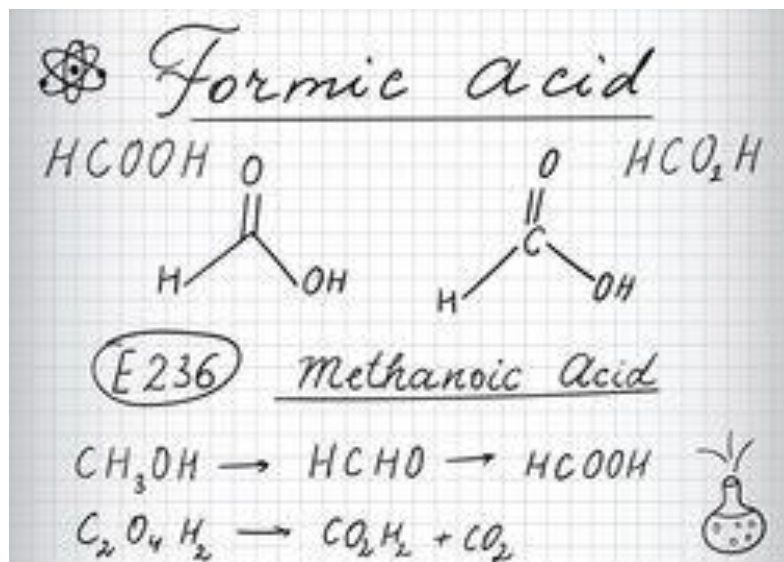


CHAPTER 10.0

CARBOXYLIC ACIDS AND ITS DERIVATIVES



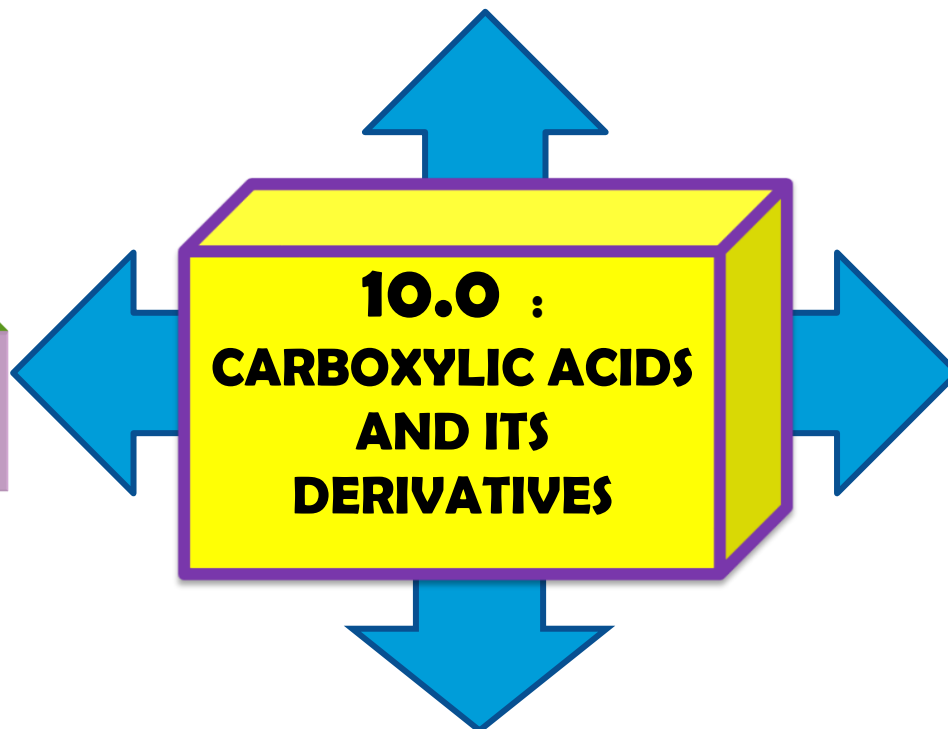
10.1
Introduction

**10.2 Physical
Properties**

**10.0 :
CARBOXYLIC ACIDS
AND ITS
DERIVATIVES**

**10.4
Chemical
Properties**

**10.3
Preparation**



Learning outcomes

10.1 Introduction

a) State the general formula of carboxylic acids : (C1)

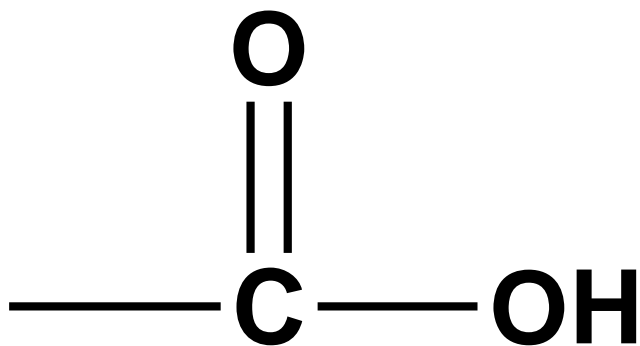


b) Give the name carboxyl compounds according to the IUPAC nomenclature (C2)

c) State the common names of carboxylic acids with parent chain $\leq \text{C}_5$ (C1)

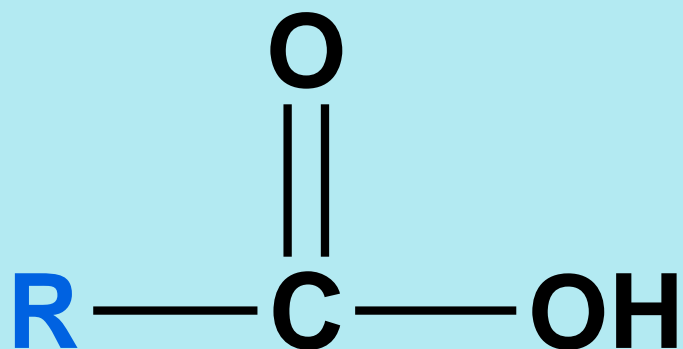
d) Give the structural formulae of carboxyl compounds (parent chain $\leq \text{C}_{10}$) (C2)

Introduction

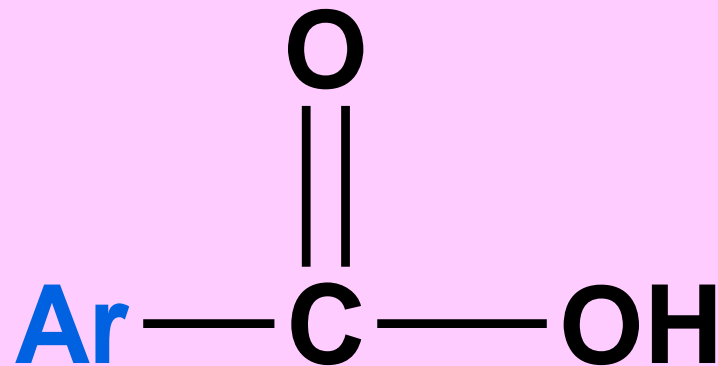


Functional group: Carboxyl

GENERAL FORMULA OF CARBOXYLIC ACIDS



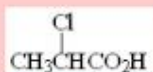
(**R** \equiv alkyl or H)



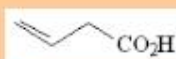
(**Ar** \equiv aryl)

Also can be written : **RCOOH** or **RCO₂H**

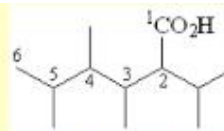
NOMENCLATURE OF CARBOXYLIC ACIDS



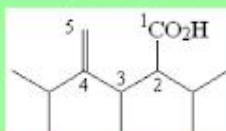
Ácido 2-cloropropanoico
2-Chloropropanoic acid



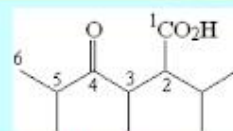
Ácido 3-butenico
3-Butenoic acid



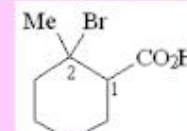
Ácido 2-(1-metiletil)-
3,4,5-trimetilhexanoico
2-(1-Methylethyl)-3,4,5-
trimethylhexanoic acid



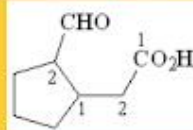
Ácido 2,4-bis(1-metiletil)-
3-metil-4-pentenoico
2,4-bis(1-methylethyl)-3-methyl-
4-pentenoic acid



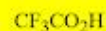
Ácido 2-(1-metiletil)-
3,5-dimetil-4-oxohexanoico
2-(1-Methylethyl)-3,5-dimethyl-
4-oxohexanoic acid



Ácido 2-bromo-2-metil-
ciclohexanocarboxílico
2-Bromo-2-methyl-
cyclohexanecarboxylic acid



Ácido 2-(2-formilciclopentil)
acético
2-(2-formylcyclopentyl)acetic
acid



Ácido trifluoracético
(TFA)

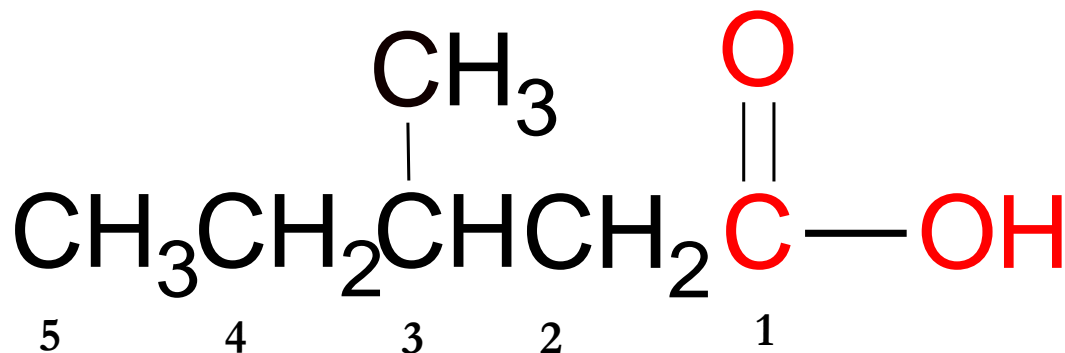
Trifluoroacetic acid

STRUCTURAL FORMULA	IUPAC NAME
HCOOH	Methanoic acid
CH ₃ COOH	Ethanoic acid
CH ₃ CH ₂ COOH	Propanoic acid
CH ₃ CH ₂ CH ₂ COOH	Butanoic acid
CH ₃ CH ₂ CH ₂ CH ₂ COOH	Pentanoic acid
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ COOH	Hexanoic acid
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ COOH	Heptanoic acid
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ COOH	Octanoic acid
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ COOH	Nonanoic acid
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ COOH	Decanoic acid

ALIPHATIC CARBOXYLIC ACID

According to IUPAC nomenclature, for carboxylic acids:

- Parent chain is the longest carbon atoms that contain the **carboxyl group**.
- The chain is numbered starting from the carboxyl carbon atom as C1.



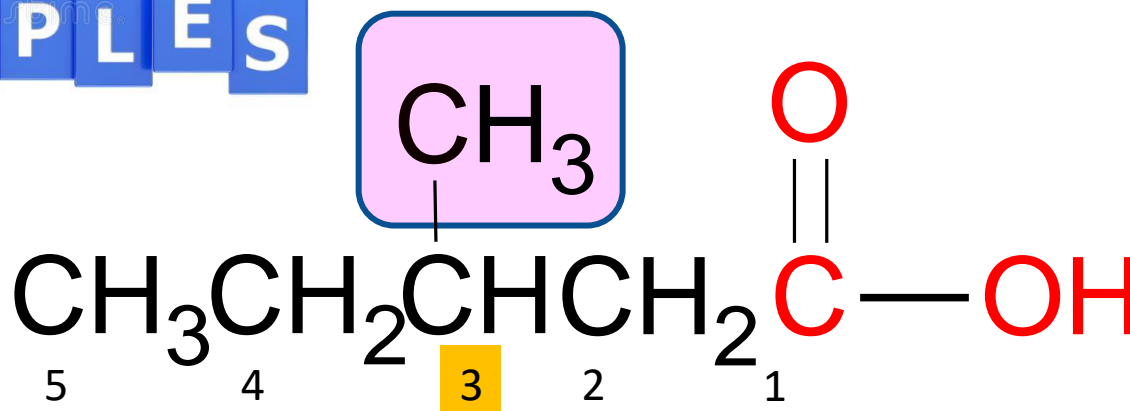
- The carboxyl group is at the **terminal**.

One COOH – carboxyl group is at one end

Two COOH – carboxyl groups are at both ends

- Replace **-e** in the alkanes by '**oic acid**' (eg: methano**oic acid**).

EXAMPLES

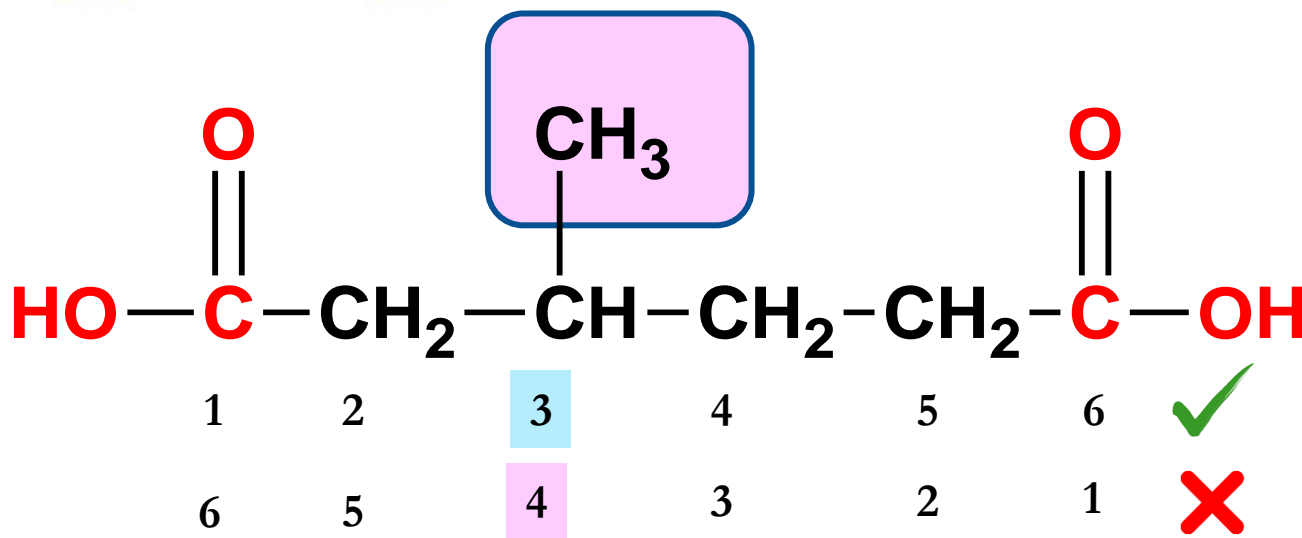


3-methylpentanoic acid



- If two carboxyl groups present, add – **dioic acid** to the name of parent alkane; **alkanedioic acid**.

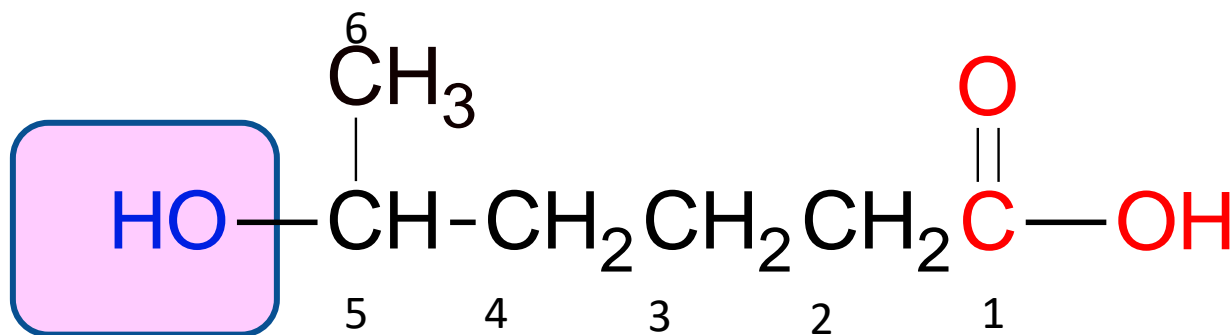
EXAMPLES



3-methyl**hexan**edioic acid

- The **carboxyl group** is given priority over other functional groups.
- Other functional group is treated as **substituents**, if present.

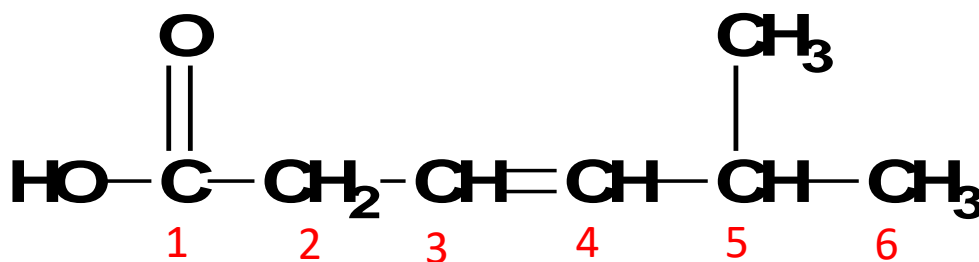
EXAMPLES



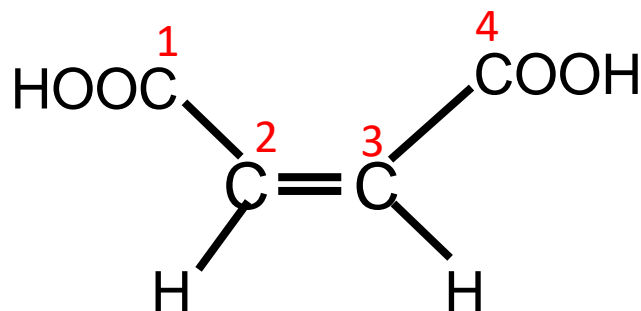
5-hydroxyhexanoic acid

- Carboxylic acid with double bond are named as **x – alkenoic acid** [x = position of double bond]

EXAMPLES



5-methyl-3-hexenoic acid



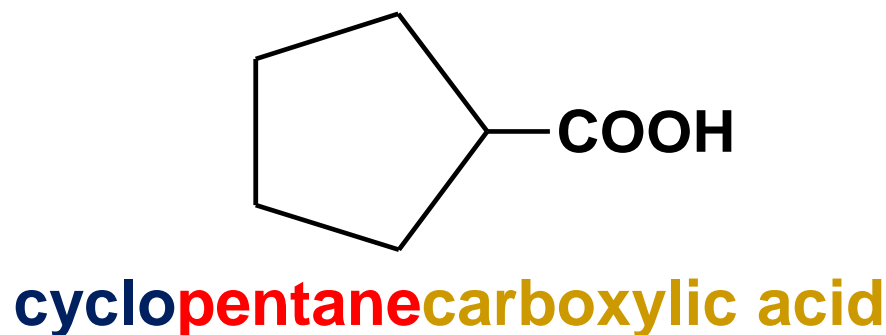
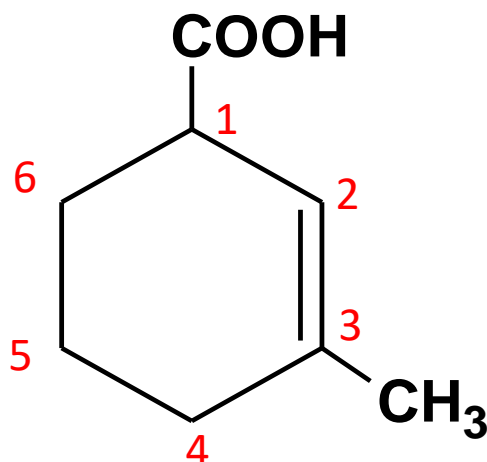
cis-2-butenedioic acid

➤ A cyclic carboxylic acid is named as:

- **cyclo****alkane****carboxylic acid**
- **cyclo****alkene****carboxylic acid**

➤ The C atom which is attached to **–COOH** is numbered as C1

EXAMPLES



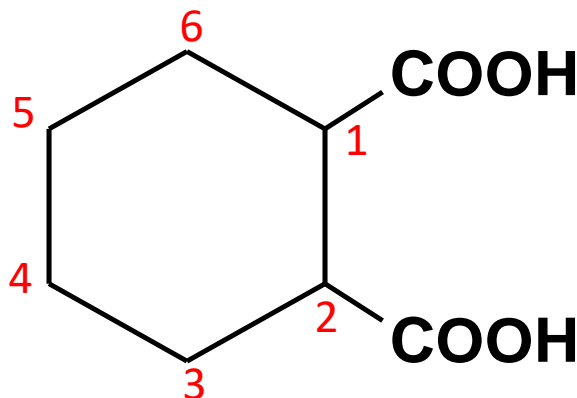
cyclopentane**carboxylic acid**

3-methyl-2-cyclohex-2-enecarboxylic acid

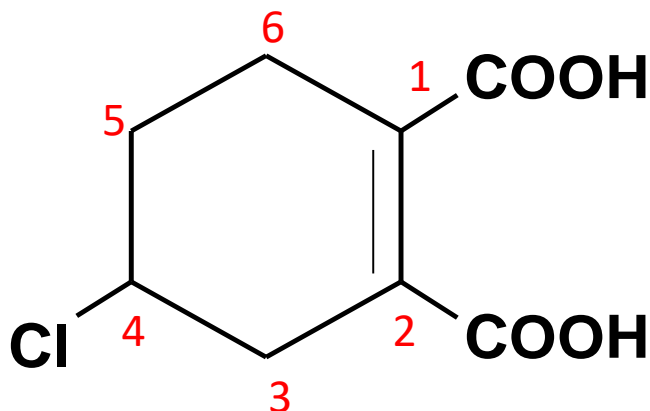
➤ A cyclic dicarboxylic acid is named as:

- 1,x – **cyclo****alkane****dicarboxylic acid**
- 1,x – **cyclo****alkene****dicarboxylic acid**

EXAMPLES



1,2-cyclohexanedicarboxylic acid

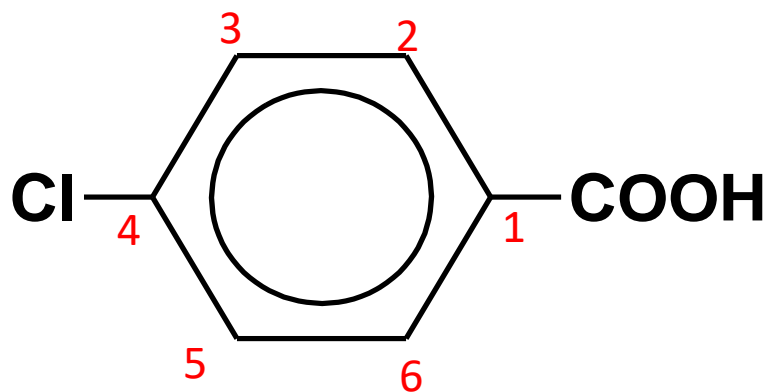


4-chloro-1,2-cyclohex-1-enedicarboxylic acid

AROMATIC CARBOXYLIC ACID

- When **R** is an **aryl group**, the parent name is **benzoic acid**.

EXAMPLES

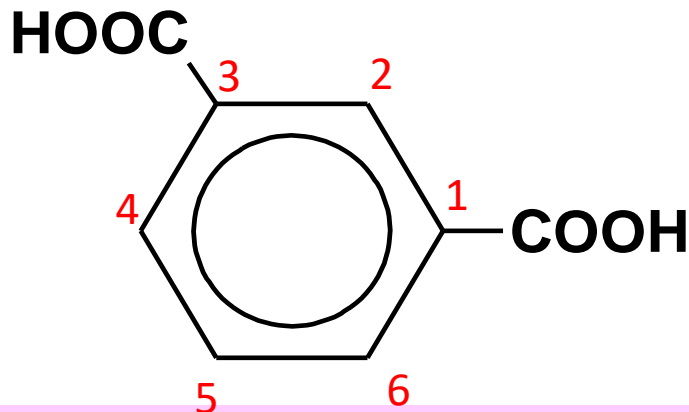


4-chlorobenzoic acid @

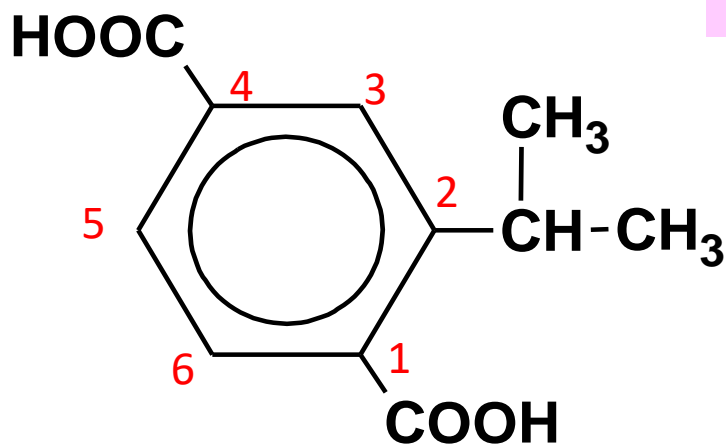
p-chlorobenzoic acid

- An aromatic dicarboxylic acid is named as **1,x-benzenedicarboxylic acid**

EXAMPLES



1,3-benzenedicarboxylic acid



2-isopropyl-1,4-benzenedicarboxylic acid

Common names with parent chain $\leq C_5$

STRUCTURAL FORMULA	IUPAC NAME	COMMON NAME
HCOOH	Methanoic acid	Formic acid
CH ₃ COOH	Ethanoic acid	Acetic acid
CH ₃ CH ₂ COOH	Propanoic acid	Propionic acid
CH ₃ CH ₂ CH ₂ COOH	Butanoic acid	Butyric acid
CH ₃ CH ₂ CH ₂ CH ₂ COOH	Pentanoic acid	Valeric acid

Learning outcomes

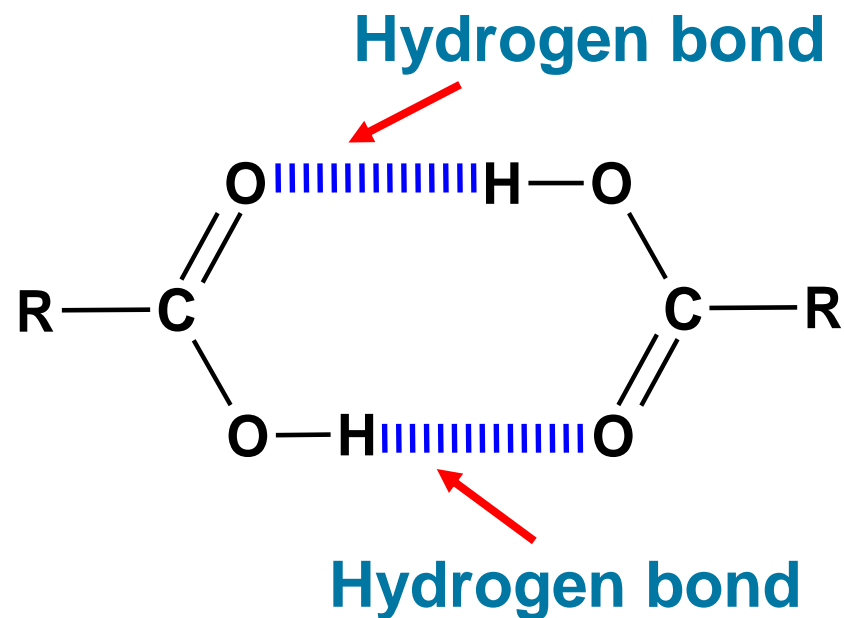
10.2 Physical Properties of Carboxylic Acids

- a) Explain the physical properties : (C2, C3 & C4)
 - i. Boiling point
 - ii. Solubility in water



BOILING POINT

- The boiling point of **carboxylic acid** is **higher than alcohol, ketone or aldehyde** of **similar molecular weight**.
- It is due to **carboxylic acids** molecule **are arranged closely packed**, as stable **dimers**, at which the hydrogen bonds formed between the molecules are **relatively strong**.
- Thus, **more energy** is needed to overcome the strong hydrogen bonding, **boiling point increase**.



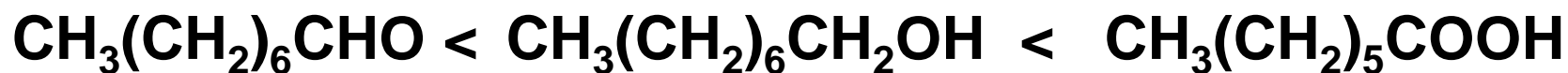
Dimerisation of Carboxylic Acid

EXAMPLES

Arrange the compounds in each set in order of increasing boiling point and explain.

(a) $\text{CH}_3(\text{CH}_2)_5\text{COOH}$, $\text{CH}_3(\text{CH}_2)_6\text{CHO}$, $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$

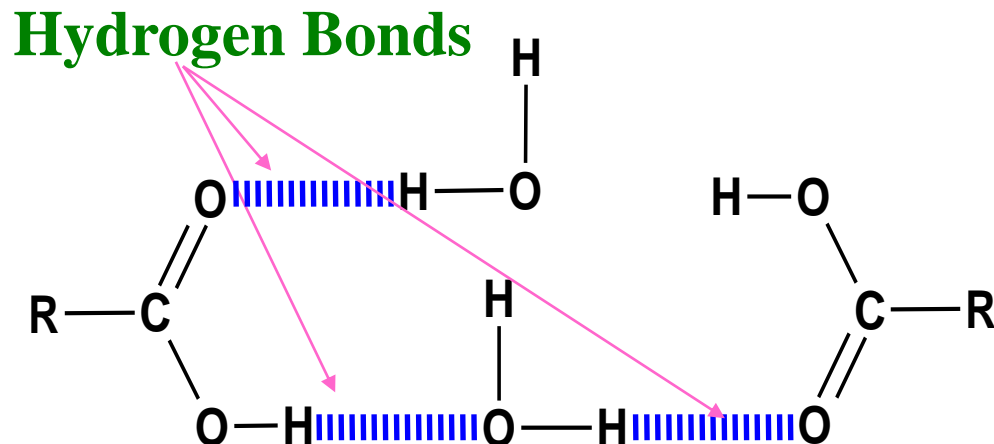
ANSWER



- ✓ **Octanal** has the lowest boiling point because it only has **weak van der Waals forces** between their molecules.
- ✓ **1-octanol** and **heptanoic acid** have **strong hydrogen bond** between their molecules.
- ✓ Boiling point of **heptanoic acid** is higher than **1-octanol** because heptanoic acid has the $-\text{COOH}$ group that exists as **stable dimers** through hydrogen bonds.
- ✓ The **hydrogen bond** of **heptanoic acid** is stronger than **1-octanol**.

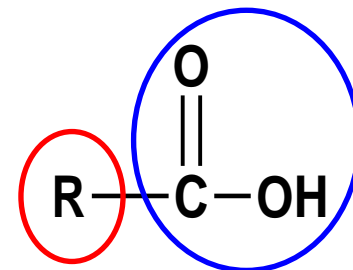
SOLUBILITY IN WATER

- Carboxylic acids are soluble in water due to the formation of **hydrogen bond between the water molecules and carboxylic acid molecules.**



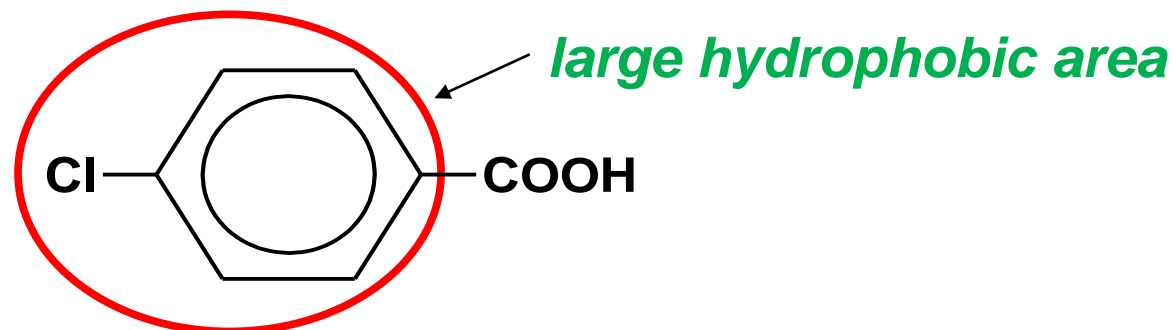
- The solubility of carboxylic acid in water is almost the same as alcohol.
- Simple carboxylic acids (**C1-C5**) are **completely soluble** in water.
- **Aliphatic carboxylic acids** with **C > 5** are **insoluble** in water. As the length of the hydrocarbon chain increases, **hydrophobic area increase**, hydrogen bonding with water molecule hardly formed thus the **solubility of the acid in water decreases.**

Hydrophilic area

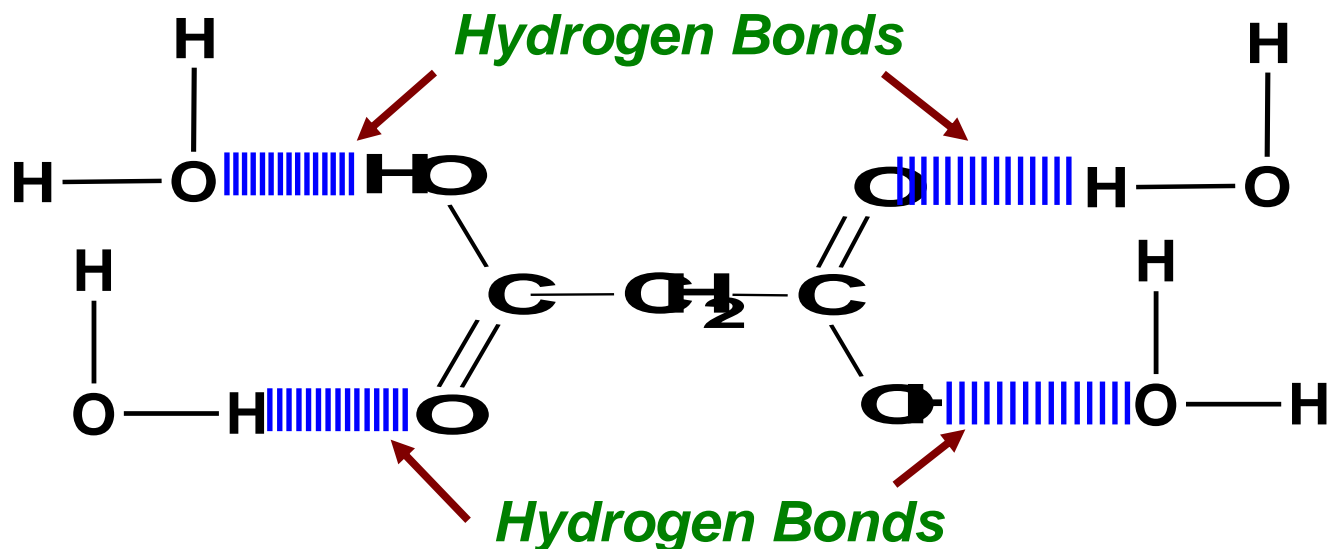


Hydrophobic area

- **Aromatic carboxylic acids** are **slightly soluble** in water due to the huge aromatic ring (**large hydrophobic area**).

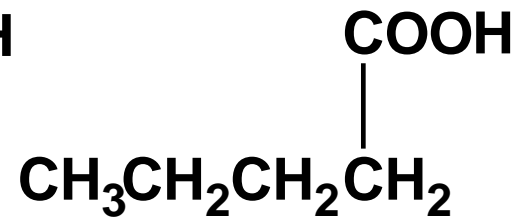
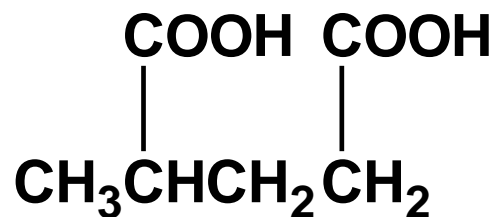
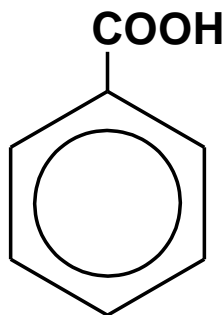
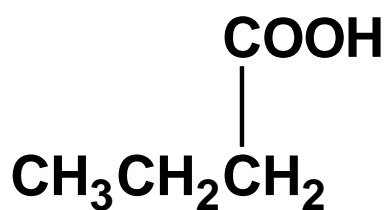


- **Dicarboxylic acids** are relatively **more soluble** since **more hydrogen bonds** can be formed with water molecules.

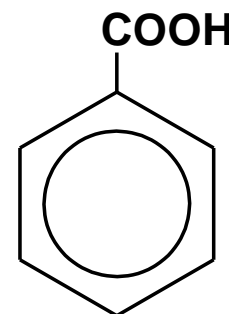
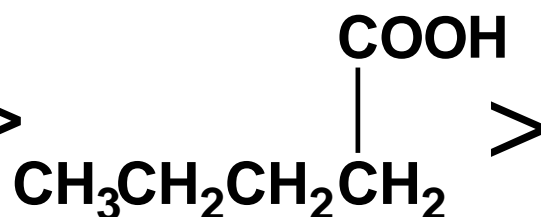
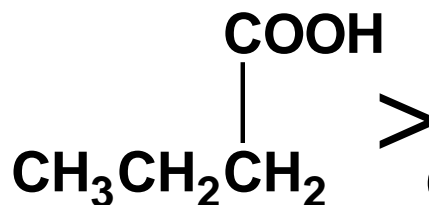
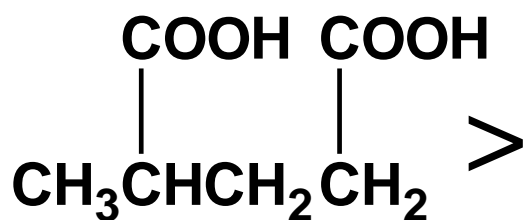


EXAMPLES

Arrange the solubility of compounds in water in descending order.



ANSWER



Learning outcomes

10.2 Physical Properties of Carboxylic Acids

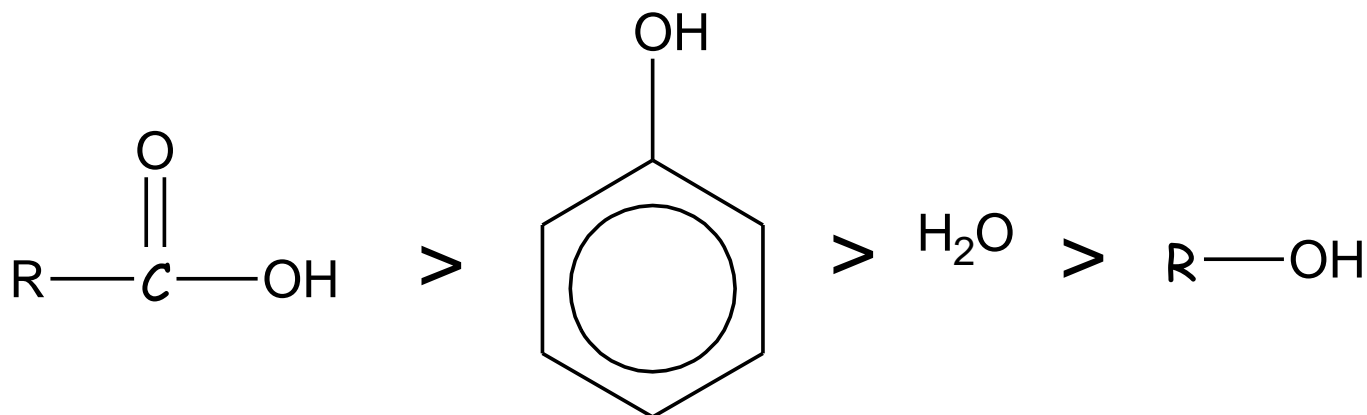
b) Explain the acidity of : (C2, C3 & C4)

- i. Carboxylic acid in comparison with alcohol & phenol
- ii. halogenated carboxylic acids based on the ;
 - number of halogens
 - position of halogens

❖ *Include inductive effect or function of halogen as Electron Withdrawing Group (EWG)*

ACIDITY

- **Carboxylic acid** is relatively a **weak acid** however it is **stronger than phenol & alcohol**.



- Two factors that influence the acidity of carboxylic acid are:

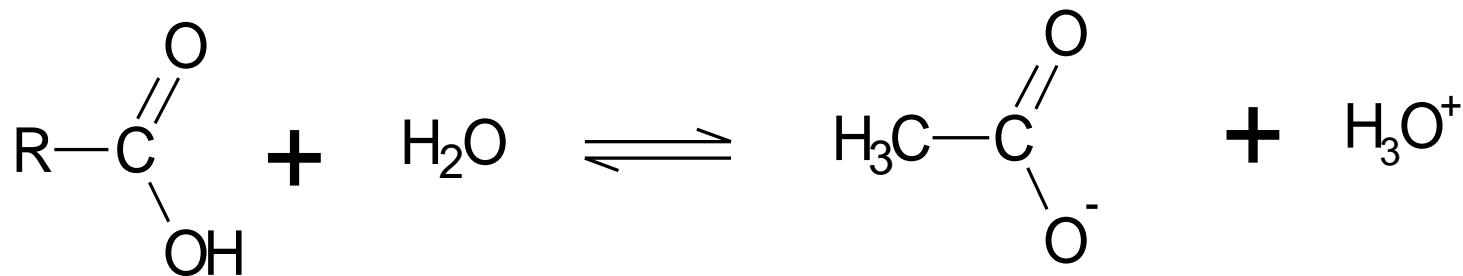
☐ **Resonance effect**

☐ **Inductive effect**

(Inductive effect is the shift of electron density from one atom to another to form a polar bond)

RESONANCE EFFECT IN CARBOXYLATE ION

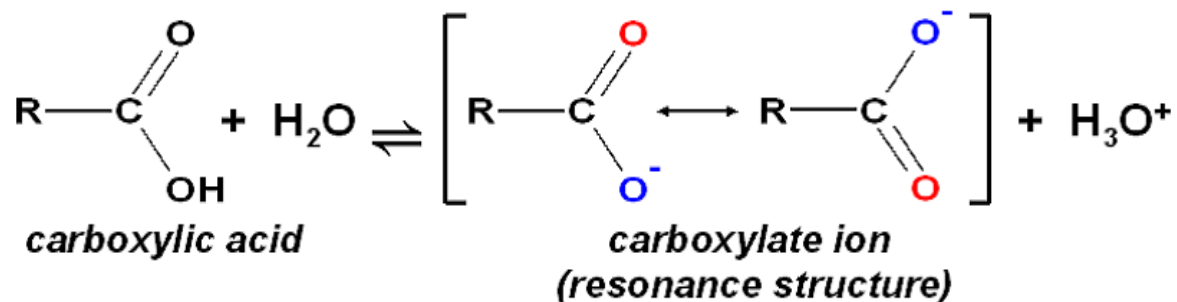
- **Carboxylic acid** dissociate in water to form **carboxylate ion**.



carboxylic acid

carboxylate ion

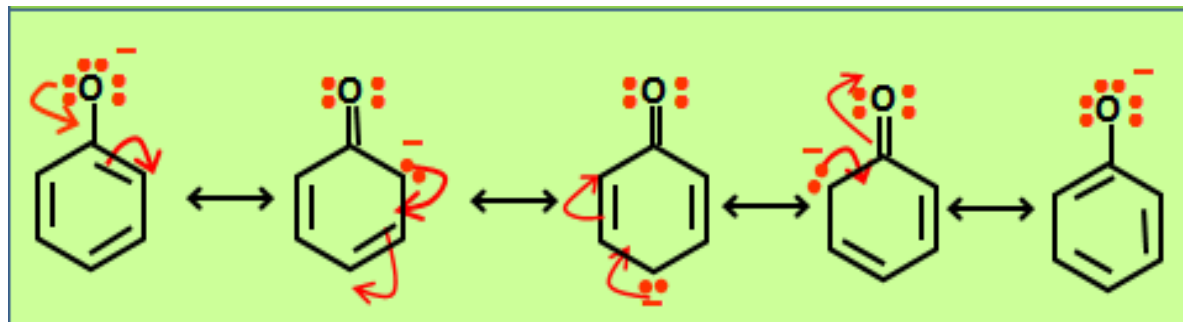
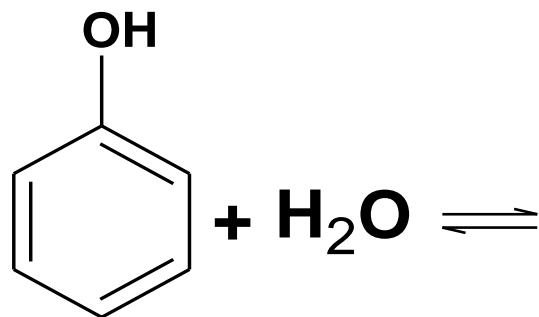
- **Carboxylate ion** is stabilized through **resonance** where the **electrons are delocalized over two electronegative oxygen atoms** (resonance stabilization).



- Due to the resonance stabilization of the carboxylate ion, **carboxylic acid** is more acidic than **phenol** and **alcohol**.

RESONANCE EFFECT IN PHENOXIDE ION

- **Phenol** dissociate in water to form **phenoxide ion**.
- In **phenoxide ion**, the **electrons** are **delocalized** within the **benzene ring**.



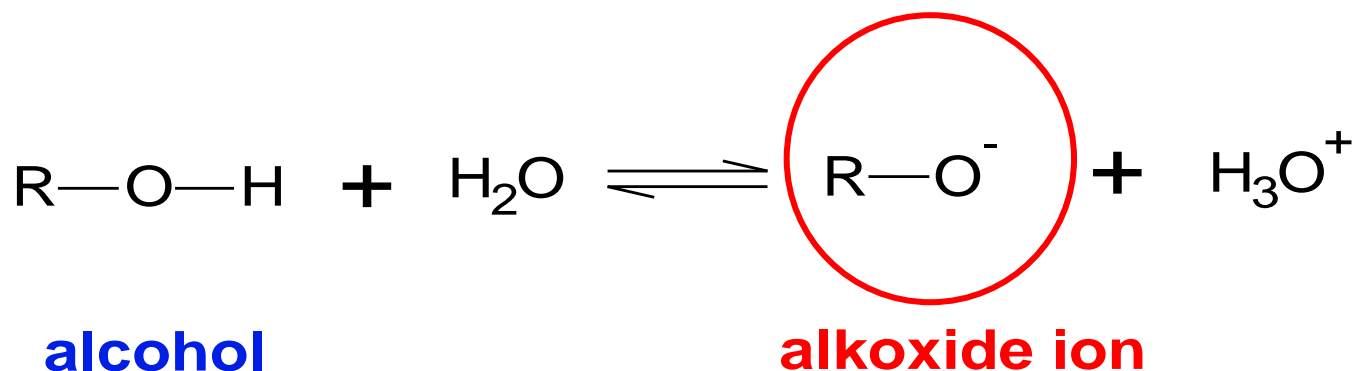
phenol

resonance structure of **phenoxide ion**

- The **resonance structure** of **carboxylate ion** is **more stable** than the **phenoxide ion**.
- Therefore **carboxylic acid** are **more acidic** than **phenol**.

** The ability to spread the negative charge over four atoms rather than concentrated it on just one atom produces more stable phenoxide ion.*

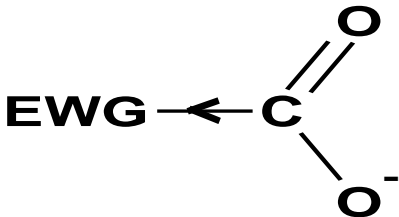
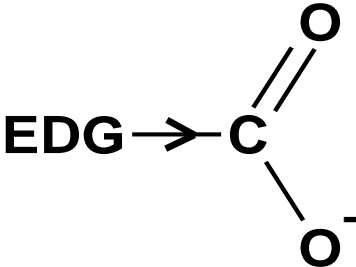
- **Alcohol** dissociate in water to form **alkoxide ion**.
- Alcohol is the **least acidic** compare to carboxylic acid and phenol due to the **electrons are localized at oxygen atom** in alkoxide ion.



- Thus **alcohol** is **less acidic** than **phenol**.

INDUCTIVE EFFECT

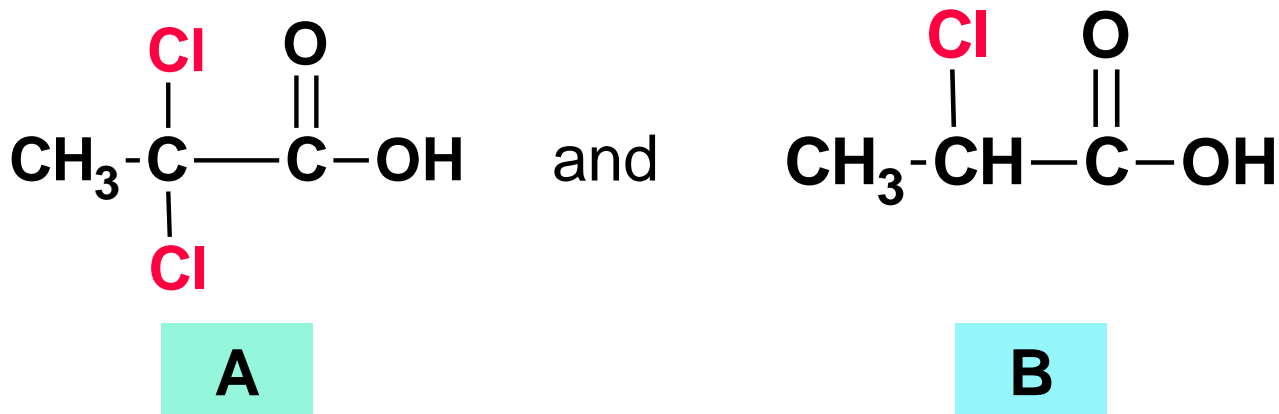
- Substituent group that attached to the carbon of the carboxyl plays major role in determining the acidity of a carboxylic acid.

Electron withdrawing group	Electron donating group
	
An electron withdrawing group, EWG that attached to a carboxylate ion will stabilises the carboxylate ion and increases acidity .	An electron donating group, EDG will destabilise the carboxylate ion and decreases acidity .
Example : NO ₂ , -F, -Cl, -Br, -I	Example : -NH ₂ , -NHR, -NR ₂ , -OH, -OR, -NHCOR, -R

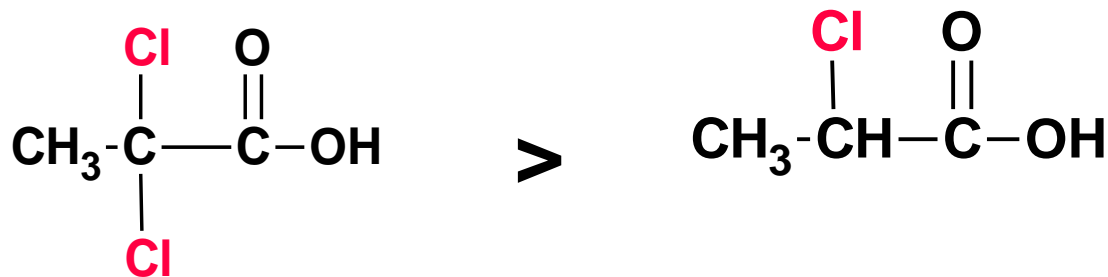
How electron withdrawing group increases the acidity ?

- Electron Withdrawing Groups(EWG) **reduce the electron density of -O-H bond.**
- Thus the -O-H bond becomes **weaker** and H^+ can be **easily released** and **form stable carboxylate ion.**
- An **electron withdrawing group, EWG** that attached to a **carboxylate ion** will stabilises the carboxylate ion.
- The compound is said to be **more acidic.**
- There are **two factors** that can **effect the stability of carboxylate ion** through **inductive effect** :
 - ✓ **Number of halogens**
 - ✓ **Position of halogens**

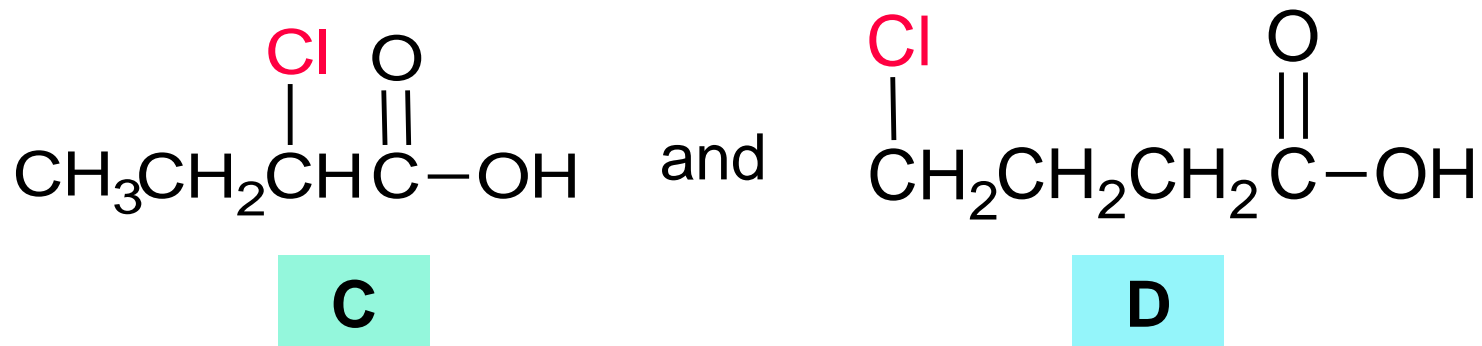
NUMBER OF HALOGENS



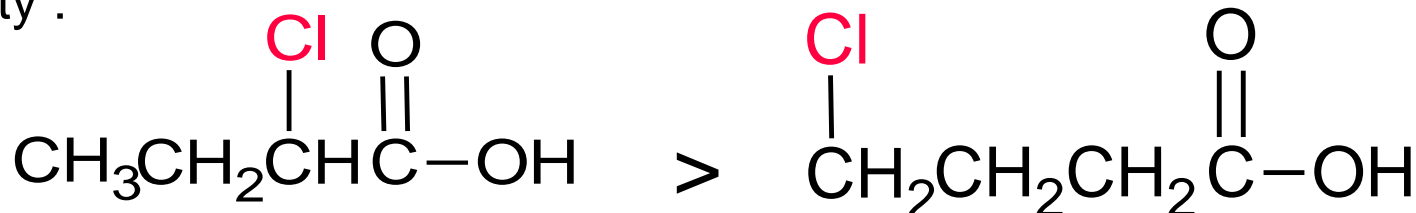
- **Compound A** contains **2 atoms of Cl** that make the bond of **–O–H bond** weaker than **Compound B** (with **only one Cl atom**). Thus, **H⁺ is easily donated**.
- **Compound A** contains more electron withdrawing group (EWG), Cl, that attached to carboxylate ion. The electron withdrawing group increase the stability of carboxylate ion.
- **Thus, acidity :**



POSITION OF HALOGENS



- The **distance between Cl atom and carboxyl group** in Compound C is nearer compared to Compound D.
- The **–O-H bond** in Compound C is **weaker** than in Compound D, so **H⁺ is easily donated**.
- The stability of carboxylate ion of compound C increases as the **distance between Cl atom and carboxyl group decreases**.
- Thus, acidity :



EXAMPLES

Carboxylic acid	pK _a
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OH} \end{array}$	4.74
$\begin{array}{c} \text{Cl} \quad \text{O} \\ \quad \parallel \\ \text{CH}_2\text{C}-\text{OH} \end{array}$	2.86

➤ pK_a ↓ , K_a ↑, acidity ↑

➤ Cl is an **electron withdrawing group (EWG)**, therefore **reduce the electron density of –O-H bond**.

➤ Thus the **O-H bond** in molecule becomes **weaker** and **H⁺** can be **easily released**.

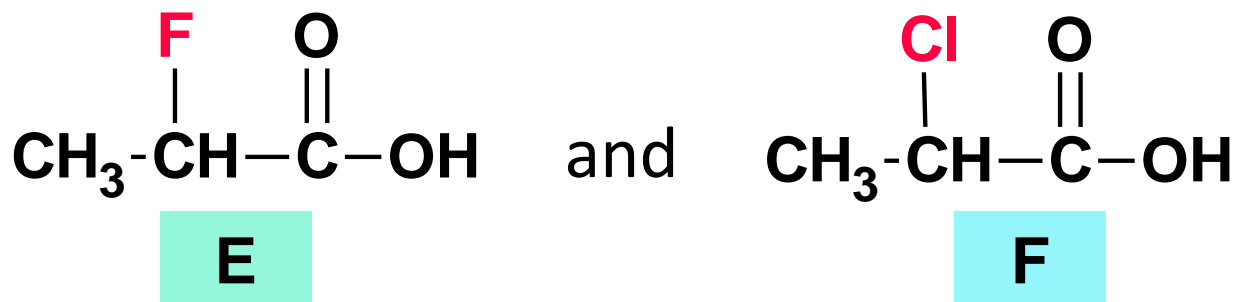
➤ The presence of **Cl** **stabilizes the carboxylate ion** through inductive effect **by withdrawing electron density** from the carboxylate ion.

➤ Therefore a **more stable carboxylate ion** is formed which makes the acidity is higher.

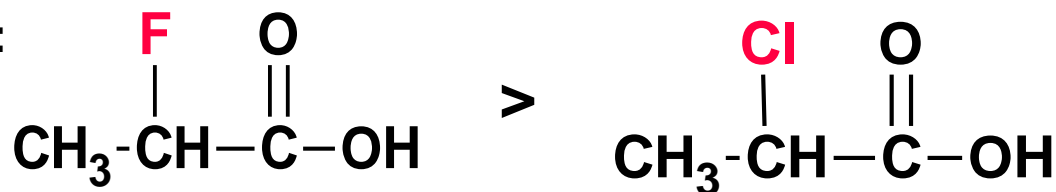
➤ Thus, acidity :

$$\begin{array}{c} \text{Cl} \quad \text{O} \\ | \quad \parallel \\ \text{CH}_2\text{C}-\text{OH} \end{array} > \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OH} \end{array}$$

EXAMPLES



- Both **F** and **Cl** are **electron withdrawing groups(EWG)**.
- The **electronegativity** of $\text{F} > \text{Cl}$, so **F** is able to attract electron stronger than **Cl**.
- The **electron density** of **–O-H bond** in Compound **E** is less, thus the **–O-H bond** is weaker than in Compound **F**. Therefore, **H⁺ is easily donated**.
- The presence of **more electronegative of F atom** in **compound E** **stabilizes the carboxylate ion** through inductive effect by **withdrawing electron density** from the carboxylate ion compared to compound **F**.
- Thus, acidity :



Learning outcomes

10.3 Preparation of Carboxylic Acids

a) Explain the preparation of carboxylic acid through :

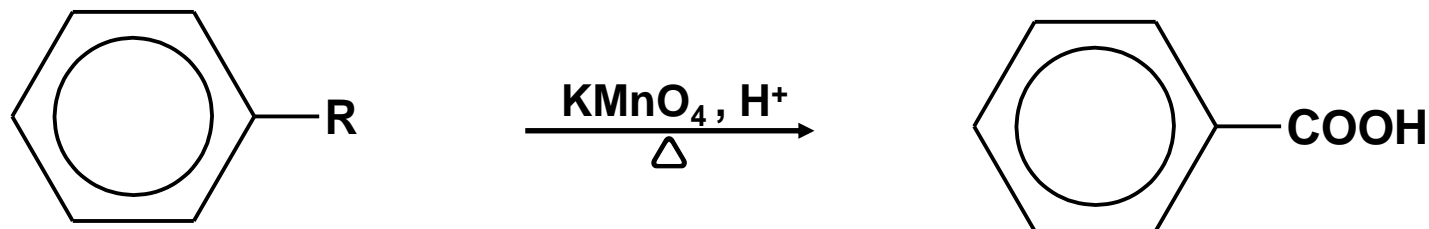
(C3 &C4)

- i. Oxidation of alkylbenzene, alcohol and aldehyde
- ii. Hydrolysis of nitrile compound
- iii. Carbonation of Grignard reagent

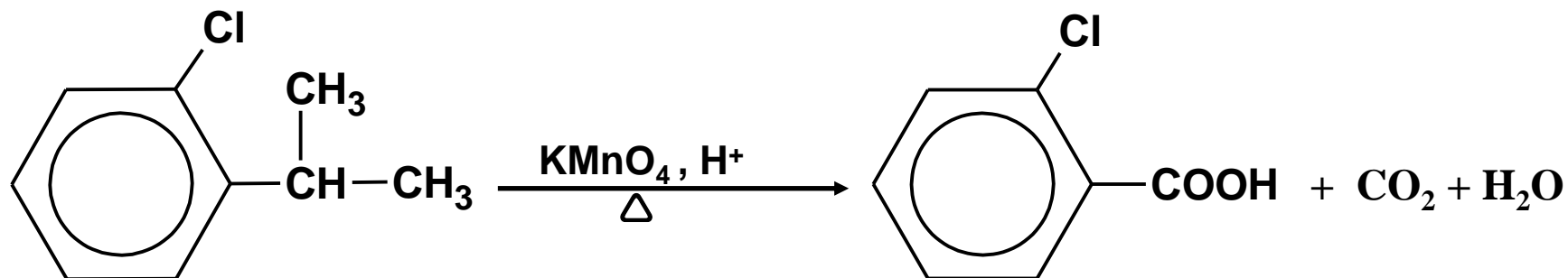


PREPARATION OF CARBOXYLIC ACIDS

➤ Oxidation of Alkylbenzene

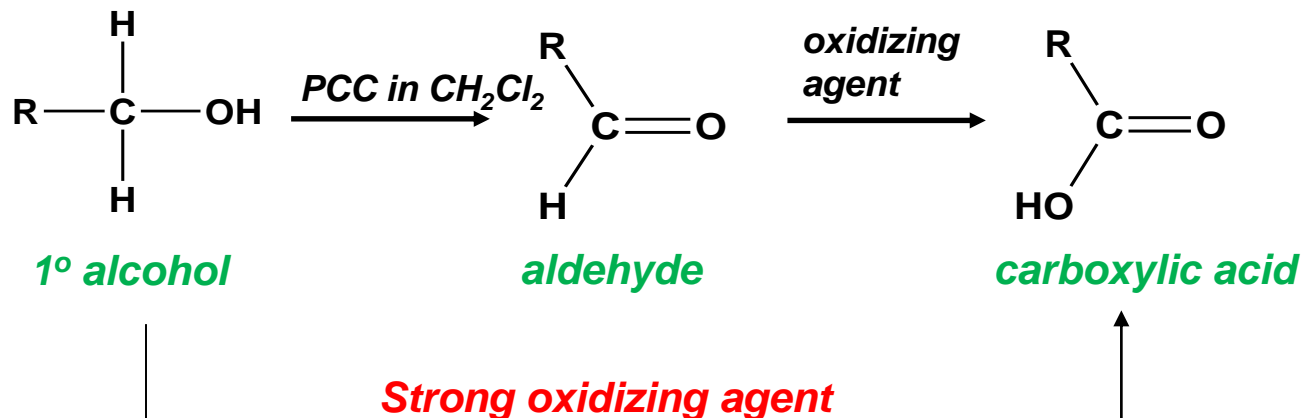


(R= alkyl group)

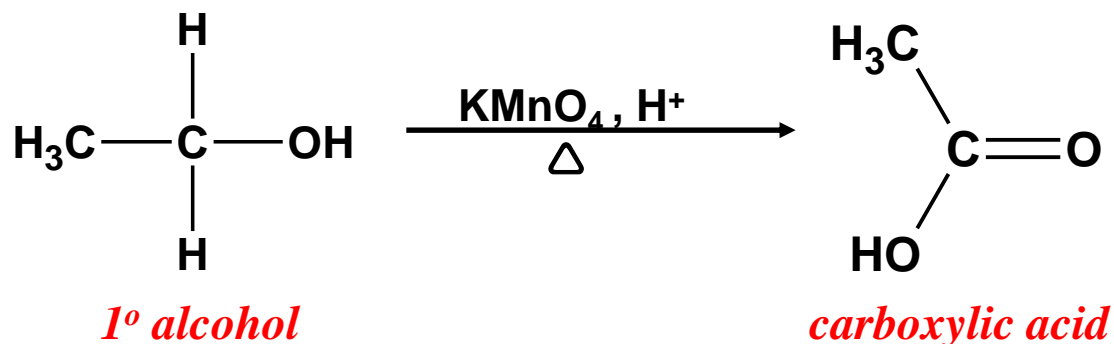


Example of strong oxidizing agent:

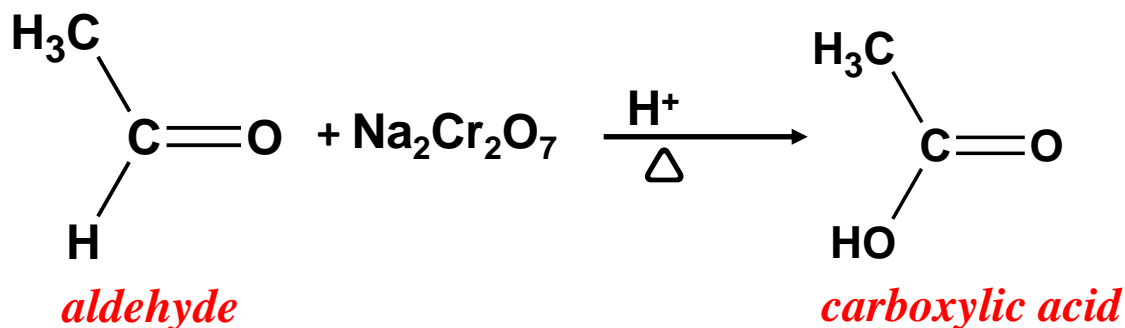
KMnO₄, H⁺, Δ or K₂Cr₂O₇, H⁺, Δ or Na₂Cr₂O₇, H⁺, Δ



➤ Oxidation of 1° Alcohol

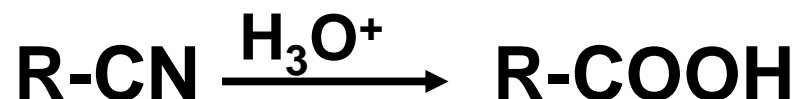


➤ Oxidation of Aldehyde

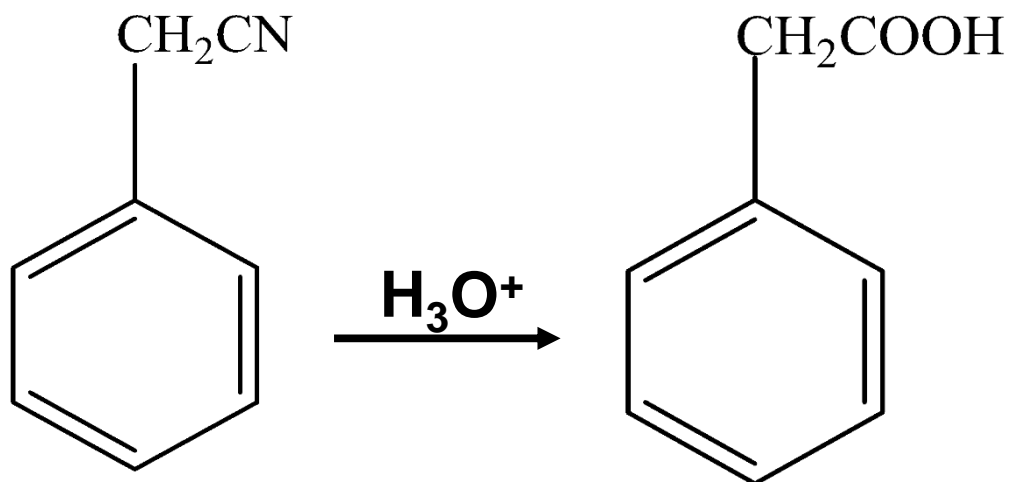


➤ Hydrolysis of nitrile compound

Hydrolysis of nitrile yields a carboxylic acid that has **one carbon atom longer** than its alkyl halide.

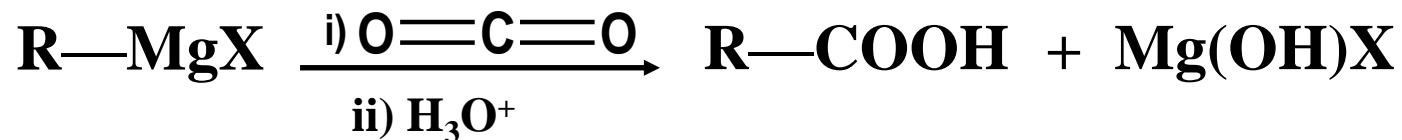


EXAMPLES

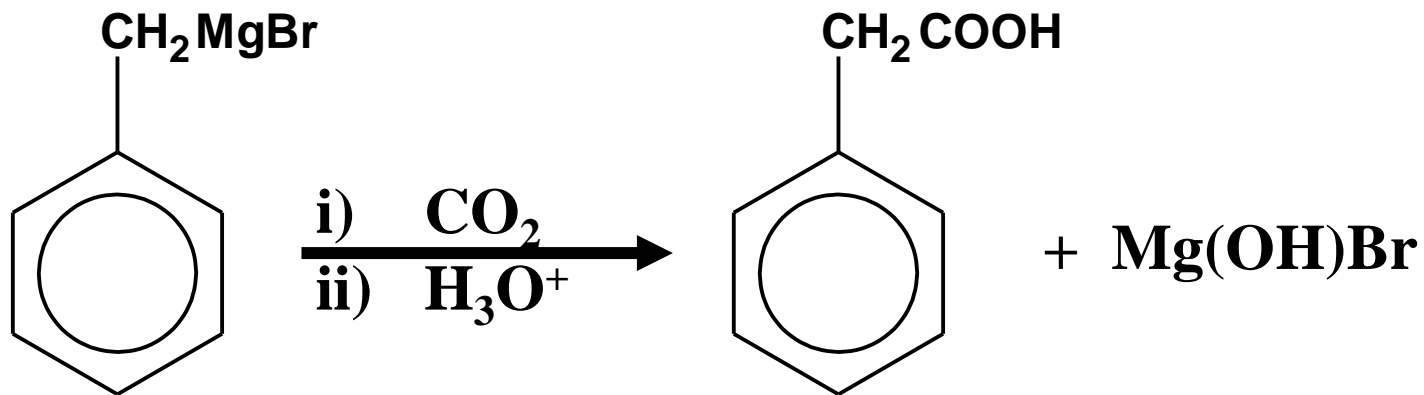


➤ Carbonation of Grignard Reagents

General reaction :



EXAMPLES



Learning outcomes

10.4 Chemical Properties of Carboxylic Acids

a) Explain the chemical properties with reference to :

(C3 & C4)

- i. Neutralisation with a base
- ii. Reaction with electropositive metals such as Na, K, Mg or Ca
- iii. Reduction with LiAlH_4 followed by H_2O
- iv. Acyl chloride formation
- v. Anhydride formation
- vi. Esterification
- vii. Amide formation

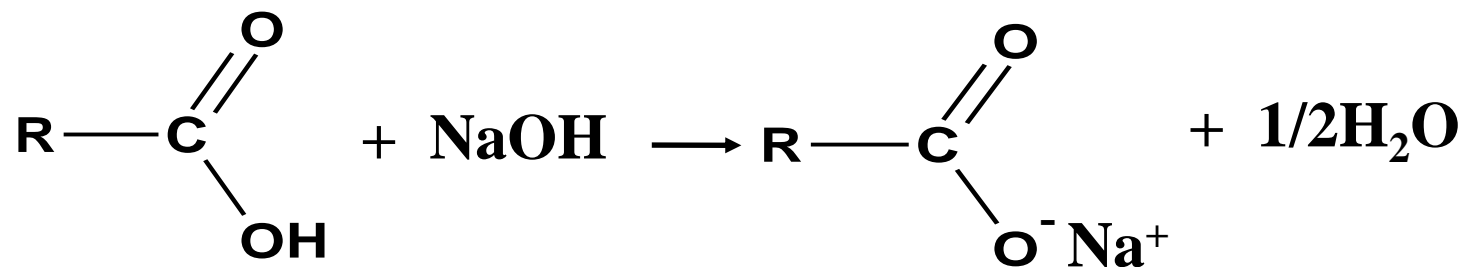


CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

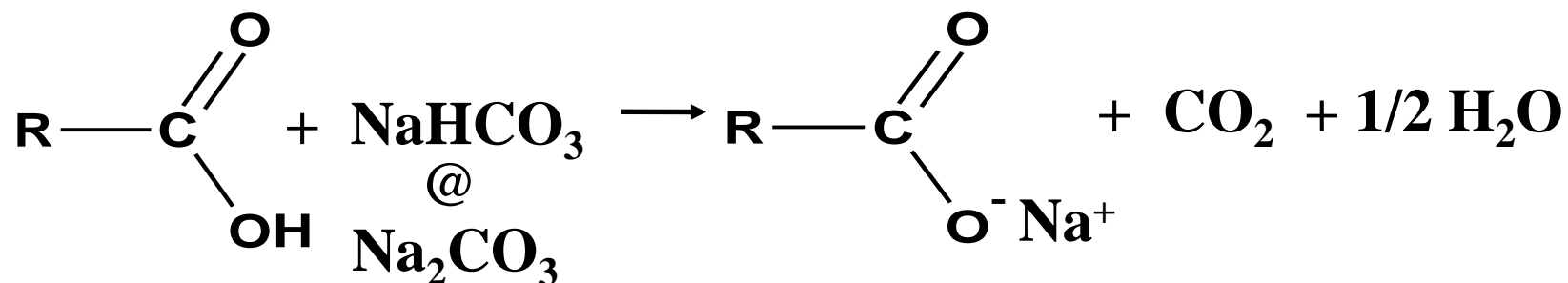
➤ Neutralisation with a base

Carboxylic acids react with base to give metal carboxylate salts.

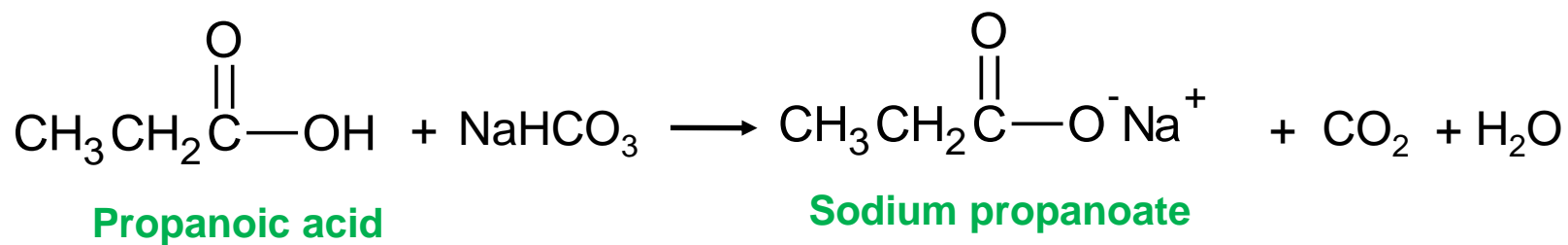
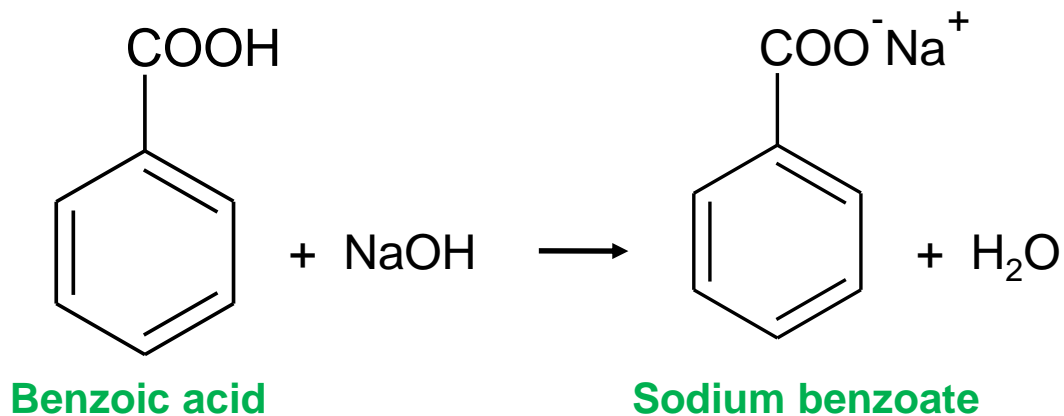
General equation:



OR

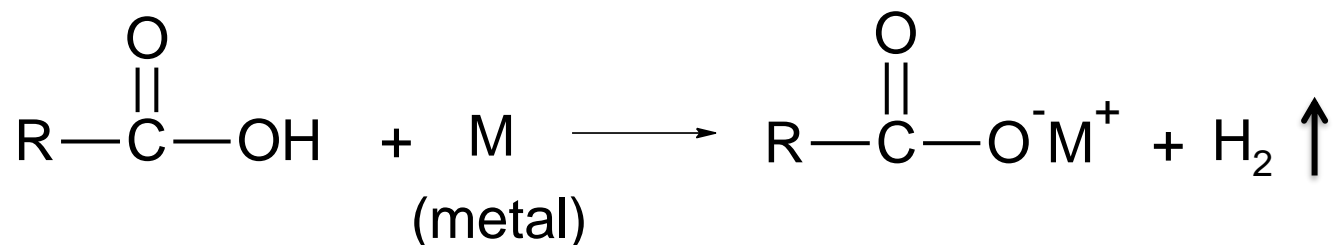


EXAMPLES

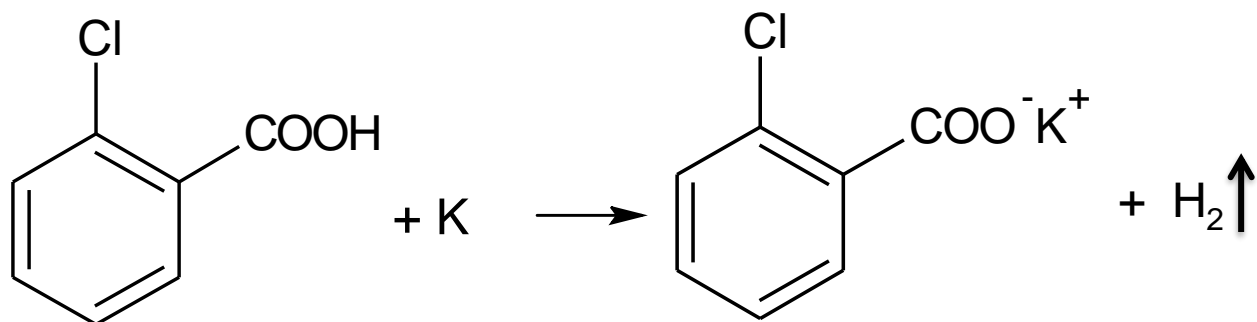


➤ Reaction with electropositive metals such as Na, K, Ca, Mg

General equation:



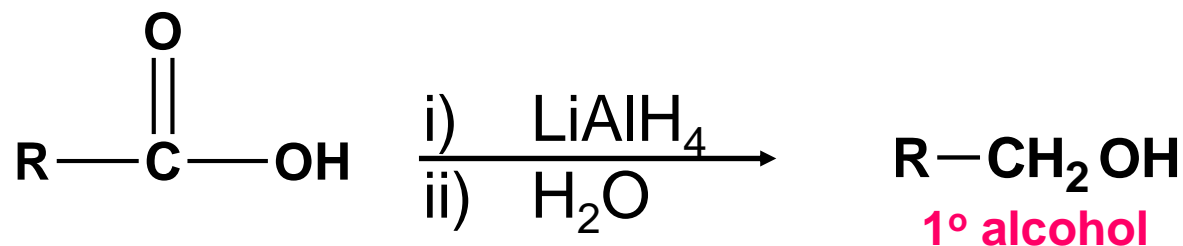
EXAMPLES



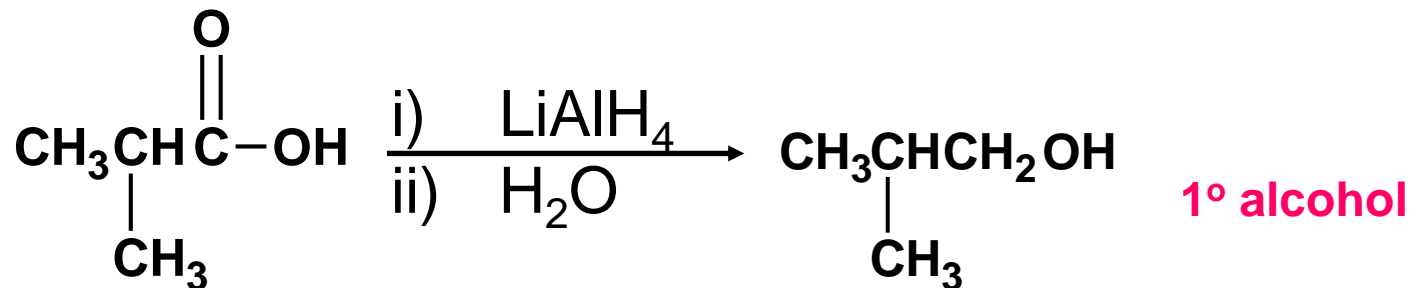
➤ Reduction with LiAlH_4 followed by H_2O

Carboxylic acids are reduced to primary alcohols by reaction with lithium aluminium hydride, LiAlH_4 followed by hydrolysis.

General equation:



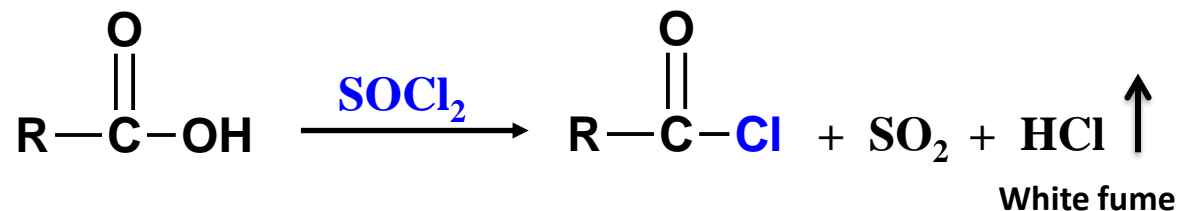
EXAMPLES



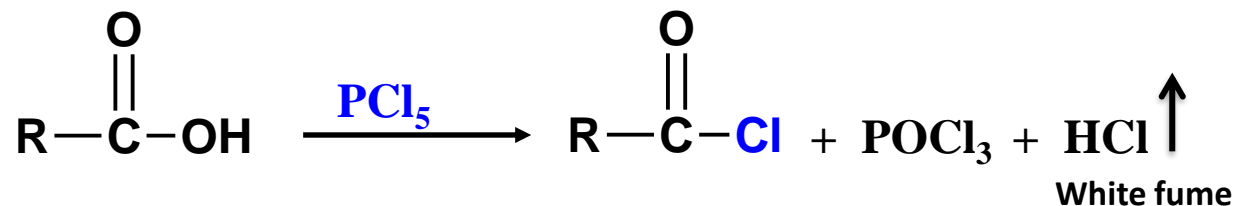
➤ Acid Chloride Formation

General equation:

- thionyl chloride, SOCl_2



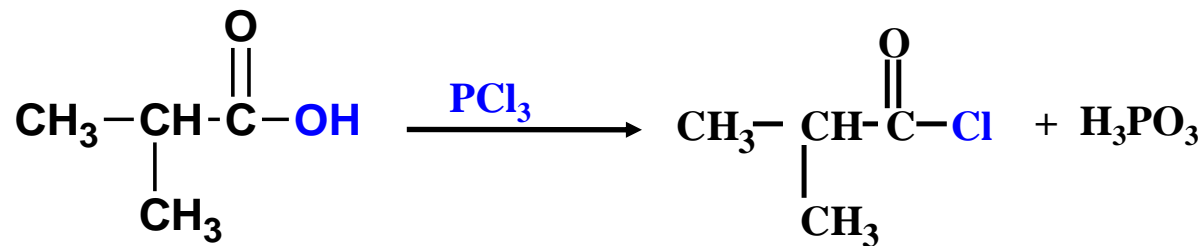
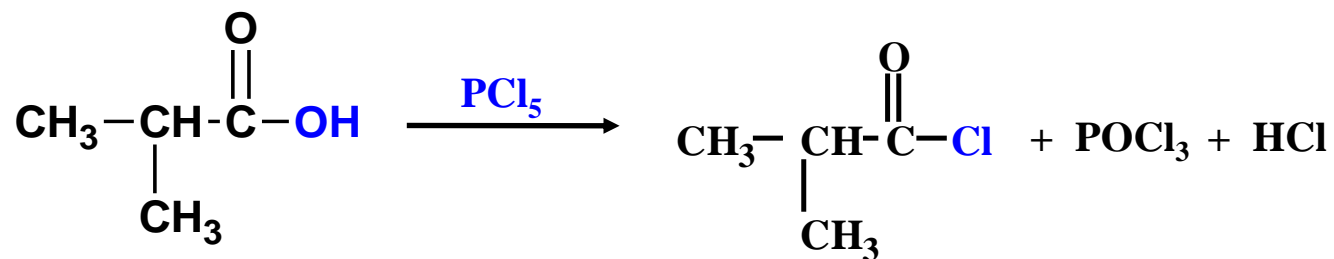
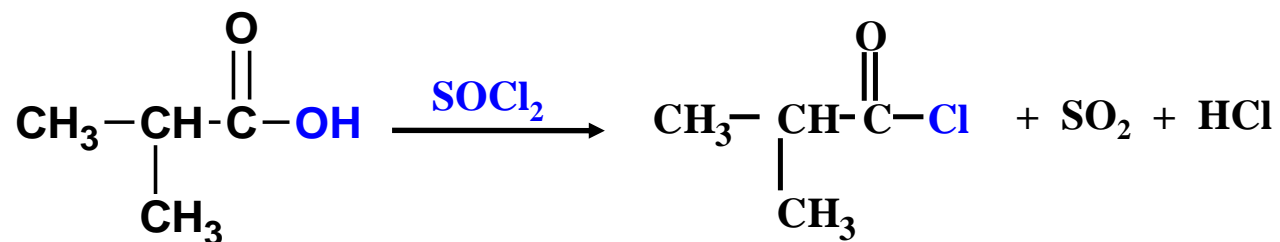
- phosphorous pentachloride, PCl_5



- phosphorous trichloride, PCl_3



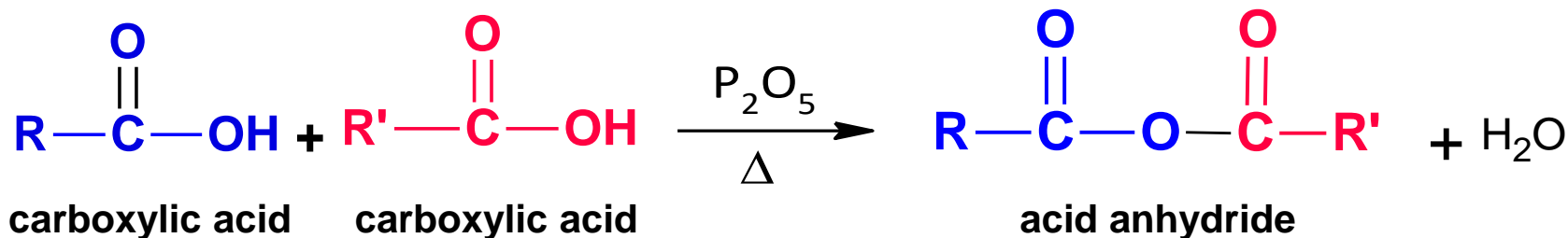
EXAMPLES



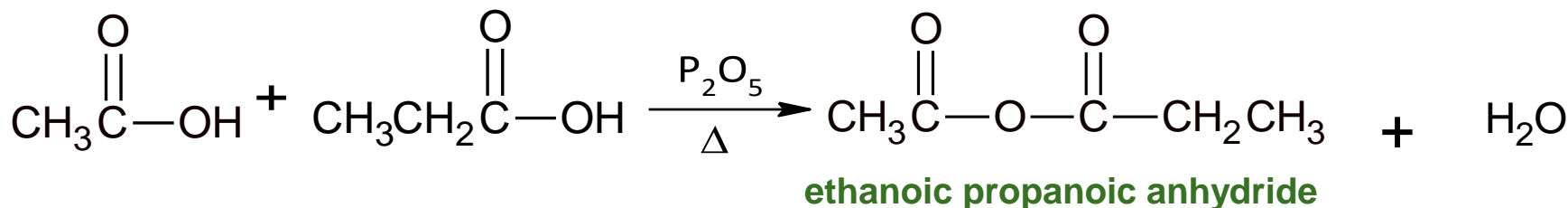
➤ Acid anhydride formation

- Acid anhydrides can be prepared from carboxylic acids in the presence **phosphorous pentoxide**, P_2O_5 , a strong dehydrating agent

General equation:

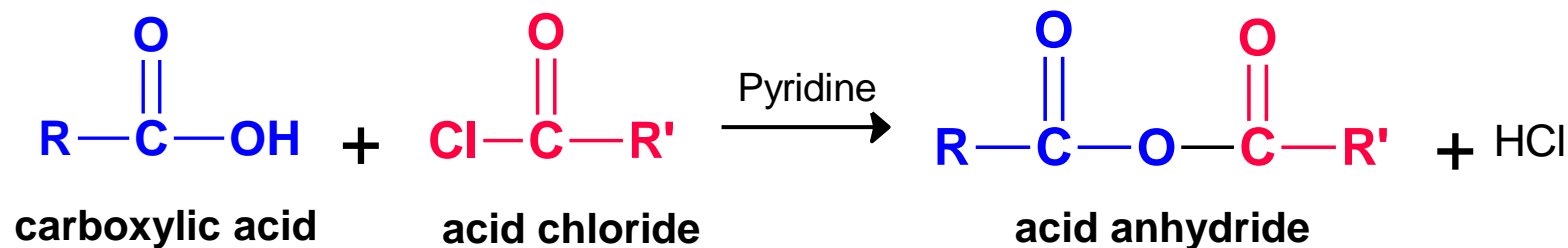


EXAMPLES

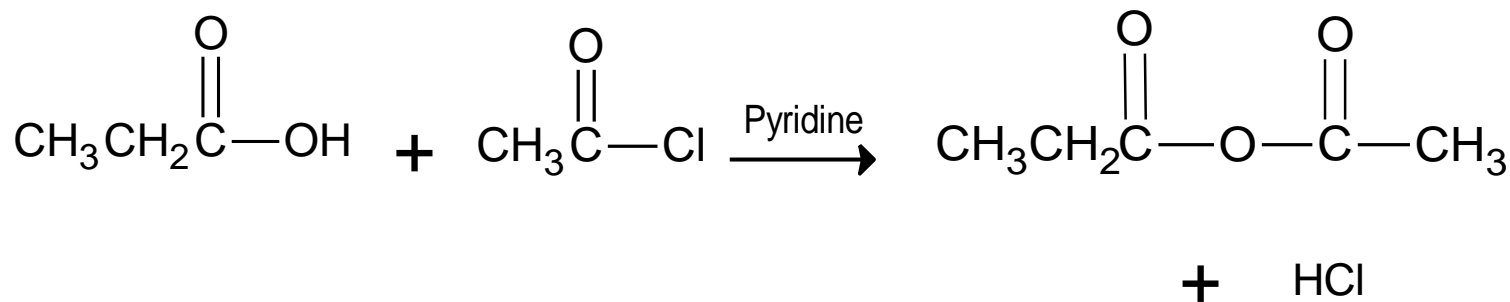


- Acid anhydride also can be prepared by reacting carboxylic acid with **acyl chloride in the presence of pyridine**.

General equation:



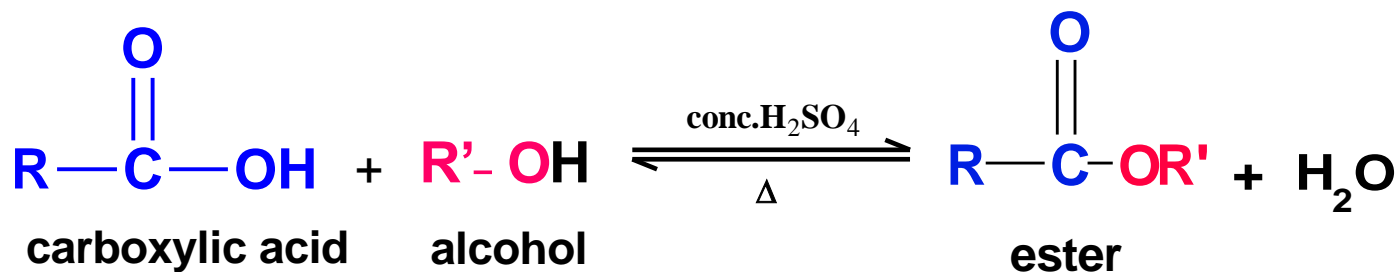
EXAMPLES



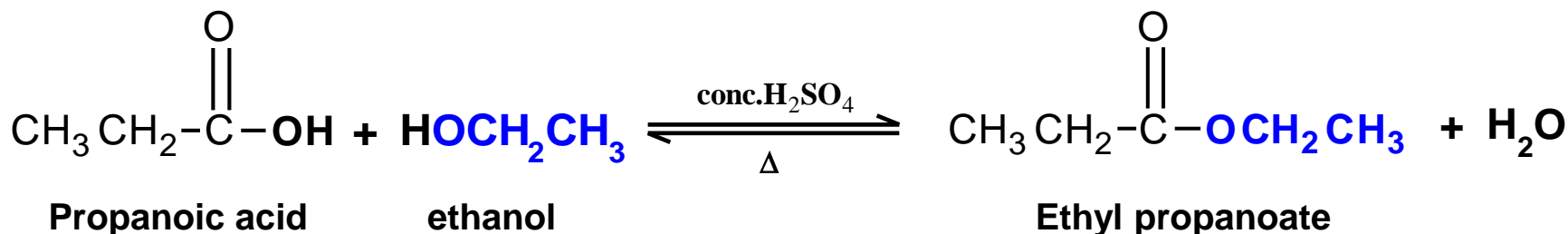
➤ Esterification

Carboxylic acids react with alcohols in the presence of mineral acid catalyst to produce **ester**

General equation:



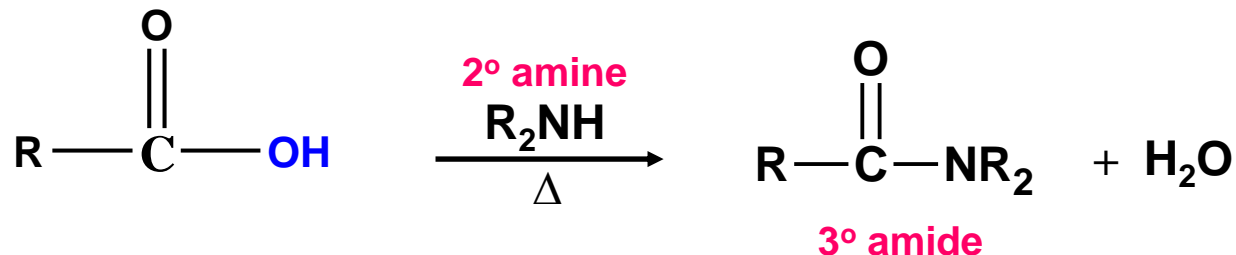
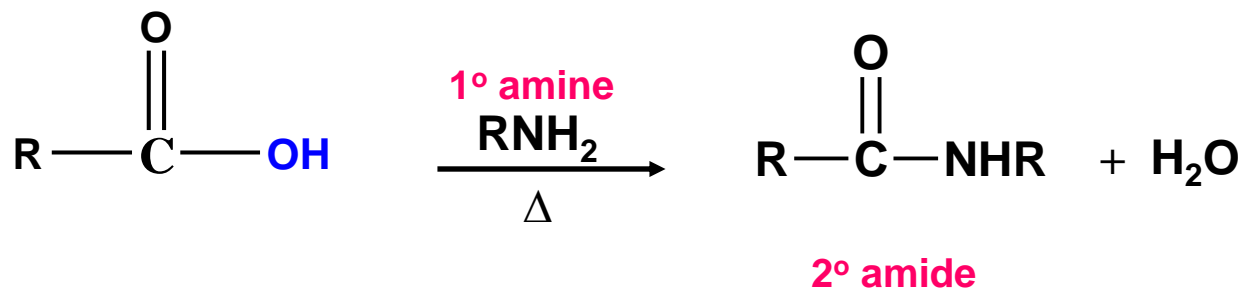
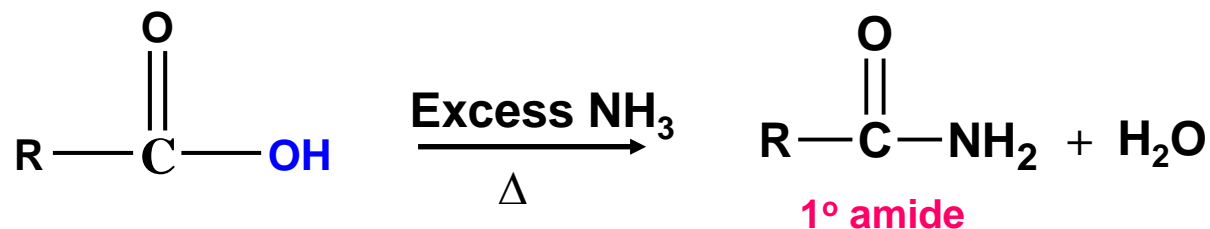
EXAMPLES



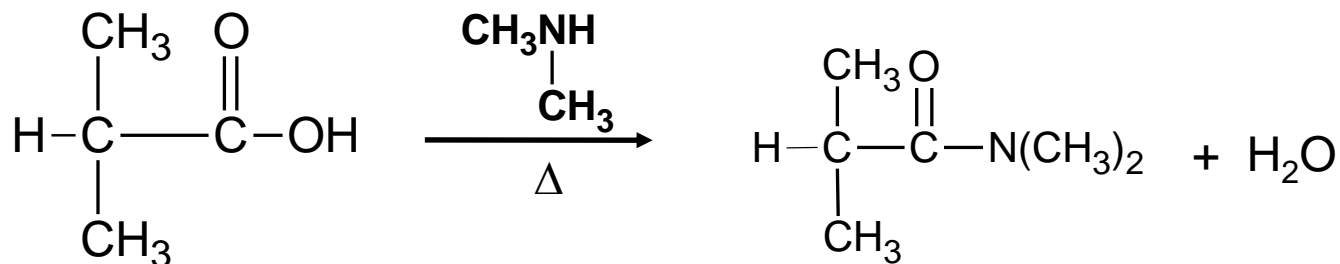
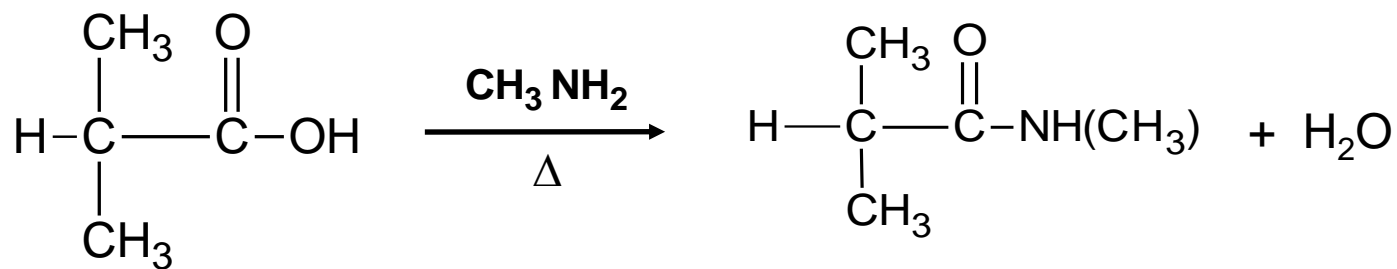
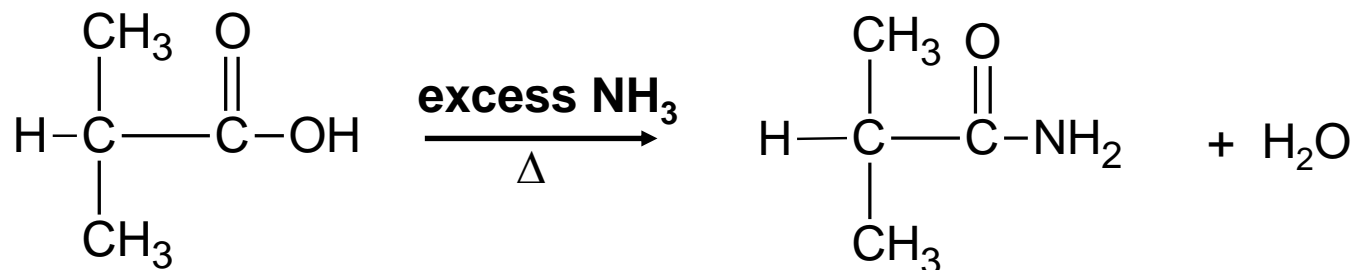
➤ Amide formation

Reaction of carboxylic acids with an ammonia or amine followed by heating.

General equation:



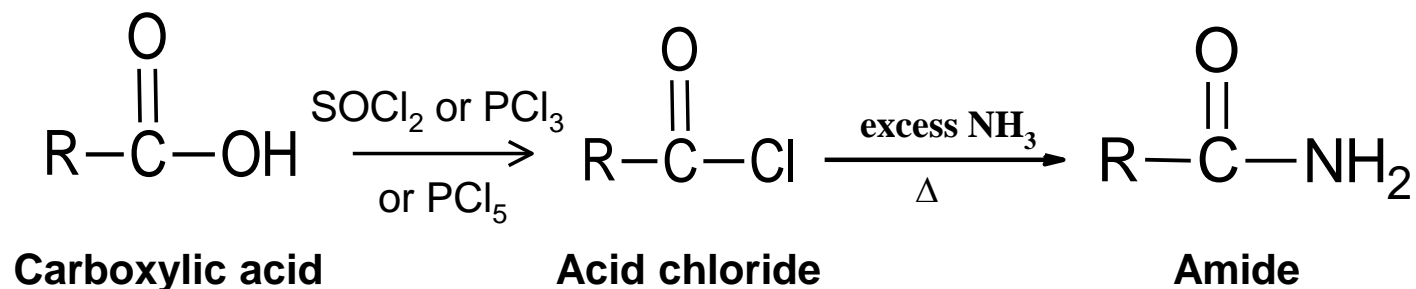
EXAMPLES



However.....

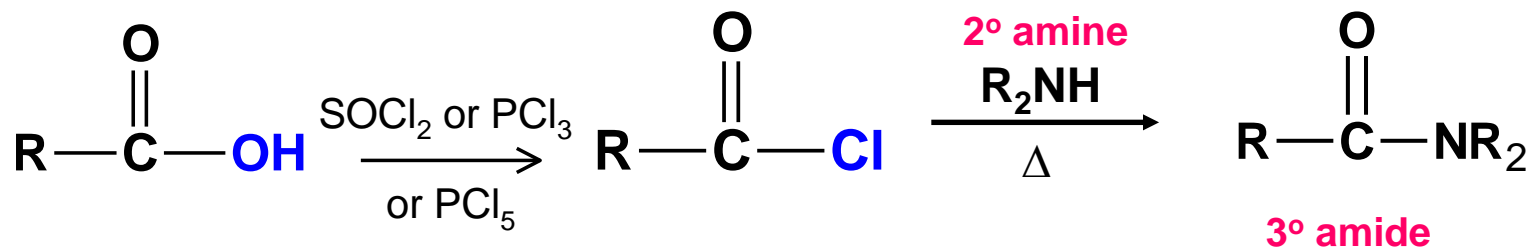
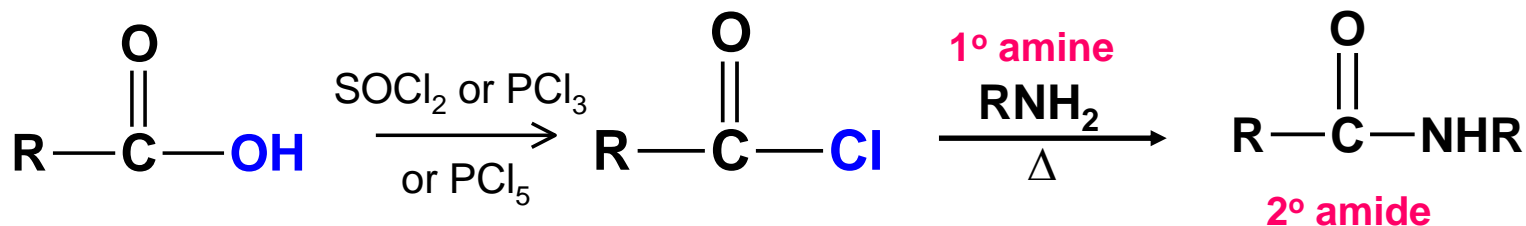
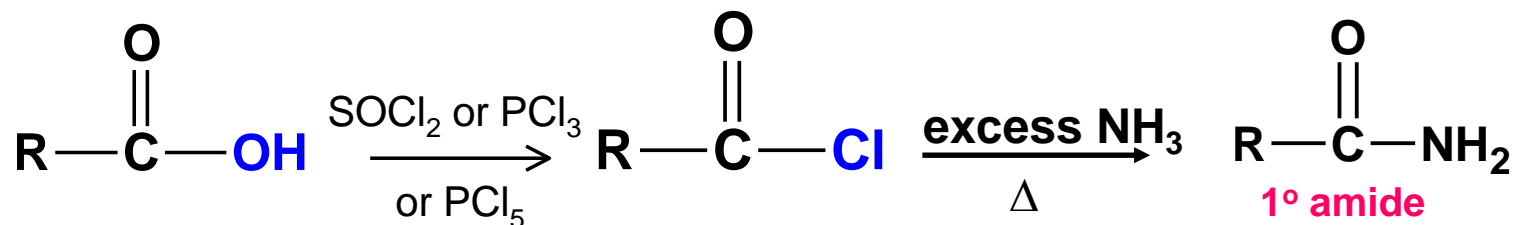
- Amide is **not favourably** prepared directly from a carboxylic acid due to its reactivity.
- It is usually prepared through **acid chloride** which is more reactive than carboxylic acid.
- The reaction of carboxylic acids with **SOCl₂/PCl₃/PCl₅** formed **acyl chloride** which is then react with **ammonia or amine**.

General equation:



EXAMPLES

Amides formation through acyl chloride



Learning outcomes

10.4 Chemical Properties of Carboxylic Acids

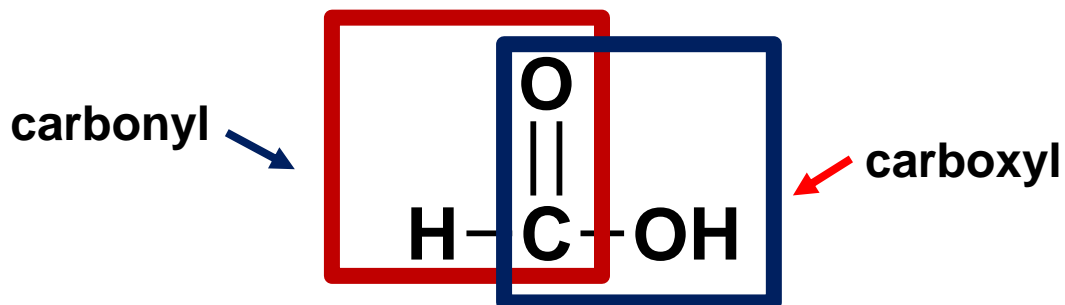
b) Explain the reducing property of methanoic acid with :
(C3 & C4)

i. $\text{KMnO}_4 / \text{H}_3\text{O}^+$

ii. Tollens' reagent

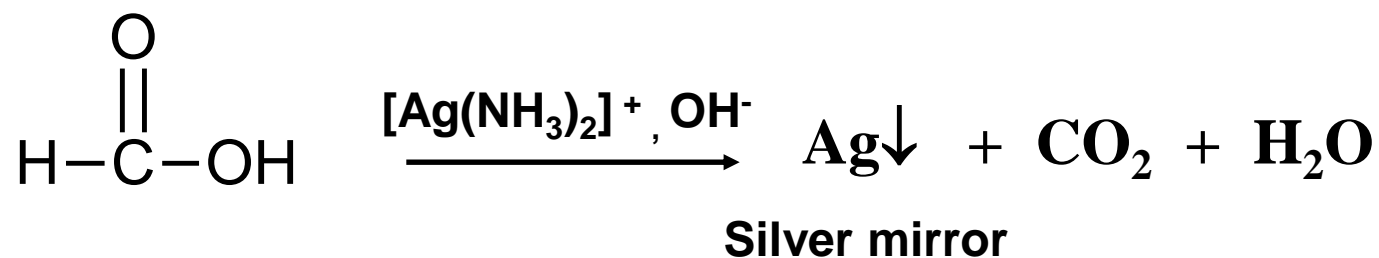
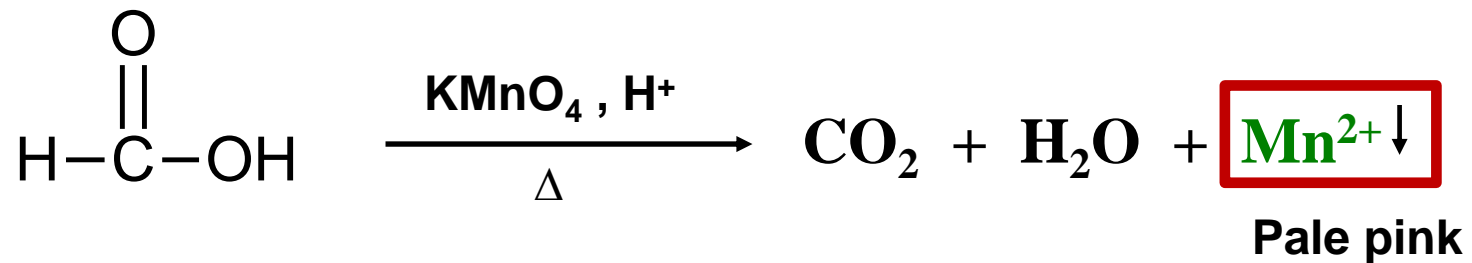


Methanoic acid, HCOOH as a reducing agent



- Methanoic acid molecule has both **carboxyl** and **carbonyl group**
- It shows the properties of both carboxylic acid and aldehyde
- It also shows reducing properties in reactions with acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ and Tollens' reagent.

EXAMPLES



Learning outcomes

10.4 Chemical Properties of Carboxylic Acids

- c) Outline the synthesis of compounds related to reactions of carboxylic acids. (C3 & C4)

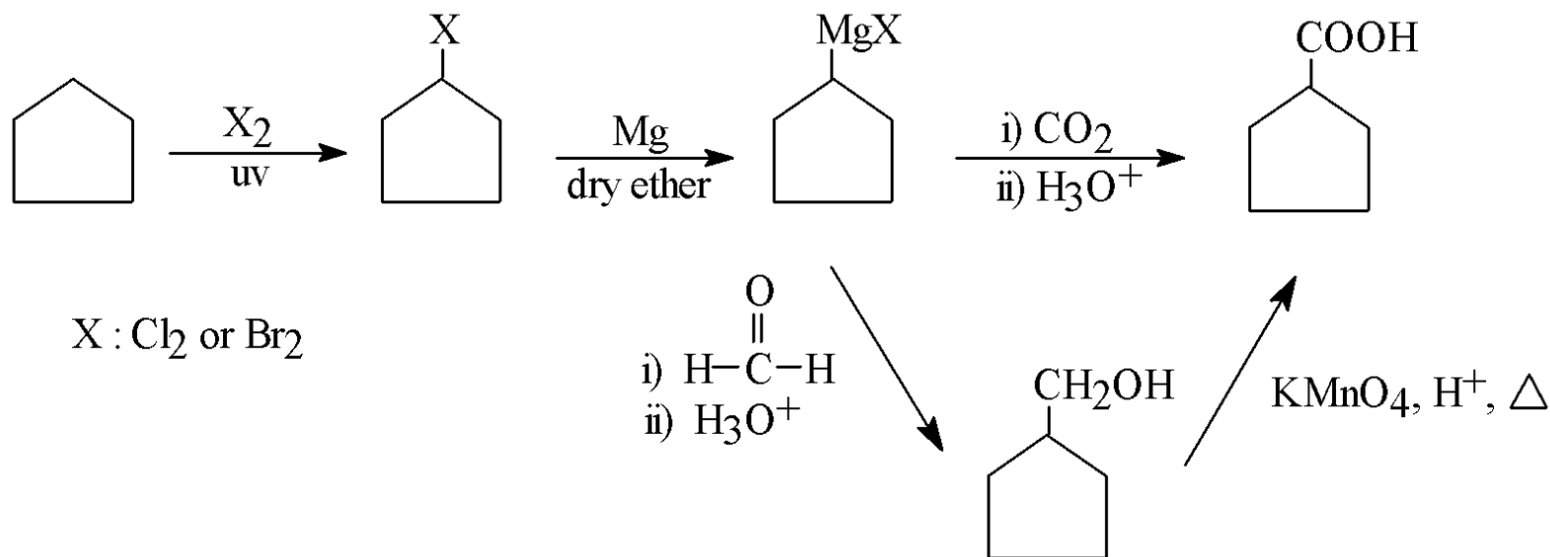
** Limit to maximum 4 steps only*



EXAMPLES

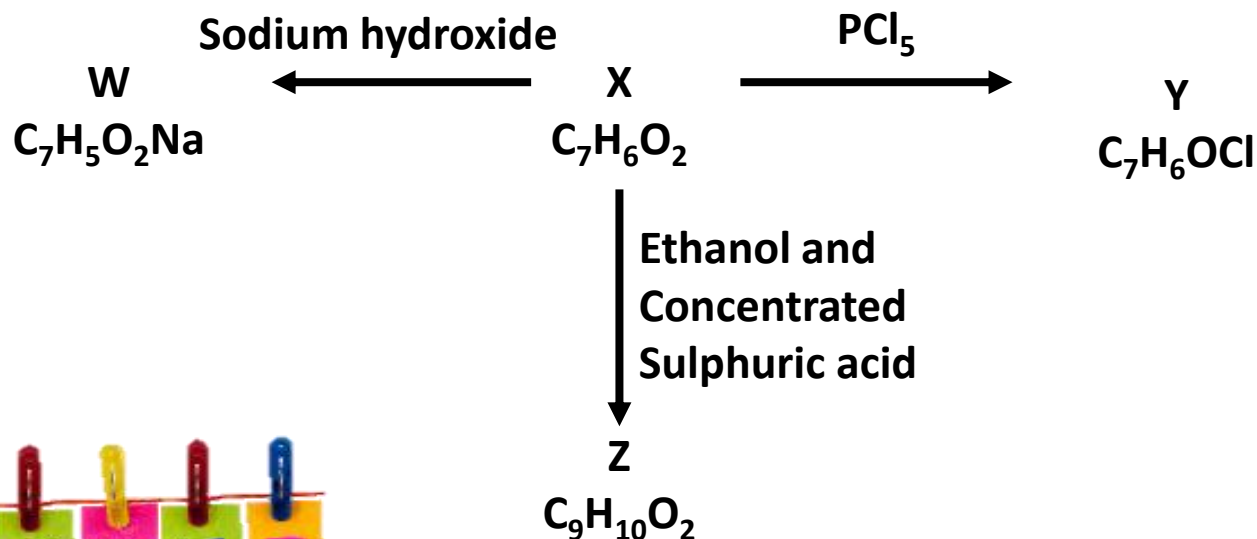
Propose a synthetic route for the preparation of cyclopentanecarboxylic acid from cyclopentane via Grignard reagent.

ANSWER



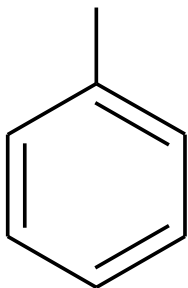
EXAMPLES

Some reactions of organic compounds W to Z are shown in the flow chart below. Suggest the structures of W, X, Y and Z.

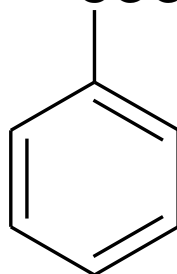


ANSWER

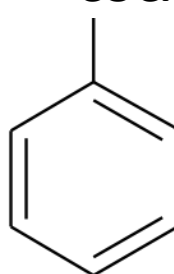
X: COOH



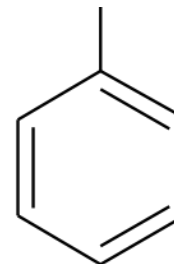
W: COO⁻Na⁺



Y: COCl



Z: COOCH₂CH₃



Learning outcomes

10.4 Chemical Properties of Carboxylic Acids

d) Explain the preparation of synthetic polymers through condensation polymerisation to produce polyamides (e.g Kevlar, nylon 6, nylon 6,6) and polyester (e.g Dacron/terylene). (C3 & C4)



PREPARATION OF SYNTHETIC POLYMERS

CONDENSATION POLYMERISATION

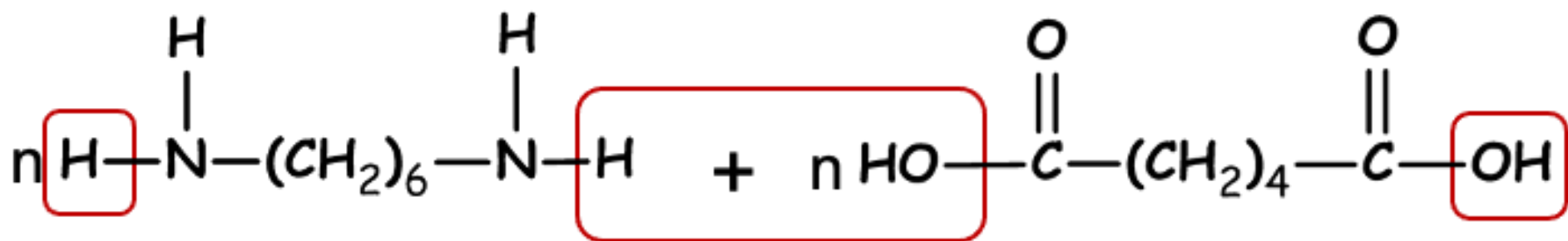
- A chemical process in which **2 monomers** react to form a **larger** molecule and **eliminate** a smaller molecule.
- Formed condensation polymers (polyamides and polyester).
- The monomers must have **at least two functional groups** to act as the reactive ends.

When a carboxylic acid with two -COOH groups reacts with an amine with two -NH_2 groups, a **polyamide** is formed.

When a carboxylic acid with two -COOH groups reacts with an alcohol with two -OH groups, a **polyester** is formed.

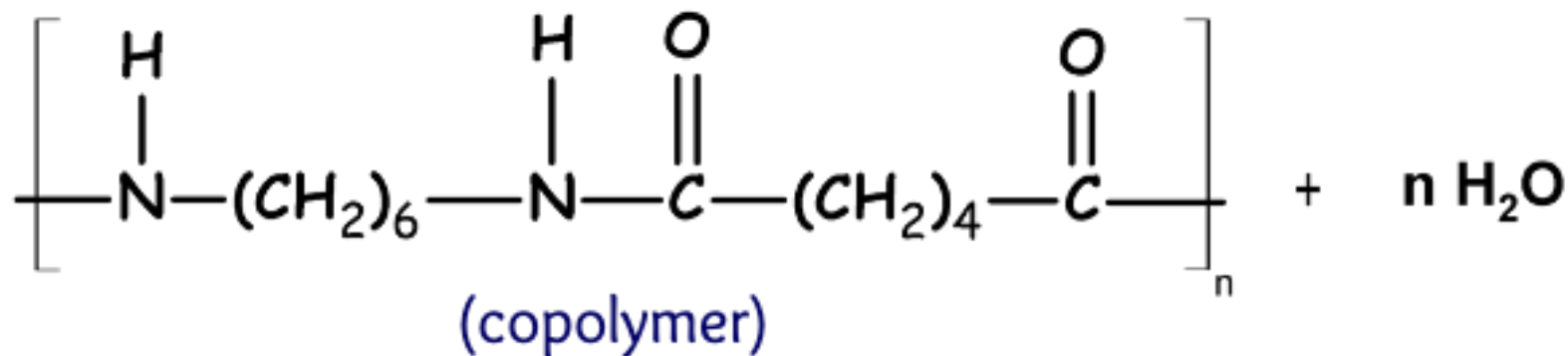
PREPARATION OF SYNTHETIC POLYMERS

CONDENSATION POLYMERISATION (POLYAMIDES): **NYLON 6,6**



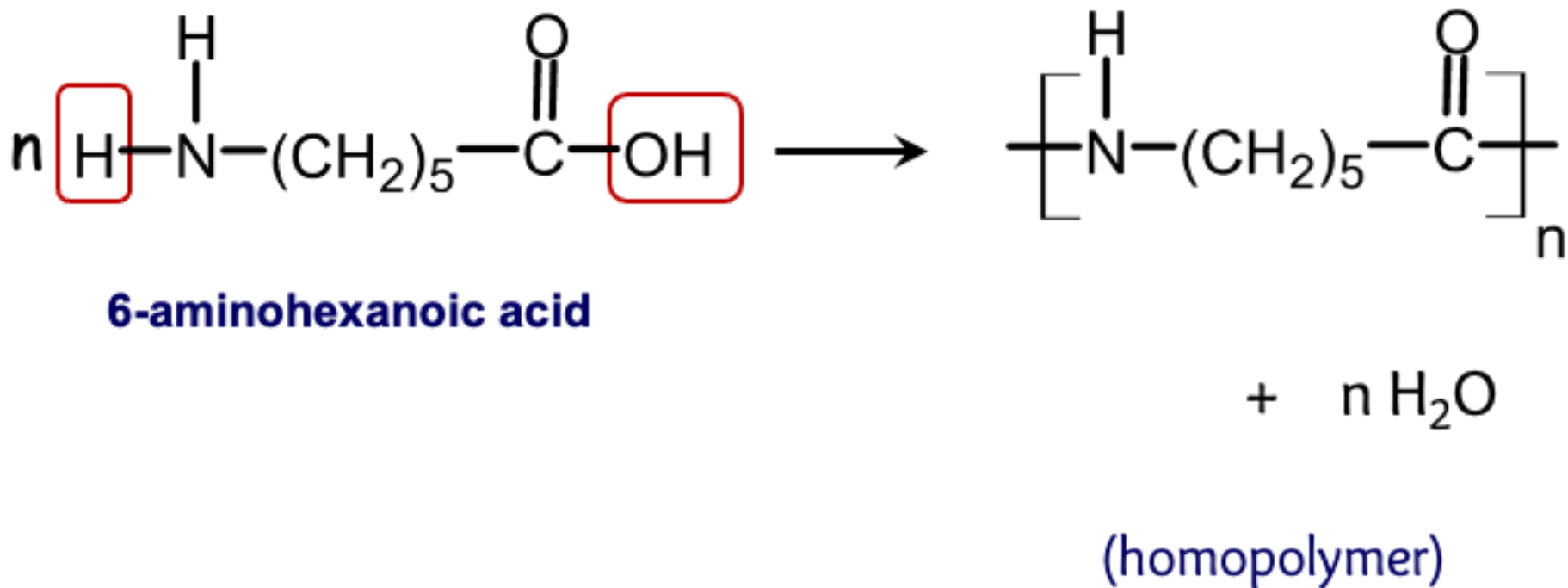
1,6-hexanediamine

hexanedioic acid



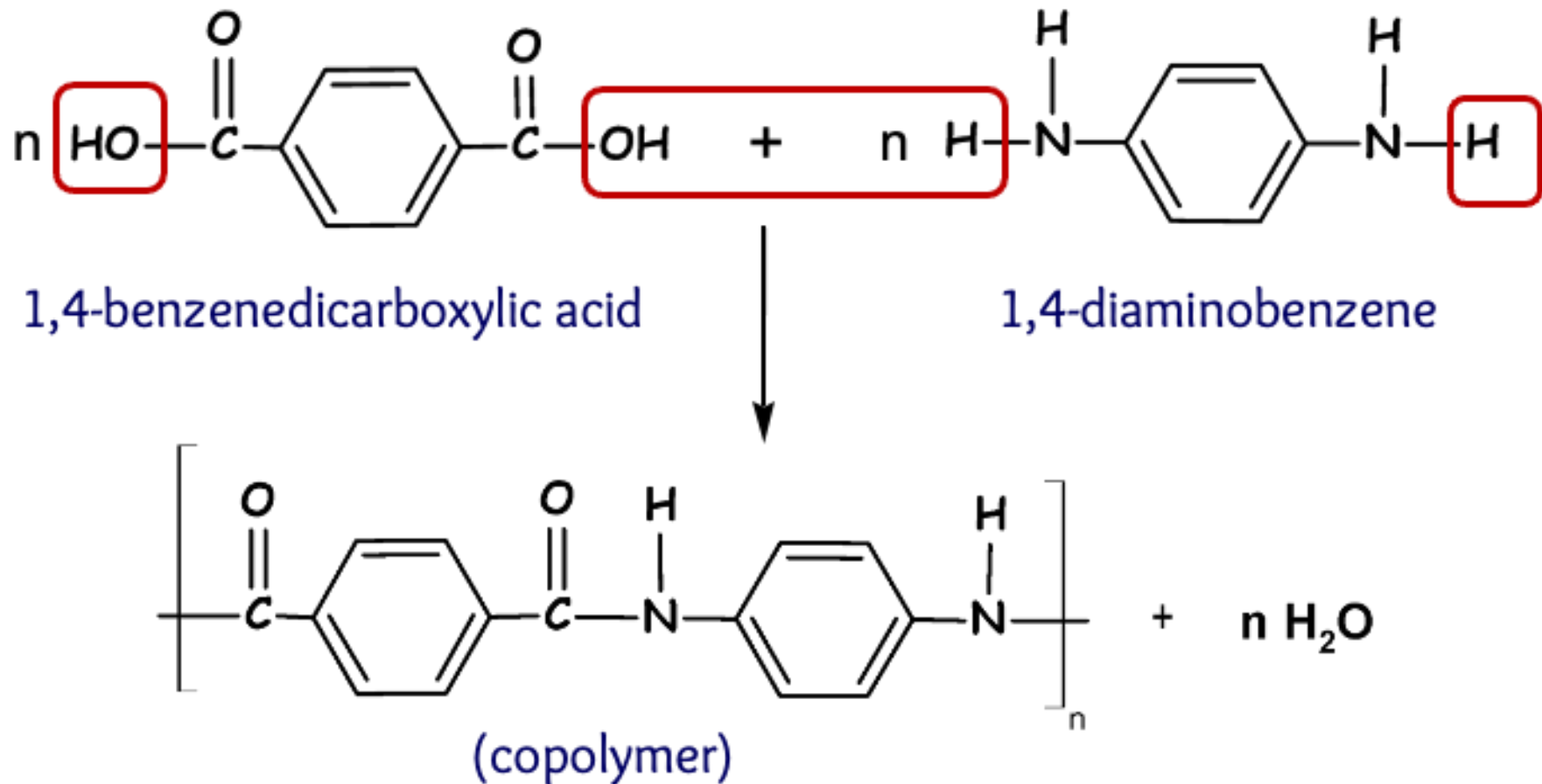
PREPARATION OF SYNTHETIC POLYMERS

CONDENSATION POLYMERISATION (POLYAMIDES): **NYLON 6**



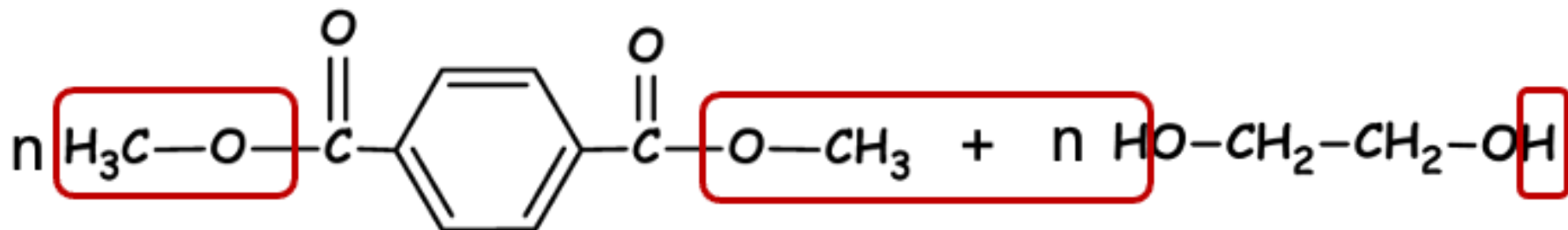
PREPARATION OF SYNTHETIC POLYMERS

CONDENSATION POLYMERISATION (POLYAMIDES): KEVLAR



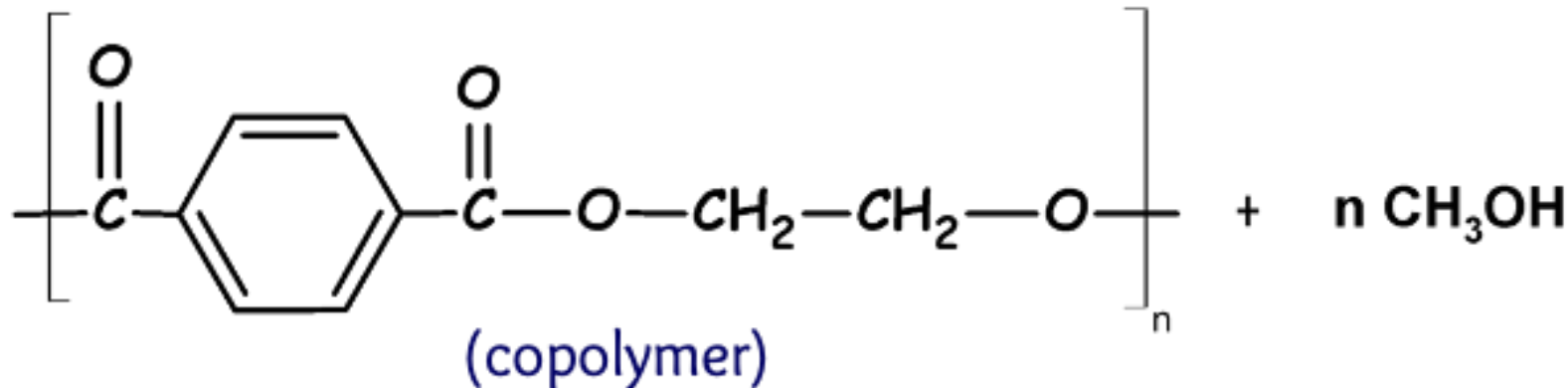
PREPARATION OF SYNTHETIC POLYMERS

CONDENSATION POLYMERISATION (POLYESTER): DACRON



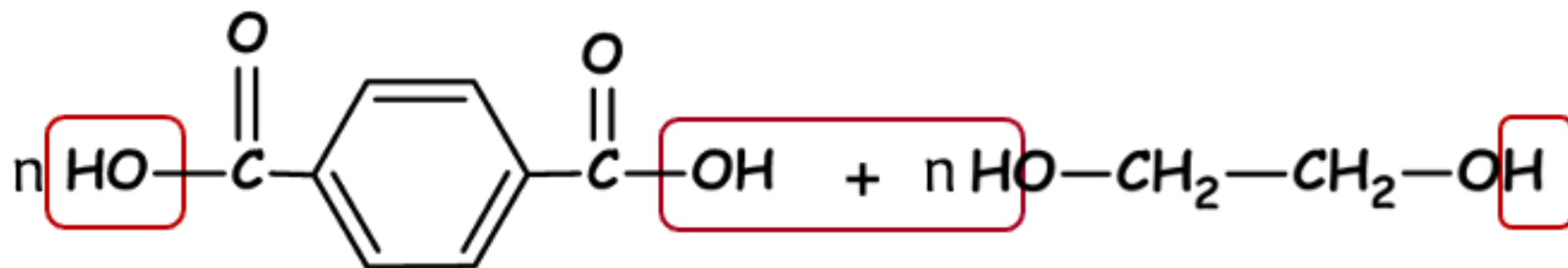
dimethyl 1,4-benzenedicarboxylate

1,2-ethanediol



PREPARATION OF SYNTHETIC POLYMERS

CONDENSATION POLYMERISATION (POLYESTER): **TERYLENE**



1,4-benzenedicarboxylic acid

1,2-ethanediol

