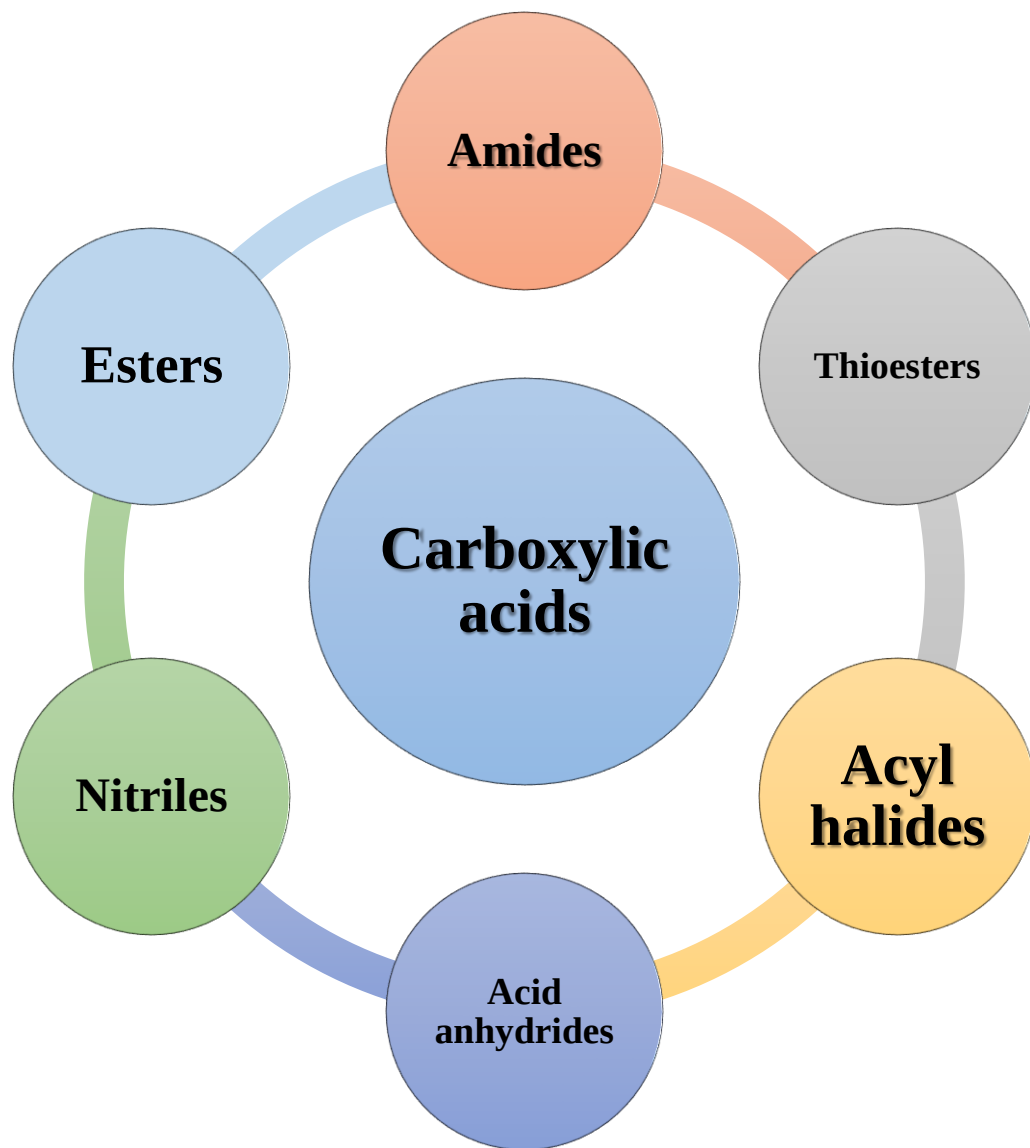


Carboxylic acids & derivatives



Carboxylic acids



Content

Introduction

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Acidity

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Reactions

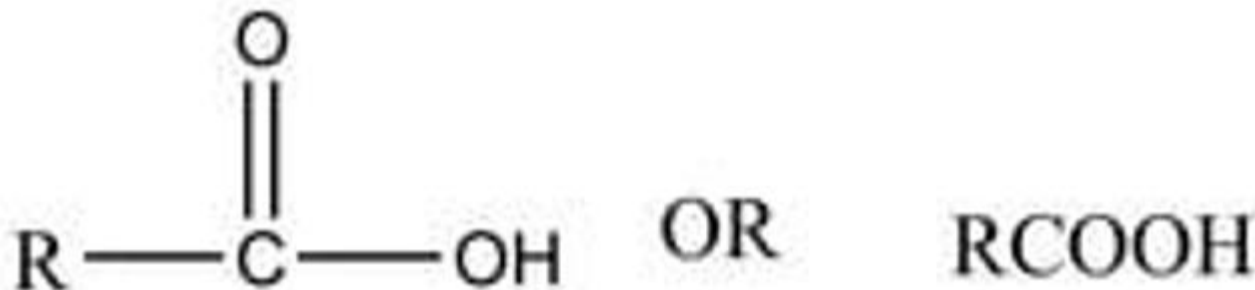
Examples



Introduction



- **Carboxylic acids:** are organic compounds that contain carboxyl functional group.
- The name carboxyl is derived from **carbonyl (C=O)** and **hydroxyl (OH)**, because in the carboxyl group these two groups are directly bonded to each other.

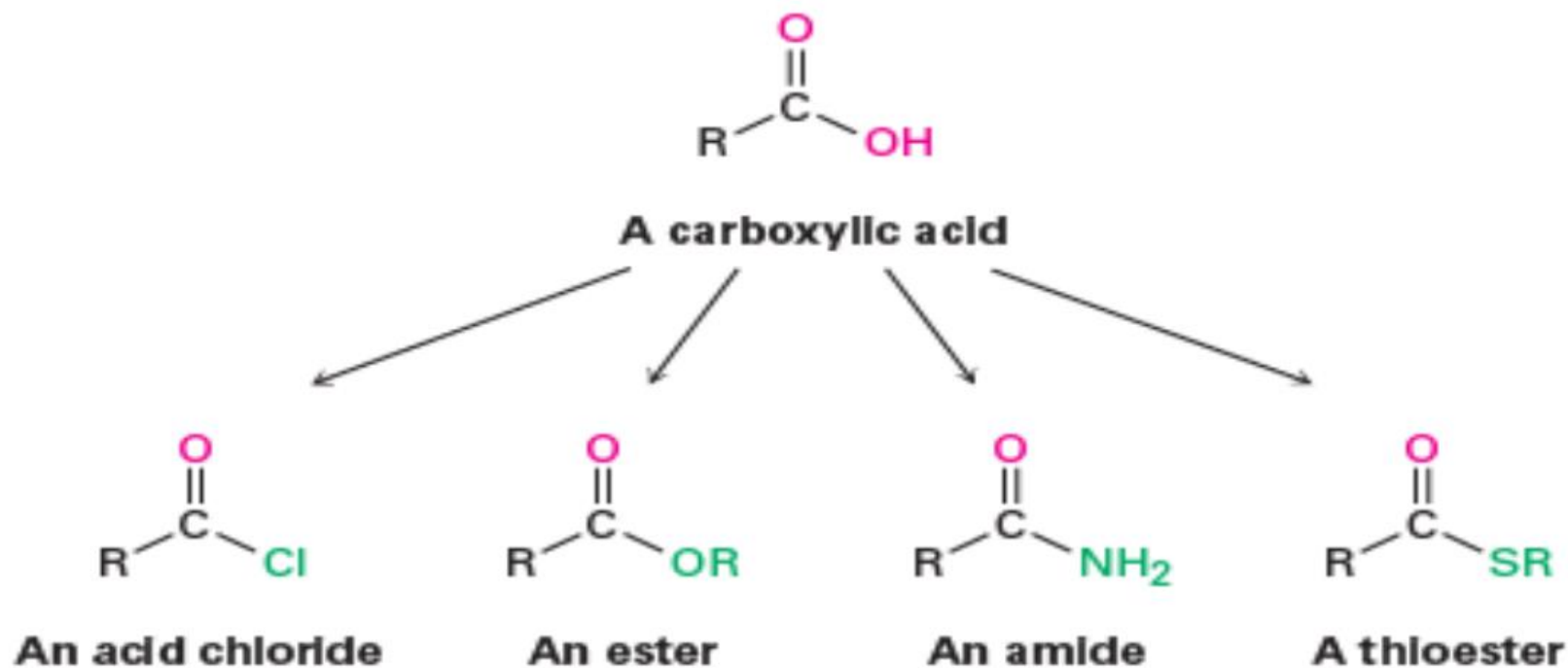


- Carboxylic acids, RCO_2H , occupy a central place among carbonyl compounds.

Introduction



- Not only are they valuable in themselves, they also serve as **starting materials** for preparing numerous carboxylic acid derivatives such as **acid chlorides**, **esters**, **amides**, and **thioesters**.



Introduction



- In addition, carboxylic acids are present in the majority of **biological pathways**.
- Carboxylic acids are further classified as **mono-**, **di-**, and **tricarboxylic acid**.
- The long chain monocarboxylic acids are commonly known as **fatty acids**.

Introduction

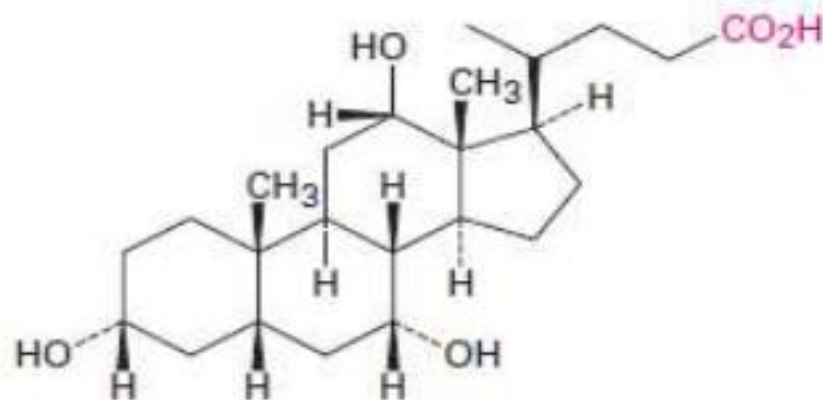


- A great many carboxylic acids are found in nature: **acetic acid**, $\text{CH}_3\text{CO}_2\text{H}$, is the chief organic component of vinegar; **butanoic acid**, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, is responsible for the rancid odour of sour butter; and **hexanoic acid (caproic acid)**, $\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$, is responsible for the unmistakable aroma of goats and dirty gym socks (the name comes from the Latin caper, meaning “goat”).

Introduction



- Other examples are **cholic acid**, a major component of human bile, and long chain aliphatic acids such as **palmitic acid**, $\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$, a biological precursor of fats and vegetable oils.



Cholic acid



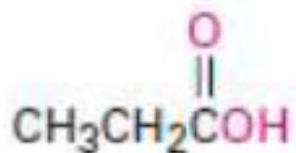
➤ Physical properties of carboxylic acids:

- ❖ Lower carboxylic acids are **liquids** with disagreeable odours.
- ❖ Boiling points and melting points of carboxylic acids increases with increasing molecular weight.
- ❖ Generally, they have **high boiling points** because of intermolecular interactions.
- ❖ Carboxylic acids are also interact with water molecules by **hydrogen bonding** through carbonyl and hydroxyl groups and because of these interactions, carboxylic acids are **more water soluble than alcohols, ethers, aldehydes, and ketones.**

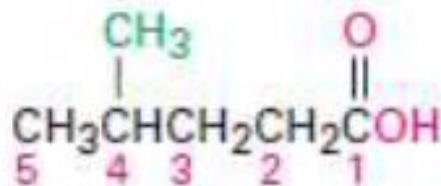
Naming



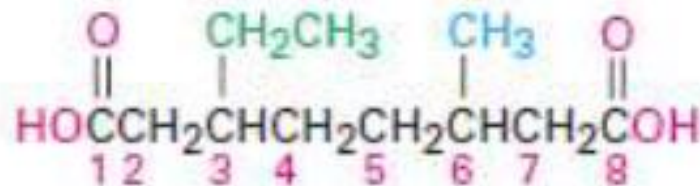
- Simple carboxylic acids derived from open-chain alkanes are systematically named by replacing the terminal **-e** of the corresponding alkane name with **-oic acid**. The CO₂H carbon atom is numbered C1.



Propanoic acid



4-Methylpentanoic acid

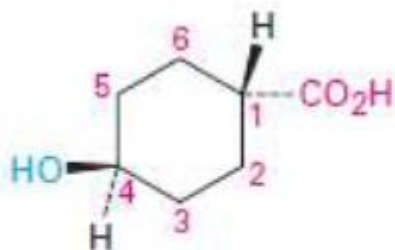


3-Ethyl-6-methyloctanedioic acid

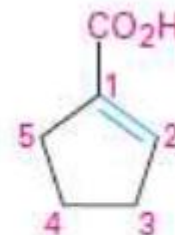
Naming



- Compounds that have a $\text{-CO}_2\text{H}$ group bonded to a ring are named using the suffix – **carboxylic acid**.
- The CO_2H carbon is attached to C1 in this system and is not itself numbered.
- As a substituent, the CO_2H group is called a carboxyl group.



trans-4-Hydroxycyclohexanecarboxylic acid



1-Cyclopentenecarboxylic acid

Naming



Molecular Structure	Common Name	IUPAC Name	Molecular Formula
	Formic acid	Methanoic acid	HCOOH
	Acetic acid	Ethanoic acid	CH ₃ COOH
	Propionic acid	Propanoic acid	CH ₃ CH ₂ COOH
	Butyric acid	Butanoic acid	CH ₃ CH ₂ CH ₂ COOH
	Valeric acid	Pentanoic acid	CH ₃ CH ₂ CH ₂ CH ₂ COOH
	Caproic acid	Hexanoic acid	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ COOH
	Acrylic acid	Propenoic acid	C ₂ H ₃ COOH
	Benzoic acid	Benzenecarboxylic acid	C ₆ H ₅ COOH

Acidity of carboxylic acids



- Carboxylic acids are **weak acids** and ionize in water according to the following equation:



- Carboxylic acids dissociate slightly in dilute aqueous solution to give **H₃O⁺** and the corresponding carboxylate anions, **RCO₂⁻**.

- The extent of dissociation is given by an acidity constant, **K_a**.

$$K_a = \frac{[\text{RCO}_2^-][\text{H}_3\text{O}^+]}{[\text{RCO}_2\text{H}]} \quad \text{and} \quad \text{p}K_a = -\log K_a$$

Acidity of carboxylic acids



- A list of K_a values for various carboxylic acids is given in table below.
- For most, K_a is approximately 10^{-4} to 10^{-5} .
- Acetic acid, for instance, has $K_a=1.75 \times 10^{-5}$ at 25 °C, which corresponds to a pK_a of 4.76.
- In practical terms, a K_a value near 10^{-5} means that only about 0.1% of the molecules in a 0.1 M solution are dissociated, as opposed to the 100% dissociation found with strong mineral acids like HCl.

Acidity of carboxylic acids



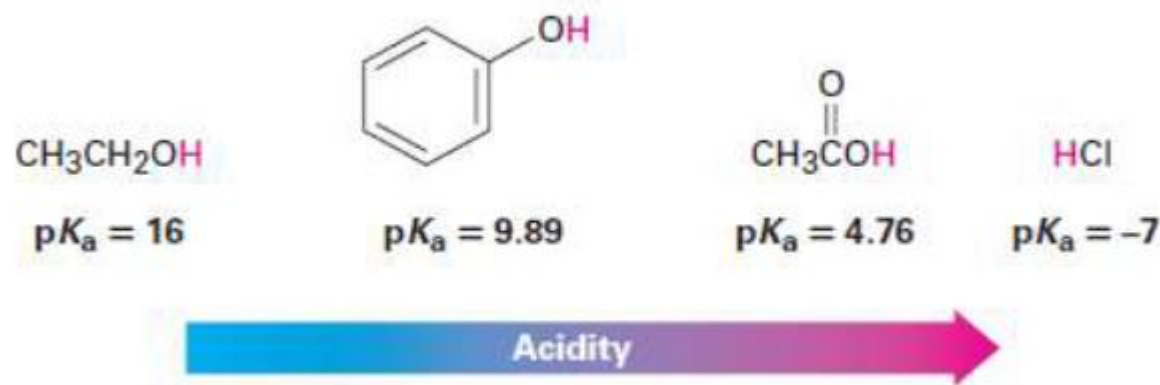
TABLE 20-3 Acidity of Some Carboxylic Acids

Structure	K_a	pK_a	
CF_3CO_2H	0.59	0.23	 Stronger acid Weaker acid
HCO_2H	1.77×10^{-4}	3.75	
$HOCH_2CO_2H$	1.5×10^{-4}	3.84	
$C_6H_5CO_2H$	6.46×10^{-5}	4.19	
$H_2C=CHCO_2H$	5.6×10^{-5}	4.25	
CH_3CO_2H	1.75×10^{-5}	4.76	
$CH_3CH_2CO_2H$	1.34×10^{-5}	4.87	
CH_3CH_2OH (ethanol)	(1×10^{-16})	(16)	

Acidity of carboxylic acids



- Although **much weaker than mineral acids**, carboxylic acids are nevertheless much **stronger acids than alcohols and phenols**.
- The K_a of ethanol, for example, is approximately 10^{-16} , making it a weaker acid than acetic acid by a factor of 10^{11} .



Why are carboxylic acids so much more acidic than alcohols, even though both contain –OH groups?

Acidity of carboxylic acids



- An alcohol dissociates to give an **alkoxide ion**, in which the negative charge is localized on a single electronegative atom.
- A carboxylic acid, however, gives a **carboxylate ion**, in which the negative charge is delocalized over two equivalent oxygen atoms.
- In resonance terms, a carboxylate ion is a stabilized resonance hybrid of two equivalent structures.
- Since a **carboxylate ion is more stable than an alkoxide ion**, it is lower in energy and more favored in the dissociation equilibrium.

Acidity of carboxylic acids

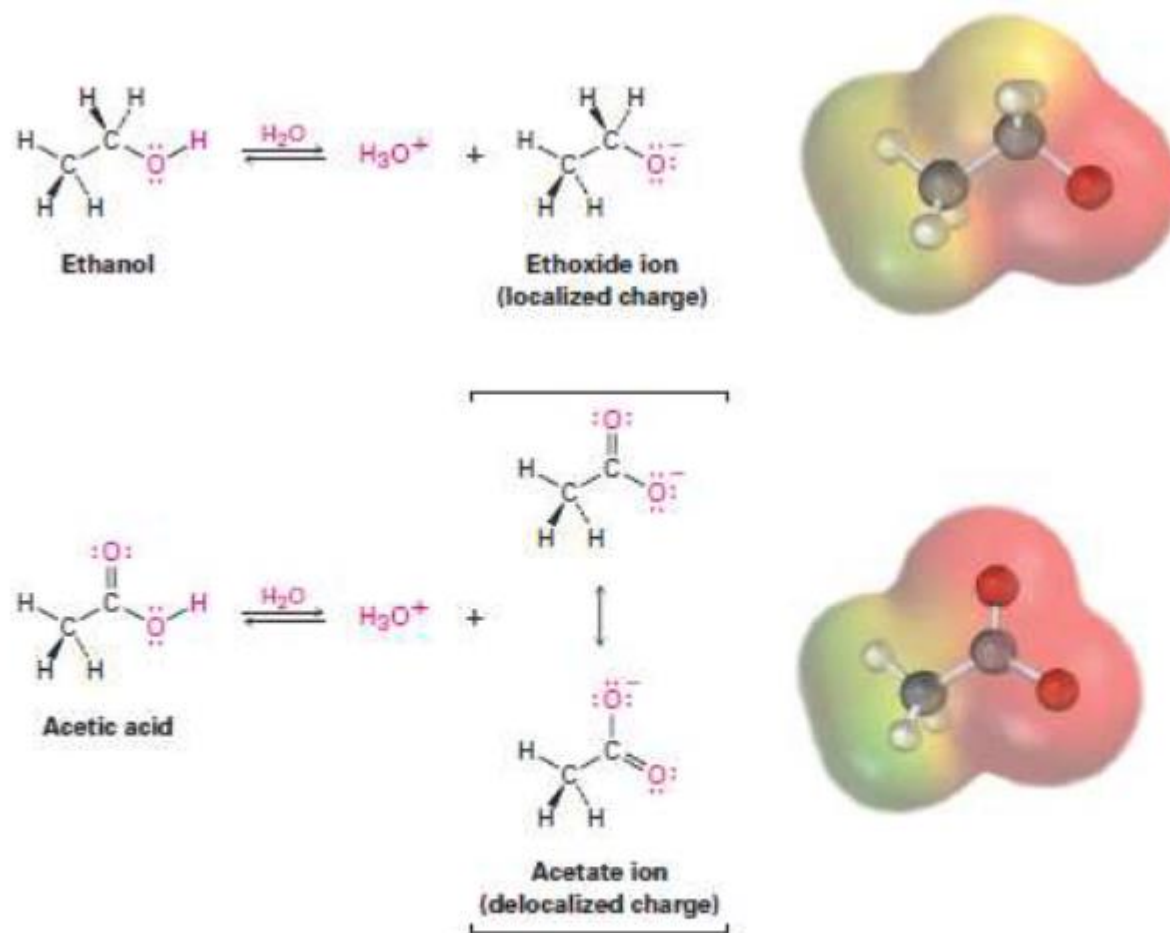


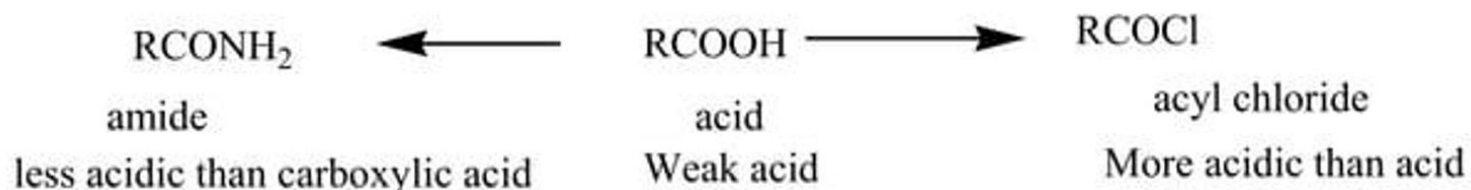
Figure 20-1 an alkoxide ion has its charge localized on one oxygen atom and is less stable, while a carboxylate ion has the charge spread equally over both oxygens and is therefore more stable.

Acidity of carboxylic acids



Effects of substituent's on acidity of carboxylic acids:

- Electron Withdrawing Groups (Cl, Br, I) increases acidity.
- EWG withdraws electron density from carboxyl group and equilibrium shifted to right that increases acidity of carboxylic acids.
- Electron Donating Groups (OH, NH₂) decreases the acidity.
- EDG add electron density to carboxyl group and equilibrium shifted to left that decreases acidity of carboxylic acid.



Methods of carboxylic acid preparation



Oxidation of primary alcohols & aldehydes

Oxidation of alkenes

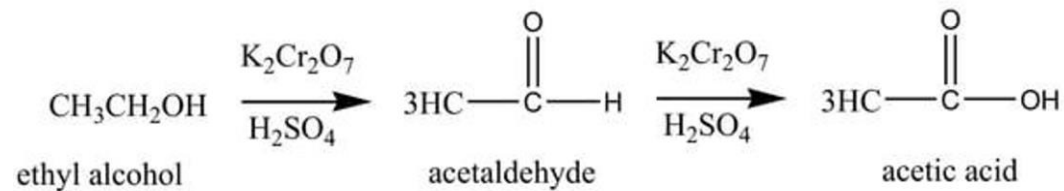
Hydrolysis of nitriles

Hydrolysis of esters

Carboxylation of Grignard method

Carboxylation of alkenes

From malonic ester

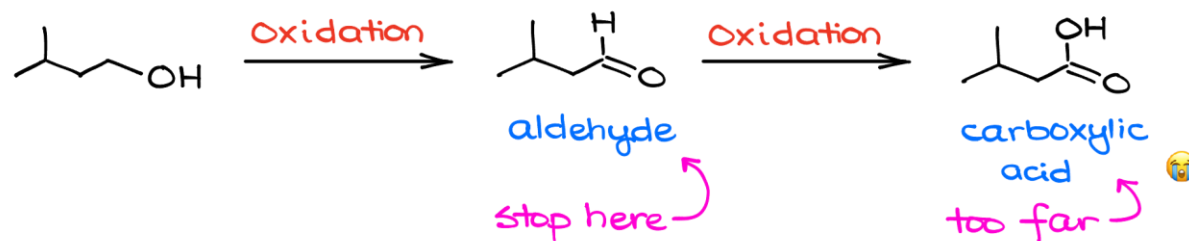
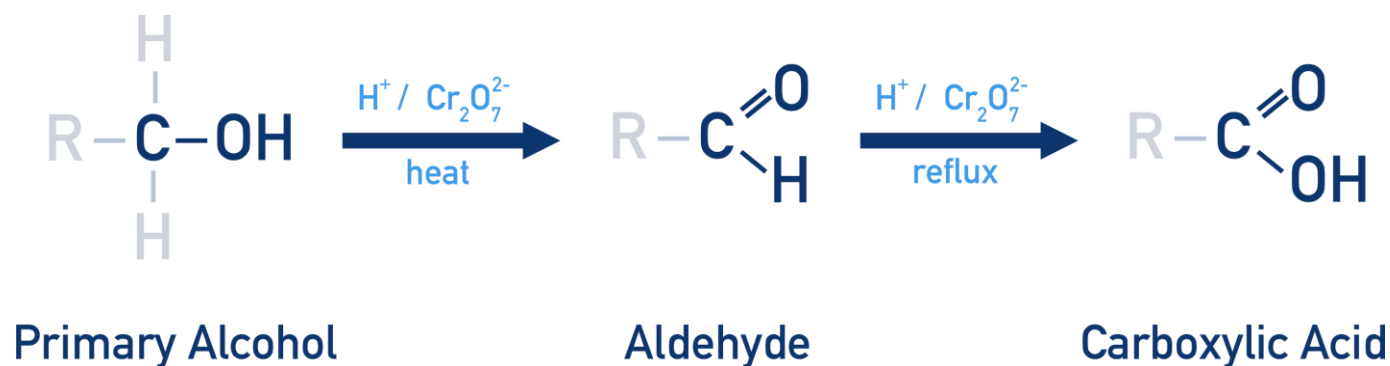


Methods of carboxylic acid preparation



❖ Oxidation of primary alcohols & aldehydes:

- A primary alcohol can be oxidised to an aldehyde, which can then (when the reaction is carried out in reflux conditions) be oxidised into a carboxylic acid.

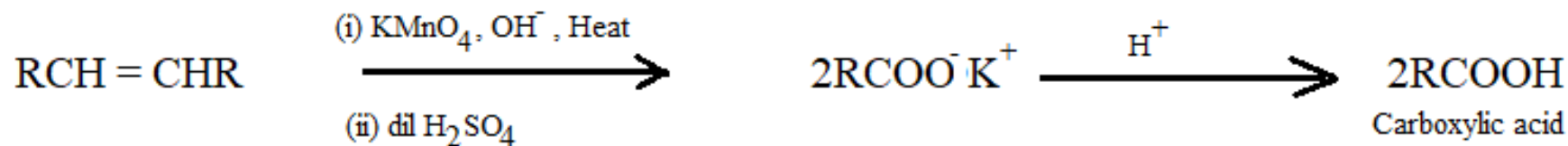


Methods of carboxylic acid preparation

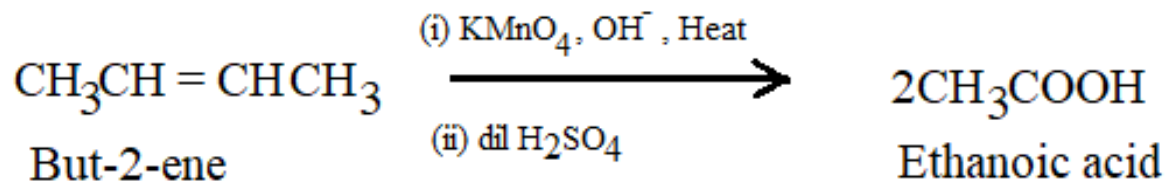


❖ Oxidation of alkenes:

- The oxidation of alkene is done by the oxidising agent like Potassium permanganate in the presence of basic medium, the whole reaction medium is then treated with Sulphuric acid.



Example :-



Methods of carboxylic acid preparation



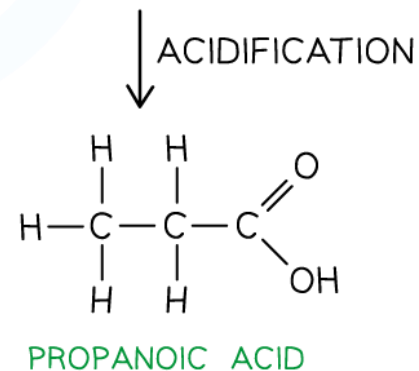
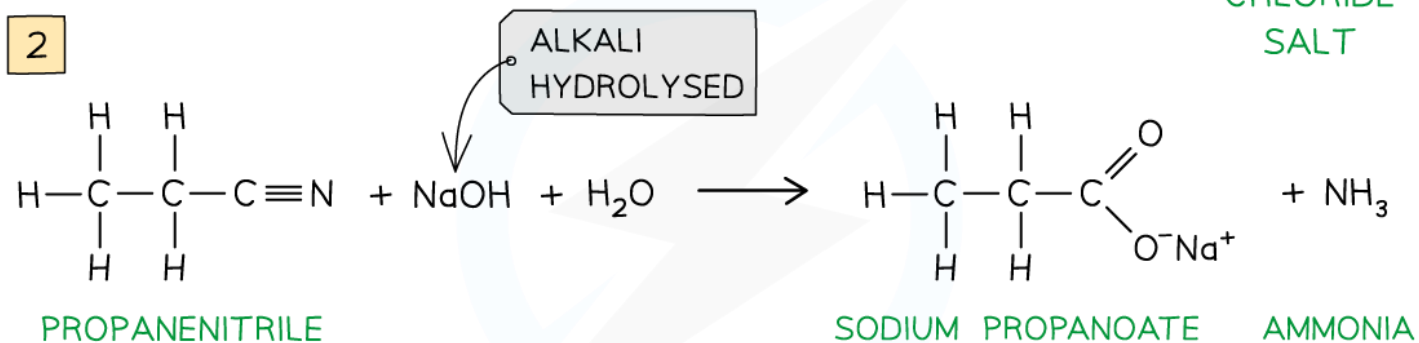
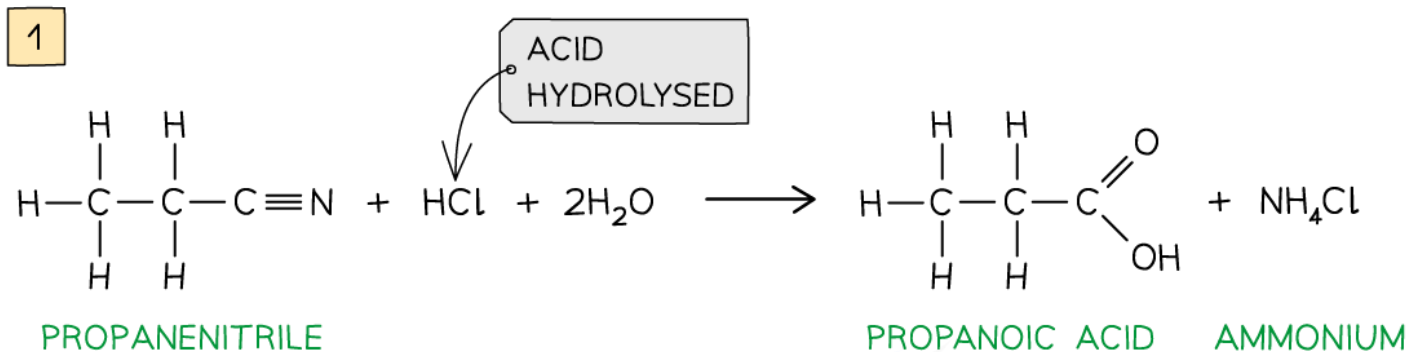
❖ Hydrolysis of nitriles:

- Nitriles are hydrolysed by either dilute acid or dilute alkali followed by acidification
- Hydrolysis by dilute acid results in the formation of a carboxylic acid and ammonium salt
- Hydrolysis by dilute alkali results in the formation of a sodium carboxylate salt and ammonia; Acidification is required to change the carboxylate ion into a carboxylic acid
- The -CN group at the end of the hydrocarbon chain is converted to a -COOH group

Methods of carboxylic acid preparation



❖ Hydrolysis of nitriles:

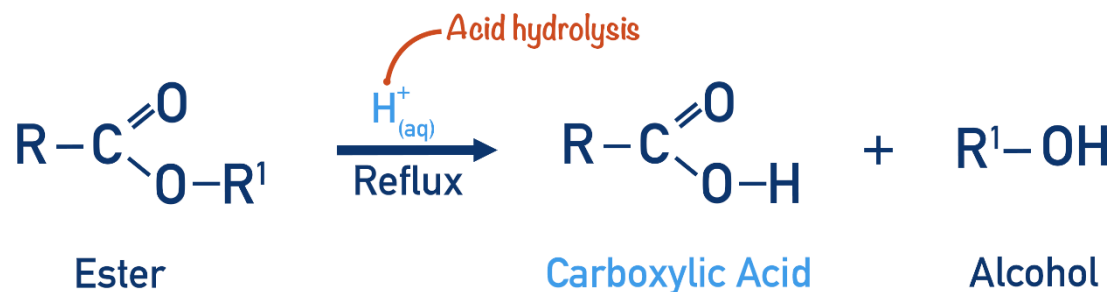


Methods of carboxylic acid preparation

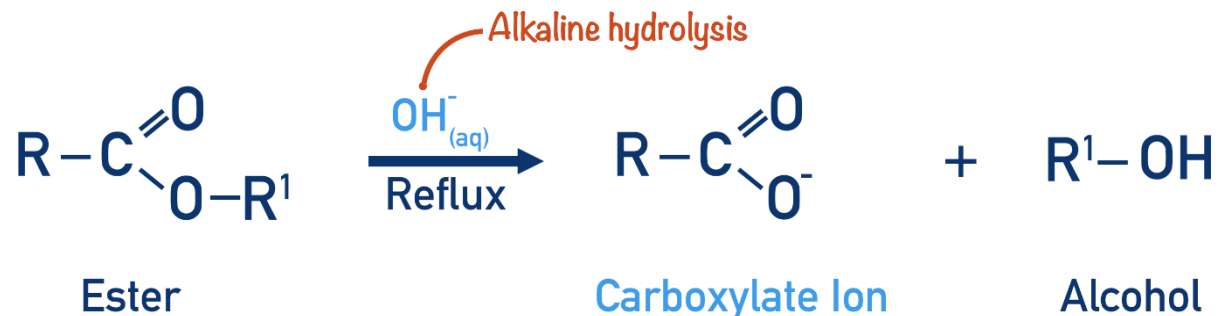


❖ Hydrolysis of esters:

- Ester links can be broken in hydrolysis reactions (addition of water).
- Hydrolysis of an ester in acidic conditions produces a carboxylic acid and alcohol.



- Hydrolysis of an ester in alkaline conditions produces a carboxylate ion and alcohol.



- Both reactions require aqueous conditions (water present) and are carried out under reflux.

Methods of carboxylic acid preparation



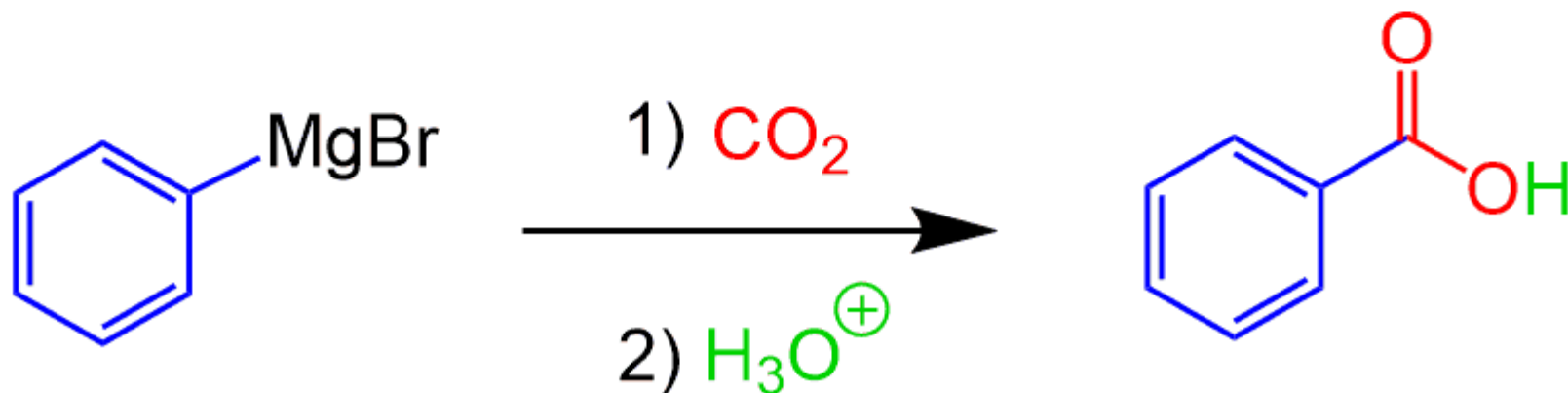
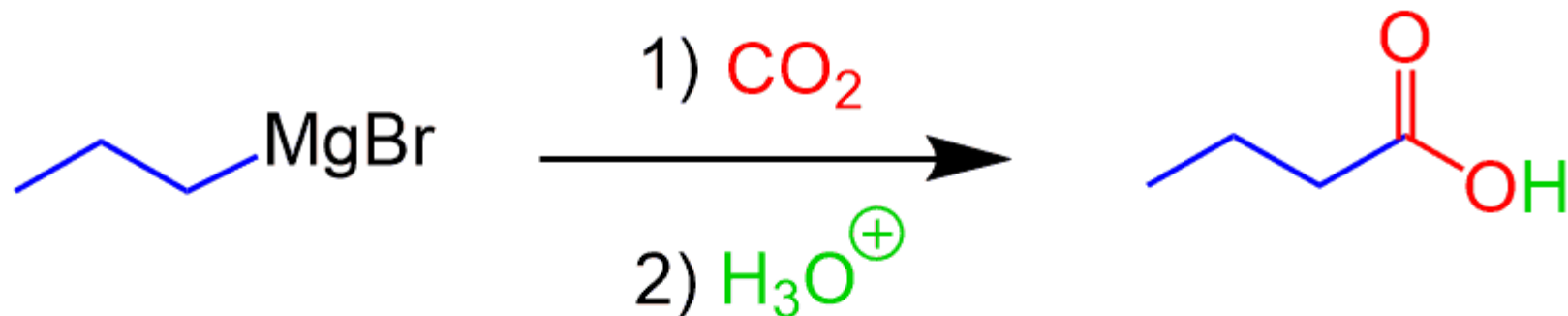
❖ Carboxylation of Grignard method:

- A Grignard reagent is a highly reactive organomagnesium halide with the general formula RMgX , where R is an alkyl or aryl group and X is a halogen.
- Carboxylic acids are prepared from Grignard reagents by first reacting the reagent with carbon dioxide (CO_2) to form a **magnesium carboxylate salt**, followed by acidification with a dilute aqueous acid to yield the final carboxylic acid.
- This carboxylation method **adds one carbon atom** to the original alkyl or aryl halide that formed the Grignard reagent.

Methods of carboxylic acid preparation



❖ Carboxylation of Grignard method:



Methods of carboxylic acid preparation



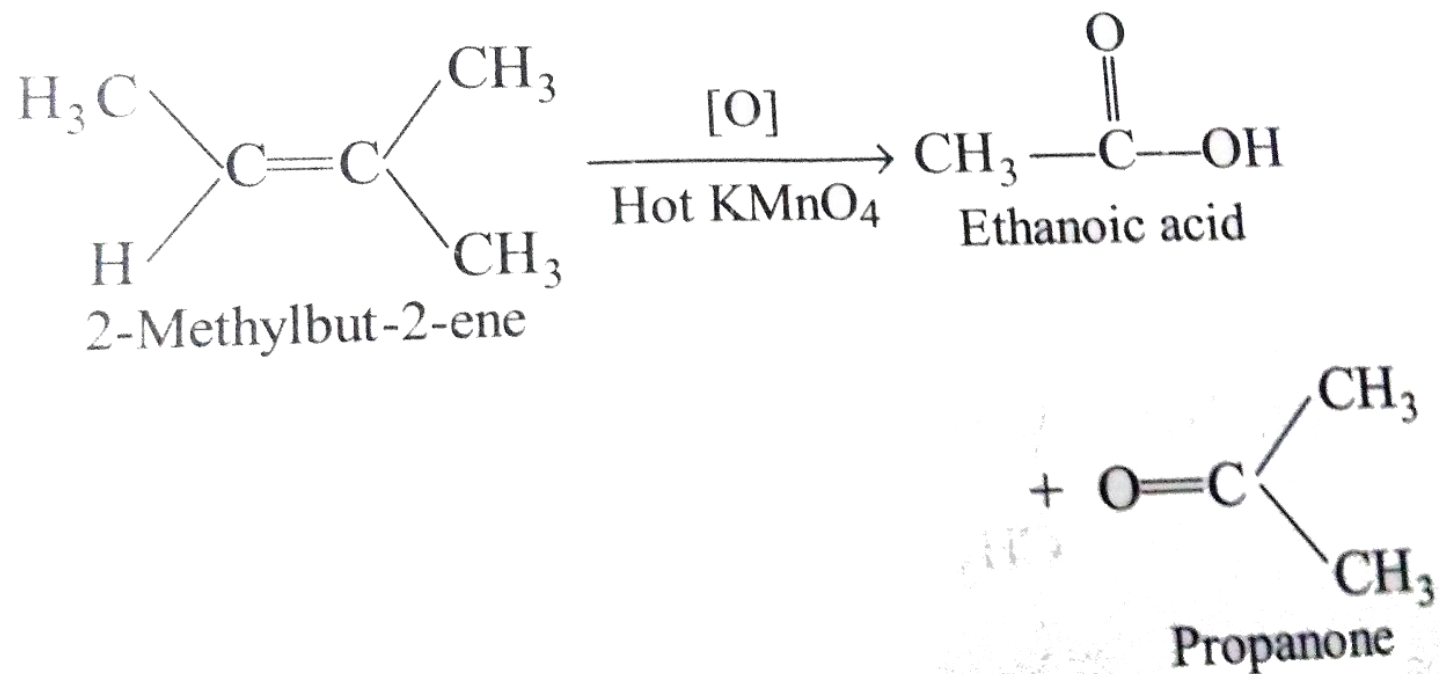
❖ Carboxylation of alkenes:

- This done by **oxidative cleavage** of alkenes with **potassium permanganate**.
- Treating an alkene with hot, concentrated potassium permanganate (KMnO_4) in a **basic solution** will cleave the double bond.
- The carbons that were part of the double bond are **oxidized to form carbonyl groups**.
- Any hydrogens attached to these carbons are further **oxidized into carboxylic acid groups**.
- **Adding acid** in a second step neutralizes the solution and ensures the products are fully converted to carboxylic acids.

Methods of carboxylic acid preparation



❖ Carboxylation of alkenes:

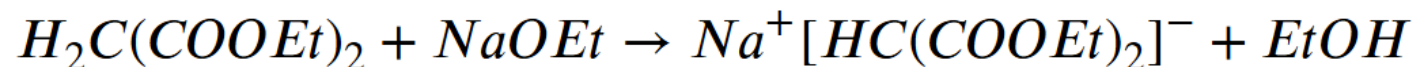


Methods of carboxylic acid preparation



❖ From malonic ester:

- The transformation of a malonic ester to a carboxylic acid is achieved through the **malonic ester synthesis**.
- A four-step process that involves **deprotonation**, **alkylation** followed by **hydrolysis** and **decarboxylation**.
- The process begins by deprotonating the acidic α -hydrogens of the malonic ester using a base like sodium ethoxide, which forms an **enolate**.

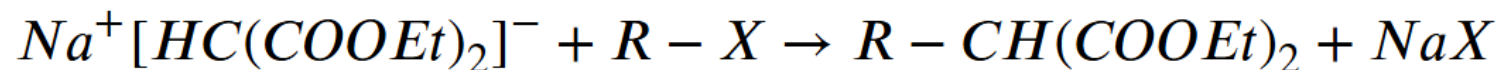


Methods of carboxylic acid preparation

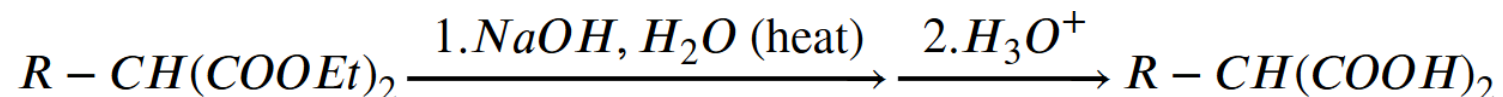


❖ From malonic ester:

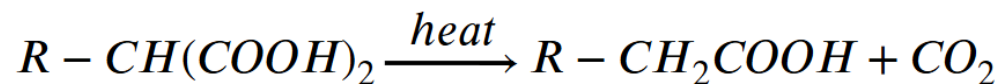
- This enolate then undergoes an SN2 reaction with an alkyl halide to form a **substituted malonic ester**.



- Finally, acidic hydrolysis converts both ester groups to **carboxylic acids**.



- And subsequent heating causes one carboxylic acid group to be lost as (CO₂) (**decarboxylation**), leaving the desired substituted carboxylic acid.



Reactions of carboxylic acid



Salt formation

Formation of acyl halides

Formation of amides

Formation of anhydrides

Formation of esters

Esterification using
diazomethane

Reduction with
aluminium hydride

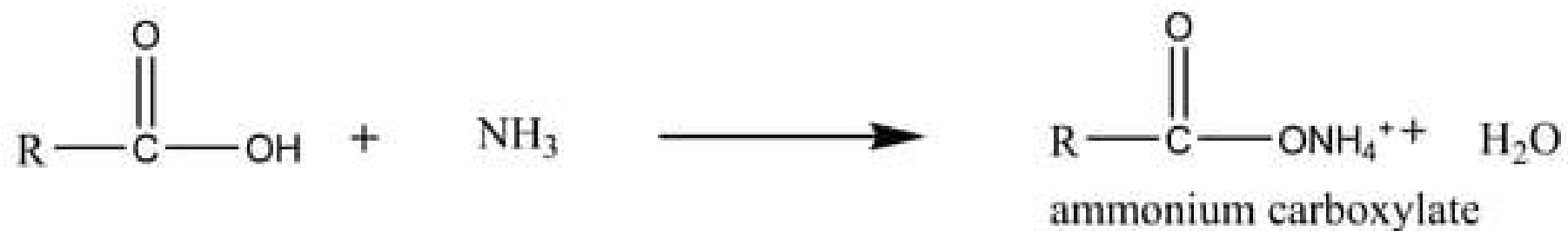
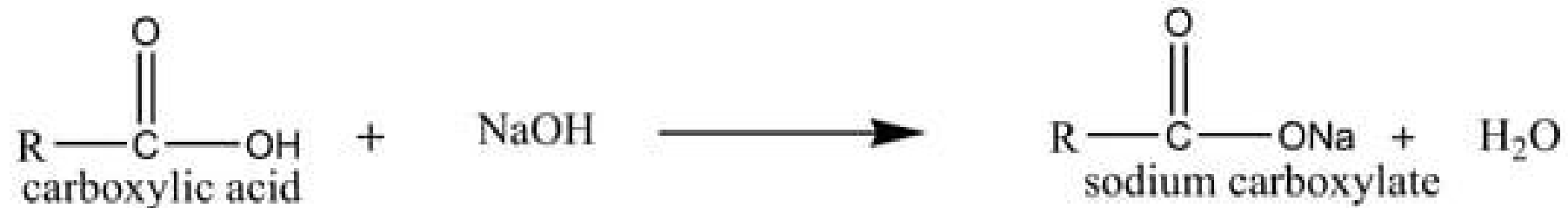
Reduction with
dibron

α halogenation

Reactions of carboxylic acid



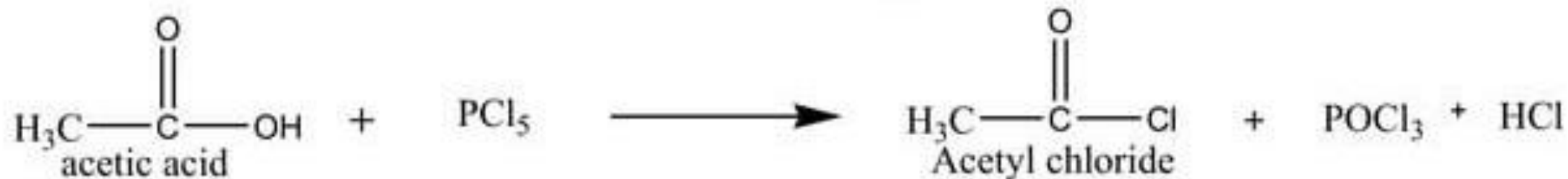
1. Salt formation:



Reactions of carboxylic acid



2. Formation of acyl halides:

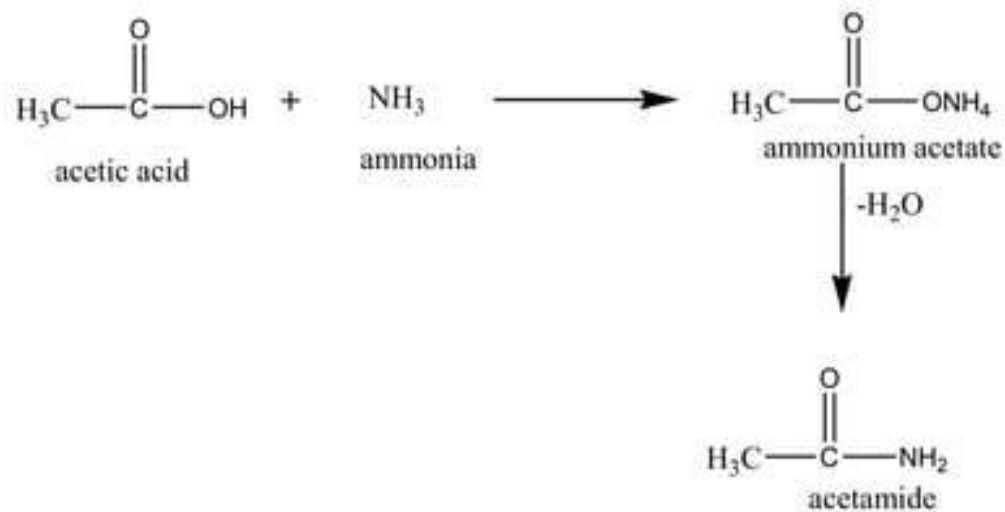
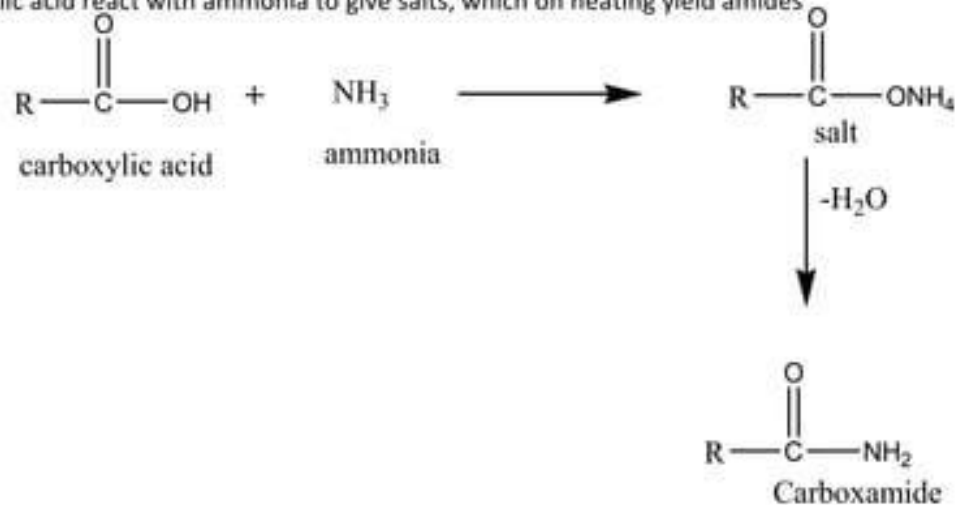


Reactions of carboxylic acid



3. Formation of amides:

- Carboxylic acid react with ammonia to give salts, which on heating yield amides

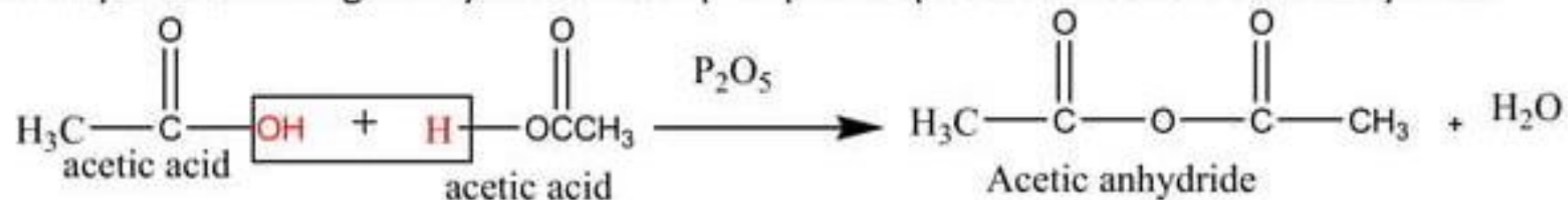


Reactions of carboxylic acid



4. Formation of anhydride:

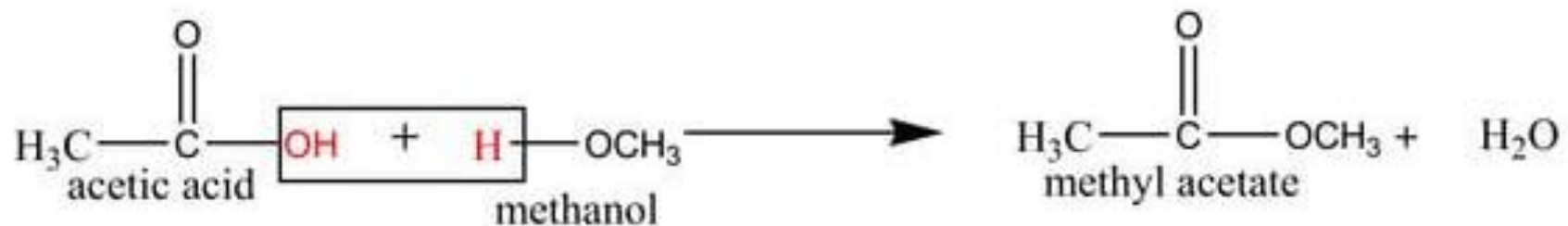
Carboxylic acid undergo dehydration with phosphorus pentoxide to form acid anhydride



Reactions of carboxylic acid



5. Formation of ester:

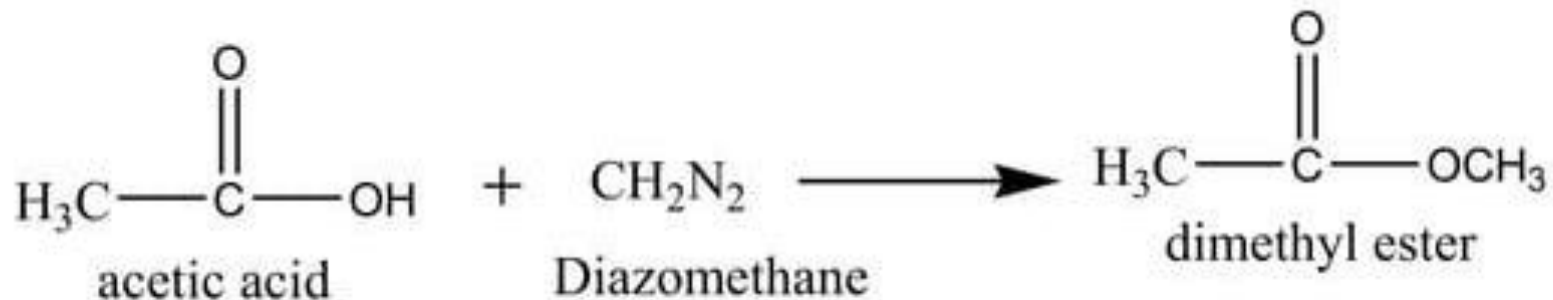
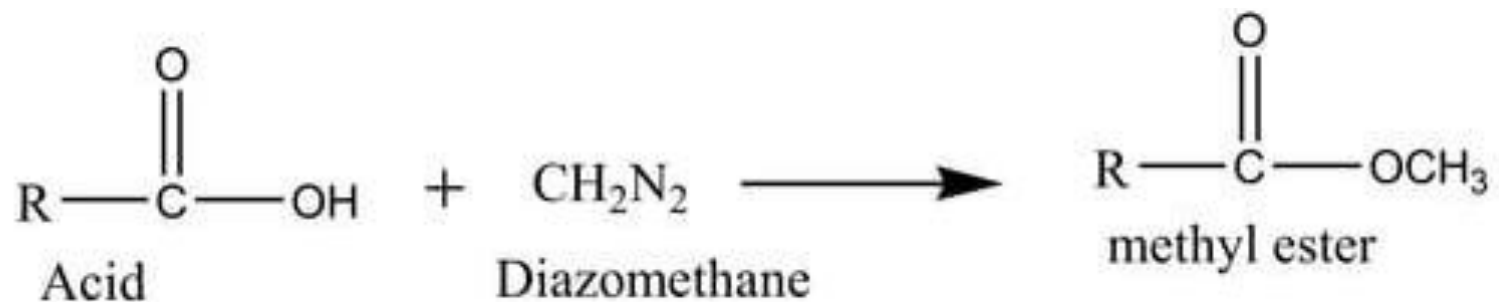


Carboxylic acid react with alcohols in the presence of strong acid to form esters

Reactions of carboxylic acid



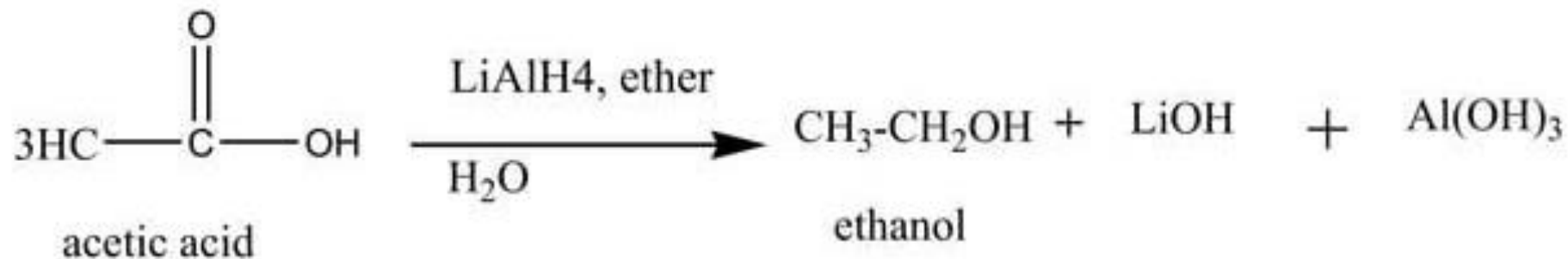
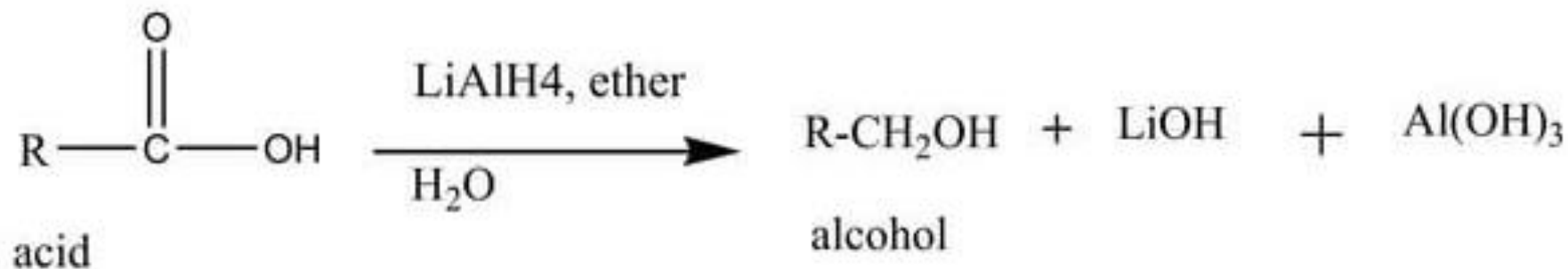
6. Esterification using Diazomethane:



Reactions of carboxylic acid



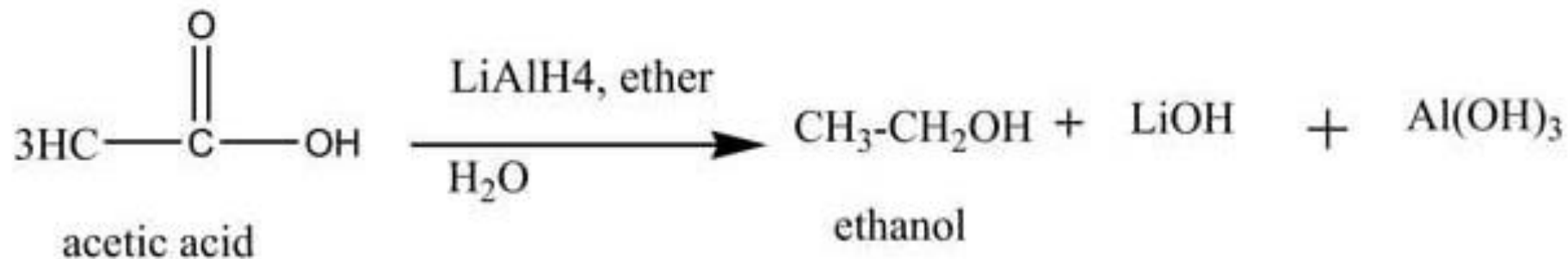
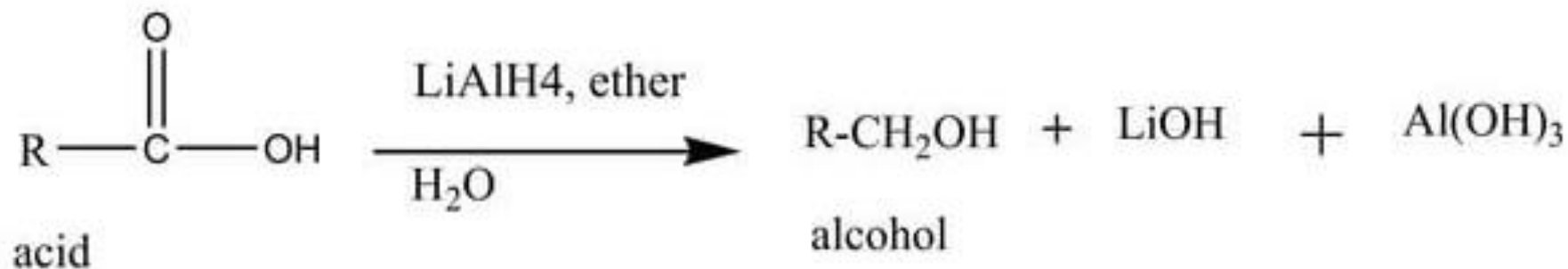
7. Reduction with lithium aluminium hydride:



Reactions of carboxylic acid



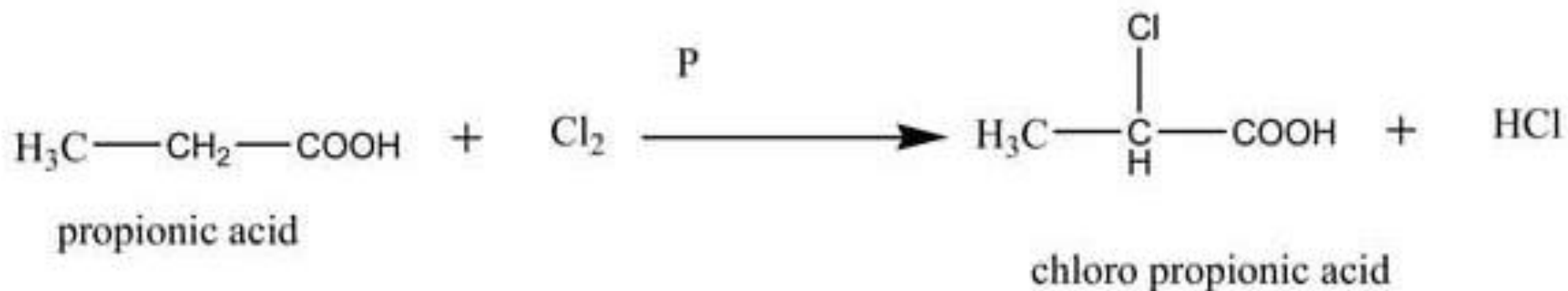
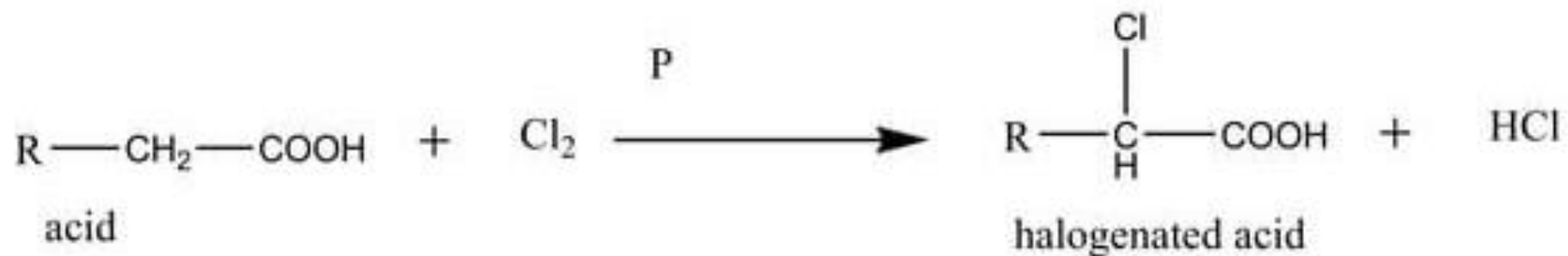
8. Reduction with diborane:

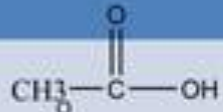
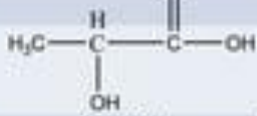
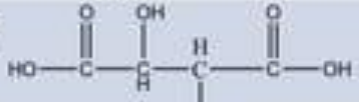
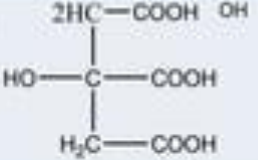
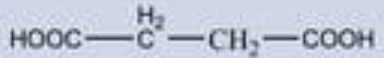
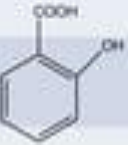
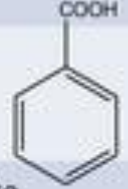
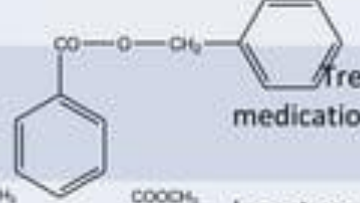
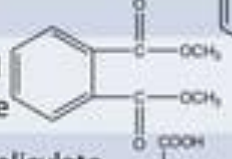
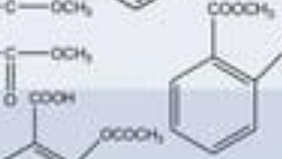


Reactions of carboxylic acid



9. α - halogenation:



Sr. No	Name of acid	Structure	Uses
1.	Acetic acid		Synthesis of acetone, ester, cellulose acetate and polyvinyl acetate, Perfumes, plastic dyes, pharmaceuticals
2.	Lactic acid		Food preservative, curing agent, flavoring agent, decontaminant for meat processing
3.	Tartaric acid		Carbonated beverages and efferevescent tablets, backing powder, as mordant, silvering of mirror, tanning, for preparation of rochelle salt, emetic tartar
4.	Citric acid		Laxative, acidulant in carbonated soft drinks, jams, jellies, candies, ferric ammonium citrate as blue print paper, esters(tributyl citrate as good plastisizers
5.	Succinic acid		Manufacturing of lacquers, dyes, volumetric analysis for acid base titration
6.	Oxalic acid		Redox titration, Ink stain remover, Mordant in dyeing and calico printing, manufacture of inks and metal polishes, allyl alcohol, formic acid.
7.	Salicylic acid		Keratolytic(peeling agent), treatment of acne, antidandruff, psoriasis,
9.	Benzoic acid		Germicide- urinary tract infection, and disinfection, food preservative- sodium benzoate
10.	Benzyl benzoate		Treatment of Scabis, spasmolytic, excipients in testosterone replacement medication
11.	Dimethyl phthalate		Insect repellent for mosquitoes and flies, ectoparasiticide, solid rocket repellent, plastic
12.	Methyl salicylate		Muscle relaxant for pain, arthritis, bruising, backaches
13.	Acetyl salicylate		Pain killer, anti-inflammatory and anticoagulant

Carboxylic acid derivatives



Content

Acid chloride

Amide

Ester

Thioester



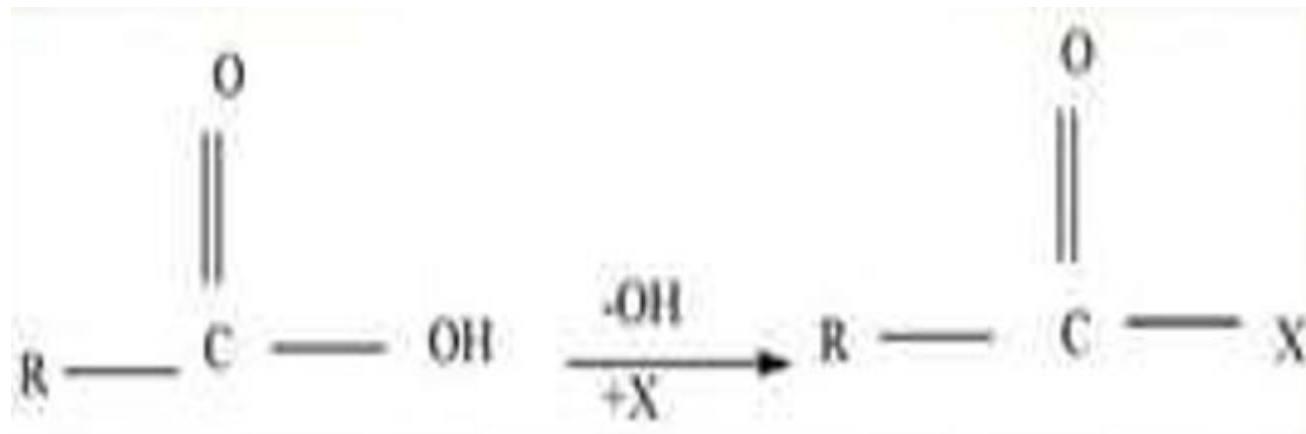
Acid halides (Acyl halides)



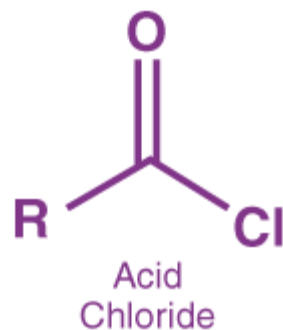
Acid chloride



- Acid halides are derivatives of acids in which OH of carboxyl group has been replaced by **halogen atom**.



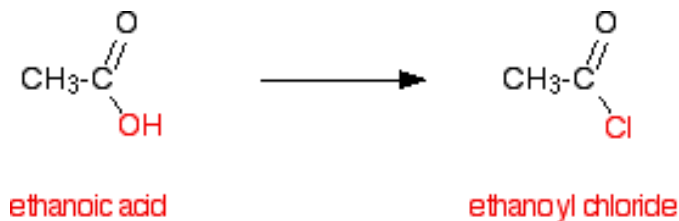
- The acid halides are also referred as **acyl halides**, acyl group is **RCO-**.
- The **acid chlorides** are the most important of all the acid halides, their structural formula represented as



Acid chloride



- Acid halides are named by dropping the ending **–ic** acid and adding the suffix **–yl chloride** or **halide**.



carboxylic acid name	acyl halide name	acyl halide formula
ethanoic acid	ethanoyl chloride	CH_3COCl
propanoic acid	propanoyl chloride	$\text{CH}_3\text{CH}_2\text{COCl}$
butanoic acid	butanoyl chloride	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$
butanoic acid	butanoyl bromide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COBr}$
butanoic acid	butanoyl iodide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COI}$

Physical properties of acid chloride

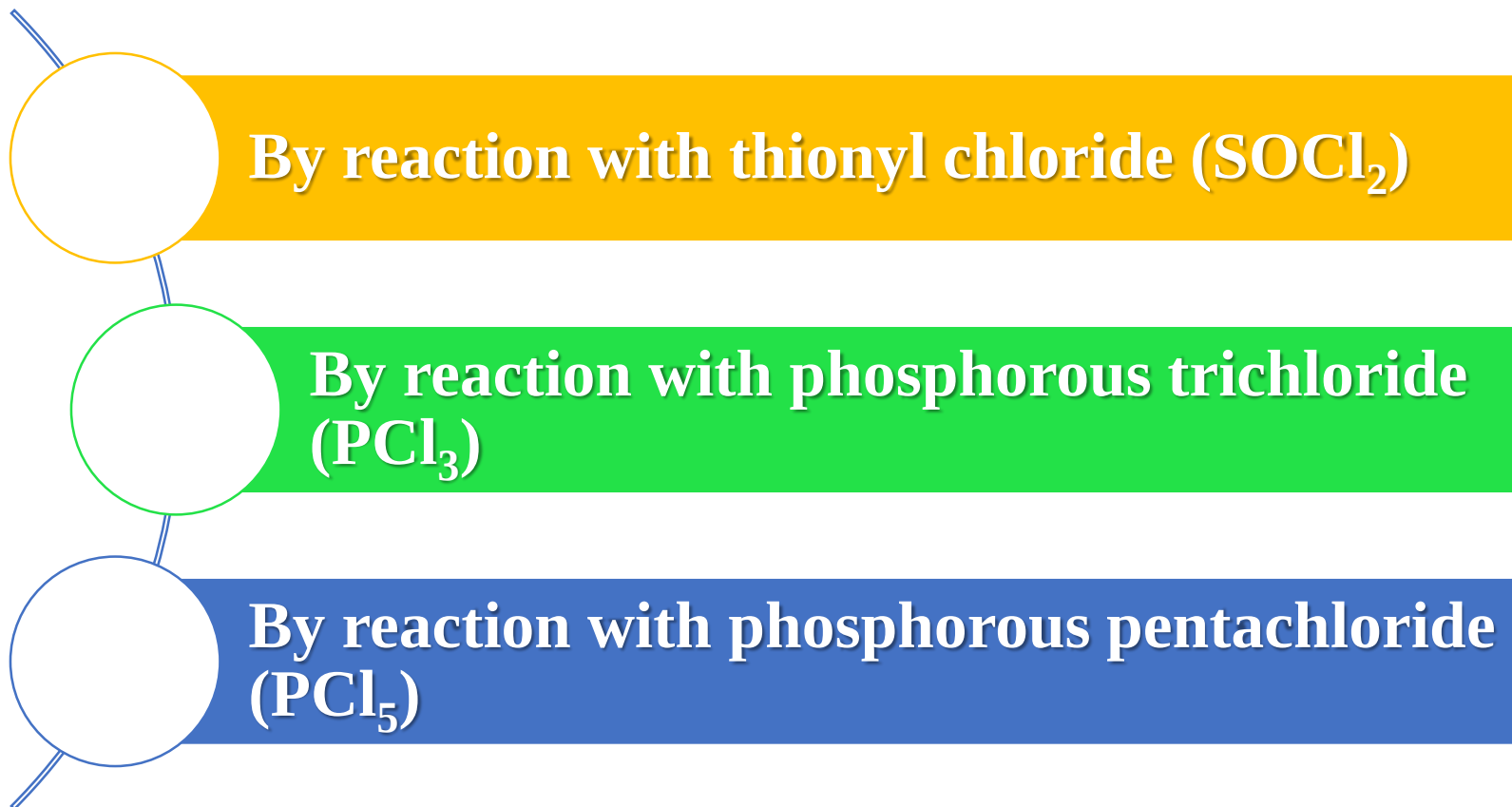


- All simple acid chlorides are **colourless liquid of lower boiling points** than the corresponding acids.
- They have sharp pungent smell, and are **lachrymators** (tear producing).
- They emit **pale fumes of hydrogen chloride** when exposed in air on account of their reaction with water vapor.
- They are **insoluble in water** but slowly dissolve in it because of hydrolysis.

Acid chloride preparation

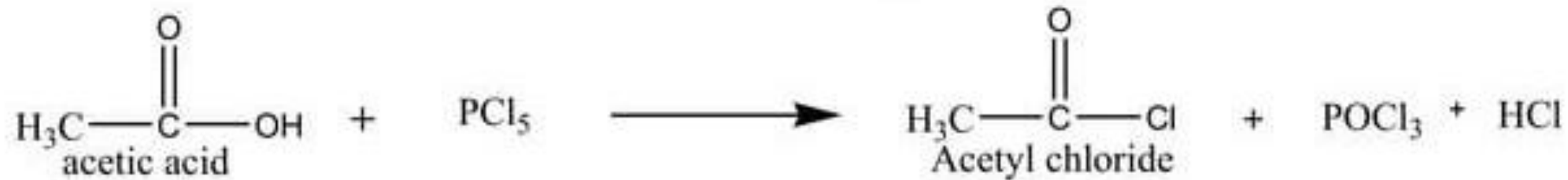


➤ Acid chlorides are prepared from carboxylic acids:



➤ It is possible to prepare **acid bromides and iodides** by reaction analogues to those used in the preparation of chlorides. However, in comparison to the chlorides, they are **seldom used**.

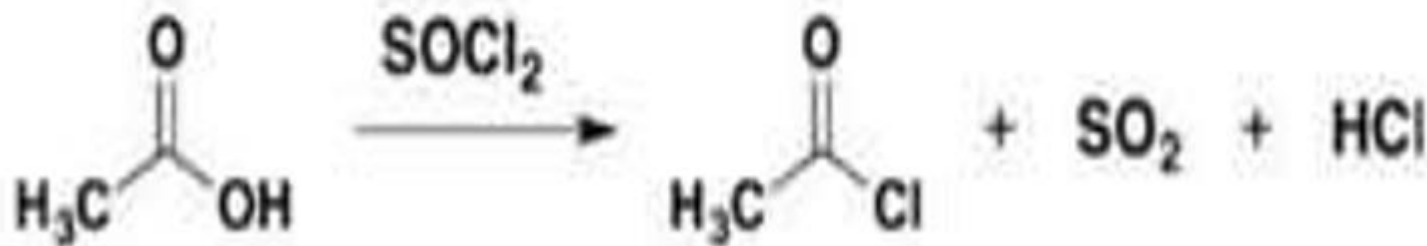
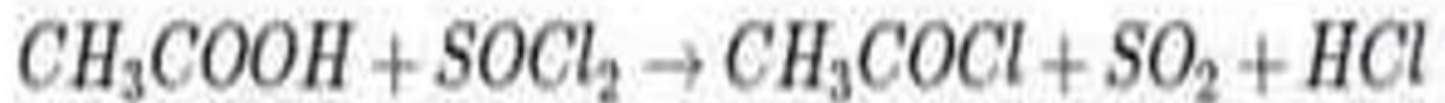
Acid chloride preparation



Acid chloride preparation



- By reaction with thionyl chloride (SOCl_2)
- Thionyl chloride reacts with carboxylic acids to produce an acyl chloride, giving off sulphur dioxide and hydrogen chloride gases:

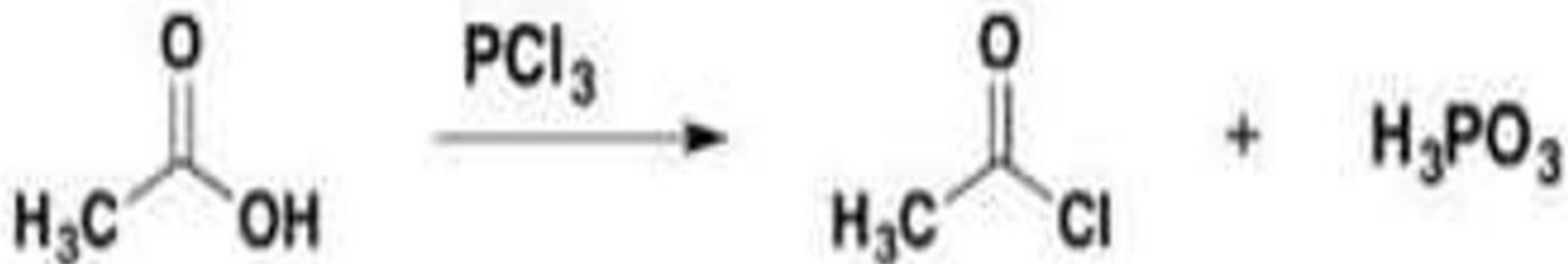
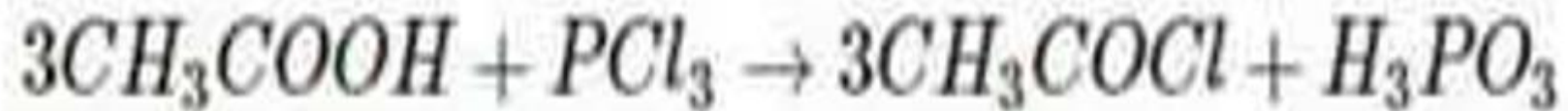


- This method is **superior** to others as the by products being gases escape leaving the acid chloride in the pure state.

Acid chloride preparation



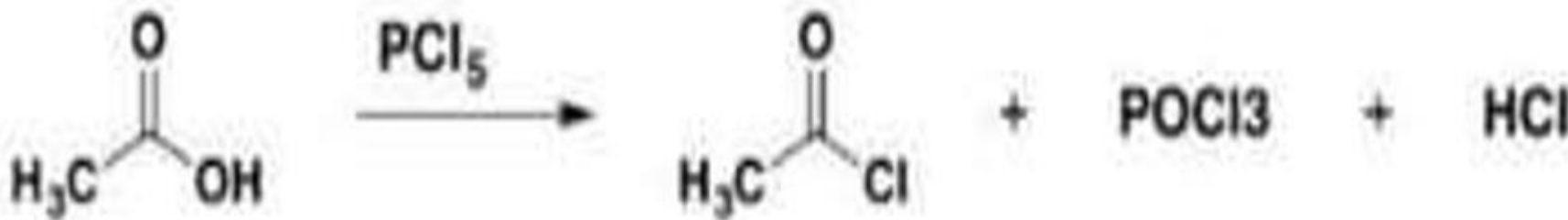
- By reaction with phosphorous trichloride (PCl_3)
- When a carboxylic acid reacts with phosphorous trichloride, a mixture of acyl chloride and phosphorous acid is produced.



Acid chloride preparation



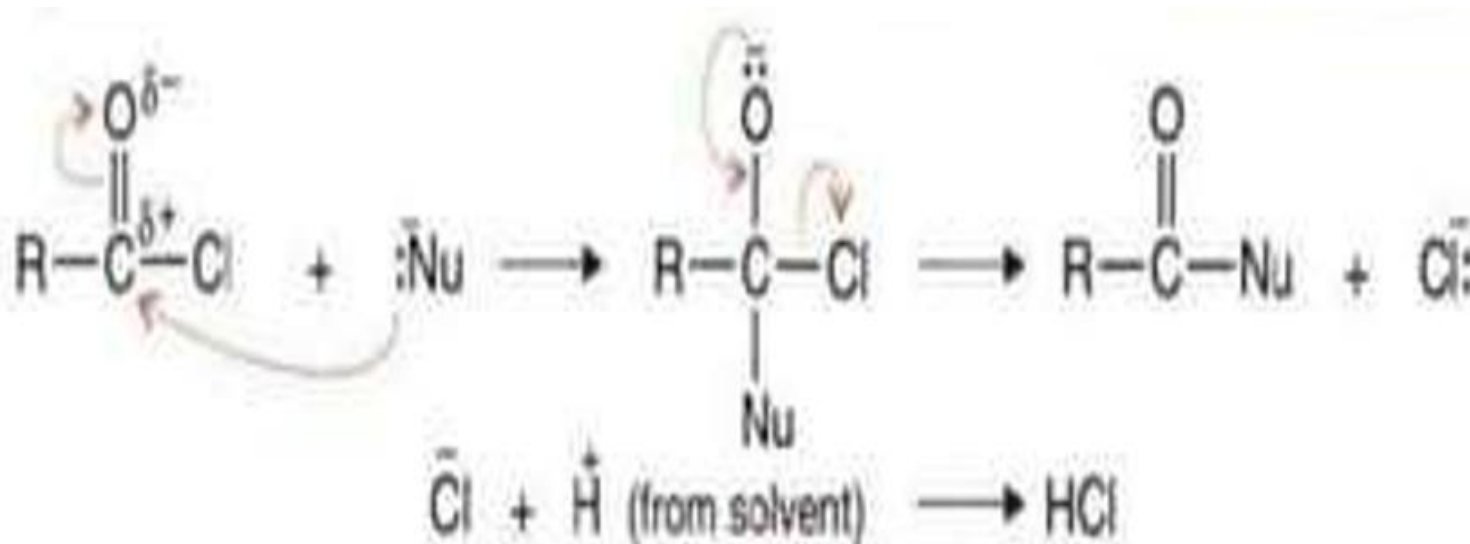
- By reaction with phosphorous pentachloride (PCl_5)
- This reaction leaves a liquid mixture of acyl chloride and phosphorous compound, phosphorous trichloride oxide (phosphorous oxychloride POCl_3).



Acid chloride reactions



- In acyl chloride (RCOCl), we have a **carbonyl group attached to a highly electronegative chlorine atom**. Due to the electron withdrawing effect of Cl atom, the electron density on the carbonyl carbon is diminished further. As a result, acid chlorides are readily attacked by nucleophiles, where by the chlorine atom is replaced by a nucleophile.
- Thus, acid chloride are **very reactive compounds**, their characteristic reactions being **nucleophilic substitution reactions**.



Acid chloride reactions

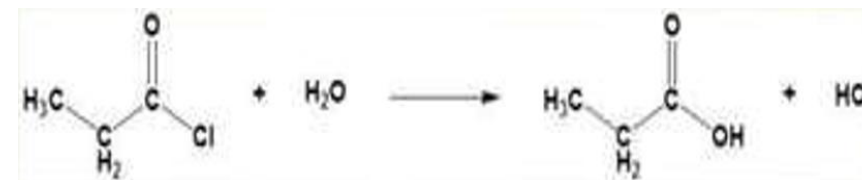


- They react with weak nucleophiles as **water, alcohol, ammonia,** and **amine** to produce the corresponding **acid, ester, amide,** and **substituted amides.**

Acid chloride reactions



Hydrolysis



Reaction with alcohol

Reaction with ammonia

Reaction with amines

Reaction with salts of carboxylic acids

Acylation (friedel crafts reaction)

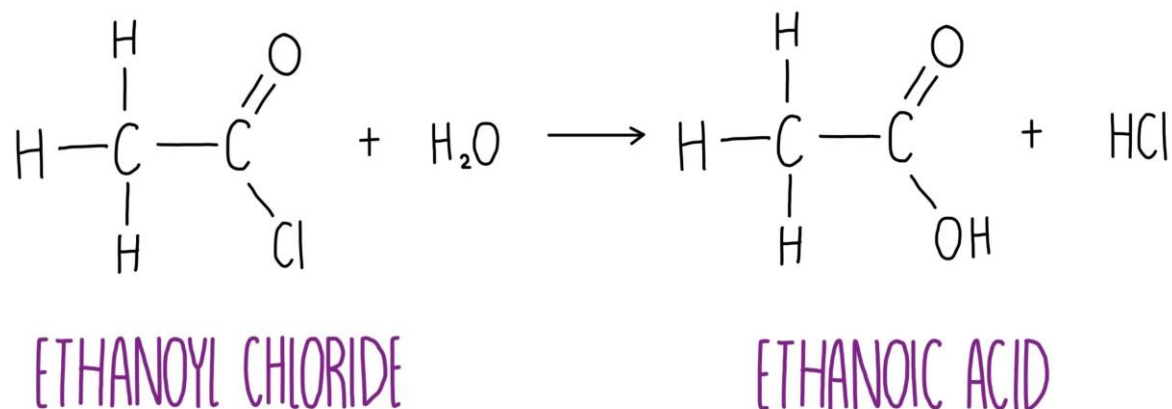
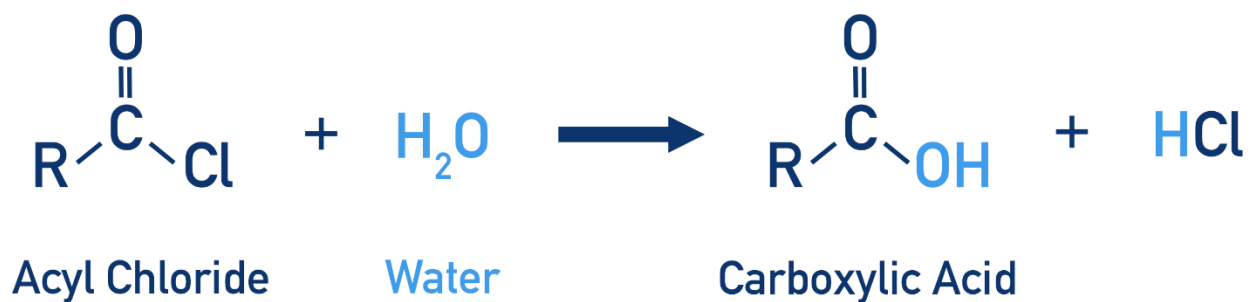


Acid chloride reactions



➤ Hydrolysis:

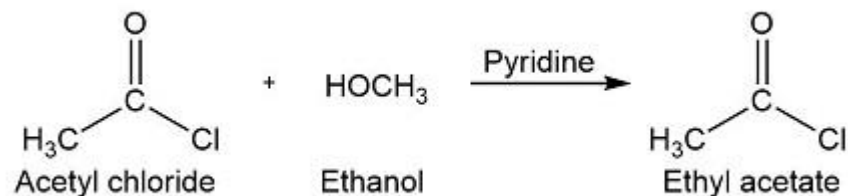
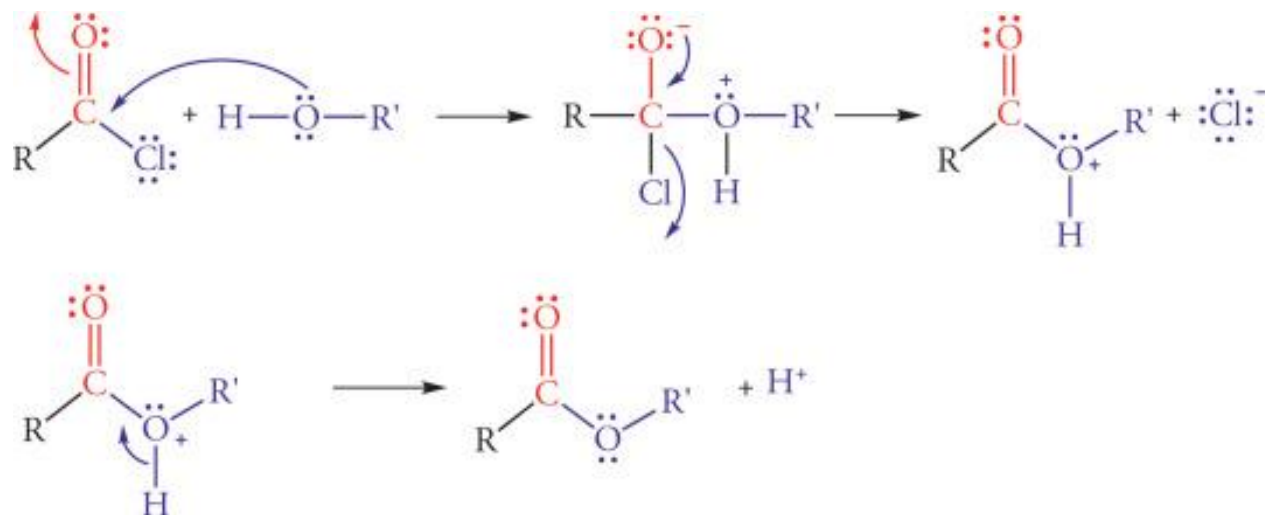
➤ Acid chlorides react with water to form **carboxylic acids**.



Acid chloride reactions



- Reaction with alcohol:
- Acid chlorides react with water to form **ester**.

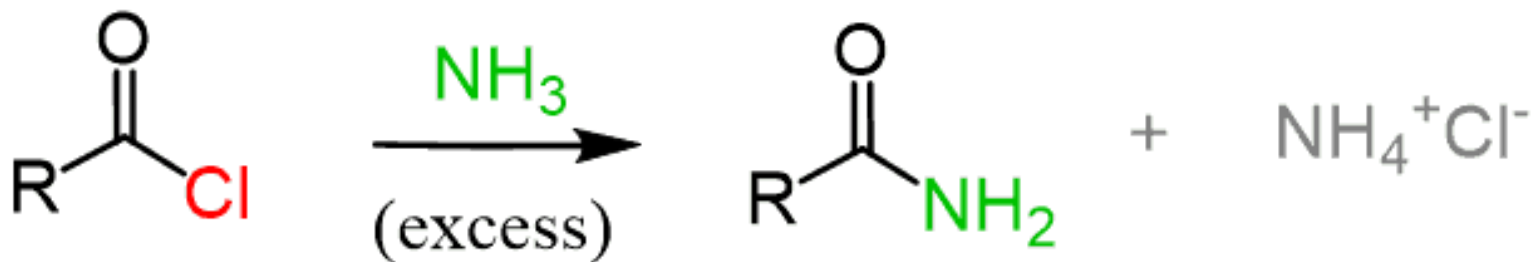


Acid chloride reactions



➤ Reaction with ammonia:

- Acid chlorides react violently with a cold concentrated solution of ammonia, a white solid product is formed which is a mixture of ethanamide (**an amide**) and **ammonium chloride**.

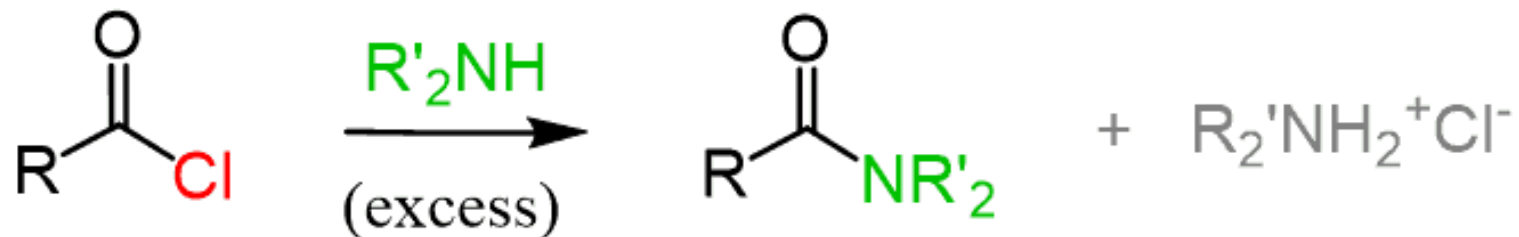
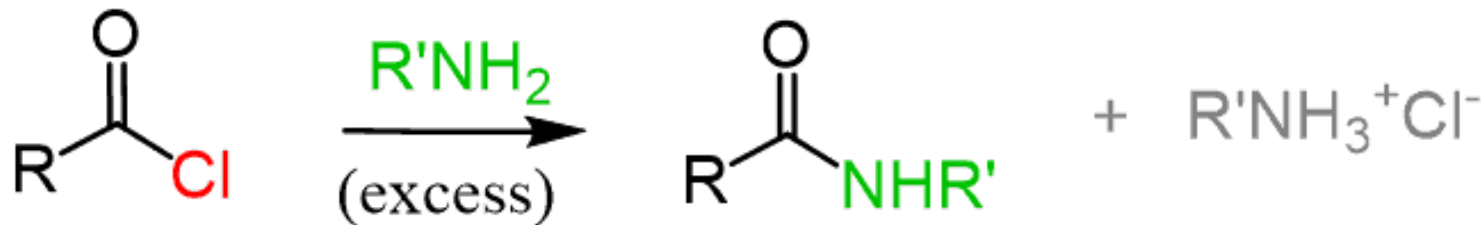


Acid chloride reactions



➤ Reaction with amines:

- Acid chlorides react with primary and secondary amines to produce **substituted amides**.

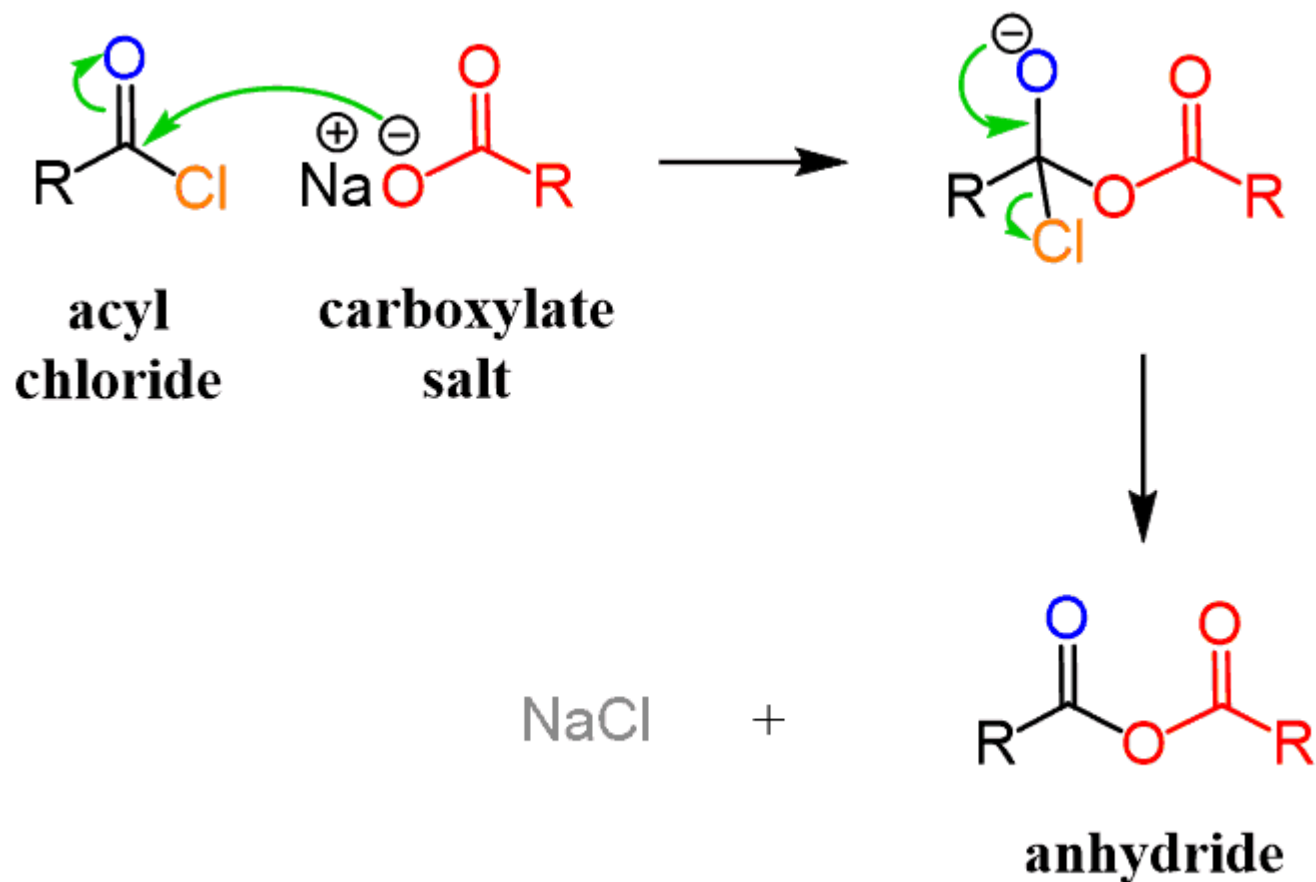


Acid chloride reactions



➤ Reaction with salts of carboxylic acids:

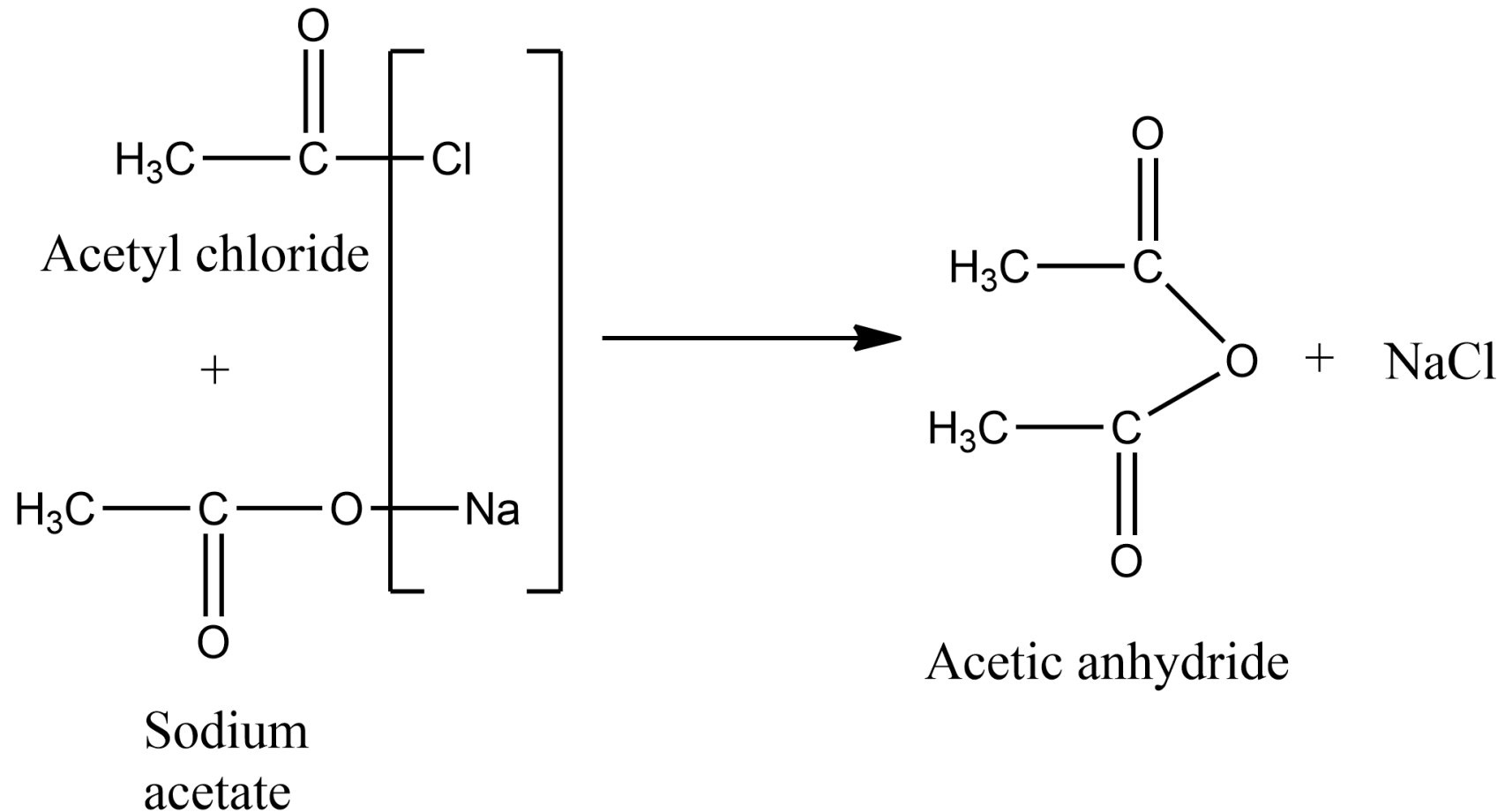
- An acid chloride reacts with the sodium salt of a carboxylic acid to form an **acid anhydride** and **sodium chloride (NaCl)**.



Acid chloride reactions



➤ Reaction with salts of carboxylic acids:

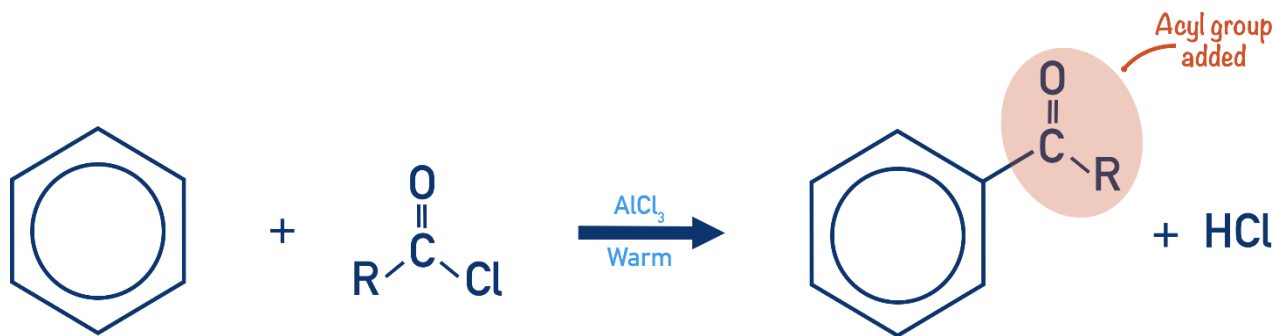


Acid chloride reactions



➤ Friedel-Craft reaction:

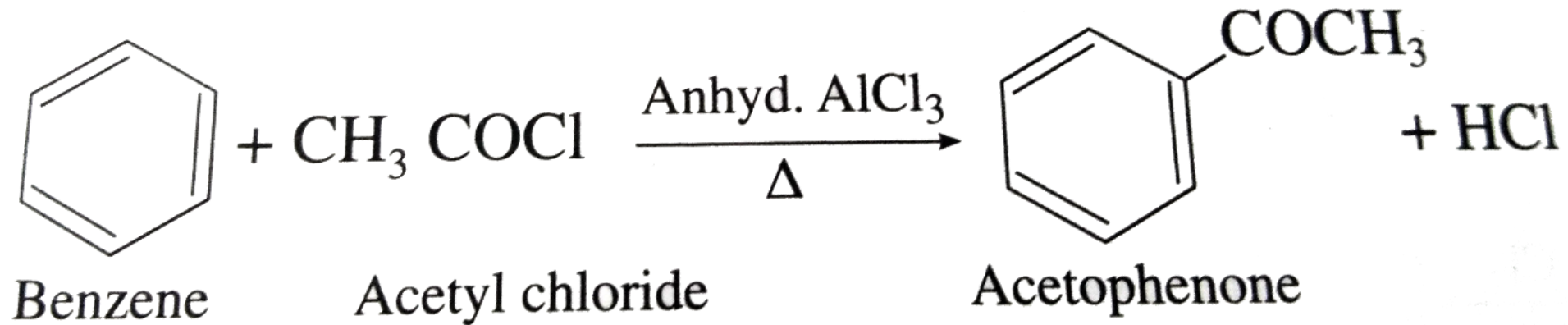
- Acylation is a term given to **substituting an acyl group** such as ethanoyl ($\text{CH}_3\text{CO}-$) onto another molecule.
- An acyl group is a hydrocarbon group **attached to a carbon-oxygen double bond**.
- If benzene reacted with ethanoyl chloride in the presence of aluminium chloride catalyst, an **ketone** would be formed.



Acid chloride reactions



➤ Friedel-Craft reaction:



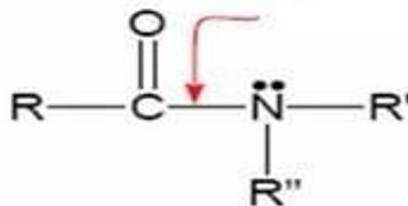
Amides



Amides

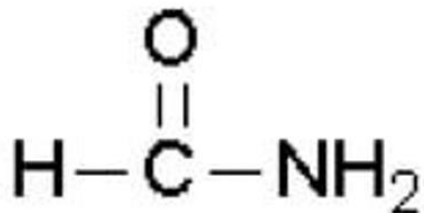


- Amides are derived from **carboxylic acids**.

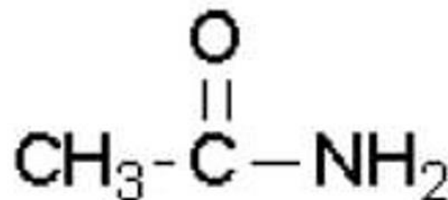


Amide

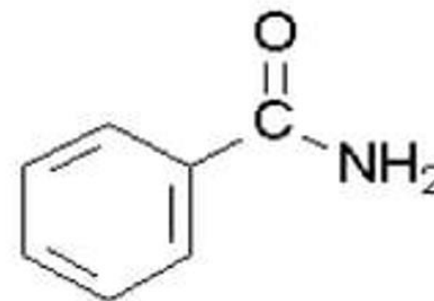
- OH** group in carboxylic acids is replaced by **-NH₂** group in amides.
- Primary amides are named by changing the name of the acid by dropping **-oic acid** or **-ic acid** ending and adding **-amide**.



Methanamide
(Formamide)



Ethanamide
(Acetamide)

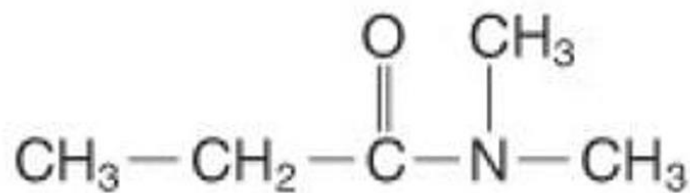


Benzamide

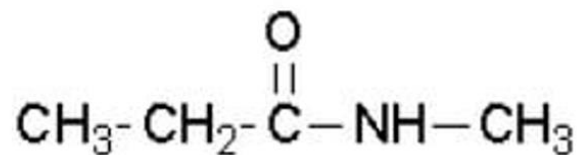
Amides



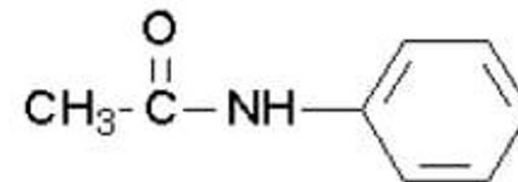
- Secondary amides are named by using an upper case **N** to designate that the alkyl group is on the nitrogen atom.
- Tertiary amides are named by the same way.



N, N- dimethylpropanamide

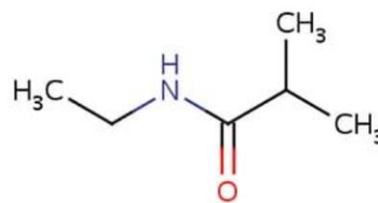
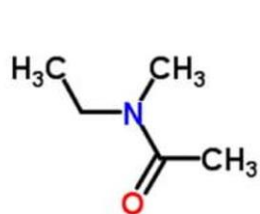


N- methylpropanamide



N- phenylethanamide (Acetanilide)

N- ethyl-N-methylethanamide

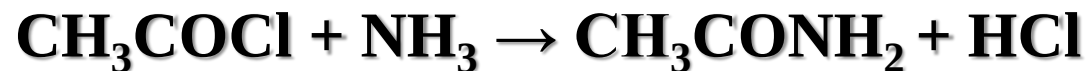


N- ethyl-2-methylpropanamide

Preparation of amides



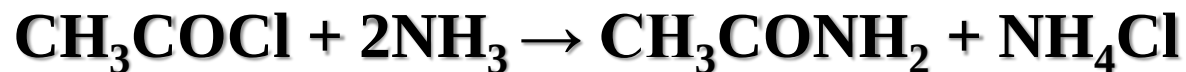
- Amides are prepared from **acid chlorides**.
- In the first stage, **ammonia** reacts with **ethanoyl chloride** to give **ethanamide** and **hydrogen chloride**.



- The hydrogen chloride produced reacts with excess ammonia to give **ammonium chloride**.



- And you can combine two equations to give one overall equation.



Reactions of amides



Acidic & alkaline hydrolysis

Reaction with nitrous acid

Reduction

Hofmann degradation

Dehydration

Reactions of amides



Acidic hydrolysis

Amides hydrolysed in the presence of **concentrated acid** to yield **ammonium salt** and **carboxylic acid**.

Example:



Alkaline hydrolysis

Amides hydrolysed in the presence of **sodium hydroxide** to yield **ammonia** and **carboxylate salt**.

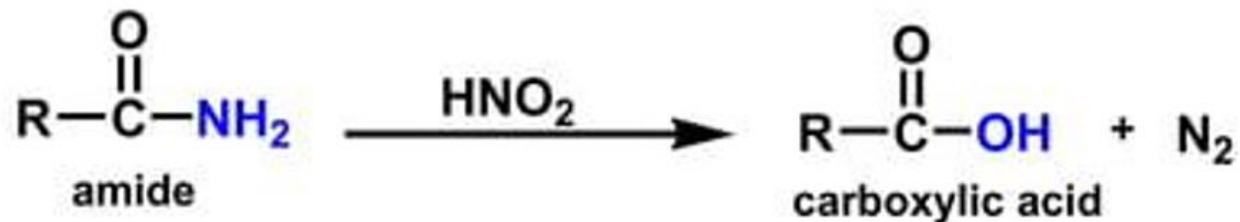
Example:



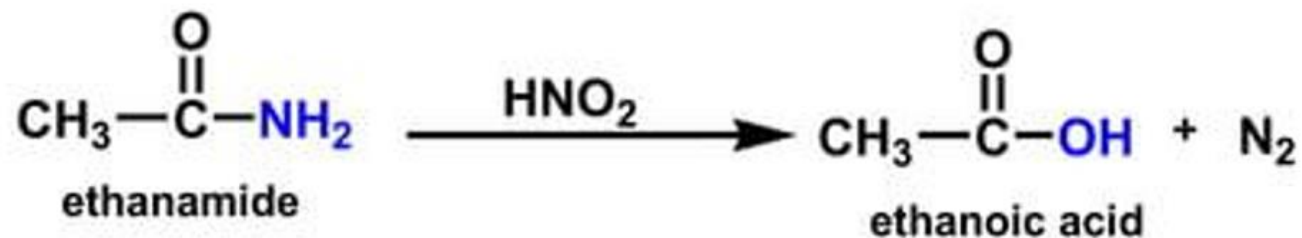
Reactions of amides



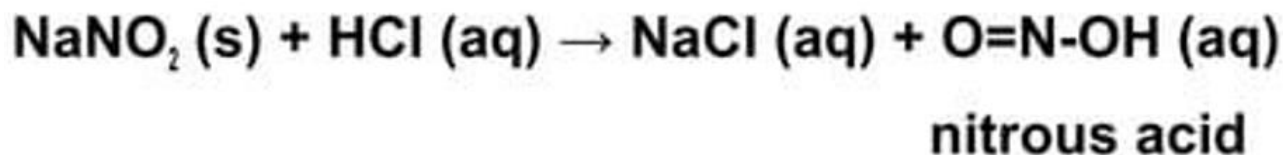
- Amides react with **nitrous acid (HNO₂)** to give **carboxylic acid** and **N₂** gas.



EXAMPLE



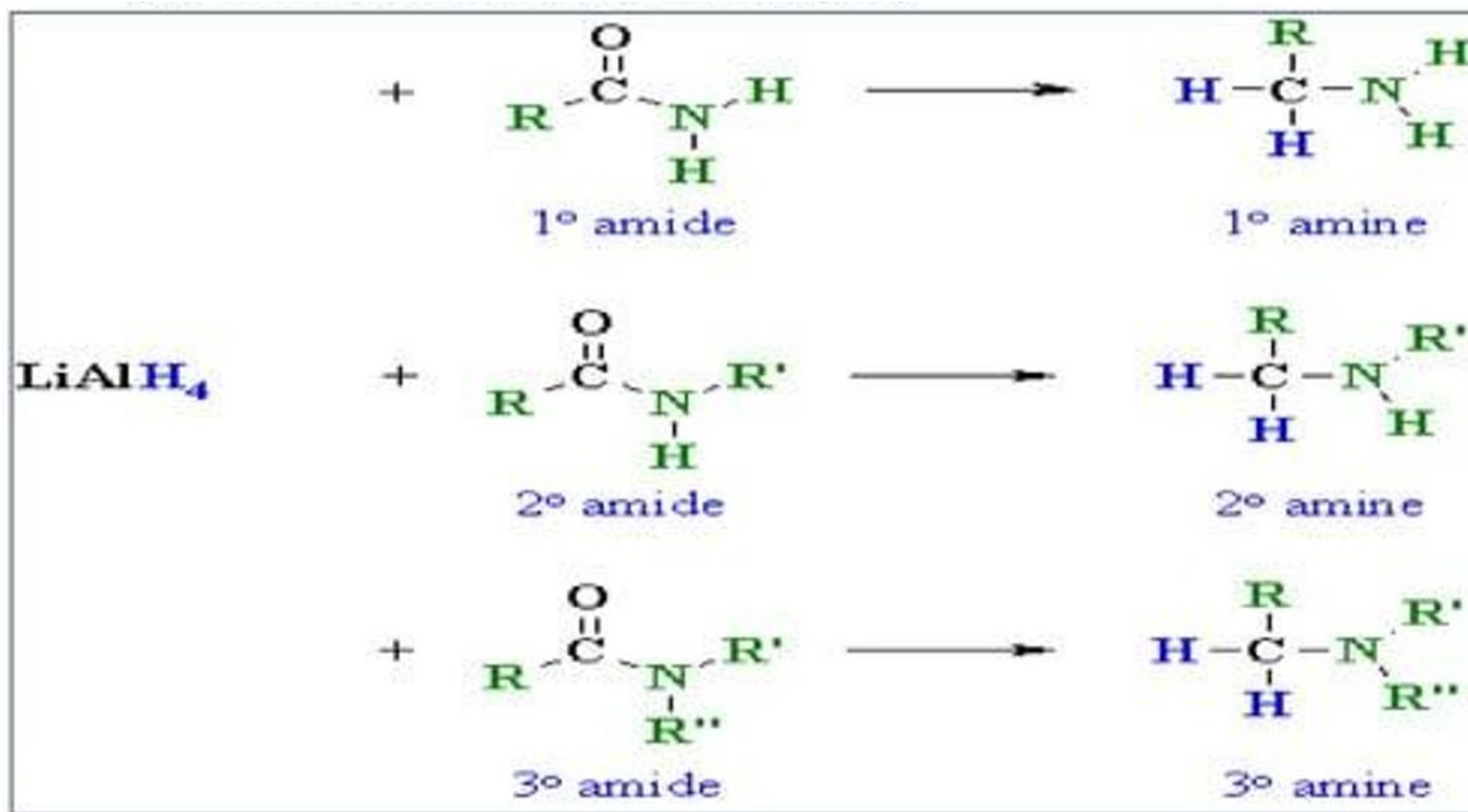
- Nitrous acid is **unstable** and is prepared in situ by the reaction of **dilute HCl or dilute H₂SO₄** with **sodium nitrite** in the absence of heat.



Reactions of amides



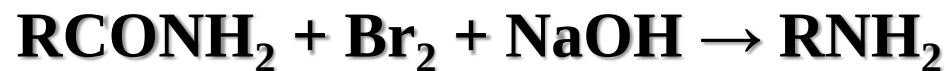
- Amides can be reduced to amine by **conversion of C=O to –CH₂**.
- Amides can be reduced by **LiAlH₄**.



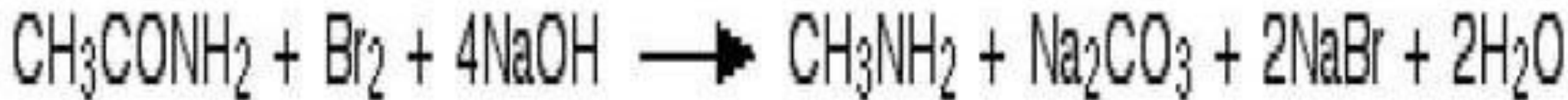
Reactions of amides



- Hofmann degradation is a reaction between an **amide** and a mixture of **bromine** and **sodium hydroxide** solution. **Heat** is needed.
- The net effect of the reaction is a **loss of the –CO- part of the amide group**.



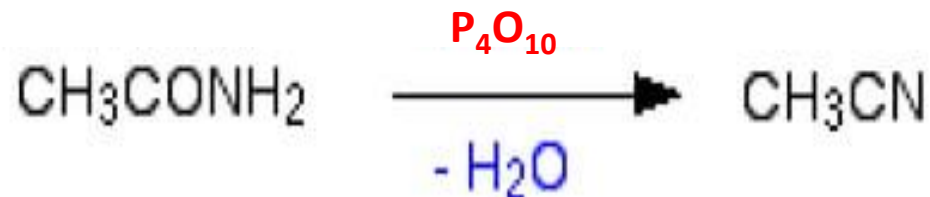
- You get primary amine with one **less carbon atom** than the original amide had (ethanamide → methylamine)
- The hofmann degradation is used as a way of cutting a single carbon atom out of a chain.



Reactions of amides



- Amides are **dehydrated** by heating a solid mixture of the **amide** and **phosphorus (V) oxide** P_4O_{10} / **phosphorus oxychloride** POCl_3 .
- Water is removed from the amide group to leave a **nitrile group** $-\text{CN}$.
- For example, with ethanamide, you will get ethanenitrile.



Esters & Thioesters



Esters

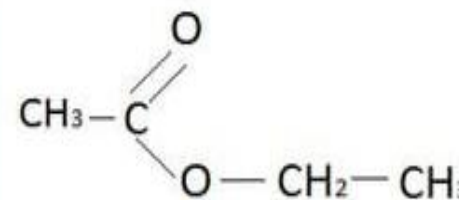


- Esters are derived from **carboxylic acids** and **alcohol**.

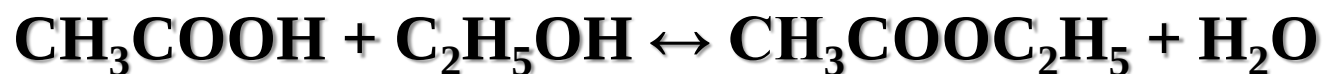


R and **R'** denotes any **alkyl** or **aryl** group, R can also be hydrogen atom.

- OH** group in carboxylic acids is replaced by **hydrocarbon group** in esters.
- The most commonly discussed ester is **ethyl ethanoate**, in this case the **hydrogen atom in -COOH** has been replaced by an **ethyl group**.



Ethyl Ethanoate

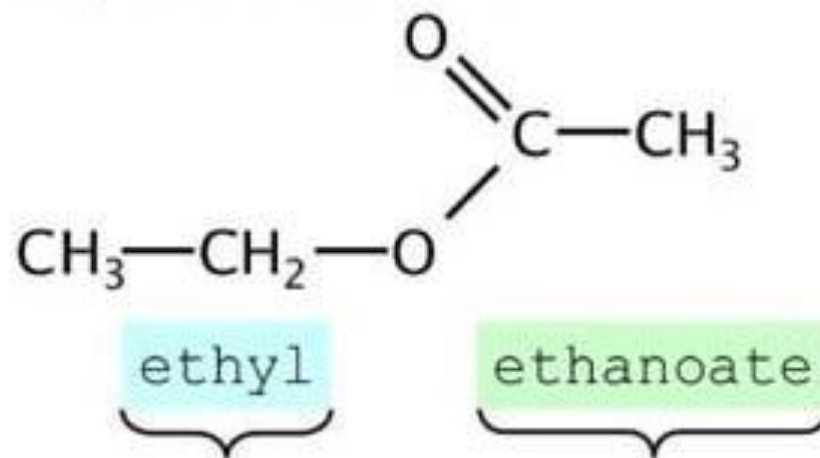


Esters



➤ Naming:

- Named after alcohol & carboxylic acid from which they derived.
- Esters name ending with **-oate**.



This part comes from the alcohol

This part from the acid and is named after it



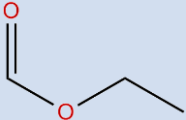
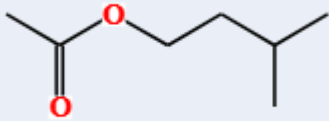
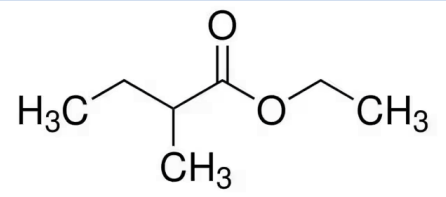
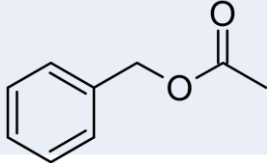
➤ Physical properties of esters:

- Esters are **sparingly soluble in water**.
- Esters are usually **volatile, pleasant smelling liquid**.
- Esters are **neutral** towards litmus.
- Esters are **colourless** natural liquids.
- Their smell is often **floral** or **fruity**.
- Esters have strong **sweet smell**.
- This means they are used in **food flavouring** and **perfumes**.
- Also, they are very good at dissolving organic compounds so often used as **solvent**.

Esters



➤ What they smell:

Ester	Fragrance	structure
Ethyl methanoate	Raspberries	
3-methylbutyl ethanoate	Pears	
Ethyl 2-methylbutanoate	Apples	
Phenylmethyl ethanoate	Jasmine	

Esters

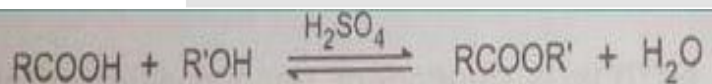


- Ester can prepared from **carboxylic acid** or **acid anhydrides**.

From carboxylic acid

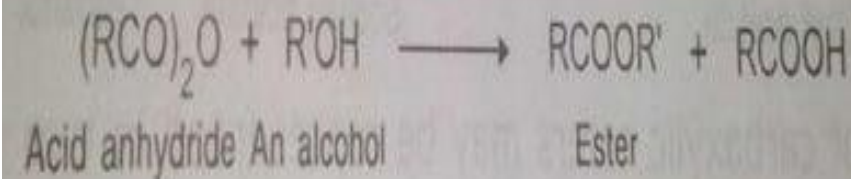
Esters prepared by refluxing the **acid** with an **alcohol** in the presence of small amount of mineral acids as catalysts (ex. 5-10% sulphuric acid).

This reaction is reversible and called **Esterification**



From acid anhydrides

Esters prepared by the reaction of **acid anhydrides** with an **alcohol**.

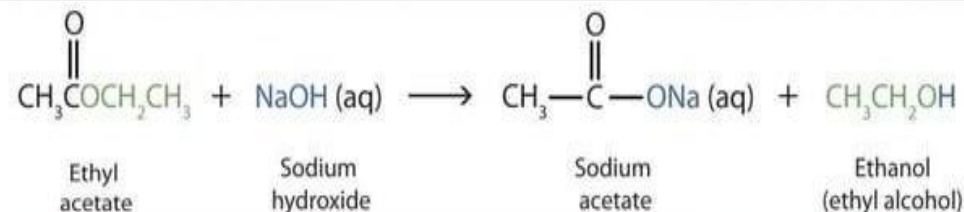




- Chemical reactions of esters

Hydrolysis

Esters are hydrolysed by acid or alkali to form alcohols and acids of their sodium salts or carboxylic acid



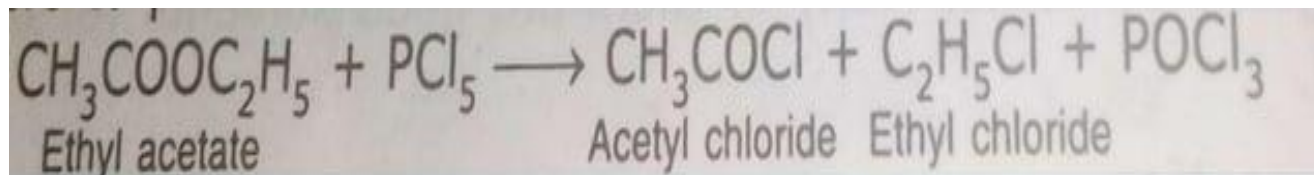
Esters



- **Chemical reactions of esters**

Reaction with
phosphorous
pentachloride

Phosphorous pentachloride reacts with esters to produce acid chloride and alkyl chlorides.



Esters



➤ Uses:

- Esters are used as **solvents for cellulose, oils, gums, resins**, etc.
- They are used in **making artificial flavours and essences**.

➤ Bar soaps:

- Soap is made by combining **sodium hydroxide** with a **liquid fat, and oils**.
- Once these ingredients are mixed, a chemical reaction start to take place.
- The result of this reaction is soap.



Esters



➤ Liquid soaps:

- The major difference between bar soap and liquid soap is the **alkali used to saponify** the oil.
- All soap whether hard or liquid start with a simple chemical reaction between **oils and alkali**.
- With bar soaps, it is **sodium hydroxide**.
- With liquid soaps, it is **potassium hydroxide**.

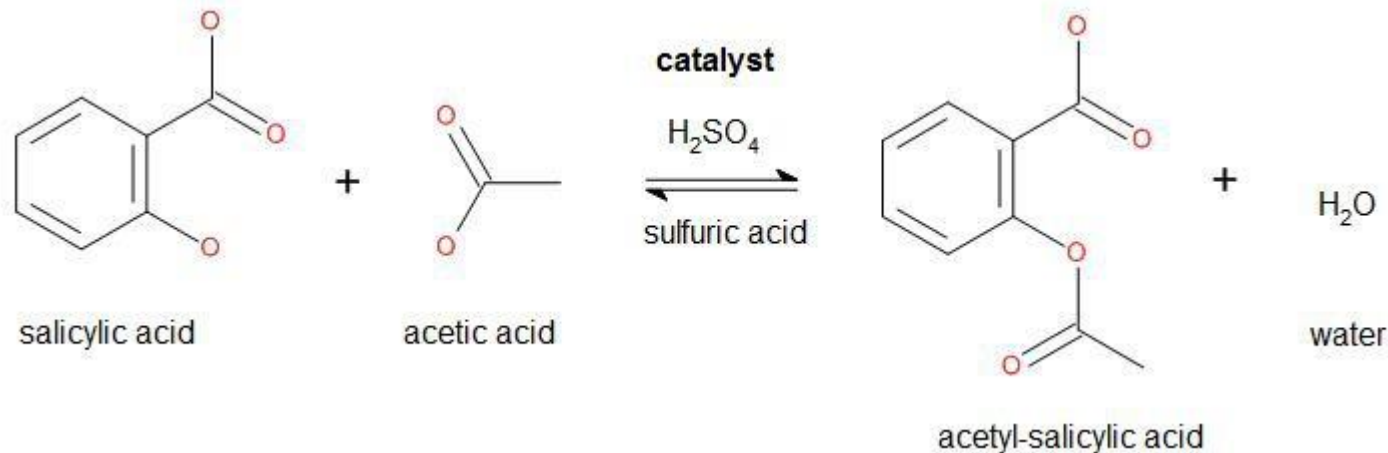


Esters



➤ Pharmaceutical applications:

- **Aspirin** is the ester of salicylic acid and acetic acid.
- It is used to **relieve pain, reduce inflammation**, and has **antiplatelet action**.

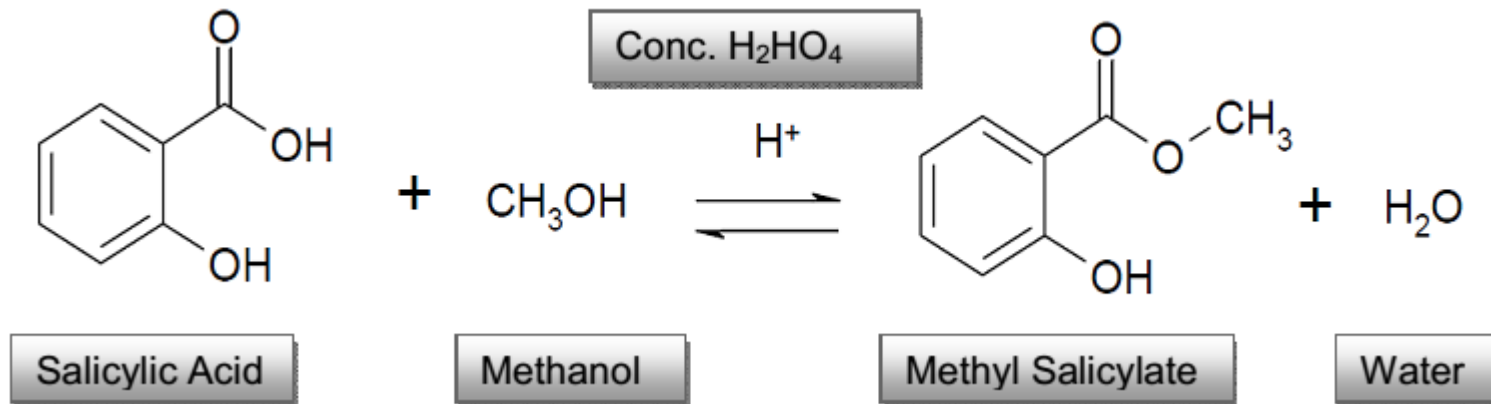


Esters



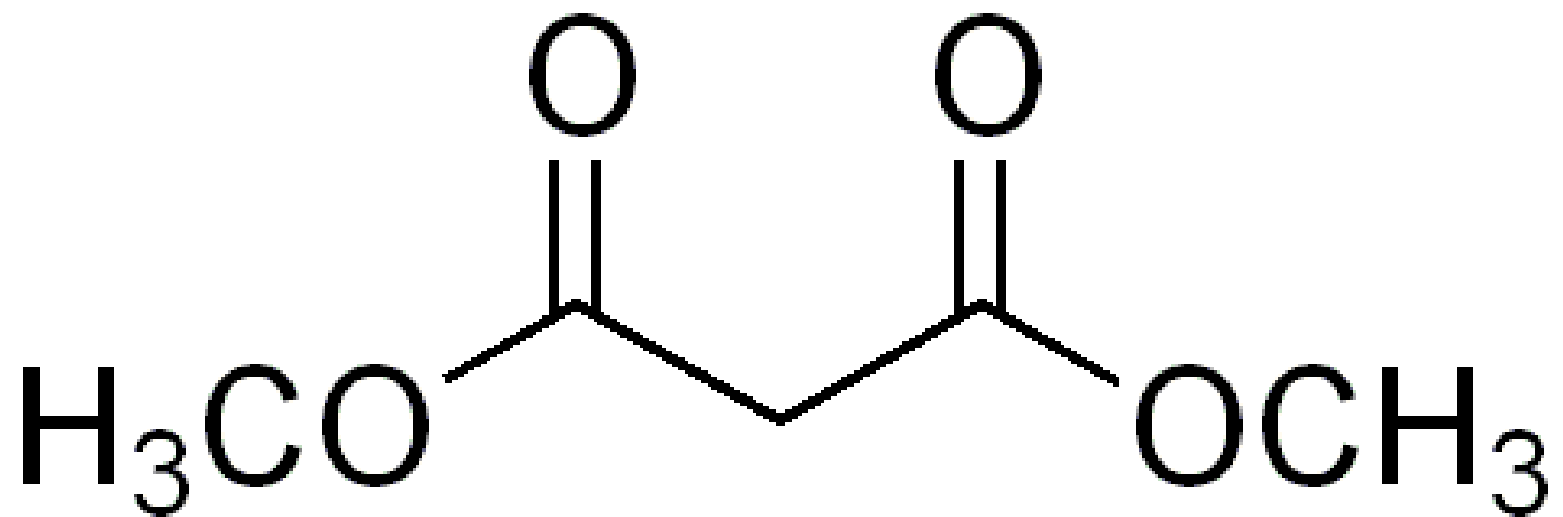
➤ Pharmaceutical applications:

- **Oil of wintergreen** (methyl salicylate) is the ester of salicylic acid and methanol.
- It is used to **soothe sore muscles**.



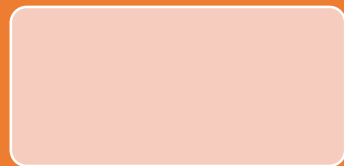


➤ Dimethyl malonate:





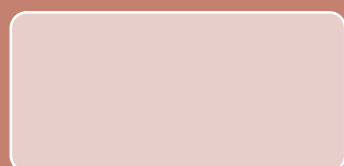
➤ Dimethyl malonate applications:



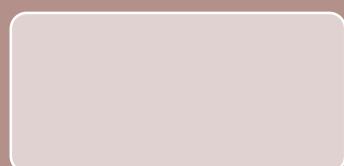
Preparation of pharmaceuticals



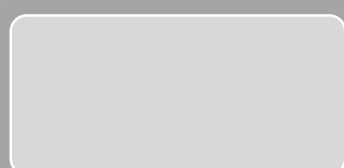
Synthesis of heterocyclic compounds



Alkylation reactions

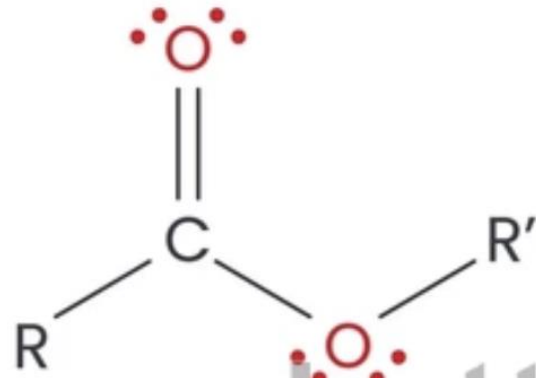


Condensation reactions

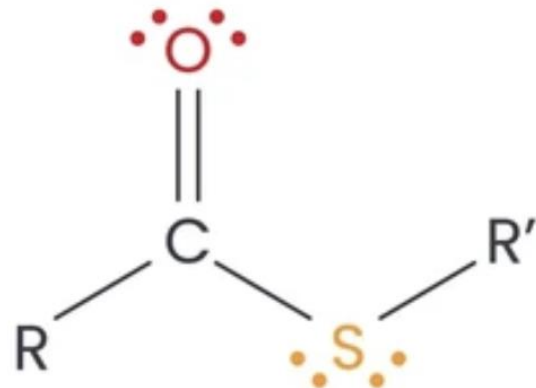


Synthesis of carboxylic acids

Esters VS Thioesters



Ester:
Low reactivity towards
nucleophiles



Thioester:
High reactivity towards
nucleophiles

C.A. derivatives chemical differentiation



	Acyl chloride	Ester	Amide
Water	Vigorous, white fume (HCl) librated	No reaction	No reaction
Acid hydrolysis	Vigorous, RCOOH formed	Reversible, produces RCOOH and alcohol	Form RCOOH and ammonium salt
Base hydrolysis	Vigorous, salt of RCOOH form	Non reversible, forms carboxylate salt and alcohol	Ammonia gas librated
Ammonia	Forms amide	Forms amide	No reaction
Reduction	No reaction	Forms two alcohols	Forms amine
Hoffman degradation	No reaction	No reaction	Forms amine

THANK YOU

