Chapter # 9

Carbonyl compound II Carboyclic acid and functional derivatives

INTRODUCTION

"Organic compounds which contain carbonyl group (C = 0) attached to hydroxyl group (-OH) are referred as carboxylic acid".

PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

i) Colour and odour

Aliphatic monocarboxylic acids are generally colorless. They have a pungent odour.

ii) Solubility

Carboxylic acids are soluble in polar solvents such as water and alcohols, due to their ability to form hydrogen bonds with these solvents.

iii) Boiling points

Compared to alcohols, carboxylic acids are more polar and have a high tendency to form hydrogen bonds among themselves.

STRUCTURE OF CARBOXYLIC ACID

Structure of carboxylic acid is explained by the hybrid orbital theory. The carbonyl carbon is sp^2 hybridized, possessing three sp^2 hybrid orbitals and one pz unhybridized orbital. These three sp^2 hybrid orbitals are oriented almost at an angle of 120° to give trigonal geometry whereas pz unhybridized orbital of carbonyl carbon form pi bond with pz orbital of oxygen atom.

Fig 9.1: Structure of carboxylic acid

ACIDITY OF CARBOXYLIC ACID

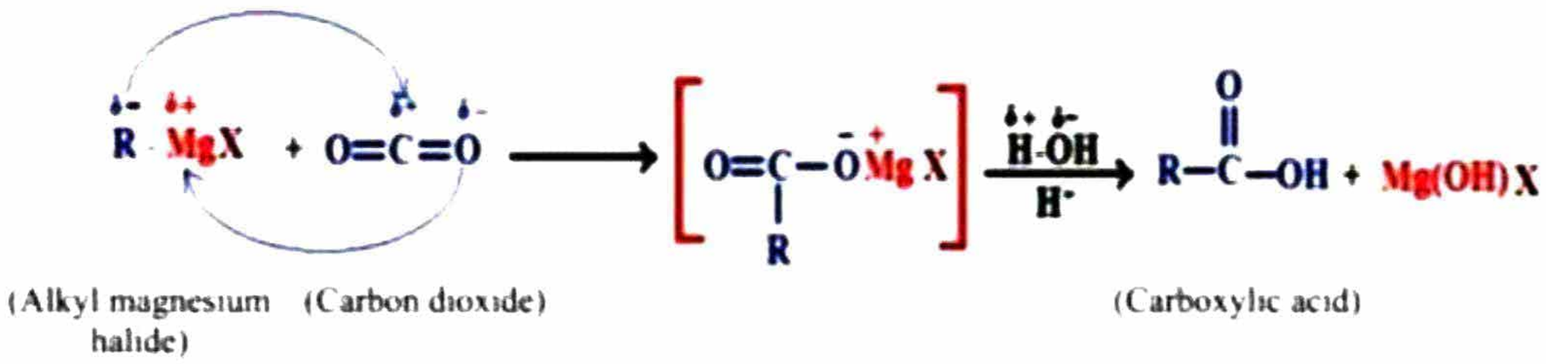
"Carboxylic acids are considerably stronger acids than alcohols, phenols and water. However, they are weaker acids compared to mineral acids",

PREPARATION OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Carboxylic acids are prepared by the following different methods.

By the Carbonation of Grignard Reagent

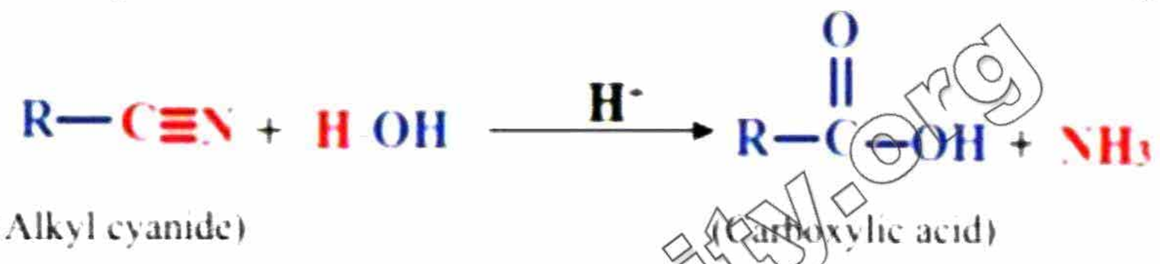
When Grignard reagent reacts with carbon dioxide, it changes into an addition product which on hydrolysis in acidic medium produce carboxylic acid.



(Alkyl magnesium halide) (Carbon dioxide) (Carboxylic acid)

By the Hydrolysis of Nitriles

Alkyl cyanide (nitrile) when reacts with water in the presence of acid, it changes into carboxylic acid with the liberation of ammonia gas.



(Alkyl cyanide) (Carboxylic acid)

By the Oxidation of Primary Alcohols

By using acidified oxidizing agents such as K,Cr,0, or KMnO4 primary alcohols can be oxidized to form carboxylic acids. This process occurs through an intermediate stage where the alcohol is converted into an aldehyde.

By the Oxidation of Aldehyde

Aldehydes oxidized when mixed with Potassium dichromate and sulphuric acid to produce carboxylic acid.

By the Oxidation of Alkyl Benzene

When an alkyl benzene reacts with potassium permanganate ($KMn0_4$) under acidic conditions, the alkyl group is oxidized to-COOH group.

REACTIONS OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Certain compounds are structurally derived from carboxylic acids by replacing a part of functional group of the carboxylic acid. Some common derivatives of carboxylic acids are given as.

(i) Esters:

They are formed by replacing the hydroxyl group of carboxylic acid with an alkyl or aryl group. Their general formula is R-COOR e.g. Ethyl acetate ($CH_3COOCH_2CH_3$), Methyl propionate ($CH_3CH_2COOCH_3$).

(i) Acid halides:

They are formed by replacing the hydroxyl group of carboxylic acid with a halogen (X) atomn. Their general formula is RCOX e.g. Acetyl chloride (CH_3COCI), Propionyl chloride (CH_3CH_2COCl).

(iii) Amides:

They are formed by replacing the hydroxyl group of carboxylic acid with an amino group. Their general formula is RCONH e.g. Acetamide (CH_3CONH_2), Benzamide ($C_6H_5CONH_2$).

(iv) Anhydrides:

They are formed by the removing a water molecule from two carboxylic acid molecules. Their general formula is $(RCO)_20$ e.g. Acetic anhydride $(CH_3CO)_2O$, Maleic anhydride ($C_4H_20_3$).

Conversion of carboxylic acids into acyl halides

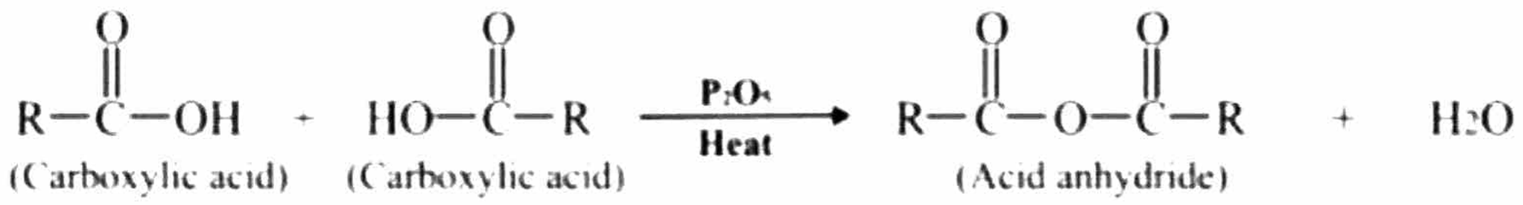
Like alcohols, the hydroxyl groups of carboxylic acids are easily replaced by halogen atom on heating with PCl_5, PCl_3, or $SOCI_2$

$$\underset{\text{(carboxylic acid)}}{R-COOH} + PCl_5 \longrightarrow \underset{\text{(Acyl halide)}}{R-CO-Cl} + POCl_3 + HCl$$

$$\underset{\text{(carboxylic acid)}}{3R-COOH} + PCl_3 \longrightarrow \underset{\text{(Acyl halide)}}{3R-CO-Cl} + H_3PO_3$$

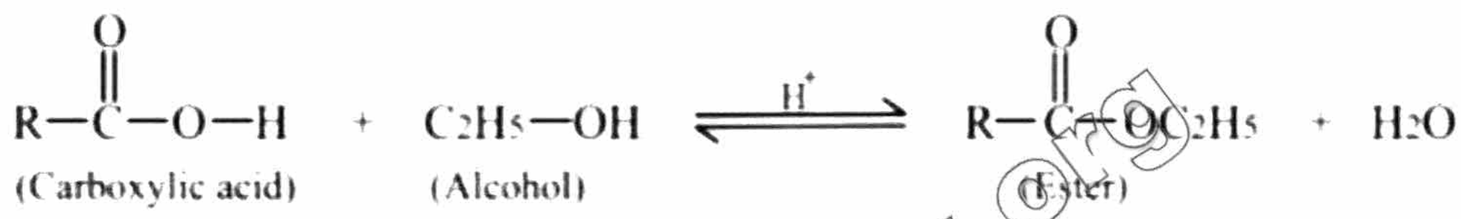
Conversion of Carboxylic Acids into Acid Anhydrides

The formation of an acid anhydride involves a condensation reaction between two carboxylic acid molecules. This reaction is typically conducted in the presence of a dehydrating agent like phosphorus pentoxide (P_2O_5).



Conversion of Carboxylic Acids into Ester

Esters are produced from carboxylic acids through a reaction called esterification. In this reaction carboxylic acid reacts with an alcohol in the presence of a catalyst usually concentrated Sulphruic acid to produce an ester and water.



Conversion of Carboxylic Acids into Amides

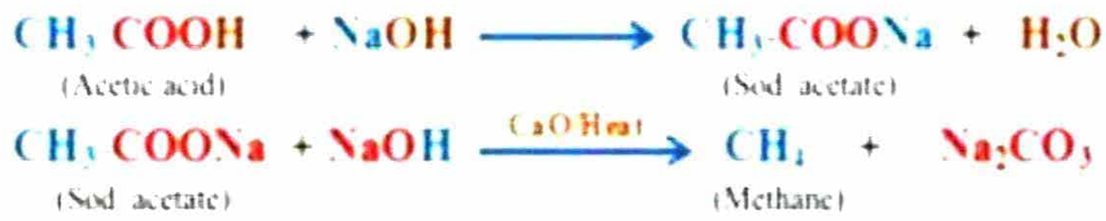
Amides can be produced by the reaction between carboxylic acid and ammonia, where an ammonium salt is formed, which upon heating yields the corresponding acid amide.

Conversion of Carboxylic Acids into Alcohols

Carboxylic acids upon catalytic reduction with lithium aluminum hydrides produce primary alcohols.

Conversion of Carboxylic Acids into Alkane

Carboxylic acids when reacted with caustic soda (base) they form salt of carboxylic acid which on further heating with soda-lime yield alkanes.



Uses of some common carboxylic acids and their derivatives

Citric Acid ($C_6H_8O_7$)

It is used as a preservative, flavor enhancer acidity regulator.

Malic Acid ($C_4H_6O_5$)
It is used as a food additive and pH control agent.

Tartaric Acid ($C_4H_6O_6$)
It is commonly used in food and beverage industry. products.

Acetic Acid (CH_3COOH)
It is used as a preservative and as a raw material of various chemicals.

Salicylic Acid (HOC_6H_4COOH)
It is used in the preparation of skin care products and in the production of aspirin.

Benzoic Acid (C_6H_5COOH)
It is used in the production of dyes, perfumes and plastics.

Acetamide (CH_3CONH_2)
It is used as a raw material in pharmaceuticals and drug synthesis.

Acetic anhydride ($C_4H_6O_3$)
It is used in making cellulose acetate and in the manufacturing of dyes.

Short Questions

1. Explain why?

i) The boiling points of carboxylic acids are high than alcohol?
Intermolecular hydrogen bonding between carboxylic acid molecules is responsible for their higher boiling points compared to alcohols.

ii) The structure of carboxylic acid is trigonal planar?
The functional group (COOH) in a carboxylic acid has a trigonal planar geometry due to sp2 hybridization of the central carbon atom.

2. What happens when:

i) Formaldehyde reacts with a mixture of Potassium dichromate & Sulphruic acid.

$$HCHO + K_2Cr_2O_7 + H_2SO_4 \longrightarrow HCOOH + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

ii) Carboxylic acid reacts with thionyl chloride

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

ii) Carboxylic acid reacts with ammonia

iv) Ethyl magnesium bromide reacts with carbon dioxide

$$C_2H_5MgBr + CO_2 \longrightarrow CH_3CH_2COOH + MgBr_2$$

3. Write down the commercial applications of carboxylic acids.

Carboxylic acids are a diverse group of organic compounds with a wide range of commercial applications. Here are some of the most important ones:

Food and Beverages: Many carboxylic acids are found naturally in food and beverages or are added as ingredients.

Chemicals and Polymers: Carboxylic acids are essential starting materials for the production of various chemicals and polymers.

Pharmaceuticals and Cosmetics: Many carboxylic acids are used in the production of medicines and cosmetics.

Other Applications: Carboxylic acids have numerous other industrial applications, including:

- **Formic acid:** Used in the textile industry for dyeing and finishing fabrics.
- **Oxalic acid:** Used as a bleaching agent and rust remover.
- **Acetic acid:** A solvent for paints, inks, and adhesives.

4. Write the natural sources of following carboxylic acids.

(a) Formic acid (b) Acetic acid (c) Valeric acid (d) Caproic acid

Here are the natural sources of the following carboxylic acids:

(a) Formic Acid (HCOOH):

- **Insects:** Formic acid is found in the venom of some ant and bee species. It's responsible for the stinging sensation and irritation caused by their bites.
- **Plants:** Stinging nettles and pine needles contain small amounts of formic acid.

(b) Acetic Acid (CH_3COOH):

- **Vinegar:** The most common source of acetic acid is vinegar, produced by the fermentation of alcoholic beverages (like wine) or sugary solutions using acetic acid bacteria.

(c) Valeric Acid ($C_5H_{10}O_2$):

- **Valeriana officinalis (Valerian Root):** This herb is a natural source of valeric acid, which is thought to contribute to its sedative and calming effects.
- **Other Plants:** Valeric acid is also found in some other plants, including catnip and cheese rind.

(d) Caproic Acid ($C_6H_{12}O_2$):

- **Milk:** Caproic acid is a short-chain fatty acid found in goat's milk and cow's milk, contributing to their characteristic flavor and odor.
- **Other Dairy Products:** It's also present in some cheeses and other dairy products.
- **Coconut Oil:** Caproic acid is a minor component of coconut oil

Descriptive Questions

1. How is carboxylic acid prepared by:

i) Carbonation of Grignard reagent

$$RMgX + CO_2 \rightarrow RCOOH + MgX_2$$

ii) Hydrolysis of alkyl nitriles

$$RCN + 2H_2O + H^+ \rightarrow RCOOH + NH_4^+$$

ii) Oxidation of primary alcohols

$$RCH_2OH + H_2CrO_4 + H_2SO_4 \rightarrow RCOOH + Cr_2(SO_4)_3 + H_2O$$

2. Explain the structure of carboxylic acid.

Notes

3. Discuss the acidic nature of carboxylic acid. How is it stronger than other organic compounds and weaker than mineral acids?

Carboxylic acids are acidic due to the stability of the carboxylate ion formed upon proton donation. This stability is a result of both electron donation from the oxygen atoms and resonance stabilization. While stronger acids than most organic compounds like alcohols, they are weaker than mineral acids due to the limitations of single proton donation and the nature of their conjugate bases.

4. Convert the followings:

i) Carboxylic acid into acid anhydride

ii) Ester into carboxylic acid

iii) Toluene into benzoic acid

5. Explain the following physical properties of carboxylic acids:

(a) Solubility (b) Boiling point

Notes

6. Write the names of four derivatives of carboxylic acids and give the equation for their preparation from acetic acid.

Notes