# IUHSS

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CHE-MM: XII

# 12. Aldehydes, Ketones & Carboxylic Acids

Ex:

Aldehydes, ketones and carboxylic acids are some of the important classes of organic compounds containing carbon-oxygen double bond (>C=O) called **carbonyl group**.

## NATURE OF CARBONYL GROUP

- **Structure**: The C=O bond is made up of one  $\sigma$  and one  $\pi$ -bond. In • the formation of carbonyl group, C uses  $sp^2$ -hybrid orbitals while O uses its unhybridised atomic orbitals.
- C-atom is joined to three atoms by  $\sigma$ -bonds. Since these bonds utilise  $sp^2$  orbitals, they lie in the same plane and are 120° apart. Hence carbonyl group is planar.



**Nature**: The C=O bond is **polarised** due to higher electronegativity of O relative to C. The polar nature of the carbonyl group can also be indicated by the following resonating structure.

 $C = 0 \iff C^+ - 0^-$ 

# ALDEHYDES

→ Aldehydes are compounds in which the carbonyl group is bonded to a carbon and hydrogen.

#### General formula



## NOMENCLATURE

**Common name**: The common names of aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –ic acid with aldehyde.

The locations of the substituent in the carbon chain is indicated by Greek letters  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , etc.

**IUPAC name:** The IUPAC names of open chain aliphatic aldehydes are derived from the names of the corresponding alkanes by replacing the ending -e with '-al'.

In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group.

Structure	Common name	IUPAC name
нсно сн₃сно	Formaldehyde Acetaldehyde	Methanal Ethanal
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	Isobutyraldehyde	2-Methylpropanal

## (2) Dehydrogenation of 1<sup>0</sup> alcohols

$$RCH_2OH \xrightarrow{Cu}{573K} RCHO$$

## (3) Ozonolysis of alkenes

Addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by Zn-H<sub>2</sub>O to aldehydes.





(5) Controlled reduction of acyl halides (Rosenmund's reduction) Acid chlorides react with hydrogen in presence of Pd supported on BaSO<sub>4</sub>, yield aldehydes.

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$$\begin{array}{c} O \\ H_{2} \\ \hline \\ Pd - BaSO_{4} \end{array} \xrightarrow{\text{CHO}} \\ Benzaldehyde \end{array}$$

(6) From nitriles and esters (Stephen reaction):

*Nitriles* when reduced with *stannous chloride* in the presence of HCl to *imines*, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3 O} RCHO$$

*Esters* reduce to aldehydes with *diisobutylaluminium hydride* (DIBAL-H). Ex:

$$CH_{3}(CH_{2})_{*} - \overset{O}{C} - \overset{O}{OC_{2}H_{5}} \xrightarrow{1. \text{ DIBAL-H}} CH_{3}(CH_{2})_{*} - \overset{O}{\overset{H}{C}} - H$$

## Aromatic aldehydes may be prepared by-

## (7) Oxidation of Methylbenzene

*Methylbenzene* oxidised with chromyl chloride (*Etard reaction*) or **Chromic oxide** (CrO<sub>3</sub>) in the presence of *acetic anhydride* yield aromatic aldehydes





CH3CH(OCH3)CHO CH3CH2CH2CH2CH0 CH2=CHCHO

CHO



Acrolein Phthaldehyde

Valeraldehyde

m-Bromobenzaldehyde

γ-Methylcyclohexanecarbaldehyde

α-Methoxypropionaldehyde

3-Methylcyclohexanecarbaldehyde

2-Methoxypropanal Pentanal Prop-2-enal

Benzene-1.2-dicarbaldehvde

3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde

## METHODS OF PREPARATION

(1) Controlled oxidation of  $1^0$  alcohols

RCH2OH Oxidation R-Ċ Aldehvde (8) By hydrolysis of benzal chloride

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method for the manufacture of benzaldehyde.



(9) Formylation of arenes (Gatterman-Koch reaction) When benzene is treated with **CO** and **HCl** in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde.



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#### Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)

#### PROPERTIES

**<u>Physical:</u>** (applicable for ketones also)

- ✓ **State:** *Liquid* or *solid* at room temperature.
- ✓ Boiling point: Boil at higher temperatures than the hydrocarbons and weakly polar compounds such as ethers of comparable molecular masses.

Reason: These are highly polar molecules.

✓ Solubility: The lower members are *soluble* in water but the higher members are *insoluble*.

**Reason**: The **lower members** form H- bonds with water. The **higher members** have large sized hydrophobic chain of Catoms.

✓ Odour: The lower aldehydes have *pungent* smell and higher members have *fruity smell*.

#### **CHEMICAL REACTIONS:**

- (i) Nucleophilic addition reactions (Mechanism: see text, page 358)
   Aldehydes undergo nucleophilic addition reactions onto the carbonyl group with a number of nucleophiles such as, HCN, NaHSO<sub>3</sub>, alcohols (or diols), ammonia derivatives, and Grignard reagents.
- a. Addition of hydrogen cyanide: Aldehydes react with hydrogen cyanide (HCN) in presence of a base to give cyanohydrins.



The cyanohydrins are useful synthetic intermediates since it can be converted to *carboxylic acids, amines, amides* etc.

b. Addition of sodium hydrogensulphite: Aldehydes with *sodium hydrogensulphite* gives the addition products (*bisulphite adduct*).

$$\begin{array}{c|c} \hline C = O + NaHSO_3 \rightleftharpoons C \swarrow SO_3H \\ \hline ONa \end{array} \xrightarrow{\text{proton transfer}} C \swarrow SO_3Na \\ \hline OH \\ \hline Bisulphite addition \\ \hline C & OH \\ \hline C &$$

compound (crystalline)

The bisulphate adduct can be converted back to the **original aldehyde** by treating it with **dilute mineral acid or alkali**. Therefore, this reaction is used for the separation and purification of aldehydes.

c. Addition of Grignard reagents: Aldehyde with *Grignard reagent* followed by hydrolysis, gives alcohols. Formaldehyde gives 1<sup>0</sup> alcohols and other aldehydes give 2<sup>0</sup> alcohols.

d. **Addition of alcohols:** Aldehydes react with monohydric alcohol in the presence of dry HCl to give *alkoxyalcohol* intermediate (known as hemiacetals), which further react with one molecule of alcohol to give a *gem-dialkoxy* compound known as **acetal**.



#### (ii) Reduction:

a. *Reduction to alcohols*: When reduced using sodium borohydride (NaBH<sub>4</sub>) or lithium aluminium hydride (LiAlH<sub>4</sub>) or H<sub>2</sub> in presence of Ni, Pd or Pt catalyst (Catalytic hydrogenation), aldehydes give 1<sup>0</sup> alcohols

 $RCHO + H_2 \xrightarrow{Pd} RCH_2OH$ 

#### b. Reduction to Hydrocarbons:

*Clemmensen reduction*: Aldehydes and ketones can be reduced to alkanes on treatment with **zinc amalgam** and **conc. HCl**. During this reaction, the carbonyl group is reduced to  $CH_2$  (methylene) group.

$$\begin{array}{|c|c|c|c|c|} \hline C = 0 & \underline{Zn-Hg} \\ \hline HCl \end{array} \xrightarrow{} CH_2 + H_2O \end{array}$$

*Wolff-Kishner reduction*: Carbonyl group can also be reduced to **methylene group**, by treating with **hydrazine** followed by heating with **sodium or potassium hydroxide** in high boiling solvent such as *ethylene glycol*.

$$C = O \xrightarrow{\text{NH}_2\text{NH}_2} C = N\text{NH}_2 \xrightarrow{\text{KOH/ethylene glycol}} CH_2 + N_2$$

#### (iii) Oxidation:

Aldehydes are easily oxidised to **carboxylic acids** on treatment with common oxidising agents like nitric acid, **potassium permanganate**, **potassium dichromate** etc.

 $R-CHO \xrightarrow{[O]} R-COOH$ 

#### (iv) Haloform Reaction:

Aldehydes or ketones having CH<sub>3</sub>-CO- group or CH<sub>3</sub>-CHOHgroup, when treated with **sodium hypohalite** or **halogen** in presence of **NaOH**, yield haloform (CHX<sub>3</sub>).

During this reaction, the methyl group is converted to haloform.

$$\begin{array}{c} O \\ \parallel \\ R - C - CH_3 \xrightarrow{\text{NaOX}} R - C - ONa + CHX_3 \quad (X=Cl, Br, l) \end{array}$$

#### (v) Aldol condensation Reaction:

The  $\alpha$ -hydrogens in aldehydes are acidic. Therefore, aldehydes



Acetals on *hydrolysis* with **aqueous mineral acids** to give corresponding aldehydes.

e. Addition of ammonia derivatives: Nucleophiles like ammonia and its derivatives  $H_2N$ -Z are added to the carbonyl group of aldehydes.

$$c = 0 + H_2 N - Z \iff \left[ c < OH \\ NHZ \right] \longrightarrow c = N - Z + H_2 O$$

having at least one  $\alpha$ -hydrogen, undergo Aldol condensation in the presence of a base to give  $\alpha$ -hydroxyaldehydes (aldol). 2 CH<sub>3</sub>-CHO  $\xleftarrow{\text{dil. NaOH}}$  CH<sub>3</sub>-CH-CH<sub>2</sub>-CHO  $\xrightarrow{\Delta}$  -CH<sub>3</sub>-CH=CH-CHO Ethanal OH But-2-enal 3-Hydroxybutanal (Aldol condensation product)

(vi) Cross aldol condensation: When aldol condensation is carried out between two different aldehydes or ketones, it gives a mixture of 4 products.



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#### (vii) Cannizzaro reaction

Aldehydes having no  $\alpha$ -hydrogen when treated with Conc. alkali (NaOH or KOH) undergo **self oxidation** and **reduction** (disproportionation) to form one molecule of the alcohol and one molecule of carboxylic acid salt.



#### (viii) Electrophilic Substitution Reactions:

Aldehydic groups are **meta directing and deactivating**. So on electrophilic substitution reactions, they give meta-derivatives.



Benzaldehyde

## Uses

- 1) **40% aqueous solution of Formaldehyde,** known as *formalin* is used to *preserve biological specimens* and to prepare **bakelite**.
- 2) Acetaldehyde is used as a **starting material** in the manufacture of **acetic acid, ethyl acetate, vinyl acetate, polymers** and **drugs**.
- 3) Benzaldehyde is used in **perfumery** and in **dye** industries.
- 4) Acetone and ethyl methyl ketone are common industrial solvents.
- 5) Many aldehydes and ketones, e.g., *butyraldehyde, vanillin, acetophenone, camphor*, etc. are well known for their odours and flavours.

# KETONES

→ Ketone: In ketones, the carbonyl group is bonded to two carbon atoms.

General formula



## NOMENCLATURE

Common name: The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group and by suffixing ketone.

The locations of the substituents are indicated by Greek letters,  $\alpha$   $\alpha'$ ,  $\beta \beta'$  and so on.

Some ketones have historical common names, **Ex:** acetone (dimethyl ketone).



IUPAC name: The IUPAC names of open chain aliphatic ketones are derived from the names of the corresponding alkanes by replacing the ending -e with '-one'.

In case of ketones the the longest carbon chain is numbered

(2) Dehydrogenation of 2<sup>0</sup> alcohols

$$\begin{array}{c} R-CH-R' \xrightarrow{Cu} 573K \\ OH \end{array} \begin{array}{c} R-C-R' \\ O \end{array}$$

(3) Ozonolysis of alkenes



## (4) Hydration of alkynes

Addition of water to alkynes (except ethyne) in the presence of  $H_2SO_4$  and  $HgSO_4$  give ketones.

Ex:  $CH_3-C=CH+H-OH \xrightarrow{Hg^{2*}/H^+} CH_3-C=CH_2$ Propyne O-HIsomerisation  $CH_3-C-CH_3$ O Propanone

## (5) Reaction of acyl chloride with dialkylcadmium

Acid chlorides react with *dialkylcadmium*, give ketones. (*Dialkyl cadmium* is prepared by the reaction of cadmium chloride with Grignard reagent).

$$2 R - Mg - X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

$$2 R' - \frac{C}{C} - Cl + R_2Cd \longrightarrow 2 R' - \frac{C}{C} - R + CdCl$$

## (6) From nitriles:

Treating a *nitrile* with **Grignard reagent** followed by hydrolysis yields a ketone.

$$CH_3 - CH_2 - C = N + C_eH_5MgBr \xrightarrow{ether} CH_3CH_2 - C_{eH_5}$$

$$H_3O^*$$
  $C_2H_5 - C_6H_5$   
Propiophenone  
(1-Phenylpropanone)

## Aromatic ketones may be prepared by-

## (7) Friedel-Crafts acylation of aromatic hydrocarbons

When *benzene* or *substituted benzene* is treated with **acid chloride** in the presence of **anhydrous aluminium chloride**, gives aromatic ketone.

O)

$$= \begin{array}{c} O \\ \parallel \\ + & Ar/R - C - Cl \end{array} \xrightarrow{Anhyd. AlCl_s} O \xrightarrow{C} Ar/R$$

## PROPERTIES

## Chemical:-

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

- **Sterically**, the presence of two bulky alkyl groups in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes.
- **Electronically**, ketones are less reactive because of the electron releasing nature of the two alkyl groups reduces the electrophilicity of the carbonyl carbon.

#### starting from the carbon of the end nearer to the carbonyl group.

Structure	Common name	IUPAC name
Ketones CH3COCH2CH2CH3 (CH3)2CHCOCH(CH3)2	Methyl n-propyl ketone Diisopropyl ketone	Pentan-2-one 2,4-Dimethylpentan-3-one
CH,	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

## METHODS OF PREPARATION



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## **CHEMICAL REACTIONS:**-

#### (i) Nucleophilic addition reactions

- a. Addition of hydrogen cyanide (HCN) gives cyanohydrins.
- b. Addition of sodium hydrogensulphite gives bisulphite adduct.
- c. Addition of Grignard reagents give 3<sup>o</sup> alcohols.
- d. Addition of alcohols form ketals



#### (ii)Reduction

a. Reduction to alcohols: Ketones give secondary alcohols. RCOR'  $\xrightarrow{\text{NaBH}}$  R- CH-R' OH

#### b. Reduction to Hydrocarbons:

*Clemmensen reduction*: Ketones can be reduced to alkanes. *Wolff-Kishner reduction*: Reduced to **methylene group**.

#### (iii) Oxidation:

Ketones when oxidised using **strong oxidising agents** and at high temperatures, yield a *mixture of carboxylic acids* having lesser number of C-atoms. During this reaction C-C bond cleavage occurs.

 $\begin{array}{ccccccc} & 1 & 2 & 3 & [O] \\ R-CH_2-C-CH_2-R' & & & & & & \\ & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & &$ 

- (iv) Haloform Reaction yield haloform (CHX<sub>3</sub>).
- (v) Aldol condensation Reaction:

Ketones having at least one  $\alpha$ -hydrogen, undergo Aldol condensation to give  $\alpha$ -hydroxyketones (ketol).



## Test to distinguish aldehydes from <u>ketones:-</u>

1. Tollens' test:

**Tollen's reagent** = Fresh *ammoniacal Silver nitrate*.

On warming Tollens' reagent, aldehydes give a **bright silver mirror**. During this reaction, the aldehyde is oxidised to corresponding **carboxylate ion** and **silver nitrate** is reduced to silver metal.

 $RCHO + 2[Ag(NH_3)_2]^* + 3 \overline{O}H \longrightarrow RCO\overline{O} + 2Ag + 2H_2O + 4NH_3$ 

## 2. Fehling's test:

Fehling reagent is a mixture of two solutions-

**Fehling solution A** = aqueous copper sulphate

**Fehling solution B** = alkaline sodium potassium tartarate (Rochelle salt)

On heating with Fehling's reagent, aldehyde gives a **reddish brown precipitate** of cuprous oxide ( $Cu_2O$ ). Aromatic aldehydes do not give this test.

 $R-CHO + 2Cu^{3+} + 5\overline{O}H \longrightarrow RCO\overline{O} + Cu_2O + 3H_2O$ 

Red-brown ppt

#### Ketones do not answer Tollens' or Fehlings' test.

# CARBOXYLIC ACIDS

→ Carboxylic acid: The carbonyl compounds in which carbonyl group is bonded to a hydroxyl group (OH).

General formula

For naming compounds containing more than one carboxyl group, the ending –e of the alkane is retained. The number of carboxyl groups is indicated by adding the prefixes di, tri, etc. to the term oic.

Names and Structures of Some Carboxylic Acids

Structure	Common name	IUPAC name
нсоон	Formic acid	Methanoic acid
сңсоон	Acetic acid	Ethanoic acid
сң сң соон	Propionic acid	Propanoic acid
CH3CH2CH2COOH	Butyric acid	Butanoic acid
(CH <sub>3</sub> ) <sub>2</sub> CHCOOH	Isobutyric acid	2-Methylpropanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC -CH2-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 -(CH2)COOH	Adipic acid	Hexanedioic acid
HOOC -CH2-CH(COOH)-CH2-COOH	-	Propane-1, 2, 3- tricarboxylic acid
Соон	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
CH <sub>2</sub> COOH	Phenylacetic acid	2-Phenylethanoic acid
СООН	Phthalic acid	Benzene-1, 2-dicarboxylic acid

## METHODS OF PREPARATION

Carboxylic acids are prepared by -

## (1) Oxidation of $1^0$ alcohols and aldehydes

 $1^{0}$  alcohols oxidise to *carboxylic acids* with oxidising agents such as *potassium permanganate* (KMnO<sub>4</sub>) or by *potassium dichromate* (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) and *chromium trioxide* (CrO<sub>3</sub>) in acidic media (Jones reagent).

$$\begin{array}{c} \text{RCH}_{2}\text{OH} \xrightarrow{1. \text{ alkaline KMnO}_{4}} \text{RCOOH} \\ \hline 2. \text{ H}_{3} \stackrel{+}{\text{O}} \\ \text{CH}_{3}(\text{CH}_{2})_{8}\text{CH}_{2}\text{OH} \xrightarrow{\text{CrO}_{3}-\text{H}_{2}\text{SO}_{4}}_{\text{Jones reagent}} \xrightarrow{\text{CH}_{3}(\text{CH}_{2})_{8}\text{COOH}} \\ \hline 1-\text{Decanol} \xrightarrow{\text{Decanoic acid}} \end{array}$$

Aldehydes on oxidation with mild oxidising agents like  $CrO_3$  or Tollen's reagent to give carboxylic acids.

$$R-CHO \xrightarrow{[O]} R-COOH$$

#### (2) Hydrolysis of nitriles

Hydrolysis of nitriles in presence of acid or alkali as catalyst first give *amides*, which on further give *carboxylic acids*.

$$R-CN \xrightarrow{\stackrel{i}{H} \text{ or } \overline{OH}}_{H,O} R \xrightarrow{\stackrel{i}{C}} -NH_2 \xrightarrow{\stackrel{i}{H} \text{ or } \overline{OH}}{\bigtriangleup} RCOOH$$

## $\textbf{(3) Treatment of Grignard reagents with CO_2}$

Grignard reagents react with  $CO_2$  (dry ice) in dry ether to form salts of carboxylic acids which on acidification give corresponding carboxylic acids.



#### (4) From acyl halides and anhydrides:

Acid chlorides and anhydrides after hydrolysis and acidification



## NOMENCLATURE

- Common name: The trivial names of carboxylic acids end with the suffix –*ic* acid and have been derived from Latin or Greek names of their natural sources.
  - **Ex:** Formic acid was first obtained from ants ( $formica^{L} = ant$ ) Acetic acid from vinegar ( $acetum^{L} = vinegar$ ), Butyric acid from rancid butter ( $butyrum^{L} = butter$ ).
- IUPAC name: The aliphatic carboxylic acids are named by replacing the ending –e in the name of the corresponding alkane with – oic acid. In numbering the carbon chain, the carboxylic carbon is numbered one.

#### give carboxylic acids.

$$\begin{array}{c} H_{3}O \\ \hline RCOCI \\ \hline \hline OH/H_{3}O \\ \hline OH/H_{3}O \\ \hline RCOO^{-} + \overline{Cl} \\ \hline H_{3}O^{+} \\ \hline RCOOH \\ \hline \end{array}$$

#### (5) From esters:

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives salt of carboxylic acids which on acidification give corresponding carboxylic acids.



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## Aromatic carboxylic acids may be prepared by-

#### (6) Side-chain oxidation of *alkylbenzenes*

Oxidation of alkyl benzenes with chromic acid or acidic or alkaline **potassium permanganate** gives aromatic carboxylic acids.  $1^{\circ}$  and  $2^{\circ}$  alkyl groups are oxidised in this manner while  $3^{\circ}$  group is not affected.



## PROPERTIES

#### **Physical**:-

✓ *Physical state*: Aliphatic carboxylic acids upto 9 C-atoms are colourless liquids with unpleasant smell.

The higher acids are **waxy solids** and are **odourless**.

- ✓ *Boiling point*: Carboxylic acids are higher boiling liquids than aldehydes, ketones and alcohols of comparable molecular masses. **Reason:-** Presence of intermolecular H-bonding.
- ✓ Solubility: The first 4 acids are soluble in water and the solubility **decreases** with increasing number of C- atoms.

**Reason:-** Simple acids have the ability to form H-bonds with water while higher acids are insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.

Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

#### Chemical:-

Acidity: Carboxylic acids are more acidic than alcohols and most of simple phenols. (For details, see text, page 372)

## **CHEMICAL REACTIONS:**

(i) Reactions with metals and alkalies: Like alcohols and phenols, carboxylic acids react with electropositive metals and liberate H- gas.

$$2R-COOH + 2Na \longrightarrow 2R-COONa^{*} +$$
  
Sodium carboxylate

(ii) Reactions with mineral acids: Carboxylic acids on heating with mineral acids like H<sub>2</sub>SO<sub>4</sub> or with P<sub>2</sub>O<sub>5</sub> undergo dehydration to give 2) Ethanoic acid (acetic acid) is used as solvent and as vinegar in food acid anhydrides.

Н,



(iii) Reaction with alcohol (*Esterification*): Carboxylic acids when heated with alcohols or phenols in the presence of a mineral acid like conc. H<sub>2</sub>SO<sub>4</sub> or HCl gas, gives esters.

 $RCOOH + R'OH \xrightarrow{H^*} RCOOR' + H_2O$ 

(iv) Reactions with PCl<sub>3</sub>, PCl<sub>5</sub> and SOCl<sub>2</sub>: Carboxylic acids on treating with PCl<sub>3</sub>, PCl<sub>5</sub> or SOCl<sub>2</sub>, gives acid chlorides. Reaction with thionyl chloride (SOCl<sub>2</sub>) is preferred because the (vi) **Reduction:** Carboxylic acids when reduced with lithium **aluminium hydride** or with **diborane** in ether solution,  $1^{\circ}$ alcohols are formed.

$$R-COOH \xrightarrow{(i) LiAlH_{q}/ether \text{ or } B_{2}H_{s}} R-CH_{2}OH$$

$$(ii) H_{3}O^{*}$$

#### (vii) Decarboxylation:

a. When sodium salts of carboxylic acid are heated with sodalime (a mixture of NaOH and CaO), they undergo decarboxylation to form alkanes.

$$\begin{array}{c} \text{R-COONa} & \xrightarrow{\text{NaOH \& CaO}} & \text{R-H} + & \text{Na}_2\text{CO}_3 \\ & & \text{Heat} \end{array}$$

b. Kolbe's electrolysis: When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, it produce alkanes having twice the number of C-atoms that present in the alkyl group of the acid.

> Electrolysis  $\rightarrow$  CH<sub>3</sub>-CH<sub>3</sub>+2CO<sub>2</sub>+H<sub>2</sub>+2NaOH 2CH<sub>3</sub>COO<sup>-</sup>Na<sup>+</sup> + 2H<sub>2</sub>O Sodium acetate

#### (viii)Halogenation [Hell-Volhard Zelinsky reaction]

Carboxylic acids undergo  $\alpha$ -halogenation with Cl<sub>2</sub> and Br<sub>2</sub> in the presence of **red phosphorus**, gives  $\alpha$ -halocarboxylic acids.

$$R-CH_2-COOH \xrightarrow{(i) X_2/Red phosphorus} R-CH-COOH$$
$$\downarrow X$$
$$X = Cl, Br$$

#### α – Halocarboxylic acid

#### (ix) Electrophilic substitution reactions:

The –COOH group is a deactivating group and meta-directing. So on electrophilic substitution reactions, they yield meta derivatives. Ex:



## USES

- 1) Methanoic acid (formic acid) is used in rubber, textile, dyeing, leather and electroplating industries.
- industry.
- 3) Hexanedioic acid (adipic acid) is used in the manufacture of nylon-6, 6.
- 4) Esters of **benzoic acid** are used in perfumery.
- 5) Sodium benzoate is used as a food preservative.
- 6) Higher fatty acids are used for the manufacture of soaps and detergents.

byproducts are gases and are easily escaped from the reaction mixture so that yield *pure acid chloride*.

RCOOH	+	PCl <sub>5</sub>	$\rightarrow$	RCOCI	+	POCI <sub>3</sub> -	t	HCl
3RCOOH	+	PCl,	$\rightarrow$	3RCOC1	+	H <sub>3</sub> PO <sub>3</sub>		
RCOOH	+	SOCI2	$\rightarrow$	RCOCI	+	SO <sub>2</sub>	t	HC1

(v) **Reaction with ammonia:** Carboxylic acids react with ammonia to give **ammonium salts** which on further heating at high temperature give amides.



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