

CARBOXYLIC ACIDS

These are saturated organic compounds with a general formula $C_nH_{2n}O_2$ or $RCOOH$ where R is an alkyl or aryl group.

The functional group for carboxylic acids is the carboxyl group, $-COOH$.

Nomenclature of carboxylic acids.

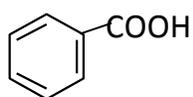
- In naming these acids, the ending "e" in the alkane is replaced by "oic acid" in the corresponding carboxylic acid.

Examples

$HCOOH$ Methanoic acid

CH_3COOH Ethanoic acid

CH_3CH_2COOH Propanoic acid



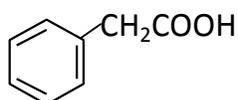
Benzoic acid

- Any other group attached on the longest continuous carbon chain containing the carboxyl group is a side chain and it is identified by its nature and its position is also specified from the side containing the carboxyl group. e.g

$CH_3CHCOOH$ 2-methylpropanoic acid
|
 CH_3

$CH_3CHCH_2CH_2COOH$ 4-hydroxypentanoic acid
|
 OH

$CH_3CH_2CHCOOH$ 2-aminobutanoic acid
|
 NH_2



2-phenylethanoic acid

Note

If the carboxylic acid has two carboxyl groups then it is a dioic acid. E.g

$HOOC-COOH$ Ethanedioic acid (Oxalic acid)

$HOOCCH_2CH_2COOH$ Butanedioic acid

$HOOCCH_2COOH$ Propanedioic acid

Isomerism in carboxylic acids.

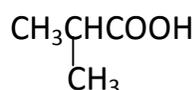
Carboxylic acid exhibit chain and functional isomerism. i.e carboxylic acids are isomeric with esters. E.g

Qn. Write the structural formulae and IUPAC names of all the isomers of $C_4H_8O_2$.

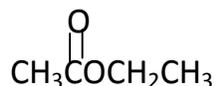
Solution



Butanoic acid



2-methylpropanoic acid



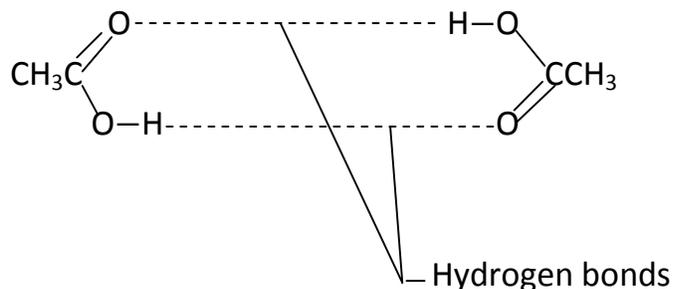
Ethylethanoate

Physical properties of carboxylic acids.

(a) Aliphatic carboxylic acid C_1 - C_{10} are liquids whose boiling points increases with increase in molecular mass while aromatic acids are crystalline solids. Ethanoic acid has a vinegar smell.

(b) The lower molecular weight carboxylic acids, C_1 - C_4 are completely soluble (miscible) with water. This is due to their ability to form hydrogen bonds with water. Higher molecular weight carboxylic acids are immiscible with water due to increase in the water insoluble hydrocarbon tail. All carboxylic acids dissolve in organic solvents.

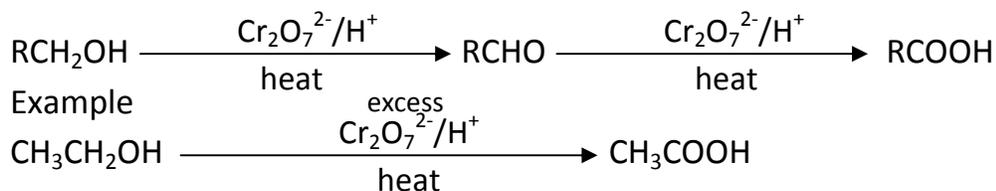
(c) They have higher boiling points than alkanes of similar formula weight due to their ability to form dimers via hydrogen bonds. e.g Ethanoic acid.



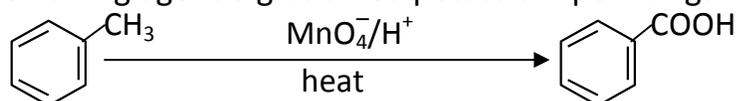
(d) The boiling point of carboxylic acids are higher than those of alcohols of similar molecular weight due to their ability to form more extensive hydrogen bond in these acid molecules than in alcohol molecules hence more energy is required to break these hydrogen bonds for the molecules to vapourise.

METHODS OF PREPARATION OF CARBOXYLIC ACIDS

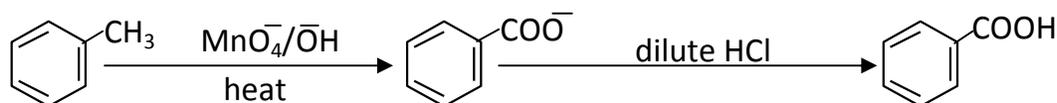
1. Oxidation of primary alcohols and aldehydes using acidified potassium/sodium dichromate solution or acidified potassium permanganate solution. i.e



2. Benzoic acid is formed from oxidation of methyl benzene using any strong oxidizing agent e.g acidified potassium permanganate solution

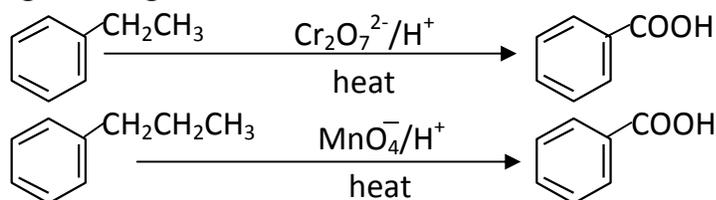


Oxidation of methyl benzene can also be done using hot alkaline potassium permanganate solution followed by dilute hydrochloric acid. i.e



Note:

All alkyl benzene compounds are oxidised to benzoic acid using strong oxidizing agents. E.g

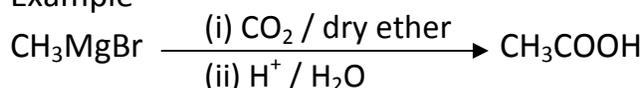


3. From Grignard reagents.

A carboxylic acid is formed when a Grignard reagent is reacted with carbon dioxide in presence of dry ether followed by acid hydrolysed. i.e

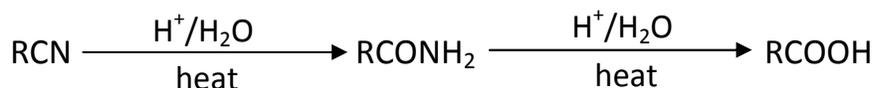


Example

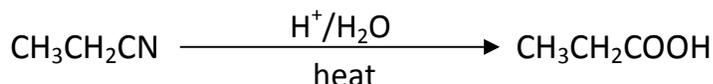
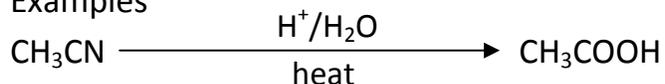


4. By hydrolysis of nitriles (RCN)

Nitriles are hydrolysed to carboxylic acids when heated with dilute mineral acids such as hydrochloric acid or with aqueous alkalis. In this reaction, an amide (RCONH₂) is formed as an intermediate. i.e



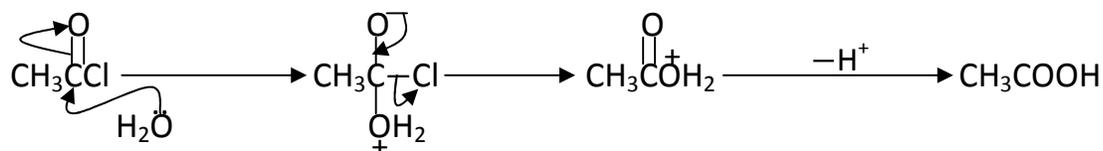
Examples



5. Hydrolysis of acid chlorides i.e

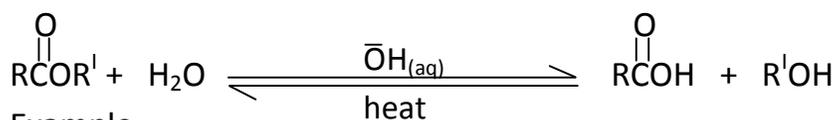


Mechanism

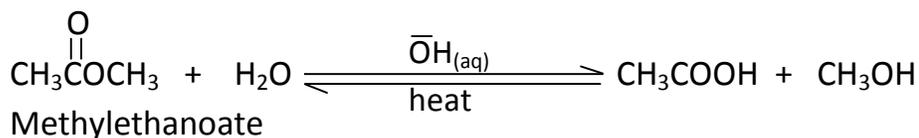


6. From acid or base catalysed hydrolysis of esters. E.g

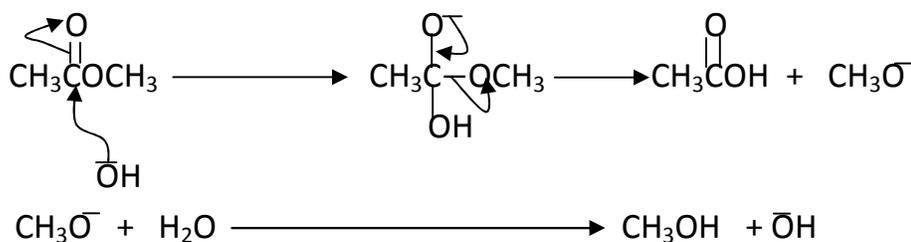
(a) Base catalysed hydrolysis of esters i.e



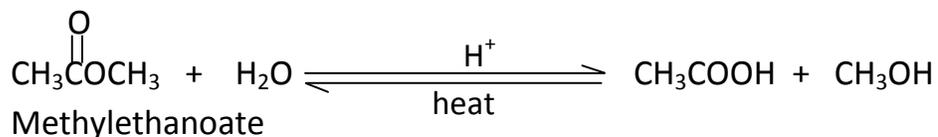
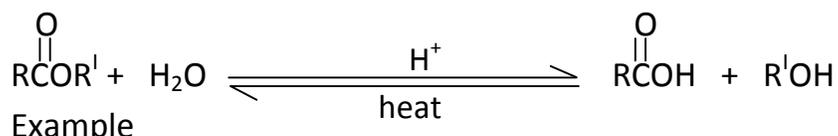
Example



Mechanism

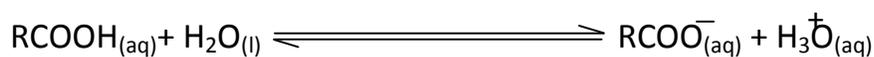


(b) Acid catalysed hydrolysis of esters. i.e



CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

Carboxylic acids are weak acids because they partially ionize in water as shown below.



The equilibrium constant K_a is given by:

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

The bigger the K_a value, the stronger the acid and the smaller the K_a value, the weaker the acid.

The more easily a proton is released, the stronger the acid and the higher is its K_a value.

Qn. Explain the following observations.

(a) Methanoic acid (HCOOH) is a stronger acid than ethanoic acid (CH₃COOH).

(The K_a of methanoic acid is 1.6×10^{-4} while that of ethanoic acid is 1.75×10^{-5})

Explanation

In methanoic acid, the hydrogen atom which is bonded to the carboxyl group has neither positive nor negative inductive effect. Therefore the hydroxyl group of methanoic acid readily loses a proton as compared to ethanoic acid.

In ethanoic acid, the methyl group which is bonded to the carboxyl group has a positive inductive effect. The methyl group therefore pushes electrons towards the oxygen-hydrogen bond which reduces the partial positive charge on the hydrogen atom. This strengthens the oxygen-hydrogen bond making the proton less readily lost compared to methanoic acid.

(b) Ethanoic acid is a weaker acid than dichloroethanoic acid.

Explanation

In ethanoic acid, the methyl group which is bonded to the carboxyl group has a positive inductive effect. It pushes electrons towards the oxygen-hydrogen bond which reduces the partial positive charge on the hydrogen atom. This strengthens the oxygen hydrogen bond making the proton less readily released.

In dichloroethanoic acid, the chlorine atoms have a negative inductive effect and they therefore pull electrons towards themselves increasing the partial positive charge on the hydrogen atom. This weakens the hydrogen-oxygen bond making the proton more easily lost.

(c) The dissociation constant, K_a , of bromoethanoic acid is greater than that of ethanoic acid at the same temperature.

Explanation

In bromoethanoic acid, the bromine atom is more electronegative than the carbon atom. It withdraws (pulls) electrons towards itself and this increases the partial positive charge on the hydrogen atom thus weakening the oxygen-hydrogen bond making the proton more easily released.

In ethanoic acid, the methyl group which is bonded to the carboxyl group has a positive inductive effect. It pushes electrons towards the oxygen-hydrogen bond which reduces the partial positive charge on the hydrogen atom. This strengthens the oxygen hydrogen bond making the proton less readily released.

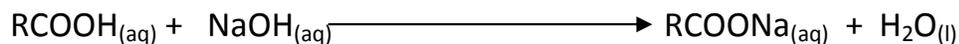
(d) Chloroethanoic acid is a stronger acid than bromoethanoic acid.

Explanation

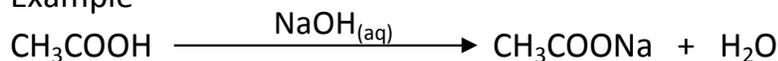
The chlorine atom is more electronegative than the bromine atom. Therefore the chlorine atom in Chloroethanoic acid strongly withdraws (pulls) electrons towards itself than the bromine atom in bromoethanoic acid thus the partial positive charge on the hydrogen atom is more increased in Chloroethanoic acid than in bromoethanoic acid hence the oxygen-hydrogen bond is more weakened in Chloroethanoic acid than in bromoethanoic acid making the proton more easily released in Chloroethanoic acid than in bromoethanoic acid.

REACTIONS OF CARBOXYLIC ACIDS

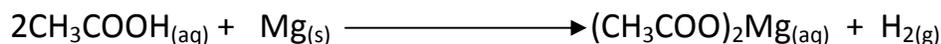
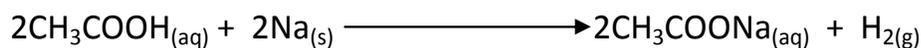
1. They react with bases to form a salt and water. i.e



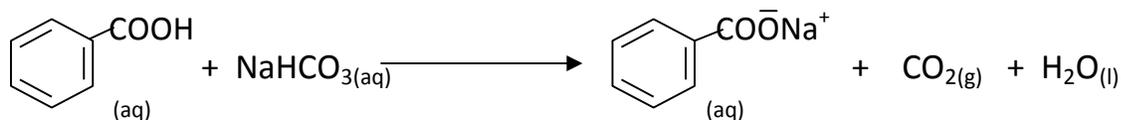
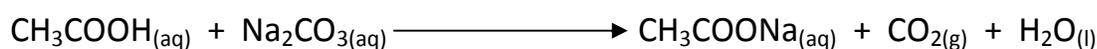
Example



2. They react with highly electropositive metals like sodium, potassium, magnesium and calcium to form salts of the metal and hydrogen gas. e.g



3. They react sodium carbonates and sodium hydrogen carbonates to liberate carbon dioxide gas. This reaction is the confirmatory test for carboxylic acids. e.g



Qn. Name a reagent can be used to distinguish the following pair of compounds. In each case state what is observed when the reagent is treated with each member of the pair.



Reagent:

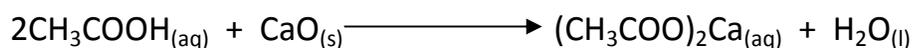
Sodium carbonate solution **or** sodium hydrogen carbonate solution.

Observations:

CH_3COOH Effervescence of a colourless gas

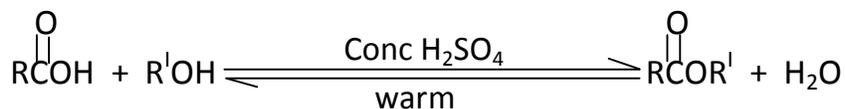
CH_3OH No observable change

4. They react with metal oxides like zinc oxide and calcium oxides to form salts and water. e.g

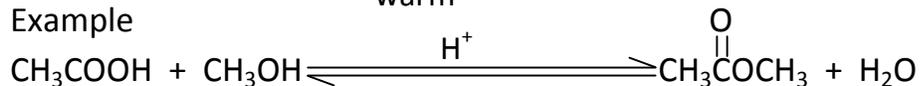


5. Esterification.

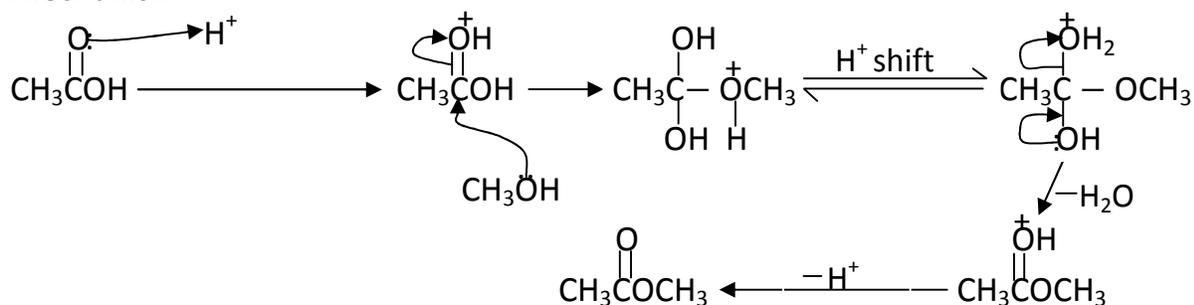
Carboxylic acids (RCOOH) react with alcohols in presence of concentrated sulphuric acid as a catalyst to form esters. i.e



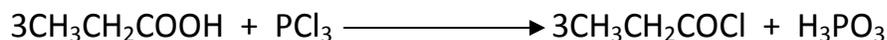
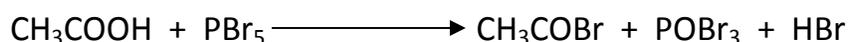
Example



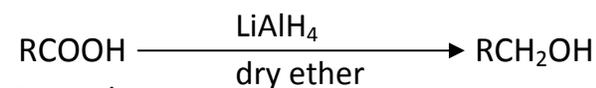
Mechanism



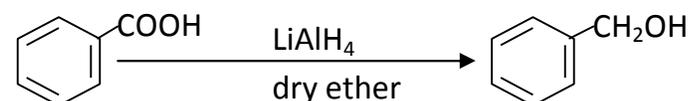
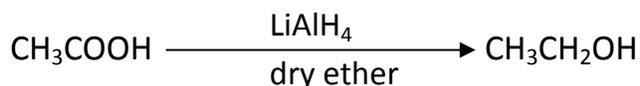
6. They react with phosphorus halides like Phosphorus pentachloride (PCl_5), Phosphorus pentabromide (PBr_5 often given as Red P/ Br_2) and phosphorus trichloride (PCl_3) or sulphur dichloride oxide (thionyl chloride, SOCl_2) to form acid halides. e.g



7. They are reduced to primary alcohols by lithium aluminium hydride in dry ether.

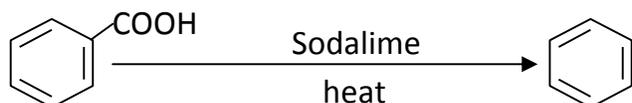
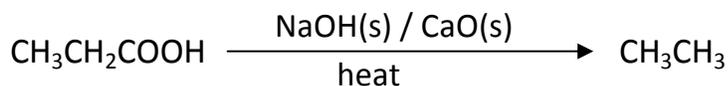


Examples



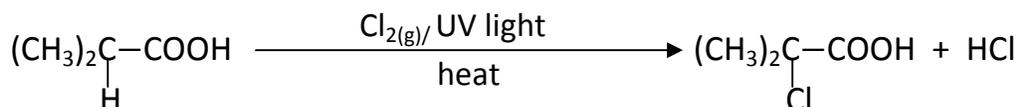
8. Decarboxylation.

A hydrocarbon is formed when a carboxylic acid is heated with soda lime (solid sodium hydroxide and solid calcium oxide). e.g

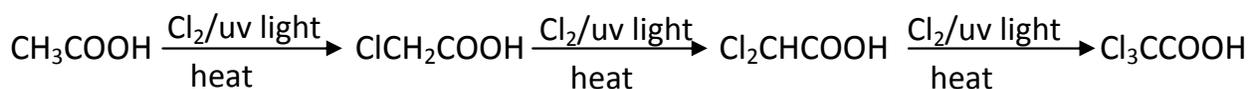


9. Reaction of hydrogen atoms adjacent to the carboxyl group (α –hydrogen atoms)

When chlorine gas is passed into the hot carboxylic acid in presence of ultraviolet light, one or all if there are more than one alpha hydrogen atoms are substituted. e.g

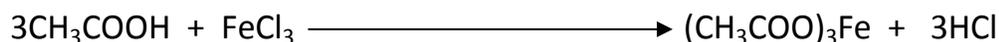


When there is more than one alpha hydrogen atoms



10. Reaction with iron (III) chloride solution.

Ethanoic acid reacts with iron (iii) chloride solution to form **a reddish brown solution which on heating forms a brown precipitate.**



Benzoic acid reacts with iron (III) chloride solution to form a **reddish brown precipitate on heating.**



Qn. State what is observed and in each case write an equation for the reaction that would take place if a mixture of the following compounds were heated.

- Benzoic acid and iron (III) chloride solution.
- Methanoic acid and Ammoniacal silver nitrate solution.
- Ethanoic acid and iron (III) chloride solution.

Note

Methanoic acid differs from other monocarboxylic acids in the following ways.

Because methanoic acid has an aldehydes group (-CHO), it undergoes the following oxidation reactions

1. On heating, methanoic acid reduces acidified potassium permanganate solution which is a purple solution to manganese (II) which is colourless in solution while itself is oxidised to carbon dioxide gas.



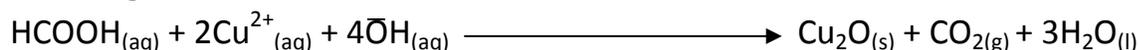
Or



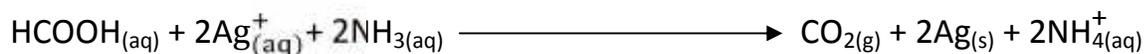
2. On heating, methanoic acid reduces the orange solution of acidified potassium or sodium dichromate to chromium (III) which is green in solution while itself is oxidised to carbon dioxide gas.



3. On warming, methanoic acid reduces Fehling's solution to a reddish brown precipitate (red precipitate) of copper (I) oxide while itself is oxidised to carbon dioxide gas.



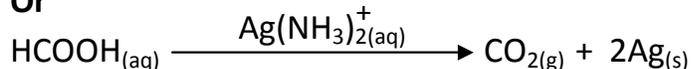
4. On warming, methanoic acid reduces ammoniacal silver nitrate solution (Tollen's reagent) to silver which is a grey precipitate (silver mirror) while itself is oxidised to carbon dioxide gas.



Or



Or

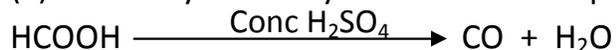


Other carboxylic acids does not have an aldehydes group hence cannot be oxidised.

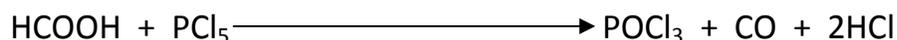
Qn. Explain why methanoic acid forms a grey precipitate (reacts) with ammoniacal silver nitrate solution whereas ethanoic acid does not

Other ways in which methanoic acids differs from other carboxylic acids include;

(a). It is dehydrated by concentrated sulphuric acid.



(b). With phosphorus pentachloride, methanoic acid forms carbon monoxide and hydrogen chloride (not the acid chloride).



Qn. Name one reagent that can be used to distinguish between the following pairs of compounds. In each case state what is observed if each member of the pair is treated with the reagent.

(a) HCOOH and CH₃COOH

Solution

Reagent: Ammoniacal silver nitrate solution (Tollen's reagent)

Observation:

HCOOH forms a silver mirror (grey precipitate) on warming

CH₃COOH No observable change

OR

Reagent: Fehling's solution.

Observation:

HCOOH forms a reddish brown precipitate on warming

CH₃COOH No observable change

OR

Reagent: Acidified potassium permanganate solution

Observation:

HCOOH purple solution turns colourless on heating

CH₃COOH No observable change

(b) HOOC-COOH and CH₃COOH

Reagent: Acidified potassium permanganate solution

Observation:

HOOC-COOH purple solution turns colourless on heating

CH₃COOH No observable change

(c) HCOOH and HOOC-COOH

Uses of carboxylic acids

- Long chain monocarboxylic acids are used in manufacture of soap.
- In food industry, they are used in the production of soft drinks, food products e.g ethanoic acid is used in making of vinegar.
- In pharmaceutical industry, they are used in manufacture of drugs e.g aspirin.
- They are used in the manufacture of dye stuff and perfumes.
- Etc

DERIVATIVES OF CARBOXYLIC ACIDS

These include; (i) Acid halides
(ii) Acid amides
(iii) Esters

ACID HALIDES

They have a general molecular formula $R-\overset{\text{O}}{\parallel}{C}-X$ where X is Cl, Br or I.

Nomenclature of acid halides

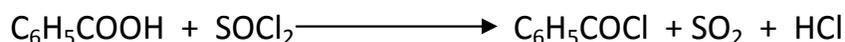
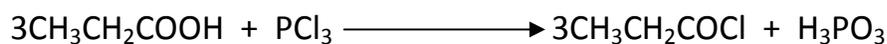
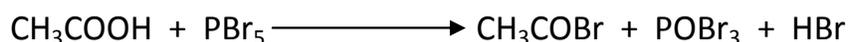
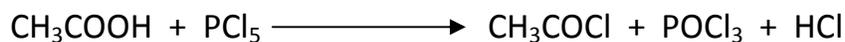
In naming these acid halides, the ending "ic acid" in the carboxylic acid is replaced by "oyl halide" in the corresponding acid halide. e.g

CH_3COCl	Ethanoyl chloride
CH_3COBr	Ethanoyl bromide
$\text{CH}_3\text{CH}_2\text{COCl}$	Propanoyl chloride
$\text{C}_6\text{H}_5\text{COCl}$	Benzoyl chloride

METHODS OF PREPARATION OF ACID HALIDES

They are prepared by reacting carboxylic acids with phosphorus halides like Phosphorus pentachloride (PCl_5), Phosphorus pentabromide (PBr_5 often given as Red P/Br_2) and phosphorus trichloride (PCl_3) or thionyl chloride (SOCl_2).

Examples

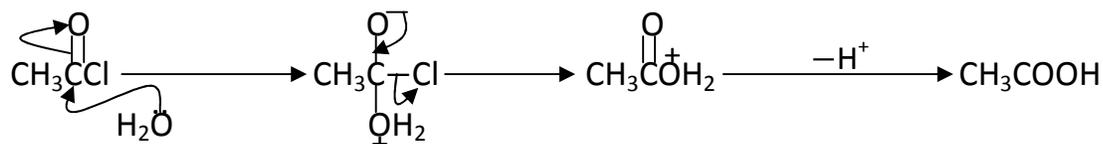


REACTIONS OF ACID HALIDES

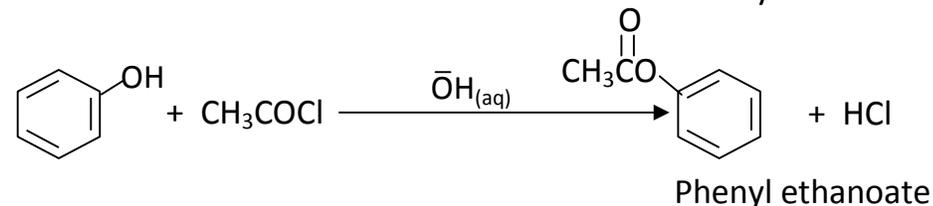
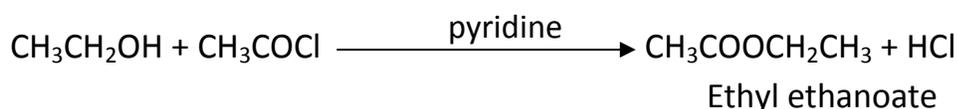
1. They hydrolyse in water forming carboxylic acids and white fumes of hydrogen chloride gas. e.g



Mechanism



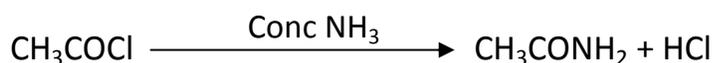
2. They react with phenol in alkaline solution or alcohols in presence of pyridine to form esters. (pyridine is a base which removes the HCl produced). e.g



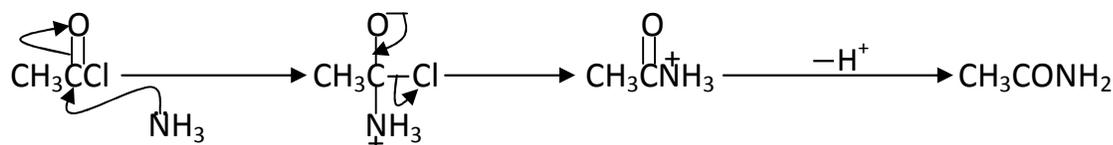
Note

The mechanisms of these reactions are similar to those between acid halides and water with the oxygen atom of the alcohol and phenol acting as the nucleophile.

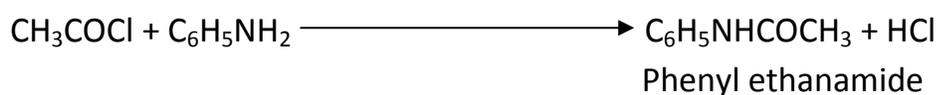
3. Acid halides react with concentrated ammonia solution to form amides. e.g

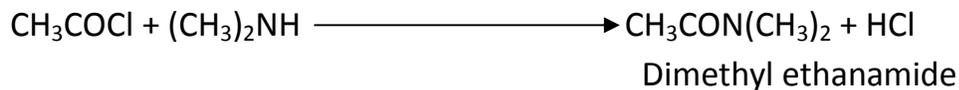


Mechanism



4. Acid halides react with primary and secondary amines to form acid amides. These reactions take place readily at room temperature. e.g

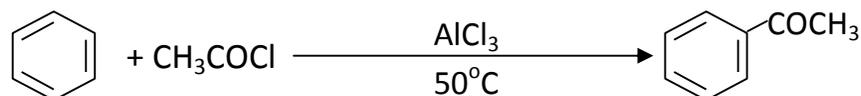




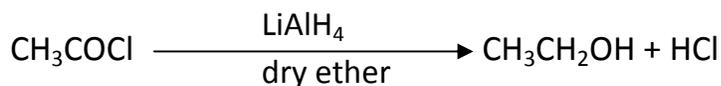
Note

The mechanisms of these reactions are similar to those between acid halides and ammonia with the nitrogen acting as the nucleophile.

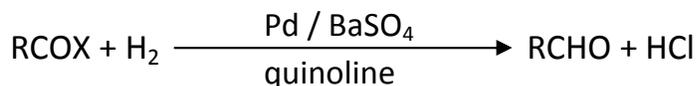
5. Acid halides react with benzene in presence of a halogen carrier like aluminium chloride, aluminium bromide, iron (III) chloride or iron (III) bromide to form aromatic ketones. e.g



6. Acid halides are reduced by lithium aluminium hydride to alcohols. e.g



If the acid halide is reacted with hydrogen in presence of Lindlar's catalyst (Pd/BaSO₄), it forms an aldehyde. i.e



ACID AMIDES

They have a general formula $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$

Nomenclature

In naming these acid amides, the ending "e" in the alkane is replaced by "amide" in the corresponding acid amide. e.g

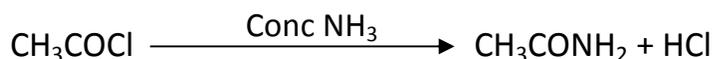
CH ₃ CONH ₂	Ethanamide
CH ₃ CH ₂ CONH ₂	Propanamide
C ₆ H ₅ CONH ₂	Benzenamide
CH ₃ CONHCH ₃	Methyl ethanamide
CH ₃ CON(CH ₂ CH ₃) ₂	diethyl ethanamide

METHODS OF PREPARATION

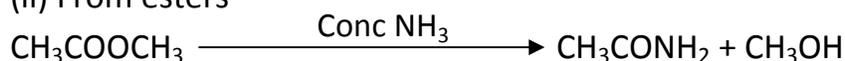
1. Reacting acid halides, esters or acid anhydrides with concentrated ammonia solution or amines.

Examples

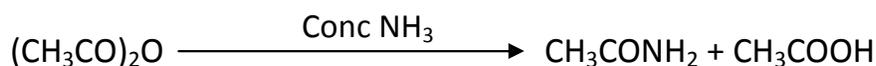
(i) From acid halides



(ii) From esters



(iii) From acid anhydrides

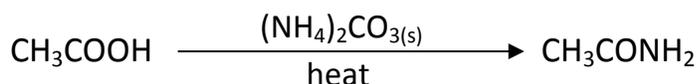


Ethanoic anhydride

(iv) Reaction with amines



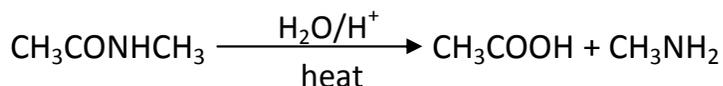
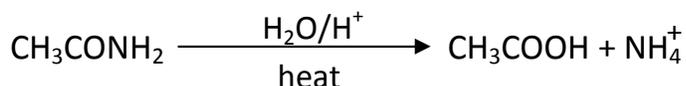
2. Heating a carboxylic acid with solid ammonium carbonate. e.g



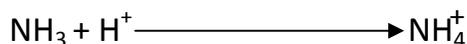
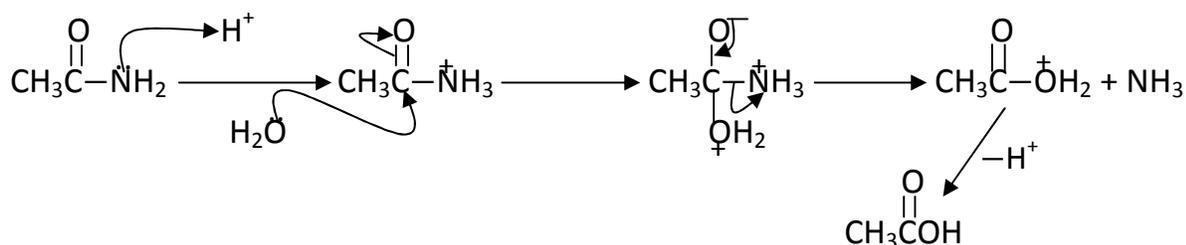
REACTIONS OF ACID AMIDES

1. Amides are hydrolysed by heating with either a mineral acid or an alkali. e.g

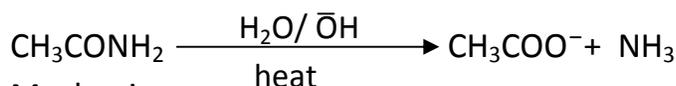
(i) Acid catalysed hydrolysis



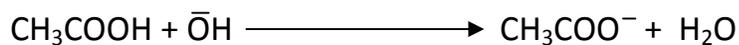
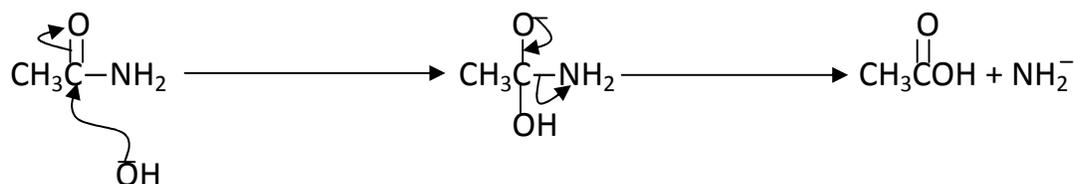
Mechanism



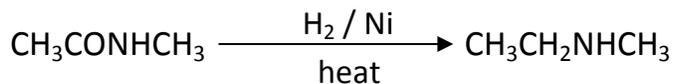
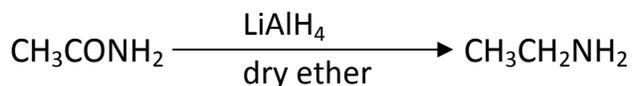
(ii) Base catalysed hydrolysis



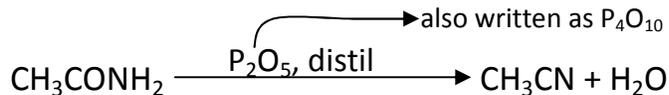
Mechanism



2. Amides are reduced to amines using lithium aluminium hydride in dry ether or hydrogen in presence of heated nickel catalyst or sodium in ethanol. e.g



3. Dehydration of an amide by distillation with phosphorus pentoxide gives a nitrile.

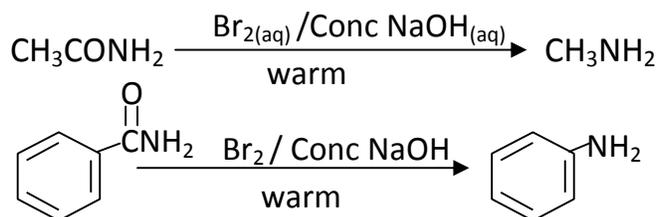


4. Amides react with nitrous acid (NaNO₂/HCl) to form carboxylic acids and nitrogen.



5. Hofmann degradation.

In this reaction, amides react with bromine and concentrated sodium hydroxide or potassium hydroxide solution to form an amine which is one carbon atom less than the amide. The reaction requires warming. e.g

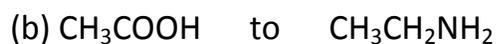
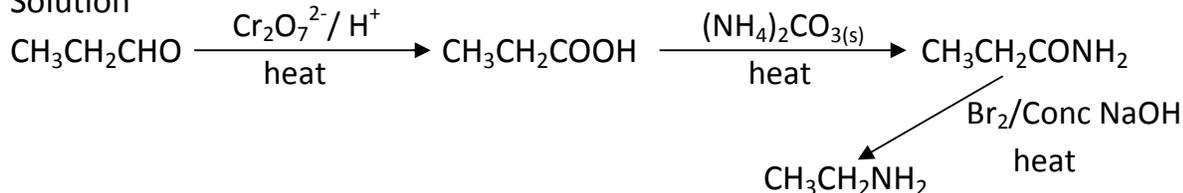


Worked example

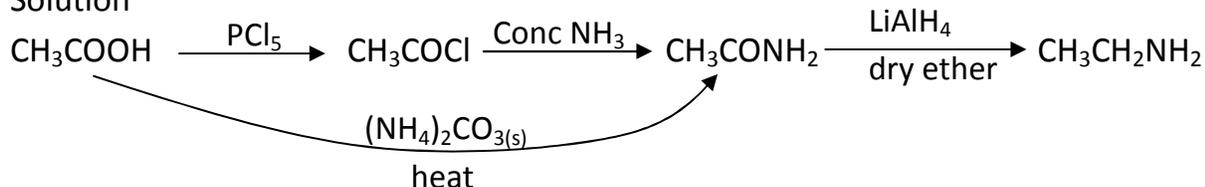
Use equations only to show how the following conversions can be effected.



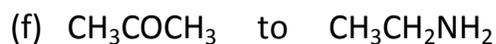
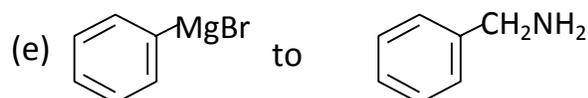
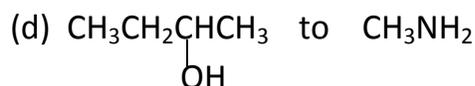
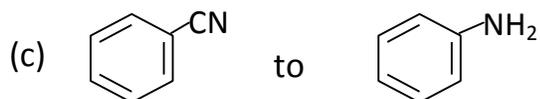
Solution



Solution



Qn. Write equation(s) to show how the following conversions can be effected.



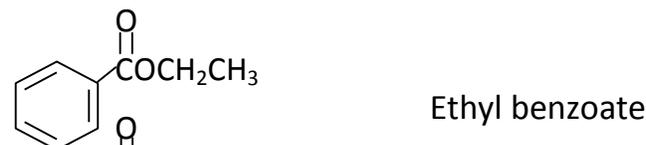
ESTERS

They have a general molecular formula RCOR where R is an alkyl group.

Nomenclature

The alkyl group is named first followed by the name of a carboxylic acid and replacing "ic acid" in the name of the acid with "oate" in the corresponding ester.

Examples



Isomerism in esters

Esters exhibit functional isomerism with carboxylic acids.

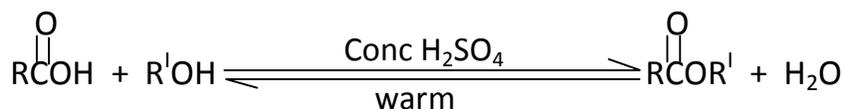
Qn. Write all the possible isomers represented by a molecular formula $\text{C}_3\text{H}_6\text{O}_2$.

Solution

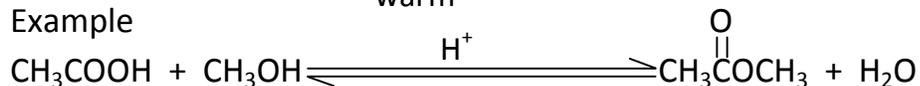


METHODS OF PREPARATION

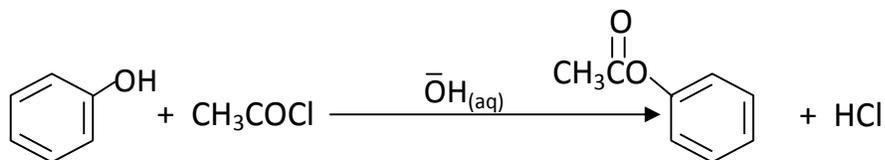
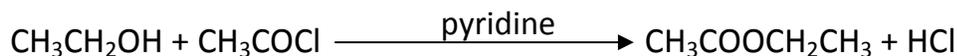
1. Reactions of alcohols with carboxylic acids in presence of concentrated sulphuric acid as a catalyst.



Example



2. Reaction of alcohols and phenol with acid halides



3. Reacting a silver salt of carboxylic acid and an alkyl halide.

Refluxing an alkyl halide with a silver salt of a carboxylic acid forms an ester. e.g



Physical properties of esters

- Are colourless liquids with a pleasant (sweet) fruity smell.
- They are insoluble in water but are soluble in organic compounds.

Note:

A mixture of an alcohol and a carboxylic acid is warmed in presence of concentrated sulphuric acid as catalyst.

Observation

A sweet fruity smell

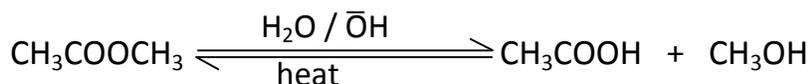
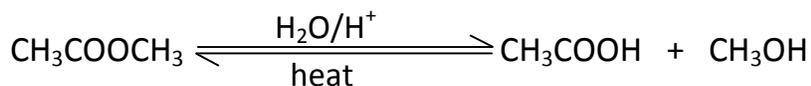
Deduction

An ester is formed (Esterification)

Therefore a sweet fruity smell is used as a test for esters in qualitative analysis.

REACTIONS OF ESTERS

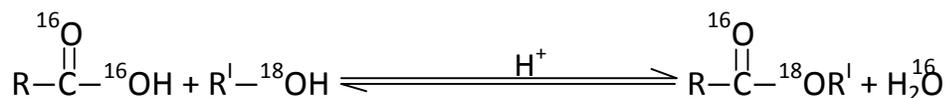
1. Esters are hydrolysed by heating with a mineral acid or alkalis to form an alcohol and a carboxylic acid. e.g



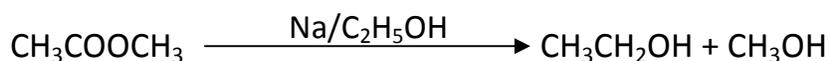
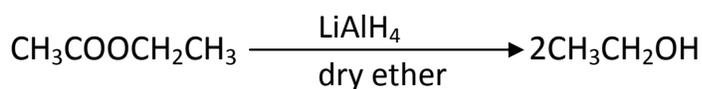
Qn. Briefly describe how oxygen-18 can be used to determine the mechanism of esterification of a monocarboxylic acid with a primary alcohol.

Solution

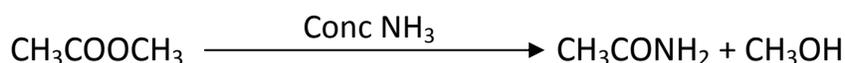
An alcohol with radioactive oxygen-18 atom is reacted with a carboxylic acid with radioactive oxygen-16 atoms. A mass spectrometer is then used to analyse the ester and water formed. It was observed that the labeled oxygen-18 is found in the ester only and not in water. This shows that during esterification, it is the oxygen-hydrogen bond in the alcohol and carbon-oxygen bond in a carboxylic acid that are broken hence the mechanism can be determined. i.e



2. Esters are reduced with lithium aluminium hydride in dry ether or sodium in ethanol to form alcohols. e.g



3. Esters react with concentrated ammonia solution or ammonia in presence of an alcohol to form acid amides.



Uses of esters

- Esters are used to manufacture drugs and antibiotics
- Are fats and oils which are used to make soap
- Are responsible for the smell and flavour of many fruits and flowers hence used to prepare artificial flavouring essences.
- Esters are used in manufacture of artificial scents.

AMINES