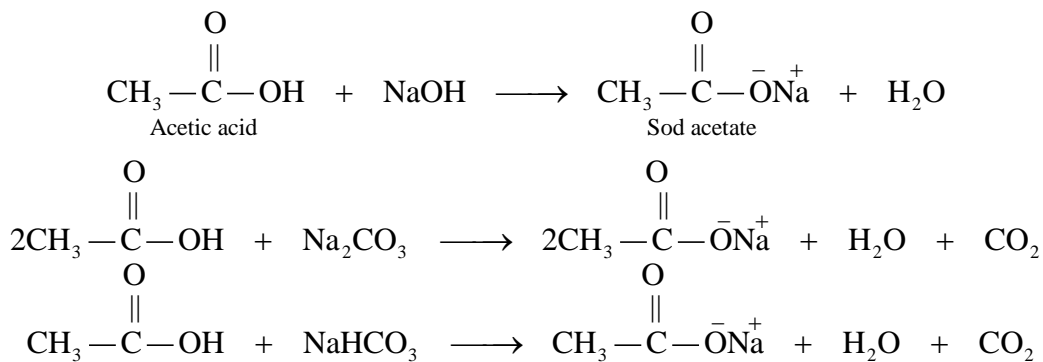
## Reactivity

The carboxylic group consists of carbonyl and hydroxyl group. The two groups influence each others to such an extent that the reactivity of carboxylic acids shows little resemblance to those of carbonyl compounds on one hand and alcohols on the other hand. As the carbon atom of carboxylic group is less positive than the carbon atom of aldehydes and ketones so carboxylic acids do not undergo nucleophilic addition reactions like carbonyl compounds. The  $\text{C}=\text{O}$  group attracts the electrons away from the  $-\text{O}-\text{H}$  group and make the  $-\text{OH}$  to leave the hydrogen as proton as compared to the case in alcohols. So carboxylic acids are more acidic than alcohols.

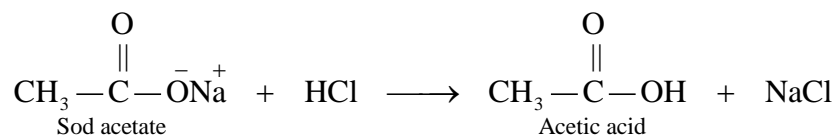
## Chemical Properties

The main chemical reactions of carboxylic acids are described below:

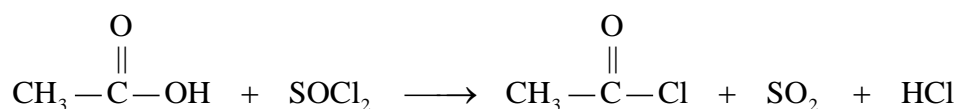
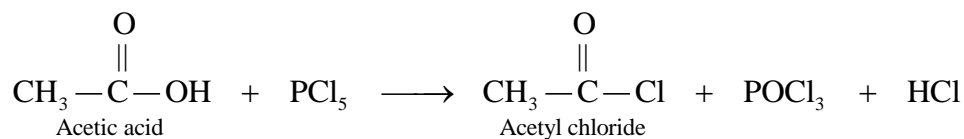
(1) **Salt Formation:** Carboxylic acids react with hydroxides, carbonates, and bicarbonates to form the corresponding salts. For example,



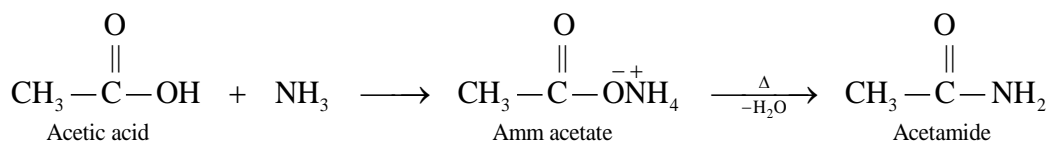
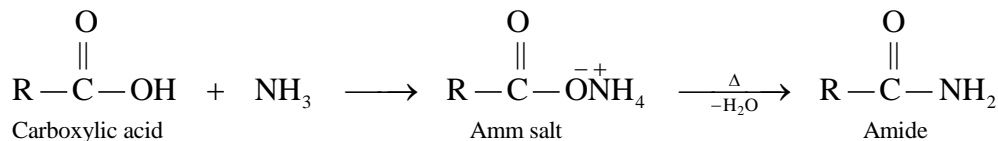
The carboxylic acid can be regenerated by treating these salts with dilute mineral acids. For example,



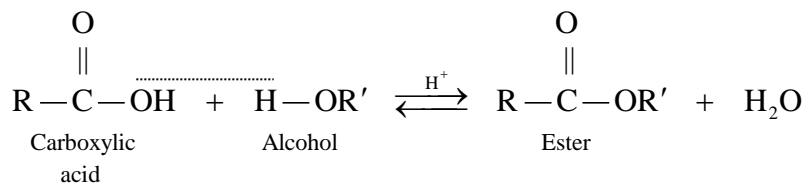
**(2) Formation of Acid Halides:** Carboxylic acids react with phosphorus halides or thionyl chloride (SOCl<sub>2</sub>), to form acid halides. For example,

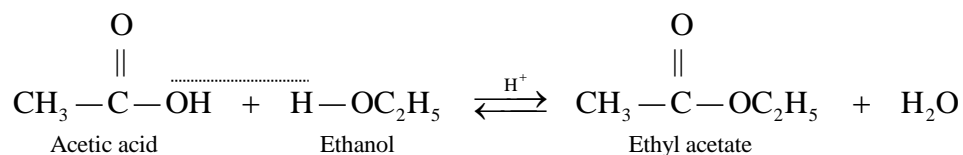


**(3) Formation of Amides:** Carboxylic acids react with ammonia to give salts, which on heating yield amides.



**(4) Formation of Esters:** Carboxylic acids react with alcohols in the presence of a strong acid catalyst like H<sub>2</sub>SO<sub>4</sub> or HCl to form esters. The reaction is reversible and is called **Esterification**.

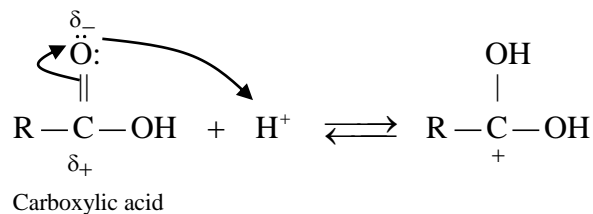




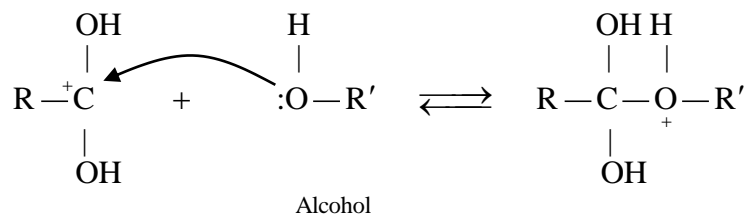
The equilibrium can be shifted to the right by using excess of alcohol or removal of water by distillation.

**Mechanism:** The mechanism of esterification involves the following steps:

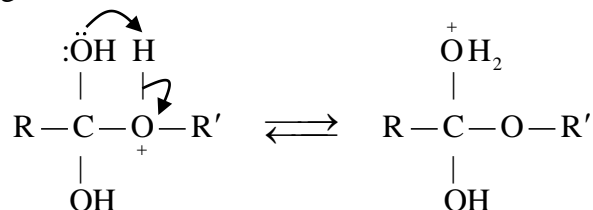
**Step 1.** Protonation of carboxylic acid.



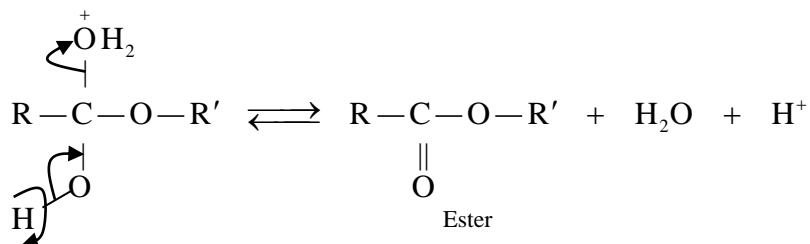
**Step 2.** Attack by nucleophilic R'OH.



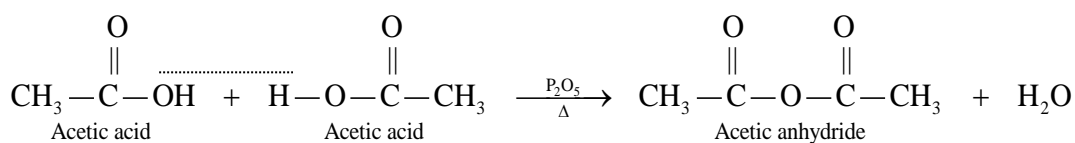
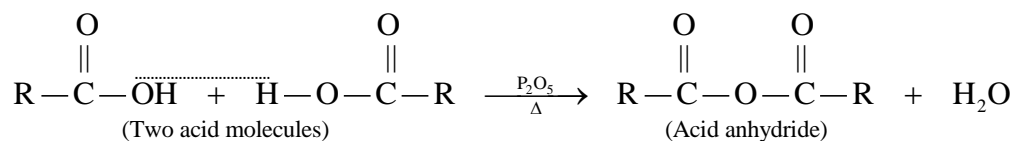
**Step 3.** Hydrogen ion transfer.



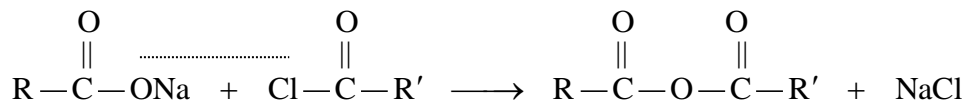
**Step 4.** Elimination of proton and water.



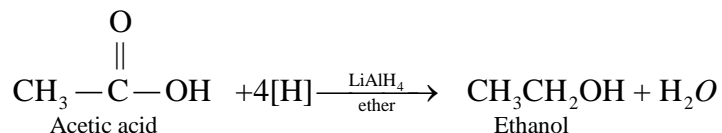
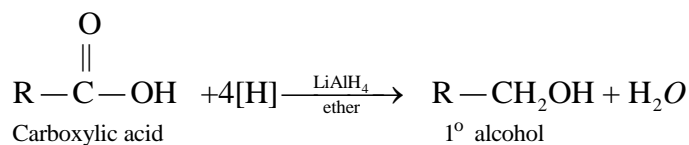
(5) **Formation of Anhydrides:** Carboxylic acids undergo dehydration with phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) to form acid anhydrides.



Anhydrides can also be prepared by treating sodium salts of acids with acid halides.

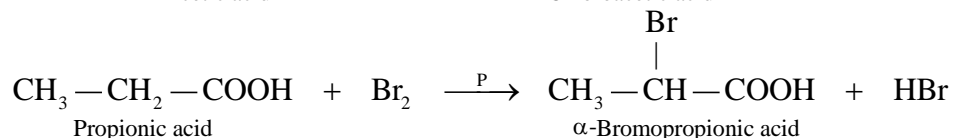
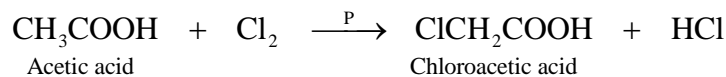
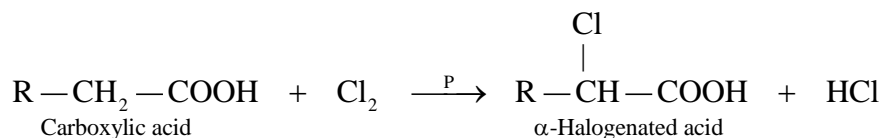


**(6) Reduction:** Carboxylic acids undergo reduction with lithium aluminium hydride to give primary alcohols.



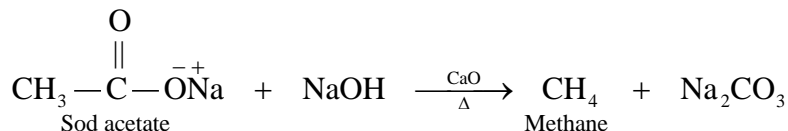
Carboxylic acids cannot be reduced with  $\text{H}_2/\text{Ni}$  or  $\text{Na}^+\text{C}_2\text{H}_5\text{OH}$ .

**(7)  $\alpha$ -Halogenation:** When a carboxylic acid that contain  $\alpha$ -hydrogens is treated with  $\text{Cl}_2$  or  $\text{Br}_2$  in the presence of phosphorus, the  $\alpha$ -hydrogen atoms are replaced by chlorine or bromine atoms. This reaction is known as the **Hell-Volhard-Zelinsky** (or HVZ) **Reaction**.

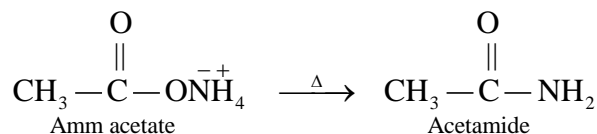


## Reactions of Salts of Carboxylic Acids

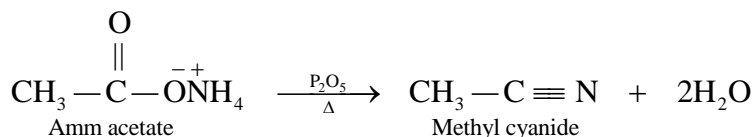
(1) **Action of Heat on Sodium Salts:** When sodium salts of carboxylic acids are heated with soda-lime (NaOH + CaO), alkanes are formed. This reaction is called decarboxylation in which the removal of carbon dioxide takes place from the carboxylic acid.



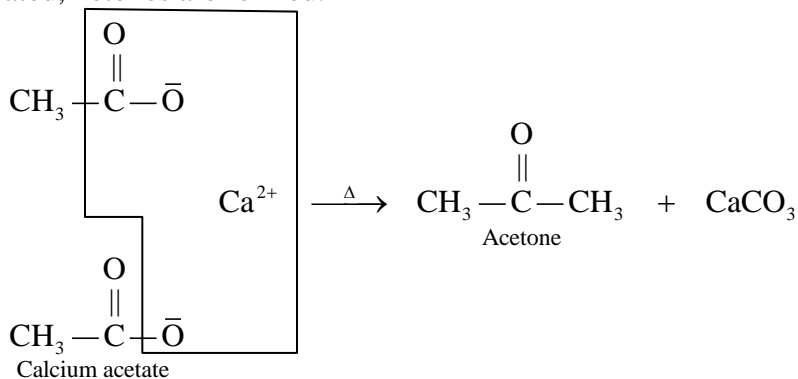
(2) **Action of Heat on Ammonium Salts:** When ammonium salts are heated alone, amides are formed.



When the ammonium salts are heated with phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>), cyanides are formed.



(3) **Action of Heat on Calcium Salts:** When calcium or barium salts of carboxylic acids are heated, ketones are formed.

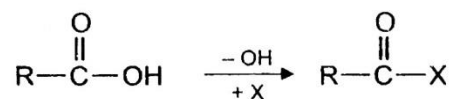


## Derivatives of Carboxylic Acids

### 1. Acid halides

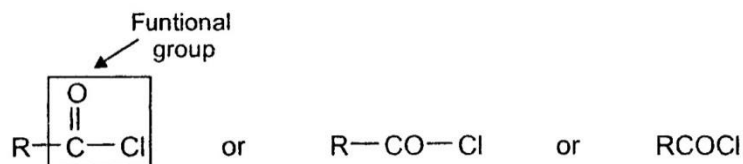
Acid halides are the derivatives of carboxylic acids in which the -OH functional group of carboxyl group has been replaced by a halogen atom.





The acid halides are also referred to as **Acyl halides**; the acyl group is R-CO-.

The acid chlorides are by far the most important of all the acid halides and will be discussed in detail. Their type formula may be represented as,



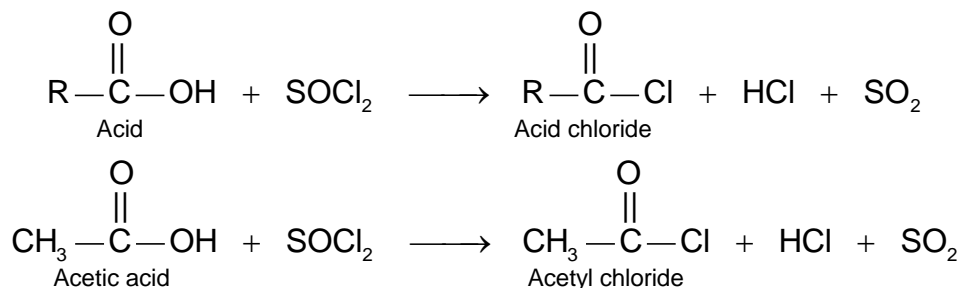
They are named by dropping the ending '*-ic acid*' from either the common name or the IUPAC name and adding the suffix '*-yl chloride*'

Formula	Common Name	IUPAC Name
CH <sub>3</sub> COCl	Acetyl chloride	Ethanoyl chloride
CH <sub>3</sub> CH <sub>2</sub> COCl	Propionyl chloride	Propanoyl chloride

### Methods of Preparation

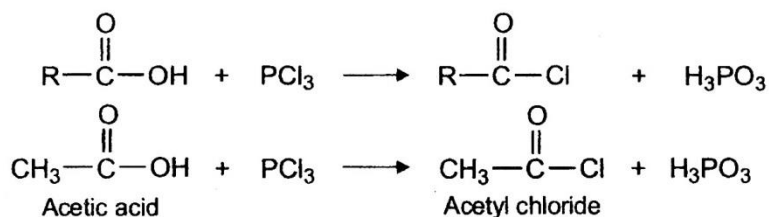
Acid chlorides are prepared from appropriate carboxylic acids:

#### (1) By the reaction of Thionyl Chloride (SOCl<sub>2</sub>) with carboxylic acid

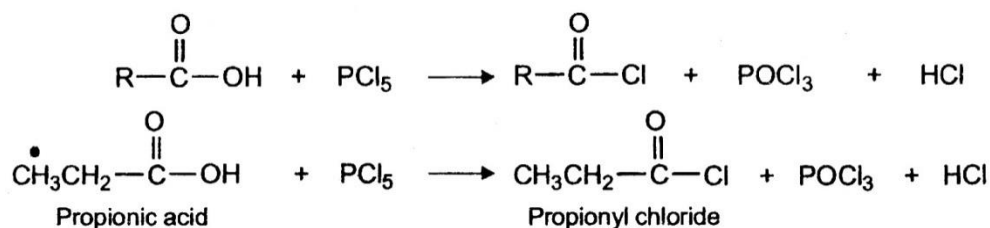


This method is superior to others as the by-products being gases escape leaving the chloride in the pure state.

#### (2) By the reaction of Phosphorus Trichloride (PCl<sub>3</sub>) with carboxylic acid



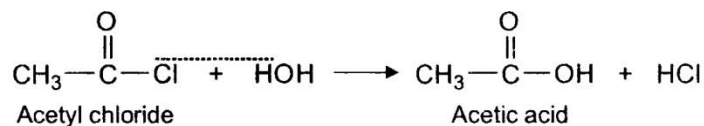
#### (3) By the reaction of Phosphorus Pentachloride (PCl<sub>5</sub>) with carboxylic acid



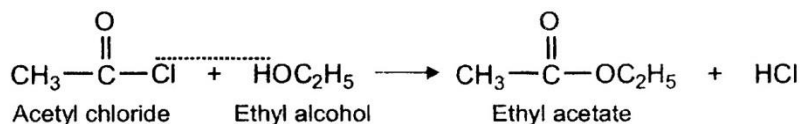
## Chemical Properties

Some of their important reactions are listed below.

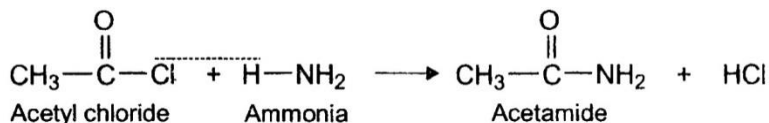
(1) **Hydrolysis:** They react with water when the chlorine is displaced by OH group to reform the original organic acid.



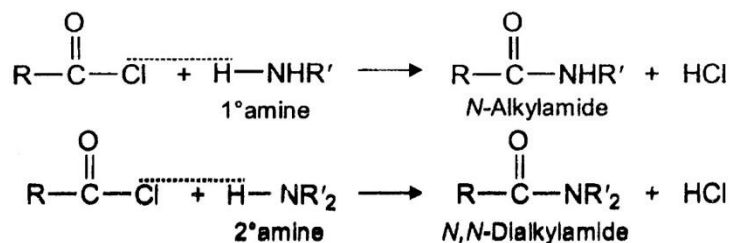
(2) **Reaction with Alcohols (Alcoholysis):** They react with an alcohol when the chlorine atom is displaced by alkoxy group,  $-\text{OR}'$ , to produce an ester.



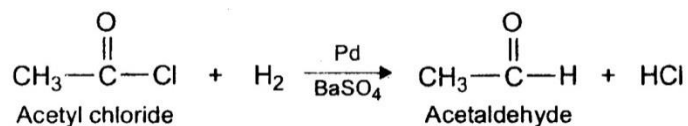
(3) **Reaction with Ammonia (Ammonolysis):** They react with ammonia when the Cl atom is displaced by an amino group,  $-\text{NH}_2$ , to produce an amide.



(4) **Reaction with 1° and 2° Amines:** Acid halides react with 1° and 2° amines to produce substituted amides.

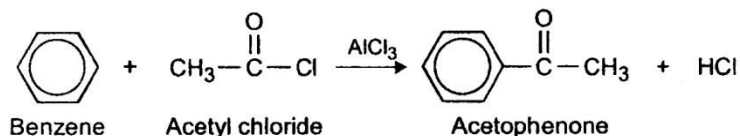


(5) **Reduction:** When reduced with hydrogen in the presence of 'poisoned' palladium catalyst, they form aldehydes.



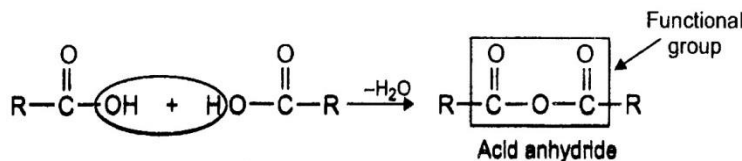
This reaction is called **Rosenmund Reduction**.

(6) **Friedel-Crafts Reaction:** They react with aromatic hydrocarbons in the presence of anhydrous  $\text{AlCl}_3$ , to form ketones.



## 2. Anhydrides

The compound derived by loss of a water molecule between two molecules of a carboxylic acid are called Acid Anhydrides or simply Anhydrides.



The functional group of this series of acid derivatives is  $-\text{CO}-\text{O}-\text{CO}-$ .

Anhydrides are named by replacing the word 'acid' in the name of the parent acid by 'anhydride'.

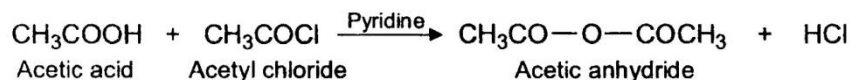
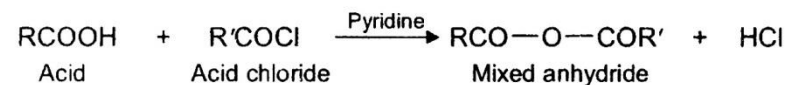
Formula	Common Name	IUPAC Name
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Acetic anhydride	Ethanoic anhydride
$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$	Propionic anhydride	Propanoic anhydride

**Mixed Anhydrides:** Anhydrides derived from two molecules of different acids are called mixed anhydrides.

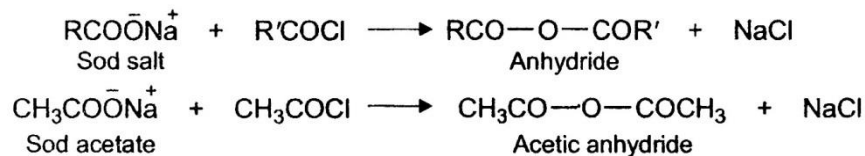
## Methods of Preparation

Acid anhydrides may be prepared:

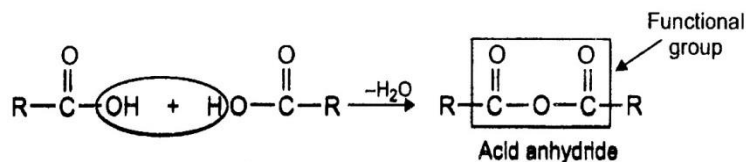
### (1) By reaction of Acid halide with a Carboxylic acid



## (2) By reaction of acid halide with Salt of a Carboxylic acid

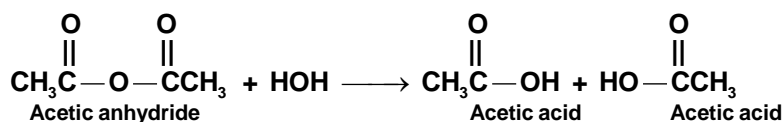


## (3) By the dehydration of carboxylic acids

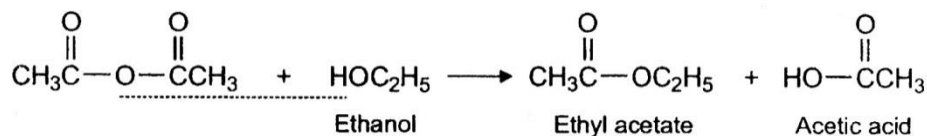


## Chemical Properties

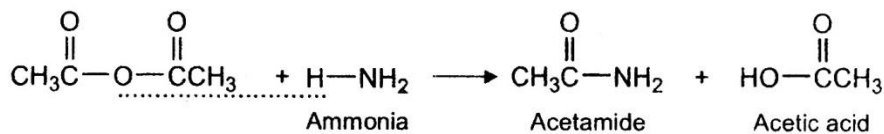
## (1) Hydrolysis



## (2) Reaction with Alcohols

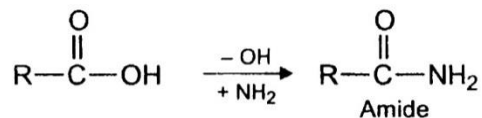


## (3) Reaction with Ammonia

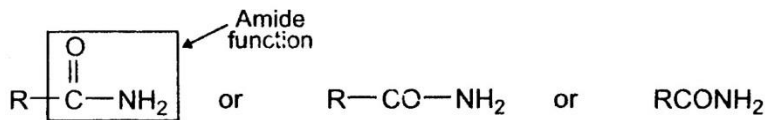


## 3. Amides

The derivatives of carboxylic acids in which the -OH of the -COOH group has been replaced by an amino group, -NH<sub>2</sub>, are called Amides or Acid Amides.



Amides are represented by the type formula



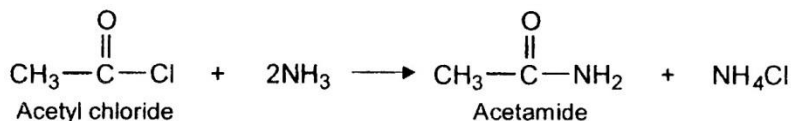
where the  $-\text{CONH}_2$  is the Amide Functional Group.

Simple amides are named by replacing the ending ‘*-ic acid*’ (Common) or ‘*-oic acid*’ (IUPAC) by the word ‘*amide*’.

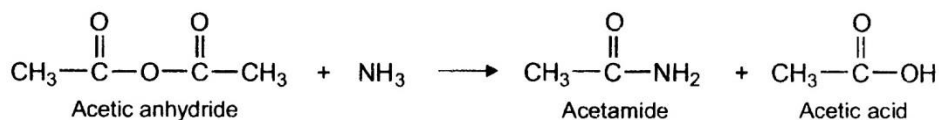
Formula	Common Name	IUPAC Name
$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{NH}_2 \end{array}$	Formamide	Methanamide
$\begin{array}{c} \text{O} \\    \\ \text{CH}_3-\text{C}-\text{NH}_2 \end{array}$	Acetamide	Ethanamide

## Methods of Preparation

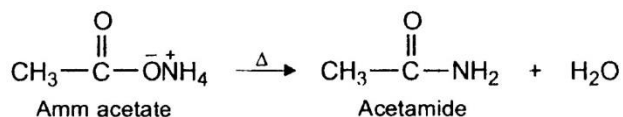
### (1) By the action of Ammonia on Acid Chlorides



### (2) By the action of Ammonia on Anhydrides

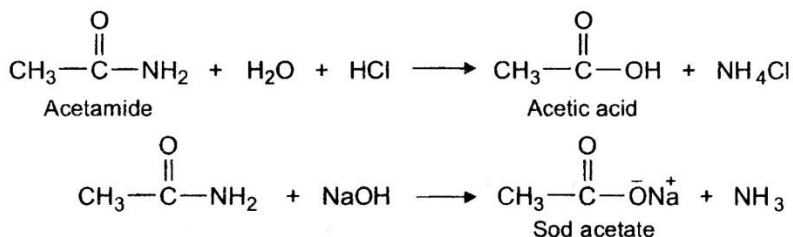


### (3) By heating Ammonium Carboxylates

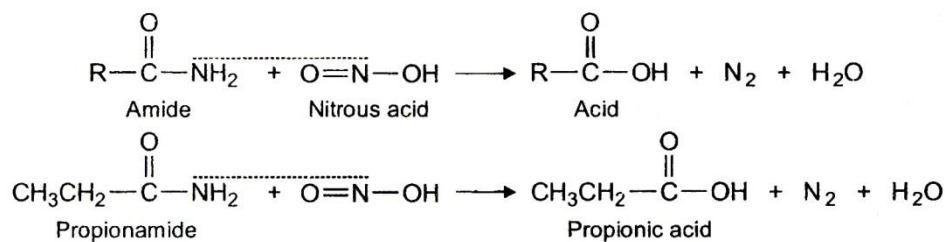


## Chemical Properties

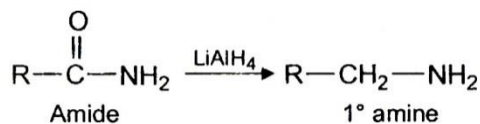
(1) **Hydrolysis:** The amides can be hydrolysed in acid or in alkaline solution on prolonged heating.



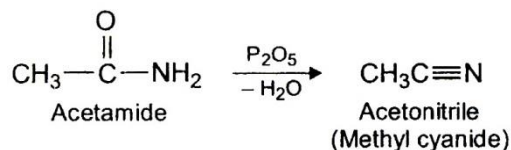
(2) **Reaction with Nitrous Acid ( $\text{NaNO}_2 + \text{HCl}$ ):** Amides on treatment with nitrous acid form carboxylic acids.



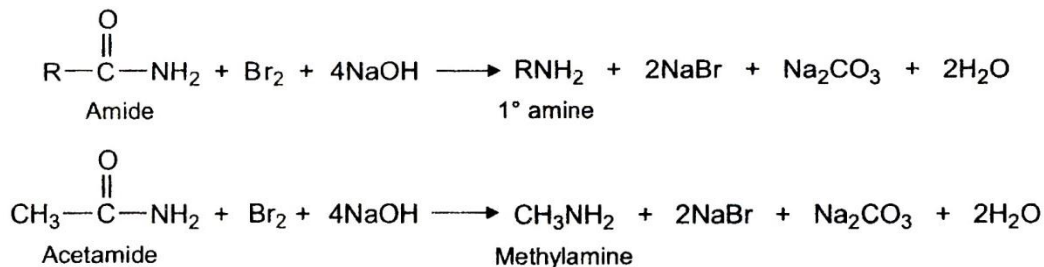
(3) **Reduction:** Lithium aluminium hydride ( $\text{LiAlH}_4$ ) reduces amides to primary amines.



(4) **Dehydration with  $\text{P}_2\text{O}_5$ :** When heated with a strong dehydrating agent such as phosphorus pentoxide, they form nitriles.



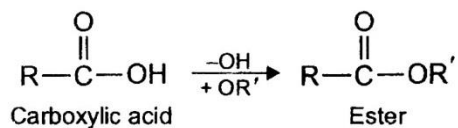
(5) **Hofmann's Degradation of Amides:** Treatment of an amide with bromide and sodium hydroxide solution produces a primary amine.



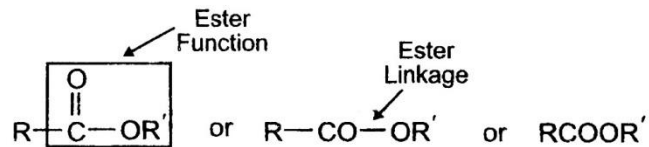
This reaction is also called **Hofmann's Rearrangement**. Notice that the overall result is the removal of the carboxyl group from the amide. The product contains one carbon less than the original amide. The reaction provides a useful method for the descent of a homologous series.

#### 4. Esters

Esters are derivatives of carboxylic acids in which the  $-\text{OH}$  group has been replaced by  $-\text{OR}$  (alkoxy) group.



The esters of carboxylic acids are often referred to as carboxylic esters. The type formula of this class of acid derivatives is:



The ester functional group (or function) may be represented as  $-\text{CO}-\text{OR}'$  or  $-\text{COOR}'$ .

Esters are by far the most important class of acid derivatives. A large number of them occur in flowers and fruits which owe their fragrance to these compounds. They are used in many synthetic products such as perfumes (for essences), pesticides, fibres, solvents and plasticizers.

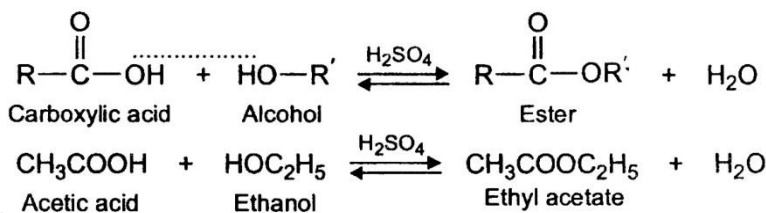
### Nomenclature

The name of an ester is of two words. The name of the alkyl group attached to oxygen is the first word. The second word is the name of the parent acid with the ending '*-ic acid*' changed to '*-ate*.'

Formula	Common Name	IUPAC Name
$  \begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{OCH}_3 \end{array}  $	Methyl formate	Methyl methanoate
$  \begin{array}{c} \text{O} \\    \\ \text{CH}_3-\text{C}-\text{OCH}_2\text{CH}_3 \end{array}  $	Ethyl acetate	Ethyl ethanoate
$  \begin{array}{c} \text{O} \\    \\ \text{CH}_3(\text{CH}_2)_2-\text{C}-\text{OCH}_3 \end{array}  $	Methyl butyrate	Methyl butanoate

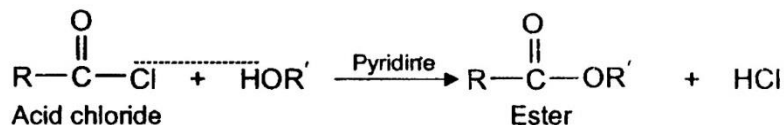
### Methods of Preparation

(1) **By Fischer Esterification:** This method consists of heating a mixture of a carboxylic acid and an alcohol in the presence of concentrated  $\text{H}_2\text{SO}_4$  or dry  $\text{HCl}$  as catalyst.

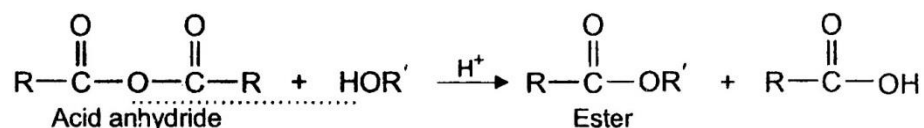


The reaction is carried to completion by using an excess of a reaction or by removing the water or ester as they are formed.

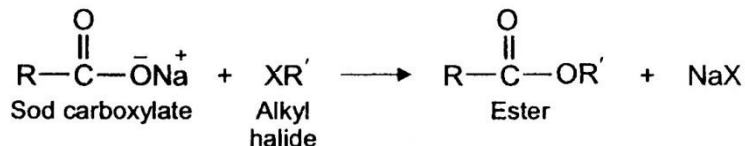
(2) **By reaction of Acid chlorides with Alcohols:** Pyridine is added to remove HCl as it is formed.



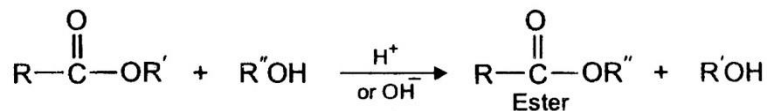
(3) **By reaction of Acid anhydrides with Alcohols**



(4) **By reaction of Carboxylate salts and Alkyl halides**



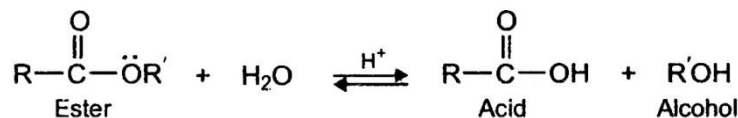
(5) **By Transesterification (Ester Interchange)**



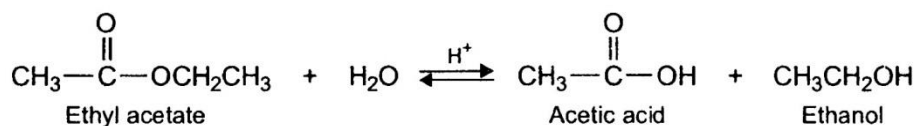
## Chemical Properties

The general reactions of esters are listed below:

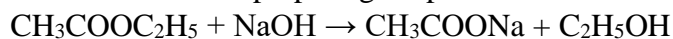
(1) **Hydrolysis:** Esters when heated with water in the presence of an acid catalyst ( $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ) are hydrolysed to give the parent carboxylic acid and alcohol. The reaction is reversible.



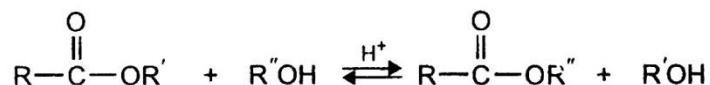




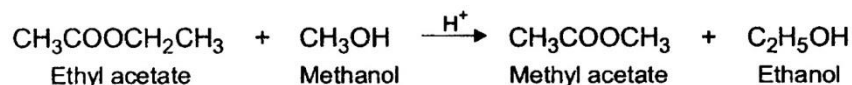
**Saponification:** The alkaline hydrolysis (basic-hydrolysis) of an ester to form sodium salt of the parent acid and alcohol is called Saponification. (Latin, *Sapon* = soap), since this type of reaction is used in preparing soaps from fats.



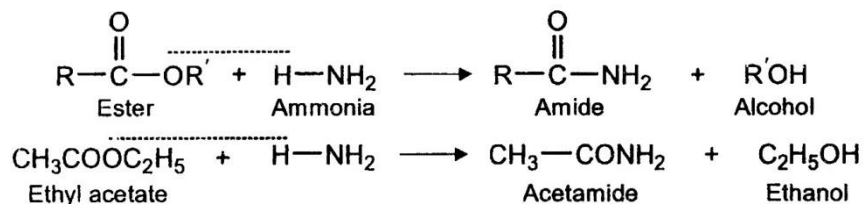
(2) **Transesterification:** Ester of an alcohol can react with another lower alcohol in the presence of a mineral acid, to give the ester of second alcohol. *The interchange of alcohol portions of the esters is termed transesterification.*



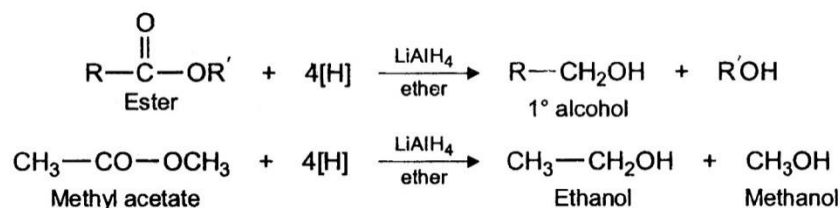
The lower alcohol being more volatile escapes and the reaction proceeds to completion.



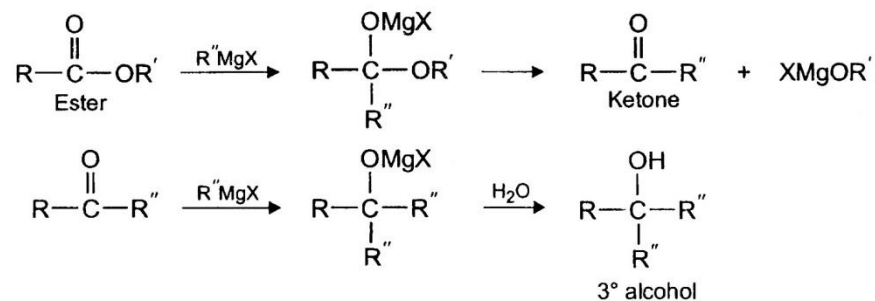
(3) **Reaction with Ammonia (*Ammonolysis*):** Esters react with ammonia, often in a solvent such as ethanol, to give amides.



(4) **Reduction to Alcohols:** Esters can be reduced to the primary alcohol corresponding to the acid from which it was derived by lithium aluminium hydride,  $\text{LiAlH}_4$ , or by sodium and alcohol.

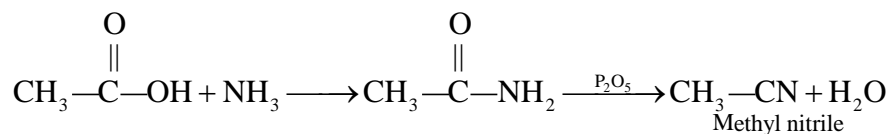


(5) **Reaction with Grignard Reagents:** Esters react with Grignard reagents to form ketones which at once react with another molecule of the Grignard reagent to yield a tertiary alcohol.



## 5. Nitriles

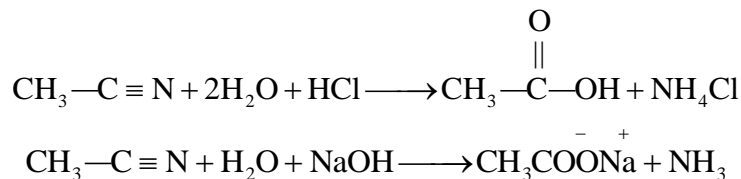
Nitriles are not the primary derivative of carboxylic acids they can be prepared from amide by dehydration (amide are primary derivative of acids).



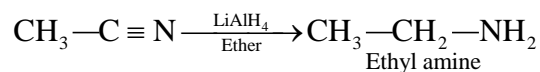
## Chemical Properties

Nitriles shows the following reactions.

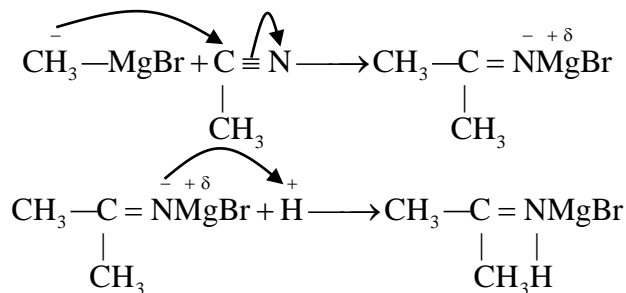
(i) **Hydrolysis:** When nitriles are boiled with dilute acid or base they are hydrolysed and form carboxylic acids.



(ii) **Reduction:** Nitriles when treated with reducing agents such as Na metal in ethanol or  $\text{LiAlH}_4$  in ether they are reduced to primary amines.



(iii) **Reaction with Grignard reagent:** Nitriles on reaction with Grignard reagent produces ketones.





Main organic product	Carboxylic acid	Ester	Amide
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## 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<sub>6</sub>H<sub>5</sub>OH  
 (c)✓ C<sub>6</sub>H<sub>5</sub>COOH (d) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH
- (ii) Which of the following acids is found in rancid butter?
- (a) C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> (b) C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>  
 (c)✓ C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> (d) C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>
- (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<sup>2</sup> 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)✓ Fluoroacetic acid
- (vi) Acetic acid can be prepared by the hydrolysis of:
- (a)✓ Methyl cyanide (b) Methylmagnesium 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) Transesterification
- (x) All the acid derivatives can be converted back into the corresponding acid

by one common reaction.

- (a) Amonolysis (b) Alcoholysis  
(c) Reduction (d)✓ Hydrolysis

## LONG QUESTIONS

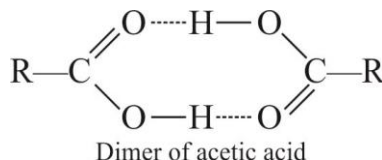
### Q.3. Explain Briefly:

**(i) Acetic acid is sometimes known as glacial acetic acid.**

**Ans.** Acetic acid is a colourless liquid with freezing point of  $17^{\circ}\text{C}$ . The low freezing point is due to the polar nature and due to the presence of hydrogen bonding among the molecules of acetic acid. On freezing it form an ice like solid therefore it is called glacial acetic acid in that state. It will exist in the glacial form when it is pure and when its temperature is 17 or below  $17^{\circ}\text{C}$ . It is miscible with water, ether and ethanol.

**(ii) Carboxylic acids have high boiling points than corresponding alcohols.**

**Ans.** In carboxylic acid the C=O bond, the C-O bond and the O-H bond are polar. The molecule as a whole is highly polar. Molecules of carboxylic acid are connected to one another by strong hydrogen bonding so the boiling points of carboxylic acids are higher than the corresponding alcohols as the alcohols are not that much polar. Hydrogen bonding between the two molecules of carboxylic acids is shown below.

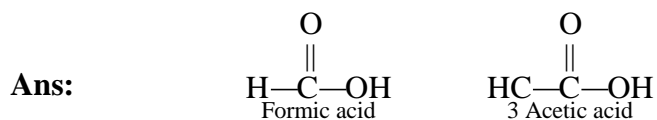


**(iii) Why carboxylic acids are stronger acids than phenol, alcohols and water but weaker than mineral acids?**

**Ans.** Carboxylic acids are stronger acids than phenol, alcohols and water but less acidic than mineral acids. Because mineral acids are completely dissociated in aqueous solution while carboxylic acids dissociates partially in aqueous solution.

**Phenol Vs Carboxylic acid:** Carboxylic acids are more acidic than phenols because when carboxylic acid dissociates the carboxylate ion formed is more resonance stabilized with the  $-ve$  charge on more electronegative oxygen atom.

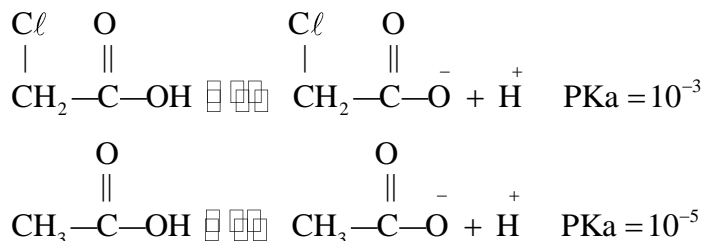




In case of formic acid H is attached to the carboxylic group while in case of acetic acid methyl group is attached to the carboxylic group. Methyl group is electron donating compared to the hydrogen atom so electron density on the oxygen bonded to H in case of acetic acid has more electron density and the H will not easily be protonated so its acidity is low. In case of formic acid as there is no electron donating group so the electron density on O bonded to H has less electron density and the O will attract electrons from the H atom and the H will be easily donated as hydrogen ion so formic acid is stronger acid compared to acetic acid.

**(v) Chloroacetic acid is stronger acid than acetic acid.**

**Ans.** Chloroacetic acid is more acidic than acetic acid because in chloroacetic acid the presence of chlorine atom makes the chloro methylene group an electron withdrawing and hence the electron density on the O bonded to H will decrease. The oxygen will attract electron from the H and its release will be easier and its acidity will be more. While in acetic acid the electron donating (CH<sub>3</sub>) methyl group is attached which increases electron density on oxygen of (OH) group due to which release of proton becomes difficult hence it is a weak acid as compared to chloroacetic acid. The PKa values are given below.



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

**Ans.** Given in the theory.

**(vii) Carboxylic acids do not undergo addition reactions compared to aldehydes.**

**Ans.** In case of aldehydes, H atom is attached to the carbonyl C atom. The carbonyl C atom always remains partial positive as O atom attached to it continuously attracts

the electron density. So nucleophile can easily attack and add to the carbonyl carbon. In case of carboxylic acids hydroxyl group (OH) which is an electron donating group is attached to the carbonyl C atom. The partial positive charge on the C atom is minimized or neutralized by the OH group attached to it. So nucleophile cannot easily attack and add to the carbonyl carbon atom of the carboxylic acid.

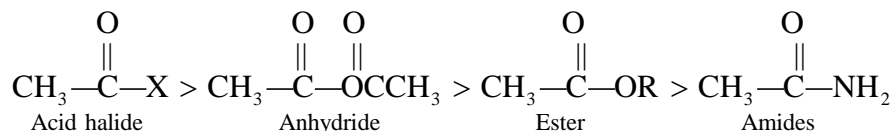


**(vii) Acid halide are most reactive of all acid derivatives towards nucleophiles.**

**Ans.** Acid halides are the most reactive among all the derivatives of carboxylic

acids because in all derivatives the Acyl group  $\left( \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}- \right)$  is attached with electron donating groups which decreases +ve charge on the carbonyl carbon except in acid halides where chlorine (halogen) is attached to the acyl group which is electron withdrawing group, attract electron density from it, make it more partial positive and hence electrophile will attack over it more easily.

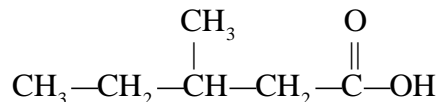
The order of reactivity of acid derivatives towards nucleophile is given below.



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

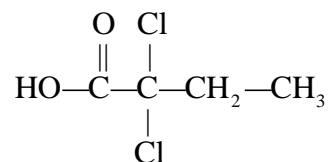
- |                                   |                                |
|-----------------------------------|--------------------------------|
| (i) 3-methylpentanoic acid        | (ii) 2,2-dichlorobutanoic acid |
| (iii) 2,2-dimethyl-3-butenic acid | (iv) Oxalic acid               |
| (v) Butanedioic acid              | (vi) Acetamide                 |
| (vii) Methanamide                 | (viii) Ethanoic anhydride      |
| (ix) Methyl Methanoate            | (x) Ethyl nitrile              |

**Ans.** (i) 3-methyl pentanoic acid

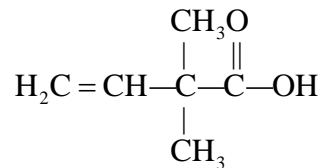


(ii) 2,2-dichlorobutanoic acid

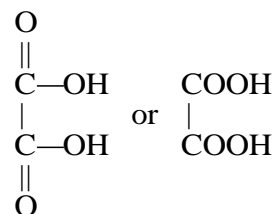




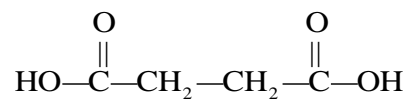
(iii) 2,2-dimethyl 3-butenoic acid



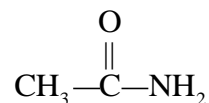
(iv) Oxalic acid



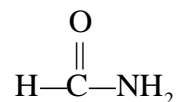
(v) Butanedioic acid



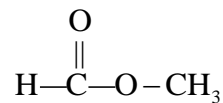
(vi) Acetamide



(vii) Methanamide



(ix) Methylmethanoate



(x) Ethylnitrile  $\text{CH}_3-\text{CH}_2-\text{CN}$

**Q.4. Write IUPAC names of the following:**

(i)  $\text{HCOOH}$

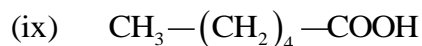
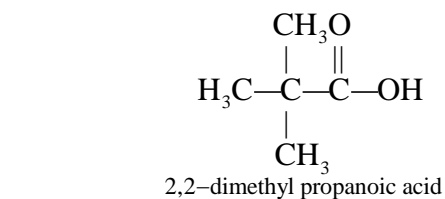
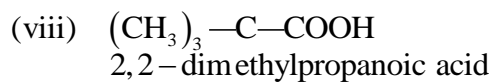
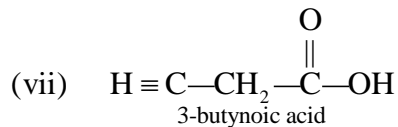
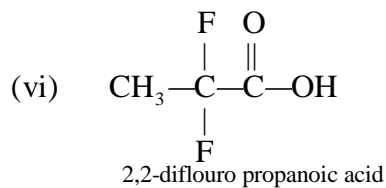
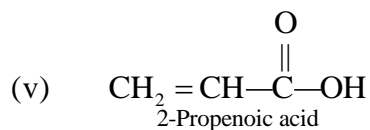
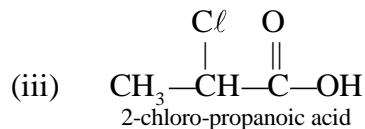
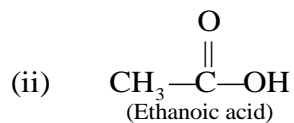
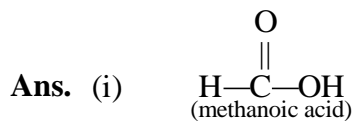
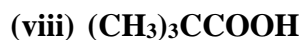
(ii)  $\text{CH}_3\text{COOH}$

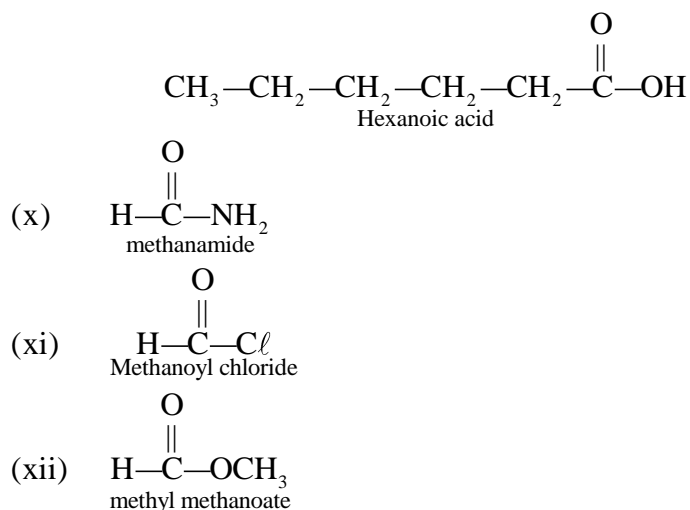
(iii)  $\text{CH}_3\text{CH}(\text{Cl})\text{COOH}$

(iv)  $\text{HOOCCH}_2\text{COOH}$

(v)  $\text{CH}_2=\text{CHCOOH}$

(vi)  $\text{CH}_3\text{CF}_2\text{COOH}$





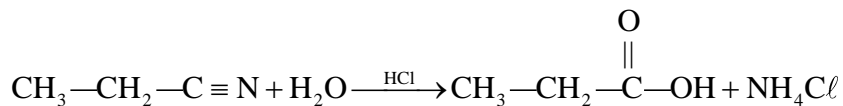
**Q.5. Explain the acidity of carboxylic acids. How their acid strength is affected by substitution?**

**Ans.** Given in the theory.

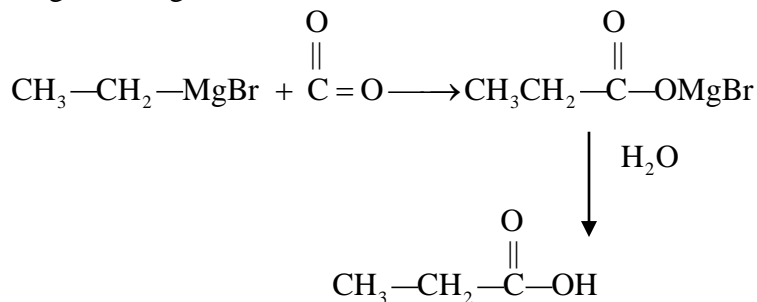
**Q.6. How will you prepare propanoic acid by using.**

- |                      |                        |
|----------------------|------------------------|
| (a) An alkyl nitrile | (b) A Grignard reagent |
| (c) An alcohol       | (d) An aldehyde        |

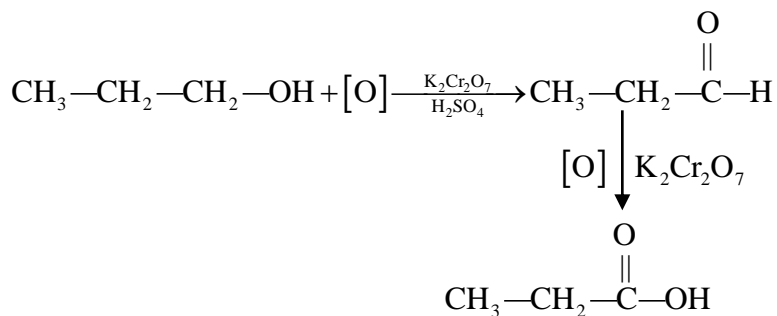
**Ans.** (a) Alkyl nitrile and water



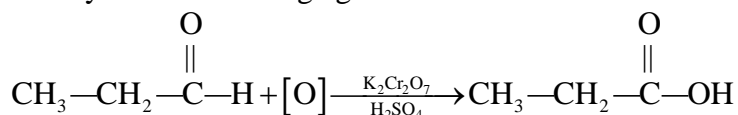
(b) Grignard reagent and carbon dioxide



(c) Alcohol and oxidizing agent



(d) Aldehyde and oxidizing agent



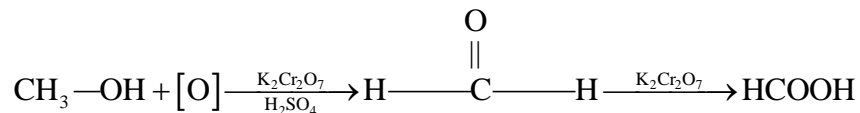
**Q.7. (a) Is there any method used for the preparation of formic acid? If yes explain with examples.**

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

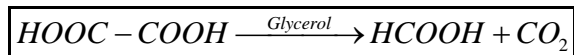
**(a) Is there any method used for the preparation of formic acid? If yes explain with examples.**

**Ans.** Yes, both laboratory and industrial scale methods are available for the preparation of formic acid.

**(i) Laboratory Method:** In laboratory formic acid can be prepared by oxidation of methanol which upon treatment with strong oxidizing agent results in the formation of formic acid.

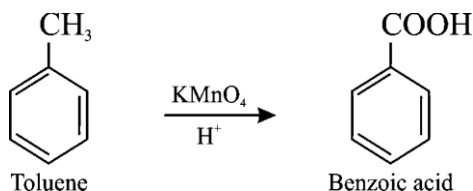


**(i) From oxalic acid:** The decarboxylation of oxalic acid gives formic acid.



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

**Ans.** Benzoic acid can be prepared by oxidation of methyl benzene or toluene with  $\text{KMnO}_4$ .



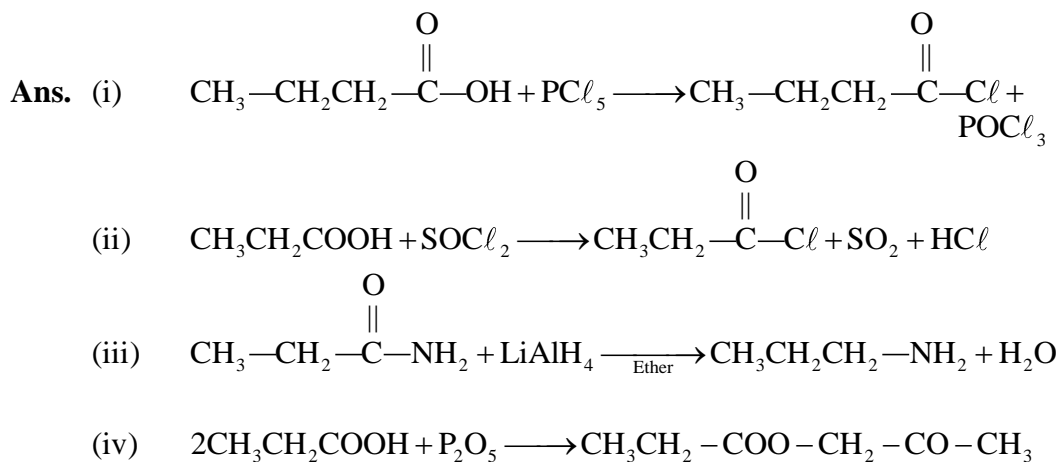
**Q.8. Write an equation for.**

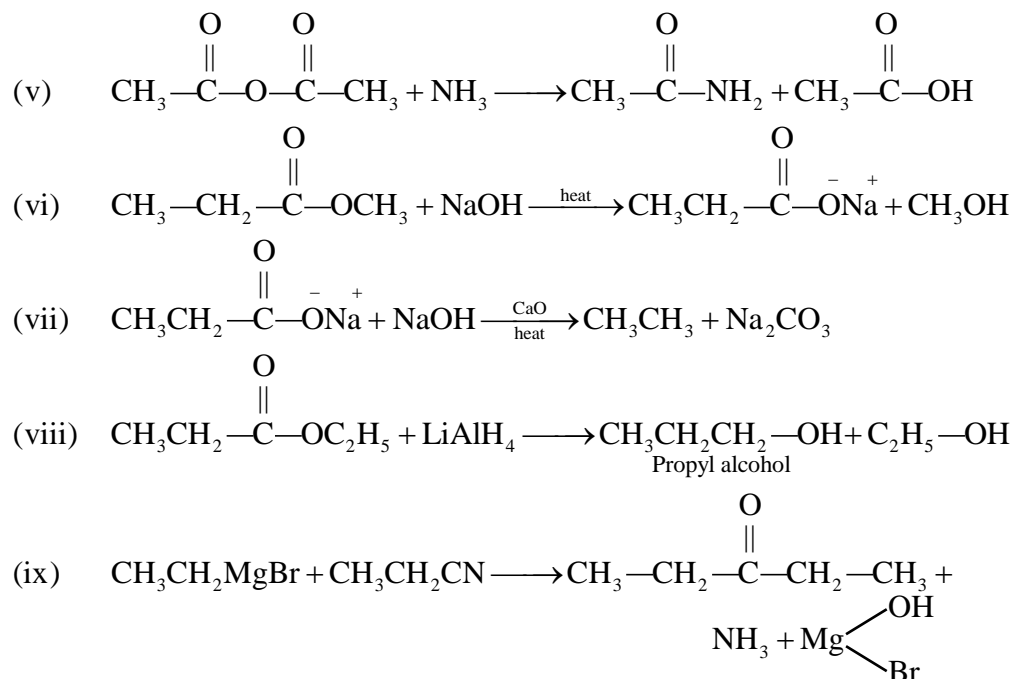
- Hydrolysis of acetyl chloride
- Reaction of benzoyl chloride with methanol.
- Esterification of 1-butanol with acetic anhydride.
- Ammolysis of butanoyl chloride.
- Fischer esterification of pentanoic acid with ethanol.
- Reaction of formic acid with ammonia.
- Hydrolysis of ethanoic propanoic anhydride.
- Reduction of ethyl cyanide.

**Ans.** Given in the theory.

**Q.9. Complete the following reactions.**

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{PCl}_5 \longrightarrow ?$
- $\text{CH}_3\text{CH}_2\text{COOH} + \text{SOCl}_2 \longrightarrow ?$
- $\text{CH}_3\text{CH}_2\text{CONH}_2 + \text{LiAlH}_4 \longrightarrow ?$
- $2\text{CH}_3\text{CH}_2\text{COOH} + \text{P}_2\text{O}_5 \longrightarrow ?$
- $\text{CH}_3\text{COOCOCH}_3 + \text{NH}_3 \longrightarrow ?$
- $\text{CH}_3\text{CH}_2\text{COOCH}_3 + \text{NaOH} \xrightarrow{\text{heat}} ?$
- $\text{CH}_3\text{CH}_2\text{COONa} + \text{NaOH} \xrightarrow{\text{CaO}} ?$
- $\text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5 + \text{LiAlH}_4 \longrightarrow ?$
- $\text{CH}_3\text{CH}_2\text{MgBr} + \text{CH}_3\text{CH}_2\text{CN} \longrightarrow ?$

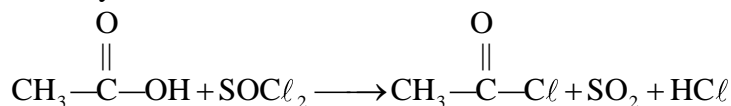




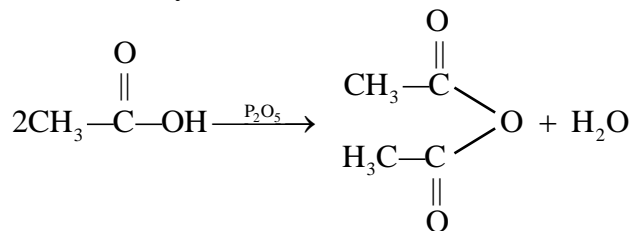
**Q.10. Starting from acetic acid, how will you prepare each of the following.**

- |                       |                         |
|-----------------------|-------------------------|
| (i) Ethanoyl chloride | (ii) Ethanoic anhydride |
| (iii) Ethanamide      | (iv) Ethyl ethanoate    |
| (v) Ethanol           |                         |

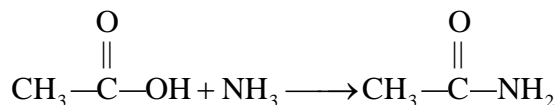
**Ans.** (i) Ethanoyl Chloride



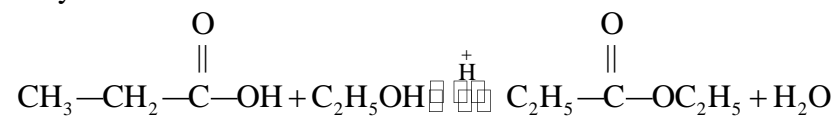
(ii) Ethanoic anhydride



(iii) Ethanamide



(iv) Ethyl ethanoate



(v) Ethanol

