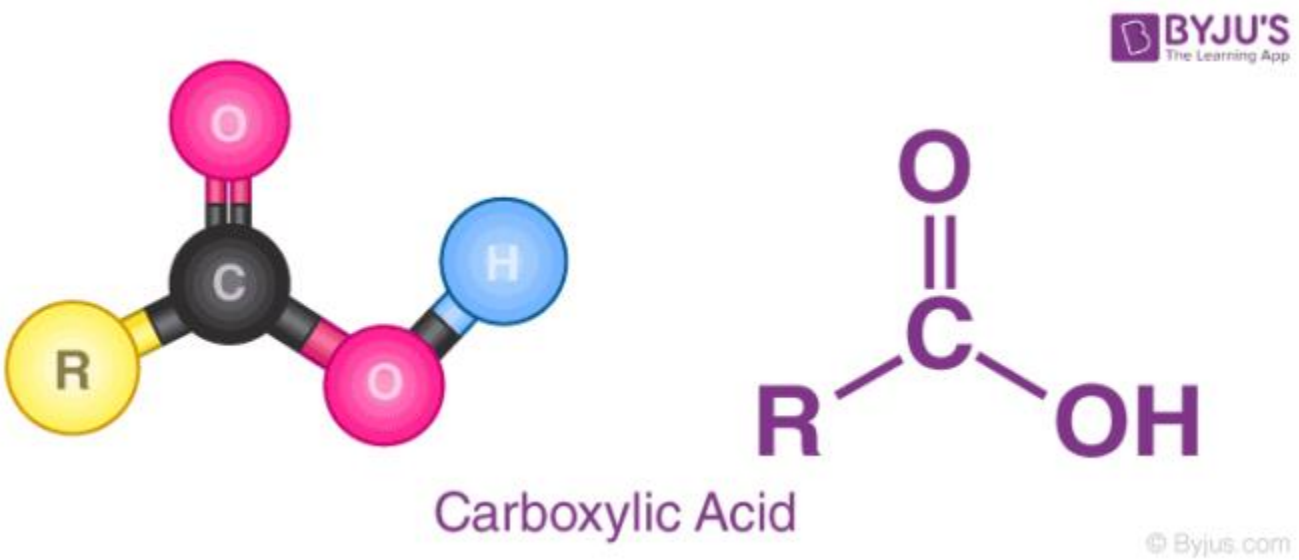
# CHAPTER 11
# CARBOXYLIC ACIDS AND DERIVATIVES




Hussein Semaan

# CARBOXYLIC ACID

**Definition :**

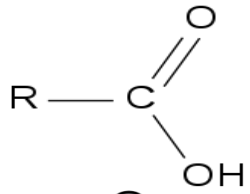
**A monocarboxylic acid is a compound which contains one carboxyl group -COOH in its structure**

**1- General formula:** $C_nH_{2n}O_2$

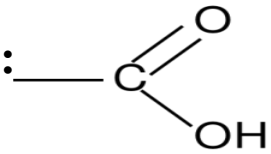
**6- Name :**

Alkane ⇨ alkanoic acid

**2- Structural formula :**

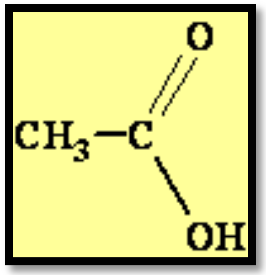



**3- Functional group:**

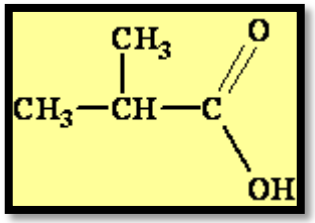



**4- Name of functional group:** carboxyl group

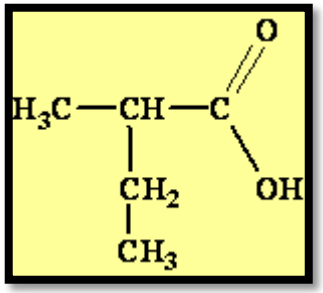
**5- Molar mass :** 14n+32



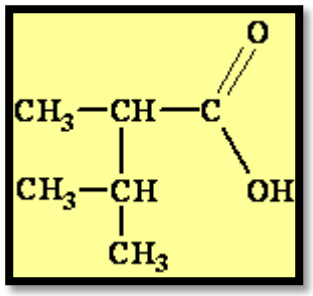

**Ethanoic acid**




**2-methylpropanoic acid**




**2-methylbutanoic acid**



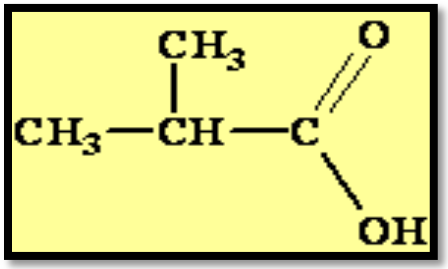

**2,3-dimethylbutanoic acid**

## 7-Isomers:

Write all possible structural formula of carboxylic acid of formula $C_4H_8O_2$

Butanoic acid : $CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH$

**2-methylpropanoic acid :**




Remark:
- Carboxylic acids have skeletal isomer and functional isomers (ester)

## 8-Reactions of carboxylic acids:

### 8.1- Reaction With calcium carbonate:

$$2RCOOH + CaCO_3 \rightarrow 2RCOO^- + Ca^{2+} + CO_2 + H_2O$$

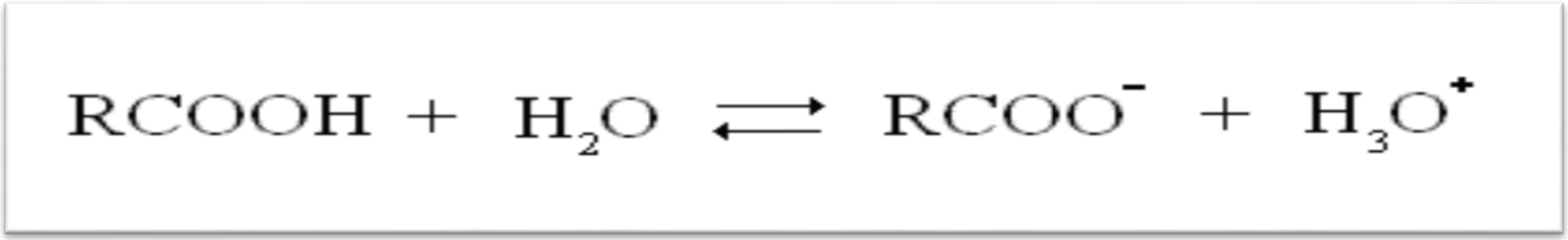
**Remark :**

**1- carbon dioxide make lime water turbid**

2- **$RCOO^-$ is called carboxylate ion and its name is alkanoate ion**

**Example :** $CH3COO^-$ **ethanoate ion**

## 8.2- reaction with water:




## 8.3-reaction with metal:

$$2RCOOH + Mg \rightarrow 2RCOO^- + Mg^{2+} + H_2$$

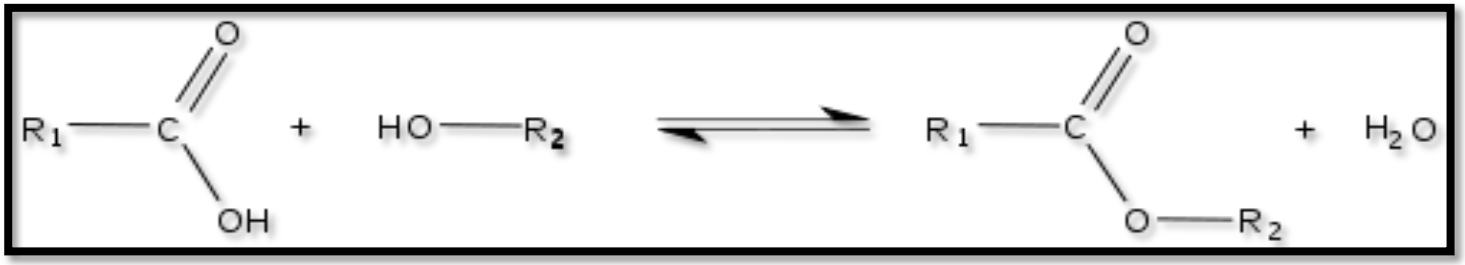
Remark :

Hydrogen gas give a pop sound

## 8.4- esterification:

Slow,reversible and athermic

Carboxylic acid + alcohol ⟷ ester + water



# Carboxylic Acid Derivatives

Hussein Semaan

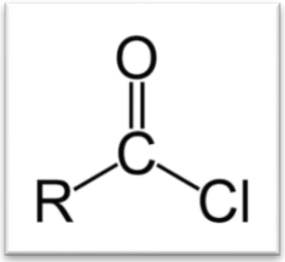
## A- acyl chlorides:

**1-General formula** : $C_nH_{2n-1}OCl$

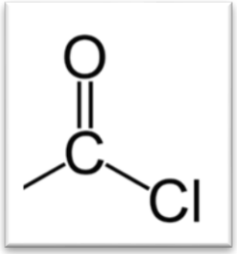
**6-Name:**

Alkane ⟹ alkanoyl chloride

**2-structural formula:**

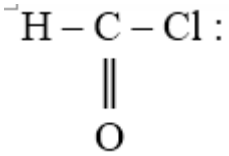



**3-Functional group:**

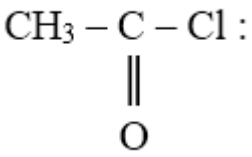



**4-Name of functional group:** acyl chloride group

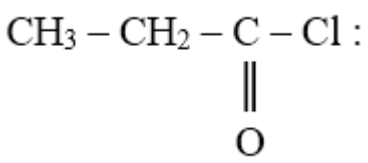
**5-Molar mass:** 14n+50,5



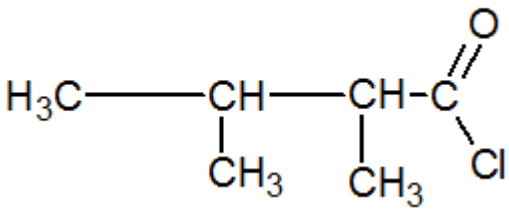
Methanoyl chloride



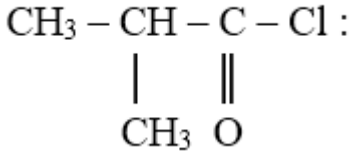
Ethanoyl chloride



Propanoyl chloride

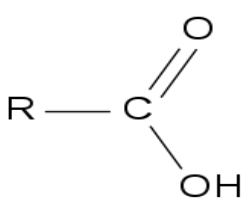


2,3-dimethylbutanoyl chloride

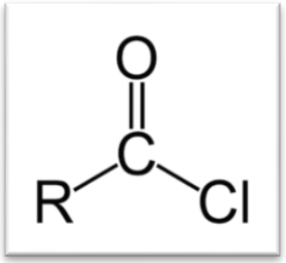


2-methylpropanoyl chloride

## 7- Preparation Of Acyl Chlorides:

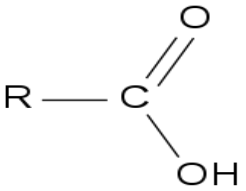



$+ SOCl_2 \rightarrow$

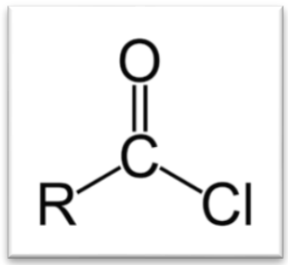



$+ SO_2 + HCl$

or




$+ PCl_5 \rightarrow$




$+ POCl_3 + HCl$

**$SOCl_2$ : thionyl chloride**

**$PCl_5$ : phosphorus pentachloride**

**Hydrolysis Of Acyl Chlorides:**

$$RCOCl + H_2O \rightarrow RCOOH + HCl$$

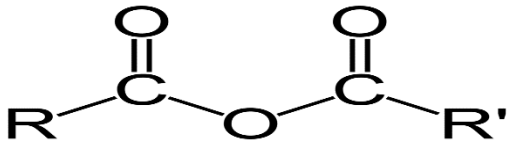
**Remark**

**Acyl chloride is conserved in dry container to avoid it hydrolysis into carboxylic acid**

## B- acid anhydride:

**1- general formula:** $C_nH_{2n-2}O_3$

**2- structural formula:**



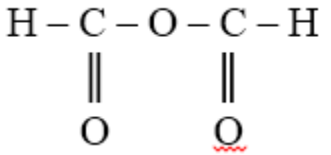

**3- functional group:**

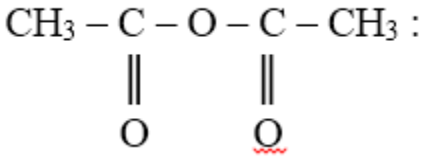

**4- name of functional group:** acid anhydride group

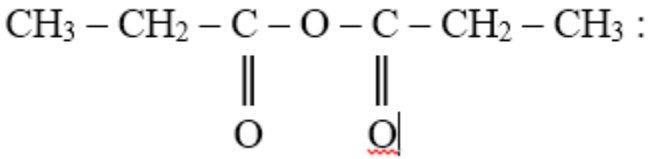
**5- molar mass:** 14n+46

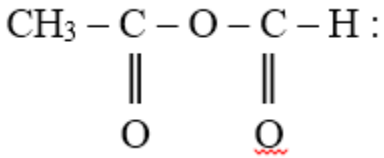
**6- name:**

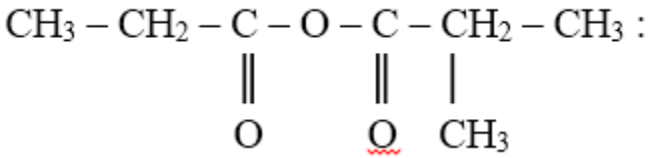
Alkane ⟹ alkanoic anhydride


: Methanoic anhydride

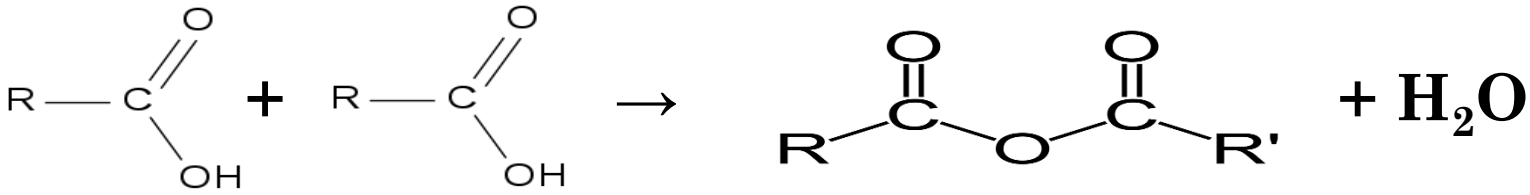

: ethanoic anhydride


: propanoic anhydride


: Ethanoic methanoic anhydride


: Propanoic 2-methylpropanoic anhydride

## 7- Preparation Of Acid Anhydrides (dehydration reaction)




This reaction took place in presence of a dehydrating agent that eliminate water and make the reaction complete

The dehydrating agent are : $P_2O_5$ ou $P_4O_{10}$

**Hydrolysis of acid anhydride:**

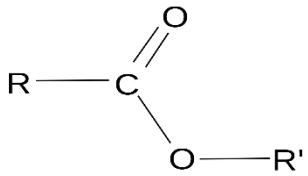
**$R–CO–O–CO–R + H_2O \rightarrow 2R–COOH$**

Acid anhydride should be conserved in a dry container to avoid its hydrolysis into carboxylic acid

## C- Ester:

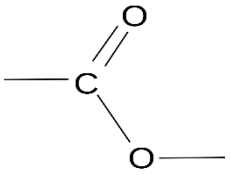
**1- general formula:** $C_nH_{2n}O_2$

**2- structural formula:**



Ester

**3- functional group :**




**4- name of functional group: ester group**

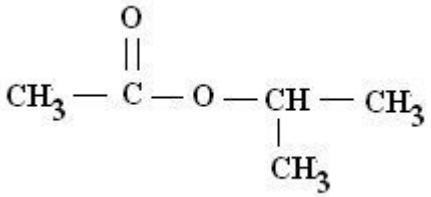
**5- molar mass:** 14n +32

**6- name:** alkyl alkanoate

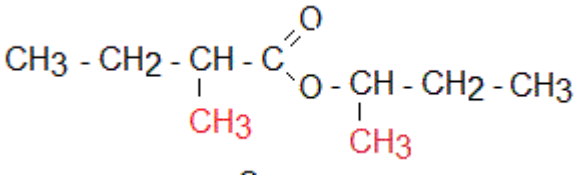
$H\text{-}COO\text{-}CH_3$ Methyl methanoate

$CH_3\text{-}\ COO\text{-}\ CH_3$ Methyl ethanoate

$CH_3\text{-}COO\text{-}CH_2CH_3$ ethyl ethanoate



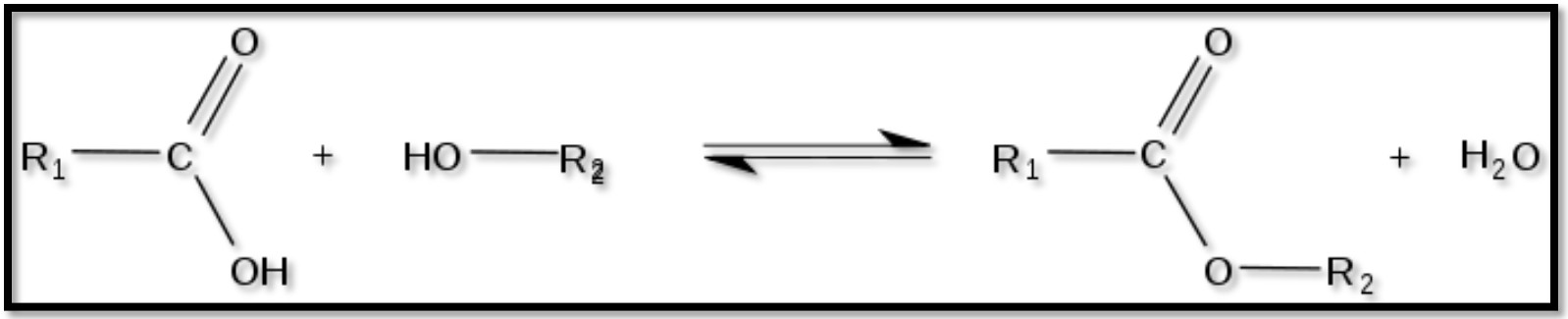
1-methylethyl ethanoate



1-methylpropyl-2-methylbutanoate

## 7- preparation of an ester :

Direct method: slow, reversible athermic

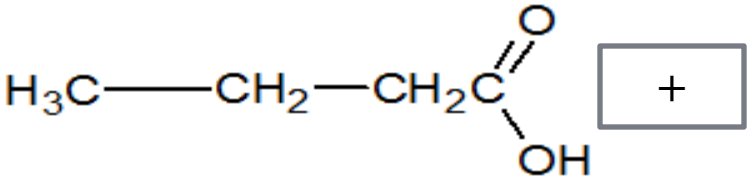



1- this reaction took place in presence of sulfuric acid as a catalyst
2- this reaction is heated using reflux heating to increase the rate of the reaction and avoid the loose of reactants and products by evaporation

At equilibrium and if the mixture is equimolar

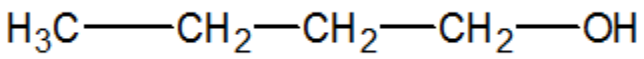
the percentage yield of esterification is

- 67% if the alcohol is primary
- 60% if the alcohol is secondary
- <5 % if the alcohol is tertiary

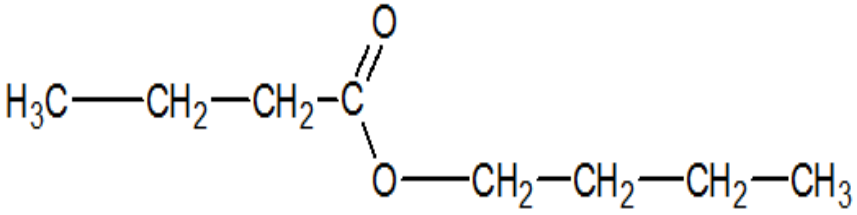


Butanoic acid

+



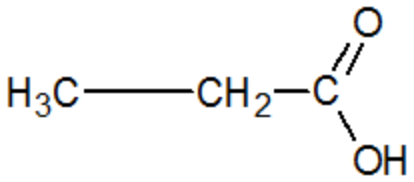
1-butanol



+

$H_2O$

Butyl butanoate

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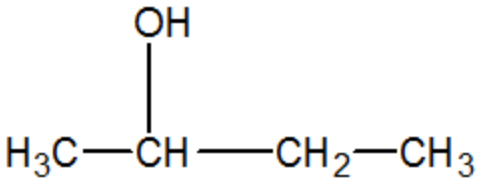
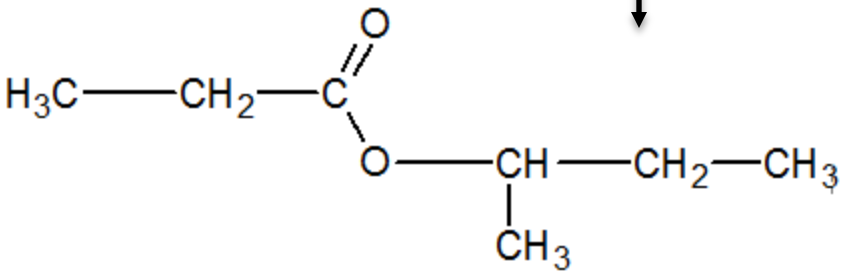



Propanoic acid

2-butanol





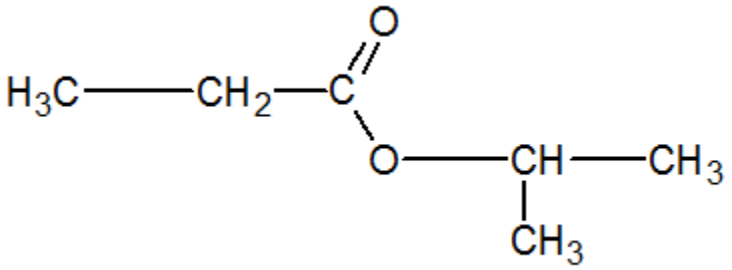

+

$H_2O$

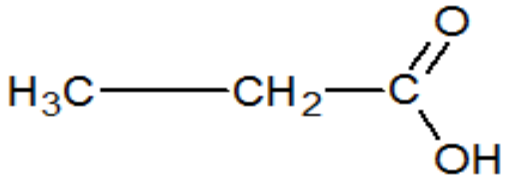
1-methylpropyl propanoate

## 8- hydrolysis of an ester in acidic medium:

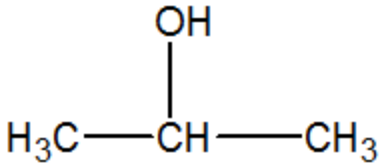

- At equilibrium and if the mixture is equimolar the percentage yield of hydrolysis is
  - 33% if the alcohol is primary
  - 40% if the alcohol is secondary
  - >95 % if the alcohol is tertiary



1-methylethyl propanoate



Propanoic acid

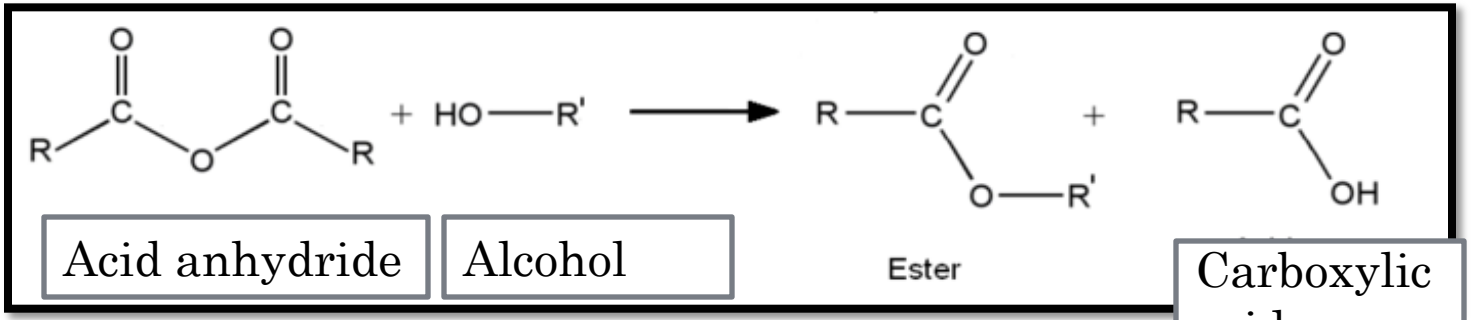


2-propanol

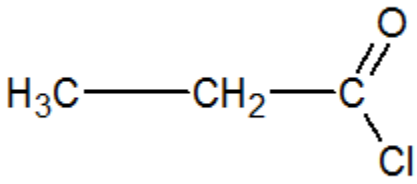
## 9- preparation of an ester using derivative of carboxylic acids

**Using derivatives of carboxylic acids such as acyl chlorides and acid anhydride make the reaction total, fast and exothermic**


Acyl chloride | Alcohol | Hydrogen Chloride




Acid anhydride | Alcohol | Carboxylic acid

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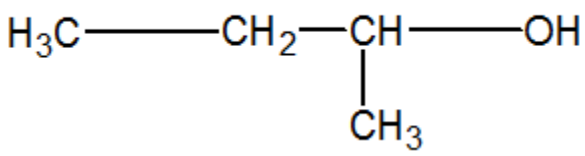
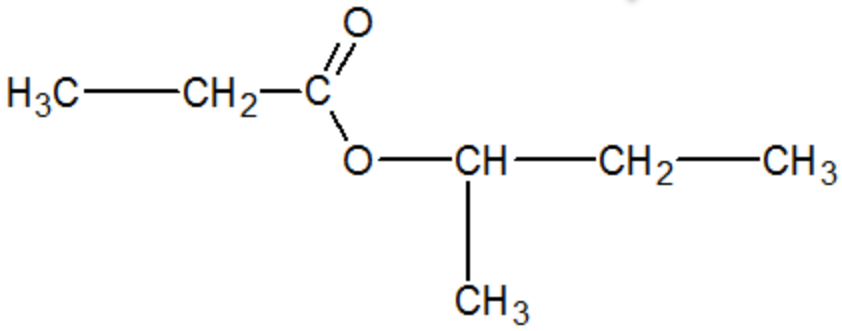



Propanoyl chloride

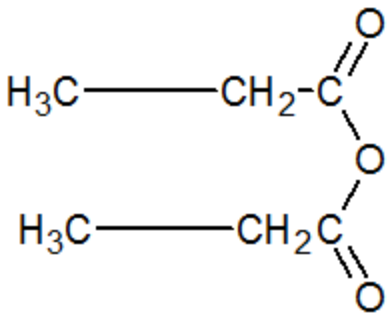
2-butanol




+

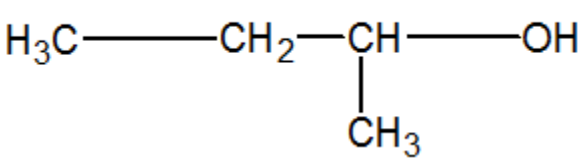
HCl

1-methylpropyl propanoate

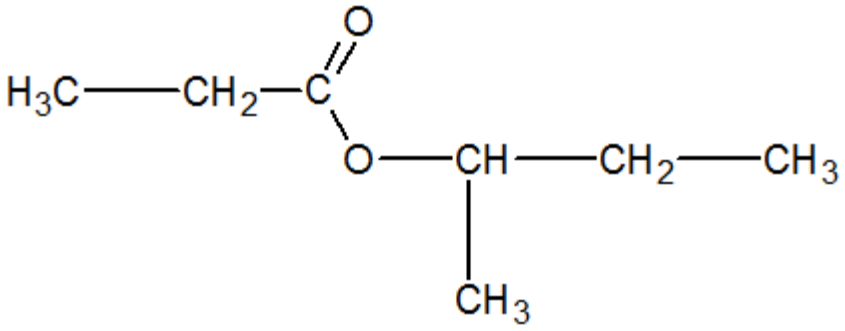


Propanoic anhydride

+

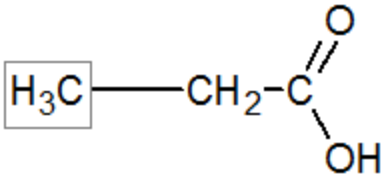


2-butanol



1-methylpropyl propanoate

+



Propanoic acid