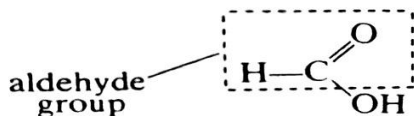


Oxidation reaction of carboxylic acids

- ❖ Carboxylic acids except methanoic acid and oxalic acid, are extremely resistant to oxidation.
- ❖ Methanoic acid gives a positive test with common oxidising agents because it contains an **aldehyde group** which makes it act as a **reducing agent**. And thus, it is **oxidized** by the common oxidising agents.



- **Observations.**
 - With acidified potassium manganate(VII) solution
Purple solution turns colourless on **heating**.
 - With acidified potassium dichromate(VI) solution
Orange solution turns green on **heating**.
- The half equation for reaction involving methanoic acid with the reagents in (i) and (ii) is:

$$\text{HCOOH}(aq) \rightarrow \text{CO}_2(g) + 2\text{H}^+(aq) + 2e^-$$
- (iii) With ammoniacal silver nitrate solution (commonly called Tollens' reagent)
Silver mirror is formed on **warming**.

$$\text{HCOOH}(aq) + 2\text{Ag}^+(aq) + 2\text{OH}^-(aq) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) + 2\text{Ag}(s)$$
- (iv) Fehling's solution and Benedict's solution

$$\text{HCOOH}(aq) + \underbrace{2\text{Cu}^{2+}(aq) + 4\text{OH}^-(aq)}_{\text{in Fehling's/Benedict's solution}} \rightarrow \text{CO}_2(g) + 3\text{H}_2\text{O}(l) + \underbrace{\text{Cu}_2\text{O}(s)}_{\text{reddish-brown precipitate}}$$

A reddish brown precipitate is formed on heating/warming.
This reaction is however **very slow** if it occurs.

❖ **Note:**

The salts of the methanoic acid (e.g. sodium methanoate, HCOONa) also give positive tests with the common oxidizing agents due to the presence of the aldehyde group.



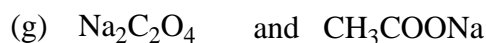
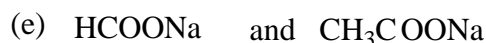
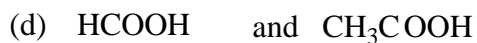
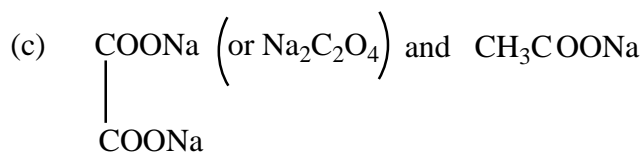
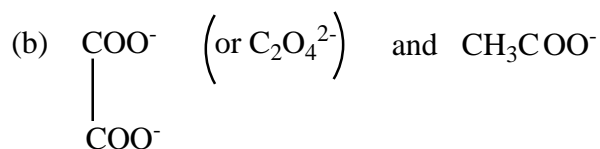
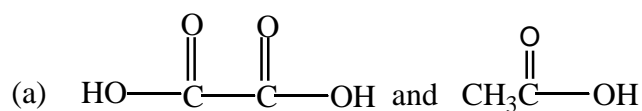
- ❖ Ethanedioic acid (commonly called oxalic acid) and its salts (e.g. sodium oxalate/sodium ethanedioate) give positive tests with some common oxidising agents.
- ❖ For example:
The acid and its salts turn acidified potassium manganate(VII) solution from purple to colourless on **heating**.
The half equation for the oxidation of the acid or salt being:

$$\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{CO}_2(g) + 2e^-$$

in acid or salt
Alternatively for the acid we may write:

$$\text{H}_2\text{C}_2\text{O}_4(aq) \rightarrow 2\text{CO}_2(g) + 2\text{H}^+(aq) + 2e^-$$

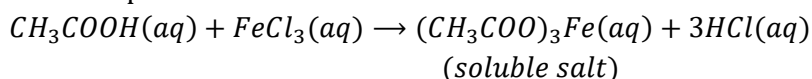
❖ Thus, it is possible to differentiate the following pairs of compounds/ions.



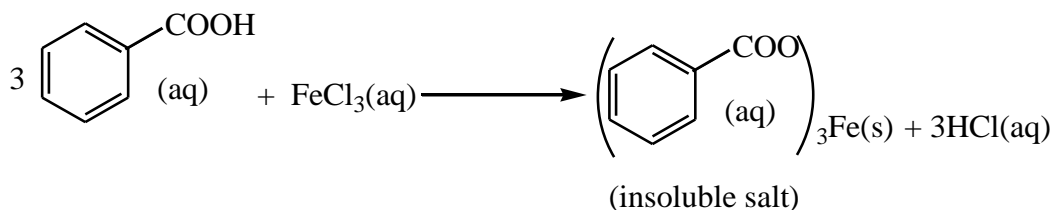
Reaction of carboxylic acids with neutral iron(III) chloride solution

❖ Aliphatic carboxylic acids produce red colouration when treated with neutral iron(III) chloride solution.

❖ For example:



❖ Aromatic carboxylic acids (e.g. benzoic acid) give a reddish-brown precipitate (or simply brown precipitate/buff coloured precipitate) when treated with neutral iron(III) chloride solution.

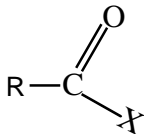
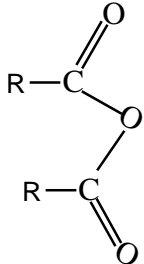
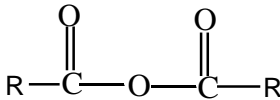
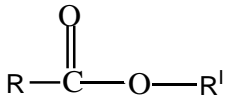
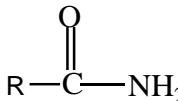


Uses of carboxylic acids

- Methanoic and ethanoic acids are used to coagulate rubber latex.
- Aqueous solution of ethanoic acid is used as vinegar.
- Ethanoic acid is used as a solvent.

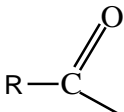
- Ethanoic acid is used as a starting material in the preparation a poly(ethenyl ethanoate), cellulose ethanoate (for artificial fibres such as varnish, films and lacquer) and the drug aspirin.
- Chloroethanoic acid is used in the manufacture of the weedkiller 2,4-D
- Benzoic acid is used as a food and drug preservative.
- Long chain carboxylic acids are used in manufacture of soaps.
- Hexanedioic acid and benzene-1,4-dioic acid are used in the manufacture of nylon-6,6 and terylene respectively.

Derivatives of carboxylic acids

Name	General formula
Acid halides	
Acid anhydride	 or 
Esters	 or $\text{RCO}_2\text{R}^{\text{I}}$
Amides	 or RCONH_2

❖ Note:

- R may be aliphatic or aromatic.
- R and R_I may be identical or not.

• All the derivatives have  called the **acyl group**

Physical properties of the acid derivatives

- ❖ Acid halides, anhydrides and esters have boiling points which are similar to those of carbonyl compounds of comparable relative molecular mass.
- ❖ Acid halides, anhydrides and esters have much lower boiling and melting points than carboxylic acids of comparable relative molecular mass. This is due to their inability to associate via hydrogen bonding since their molecules lack a highly polar oxygen–hydrogen bond.
- ❖ Molecules of amides associate via hydrogen bonding/hydrogen bonds due to the presence of a highly polar nitrogen–hydrogen bond.

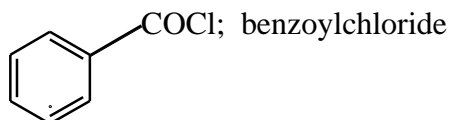
- ❖ The presence of hydrogen bonds between the molecules of amides, make amides:
 - exist as solids except methanamide, HCONH_2 .
 - boil and melt at very high temperatures (i.e. much less volatile).
 - readily soluble in water.

Acid halides

(a) Introduction, structure and nomenclature

- ❖ The most important are the **acid chlorides**, RCOCl .
- ❖ HCOCl (methanoyl chloride) has **not been isolated**.
- ❖ The other examples are:
 CH_3COCl ; ethanoyl chloride

$\text{CH}_3\text{CH}_2\text{COCl}$; propanoyl chloride



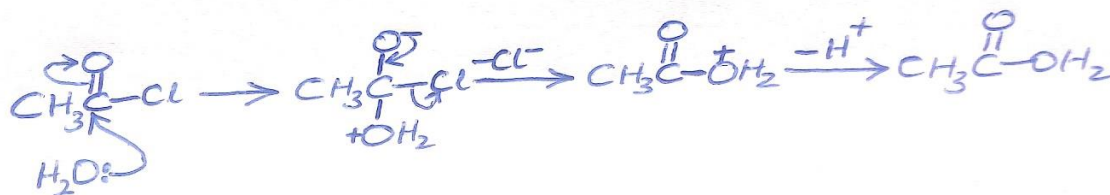
(b) Preparation of acid chlorides

- ❖ Refer to the previous sections for details.

(c) Properties of acid chlorides:

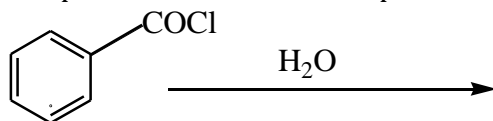
- ❖ Lower members are colourless liquids with sharp, irritating smell.
- ❖ They give misty fumes in moist air due to ready hydrolysis which liberates hydrogen chloride.
 $\text{CH}_3\text{COCl}(l) + \text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{COOH}(l) + \text{HCl}(g)$

Mechanism for the hydrolysis reaction:



Question:

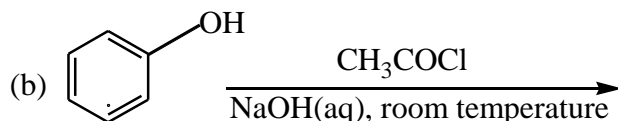
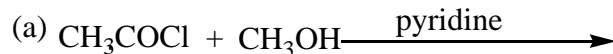
Complete and outline the acceptable mechanism for the following reaction:



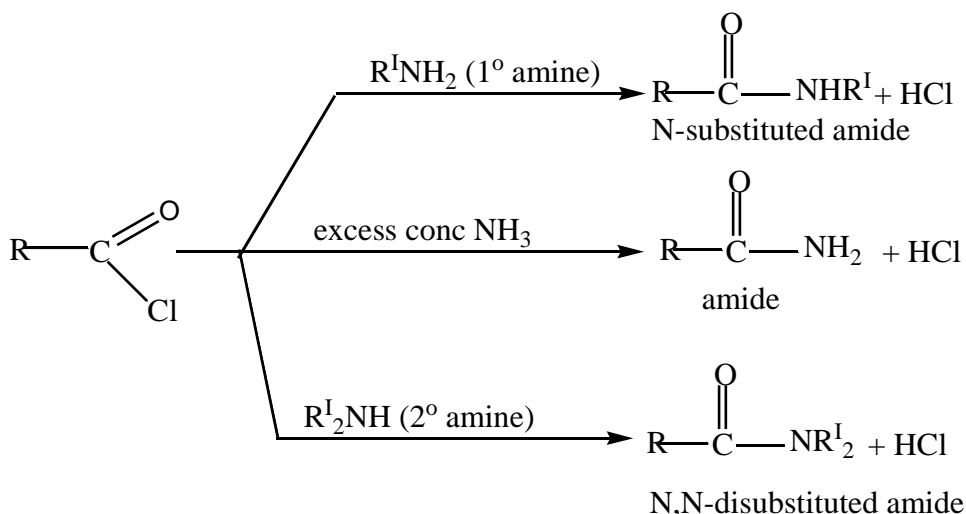
- ❖ Under suitable conditions, they react with phenols and alcohols to form esters.
 The reaction with alcohols requires pyridine, an organic base to absorb hydrogen chloride formed.
 The reaction with phenols require an alkaline medium.
 The mechanism is the same as that of hydrolysis except that the nucleophiles are the phenoxide ion and alcohol molecule, instead of the water molecule.

Question:

Complete and outline the acceptable mechanism of the following reactions:



- ❖ They react with primary amines, secondary amines and concentrated amine at **room temperature** to form **amides**.

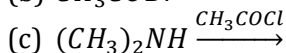
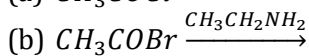
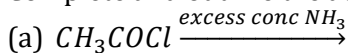


The mechanisms for the above reactions are similar to of hydrolysis already discussed.

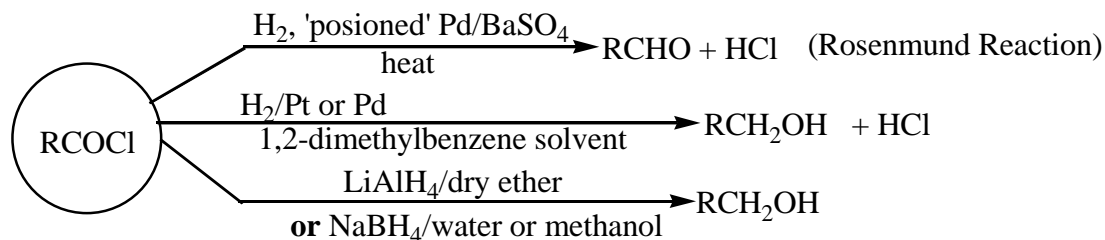
Note: Tertiary amines (R_3N) do not react due to lack of the $\text{N}-\text{H}$ bond.

Question:

Complete and outline the acceptable mechanism for the following reactions:



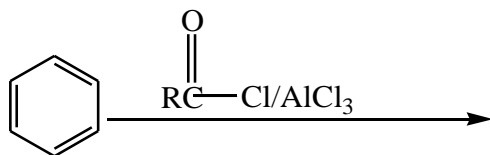
- ❖ Acid chlorides are readily reduced and the product depends on the reducing agent employed.



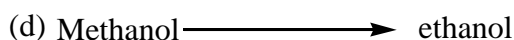
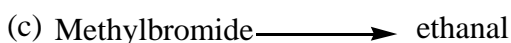
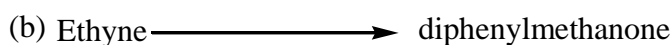
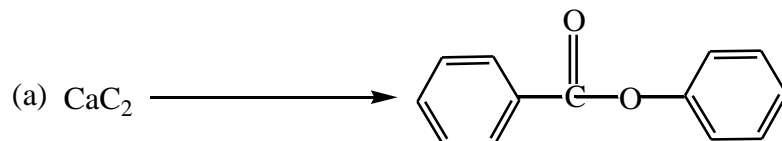
- ❖ The acid chlorides also react with benzene in the presence of a halogen carrier to form aromatic carbonyl compounds. Refer to Friedel-Crafts acylation for details.

Questions:

1. Complete and outline the mechanism for the following reaction.



2. Show how the following conversions can be effected.



Esters

(a) Introduction and nomenclature

- ❖ These occur naturally in fats, oils, many fruits, flowers and waxes.
- ❖ Examples of some esters are:

HCOOCH_3 methyl methanoate	$\text{CH}_3\text{COOCH}_2\text{CH}_3$ ethyl ethanoate	
$\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ ethyl propanoate	$\text{C}_6\text{H}_5\text{COOCH}_3$ methyl benzoate	

(b) Physical properties of esters:

- ❖ Simple esters are colourless liquids with sweet/pleasant fruity smell and are commonly used in scenting perfumes and flavouring food.
- ❖ Their boiling points are much lower than their parent acids despite having higher relative molecular masses. For example, methanoic acid (RMM=46) boils at 101°C whereas methyl methanoate (RMM=60) boils at 32°C .
- ❖ The lower members are moderately soluble in water but the solubility decreases rapidly with increasing molecular mass; esters are soluble in most organic solvents.

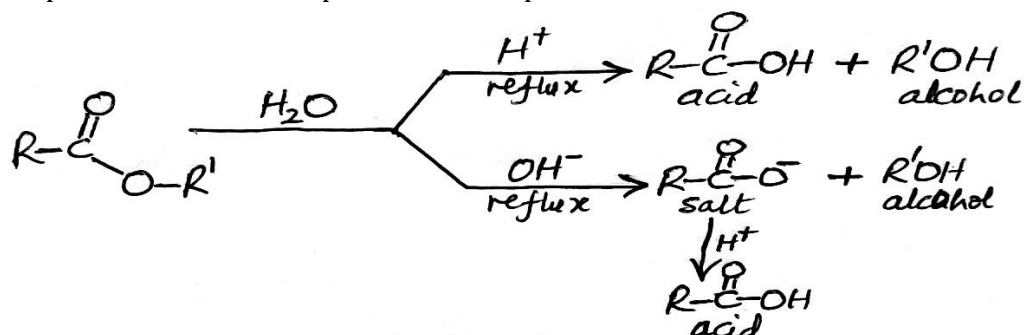
(c) Preparation of esters:

- ❖ Refer to the previous sections/topics for details.

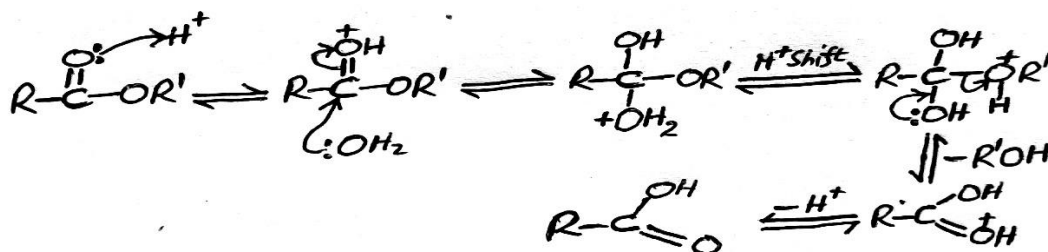
(d) Reactions of esters:

(i) Hydrolysis

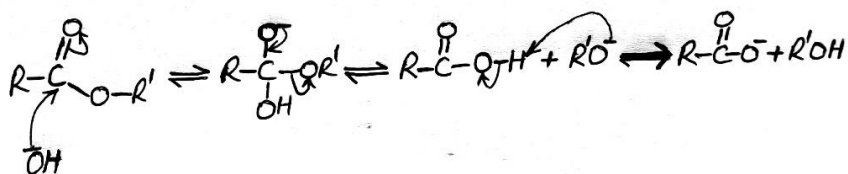
- The process can be effected by use of either acid or base catalysis.
- The products are both the parent acid and parent alcohol.



- Base catalysed hydrolysis proceeds to completion as compared to the acid catalysed hydrolysis.
This is because the acid formed is converted by the base into a salt. Equilibrium concentration of the acid formed reduces and this disturbs the equilibrium. In order, to restore the equilibrium position, further hydrolysis occurs.
- Base catalysed hydrolysis is referred to as saponification because it is the type of reaction used in preparing soaps.
- General mechanisms for both acid and base hydrolysis are:
(i) Acid catalyzed hydrolysis

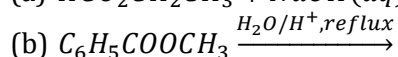
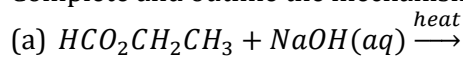


(ii) Base catalyzed hydrolysis

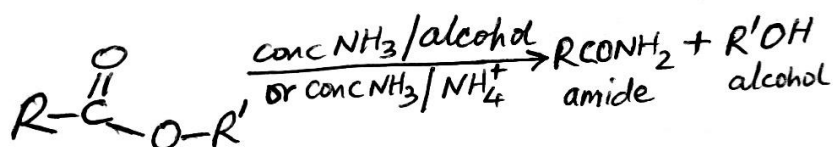


Question:

Complete and outline the mechanism for the following reaction.



(ii) Amide formation



- Mechanism is similar to the base catalysed hydrolysis of esters.
- Primary and secondary amines react with esters in a similar way like ammonia.

(iii) Reduction

- Only effected by powerful reducing agents like LiAlH_4 /dry ether **or** H_2 , CuO/CuCrO_4 catalyst at 250°C and 150 atmospheres.
- Depending on the structure of the ester used, the process yields two primary alcohols which many be identical or not.
- For example: $\text{RCOOR}^I \xrightarrow{\text{LiAlH}_4/\text{dry ether}} \underbrace{\text{RCH}_2\text{OH}}_{\text{primary alcohols}} + \text{R}^I\text{OH}$

(e) Uses of esters

❖ Esters are used:

- as solvents
- for preparation of synthetic perfumes and fruit essences.

Amides

(a) Introduction and nomenclature

❖ Amides may be classified as follows:

Primary	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ or RCONH_2
Secondary	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHR}^I$
Tertiary	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NR}_2^I$

❖ Examples of some amides are:

HCONH_2 ; methanamide	$\text{CH}_3\text{CONHCH}_3$; N-methylethanamide
CH_3CONH_2 ; ethanamide	$\text{C}_6\text{H}_5\text{CONH}_2$; benzenecarboxamide (or benzamide)
	$\text{CH}_3\text{CH}_2\text{CON}(\text{CH}_3)_2$; N,N-dimethylpropanamide

(b) Physical properties of amides:

- ❖ All are solids except methanamide.
- ❖ They possess hydrogen bonds between their molecules except tertiary amides which possess no highly polar hydrogen–nitrogen bond. The molecules of tertiary amides associate via weak van der Waals forces of attraction.
- ❖ Thus, tertiary amides have normal boiling points.
- ❖ All amides are virtually insoluble in hydrocarbon solvents like methylbenzene, benzene etc.

(c) Preparation of amides:

- ❖ Refer to the previous sections for details.

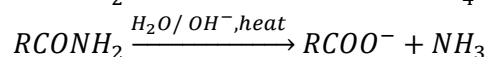
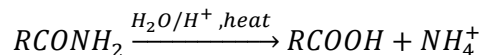
(d) **Reactions of amides:**

(i) **Basicity**

- The lone pair of electrons on the nitrogen atom gives amides a slightly basic character.
- However, amides are less basic than amines. Refer to amines for details.

(ii) **Hydrolysis**

- Can be base or acid catalysed.



- The mechanism for the hydrolysis of amides is similar to that of esters.

(iii) **Reduction**

- For example: $RCONH_2 \xrightarrow{LiAlH_4/\text{dry ether}} \underbrace{RCH_2NH_2}_{\text{primary amine}}$
- The reduction can also be effected by use of sodium in ethanol.

(iv) **Dehydration**

- For example: $RCONH_2 \xrightarrow{P_2O_5, \text{heat}} \underbrace{RC \equiv N}_{\text{nitrile}} + H_2O$

Question

Write equations to show how methanol can be converted into ethylamine.

(v) **Reaction with nitrous acid**

- For example: $RCONH_2 \xrightarrow{NaNO_2/\text{conc HCl}, <10^\circ C} RCOOH + N_2 + H_2O$
- A mixture of $NaNO_2/\text{conc HCl}$ at $< 10^\circ C$ gives a **very unstable** nitrous acid.

(vi) **Hofmann degradation**

- For example: $RCONH_2 \xrightarrow{Br_2/\text{conc OH}^-(aq), \text{warm}} \underbrace{RNH_2}_{\text{primary amine}} + \underbrace{Br^- + CO_3^{2-} + H_2O}_{\text{other minor products}}$
- This reaction leads to formation of a primary amine and is used in organic synthesis for carbon chain reduction.

Question

Write equations to show how ethanol can be converted into methylamine.