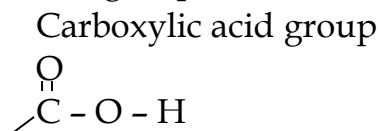
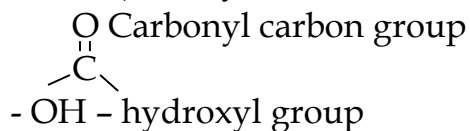


CARBOXYLIC ACIDS

CARBOXYLIC ACIDS/ALKANOIC ACIDS

Carboxylic acids are organic compounds with a general formula, $\text{R} \overset{\text{O}}{\parallel} \text{C} - \text{OH}$

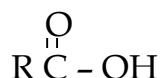
($\text{C}_n\text{H}_{2n}\text{O}_2$) if they are saturated. They contain two functional groups:



Carboxylic acids can be roughly categorized into the following:

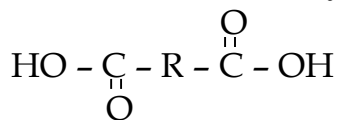
(i) Monobasic acid:

Contains a single carboxylic acid group.



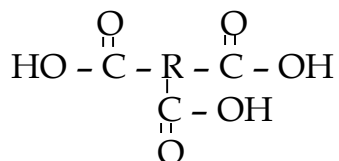
(ii) Diabasic acid

Contains two carboxylic acid groups joined to the same carbon chain.



(iii) Tribasic acid

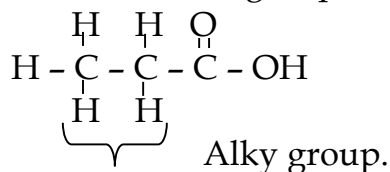
Contains three carboxylic acid groups joined to the same carbon chain.



Nature of the alkyl group

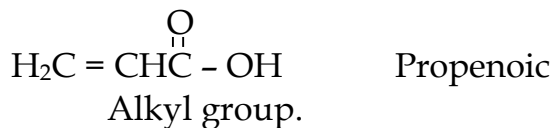
Saturated carboxylic acid

Contains the R group with single carbon-carbon bond.



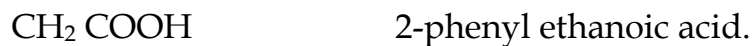
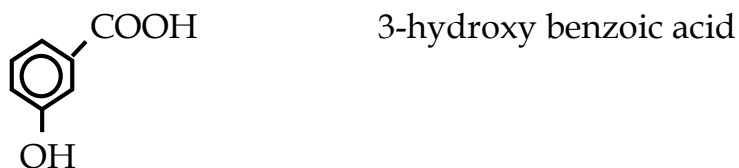
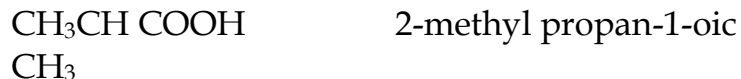
Unsaturated carboxylic acid

Contains at least a double bond in the alkyl chain.



NOMENCLATURE

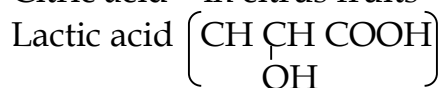
According to the IUPAC system, carboxylic acids are named after their corresponding alkanes. This is usually done by replacing a suffix-ane by OIC.



MONOBASIC CARBOXYLIC ACIDS

These contain a single carboxylic acid group. They are largely found in nature. E.g.

Citric acid - in citrus fruits



Formic acid (HCOOH) - insect bites.

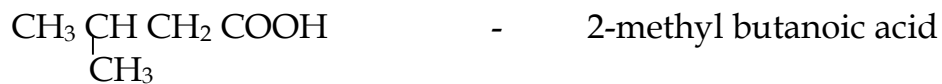
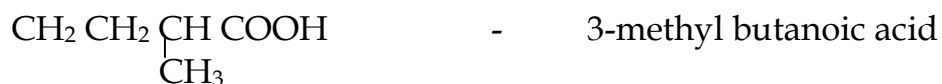
ISOMERISM

Monobasic acids show both structural and functional isomerism.

STRUCTURAL

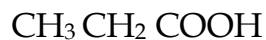
Chain isomerism:

Isomers differ from nature of the carbon chain $\text{C}_5\text{H}_{10}\text{O}_2$.

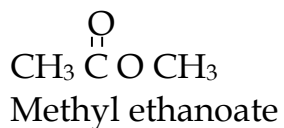


FUNCTIONAL

Monocarboxylic acids are isomeric with esters e.g. $\text{C}_3\text{H}_6\text{O}_2$



Propanoic acid



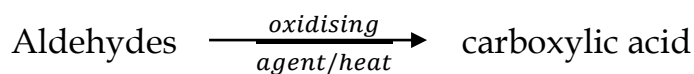
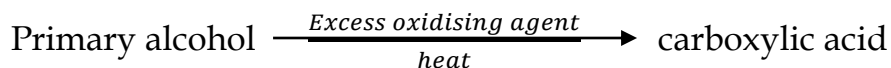
METHODS OF PREPARATION OF MONOCARBOXYLIC ACIDS

Monocarboxylic acids can be prepared from the following:

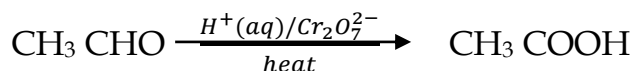
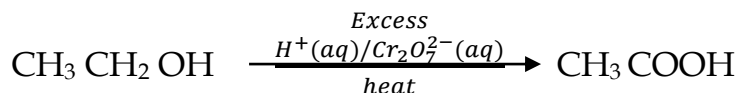
(i) **Oxidation of primary alcohols and aldehydes:**

Primary alcohols are oxidized by excess oxidizing agents until carboxylic acids are formed.

Aldehydes are also oxidized to carboxylic acids.

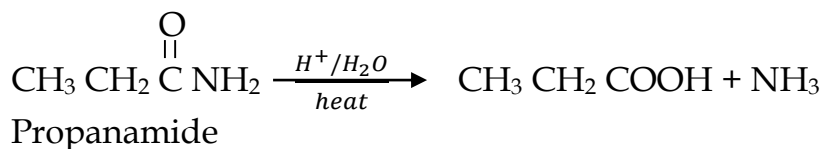
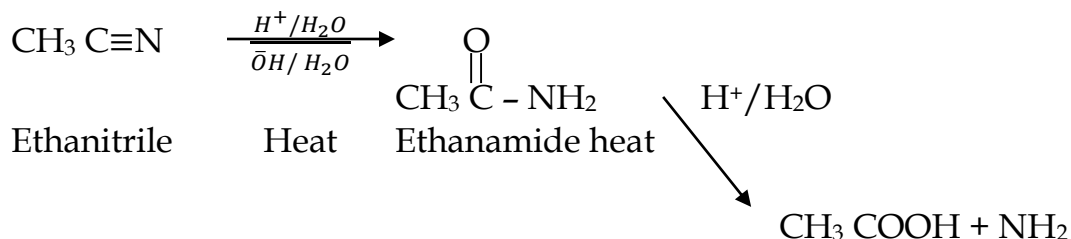


The main lab. Oxidizing agents used in this case are acidified $\text{K}_2/\text{Na}_2\text{Cr}_2\text{O}_7/$
 $\text{H}^+(\text{aq}) / \text{CrO}_3(\text{aq}), \text{H}^+(\text{aq}) / \text{KMnO}_4(\text{aq})$

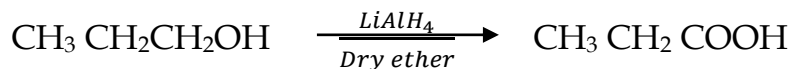
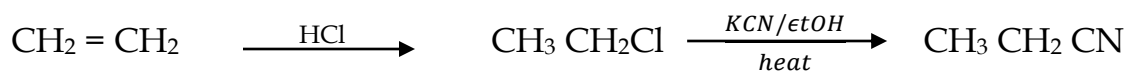


(ii) **Hydrolysis of acid nitriles and acid amides with alkaline or acid.**

When a nitrile is heated under reflux with mineral acid or alkali, an amide is first formed which later is further hydrolyzed to a carboxylic acid.

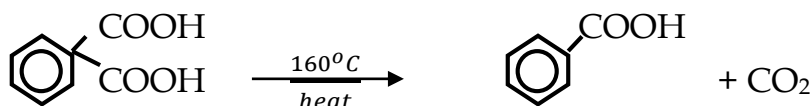


The usefulness of this reaction is, increase of the carbon chain of one carbon. E.g.
Convert $\text{CH}_2 = \text{CH}_2 \longrightarrow \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{OH}$



(iii) **From dicarboxylic acids**

When dicarboxylic acids are heated, they are decomposed by loss of CO_2 to form a monocarboxylic acid. This reaction is important in reducing the carbon chain by one carbon.



PROPERTIES OF CARBOXYLIC ACIDS

Physical properties:

Lower members ($\text{C}_1 - \text{C}_4$) are colourless liquids very soluble in H_2O .

Medium members ($\text{C}_5 - \text{C}_9$) are solids only partially soluble in H_2O .

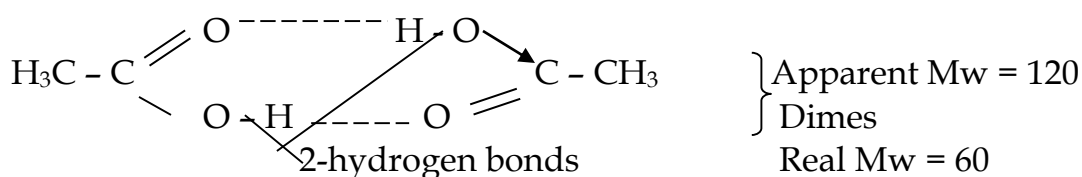
SOLUBILITY OF CARBOXYLIC ACIDS IN H_2O .

Solubility of carboxylic acids decreases with the increase in the carbon chain. This is because the more number of carbon chains which are hydrophobic outweighs the carboxylic acid group, which is responsible for forming H_2 bonds with H_2O hence low solubility.

Melting and boiling points:

Carboxylic acids show high values of melting and boiling points compared to their corresponding alcohols and alkanes. This is because a single molecule of a carboxylic acid dimerises via H_2 bonds which makes their melting and boiling points to be higher.

By them undergoing dimerisation, their apparent molecular masses when determined by **cryoscopic method** to be twice the actual molecular mass.



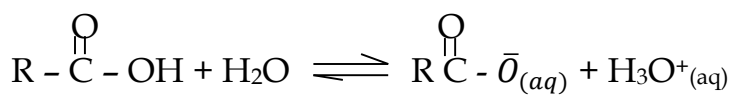
The formation of H₂ bonds also make them to be very soluble in H₂O.

CHEMICAL PROPERTIES

Acid nature:

Carboxylic acids are acidic in nature. They are more acidic than phenol but less acidic compared to mineral acids. Aqueous solutions of carboxylic acids turn litmus paper red.

When dissolved in H₂O, they dissociate. An equation is established as shown.



$$K_a = \frac{[RCO\bar{O}][H_3O^+]}{[RCOOH]} \text{ Moldm}^{-3}.$$

The K_a value is then used to denote the strength of the acid. The bigger the K_a value, the more stronger the acid.

Acid	K _a	PK _a
Methanoic, HCOOH	1.77 × 10 ⁻⁴ mol dm ⁻³	3.75
Ethanoic, CH ₃ COOH	1.75 × 10 ⁻⁵ mol dm ⁻³	4.82

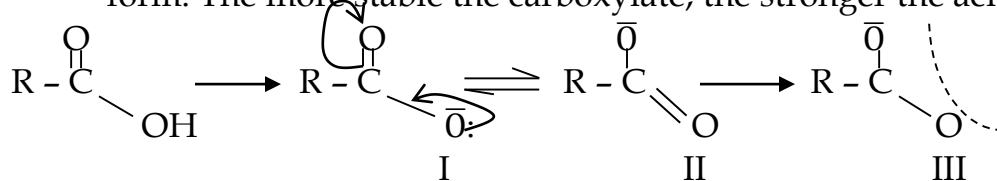
Another important value is PK_a, therefore the higher the PK_a value, the weaker the acid.

Explanation/reason for acid strength

Acidity of carboxylic acids is determined by a number of factors;

(i) **Resonance of the carboxylic ion**

When the carboxylic acid group ionizes, it forms the carboxylic ion and this ion may show several resonance structures in order to attain a more stable form. The more stable the carboxylate, the stronger the acid.



I, II and III are resonance structures of carboxylic acid.

(ii) **Inductive effect:**

Inductive effect is a tendency of an atom or groups of atoms to donate or withdraw electrons from a certain group.

Adjacent electron withdrawing substituents increase the acidity by further stabilizing the carboxylate. E.g.

Acids	Structure	PKa
Ethanoic acid	CH ₃ CO ₂ H	4.7
Fluoro ethanoic	FCH ₂ CO ₂ H	2.6
Dichloro ethanoic	ClCH ₂ CO ₂ H	1.3
Chloro ethanoic	Cl ₂ CHCO ₂ H	2.9
Tri-chloro ethanoic	Cl ₃ CCO ₂ H	0.9
Nitro ethanoic	NO ₂ CH ₂ CO ₂ H	1.7

The above table shows that the presence of an electron withdrawing atom pulls electrons from the bond decreasing electron density of that bond (O-H) and the ease of a proton release.

More atoms of such groups decreases the electron density of the O - H bond further and stabilizing the carboxylate thus high acidity.

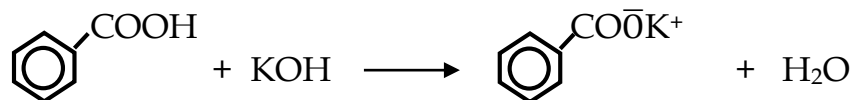
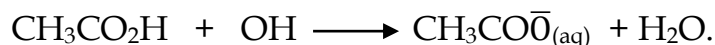
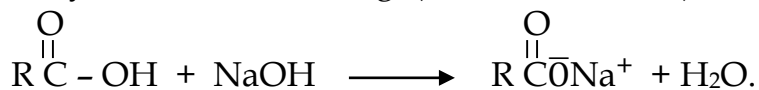
The data below shows the PKa of the following acids. Explain.

Acid	PKa
CH ₃ COOH	4.7
CH ₃ CH ₂ COOH	4.9

REACTIONS OF CARBOXYLIC ACIDS

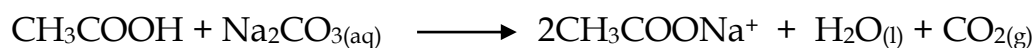
They react as weak acids.

They react with bases e.g. (KOH and NaOH) to form a salt and H₂O.

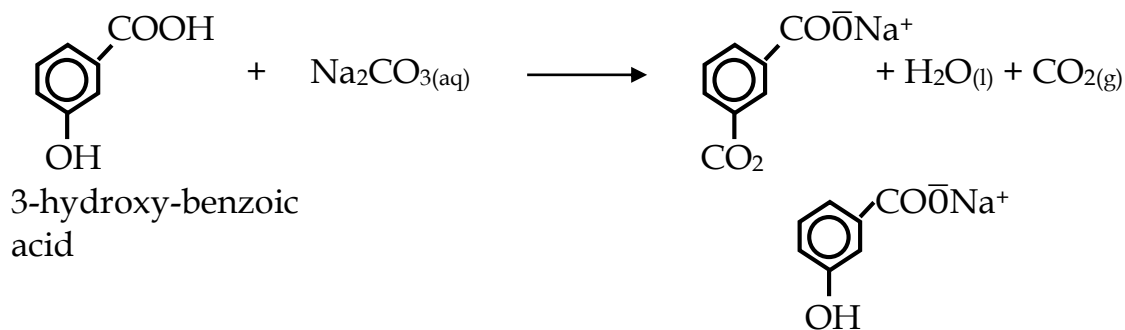
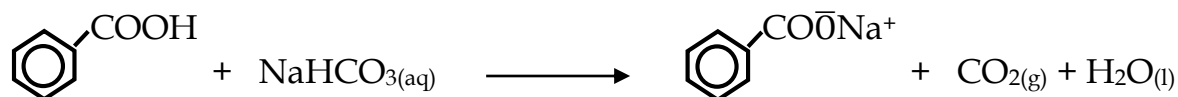


REACTION WITH SODIUM CARBONATE (Na₂CO₃)

Carboxylic acids unlike phenol react with Na₂CO₃ very slowly to liberate CO_{2(g)}. This reaction is of practical importance in distinguishing carboxylic acids from phenols. The reagent used is saturated Na₂CO₃.



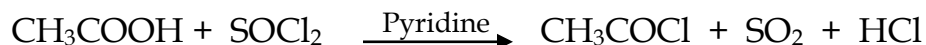
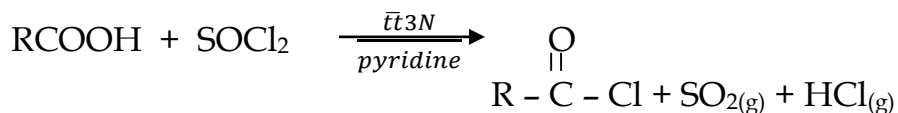
Similarly, CO₂ can also be evolved from saturated NaHCO₃.



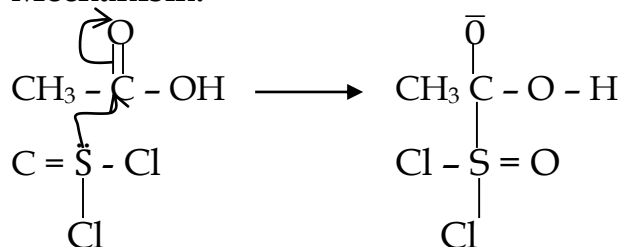
OTHER REACTIONS:

With SOCl₂.

Carboxylic acids react with SOCl₂ in presence of an organic base e.g. pyridine to form an acid chloride and SO₂. This is one useful way of preparing acid chlorides.



Mechanism:



Reaction with PCl₅.

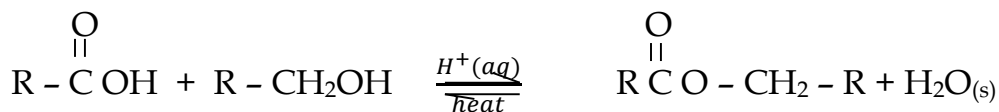
Carboxylic acids react with PCl₃ or PCl₅ to form acid halides.

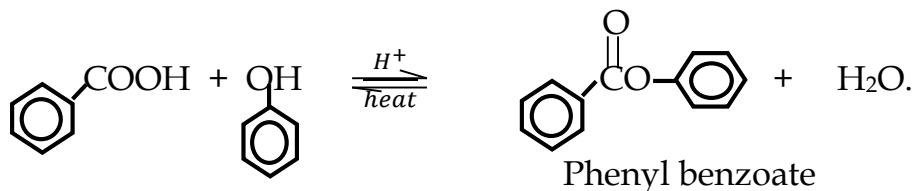
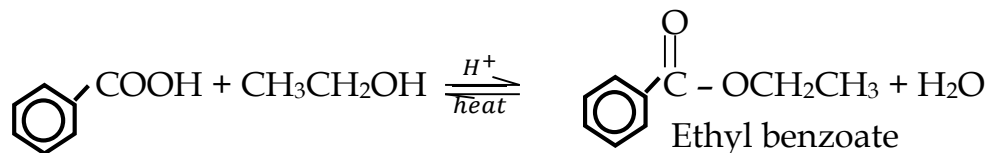
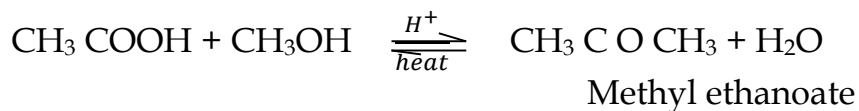


Reaction with alcohols

React with alcohols in presence of a mineral acid to form an ester under heat. This is called esterification where an ester is formed by refluxing a carboxylic acid and alcohol in presence of an acid catalyst.

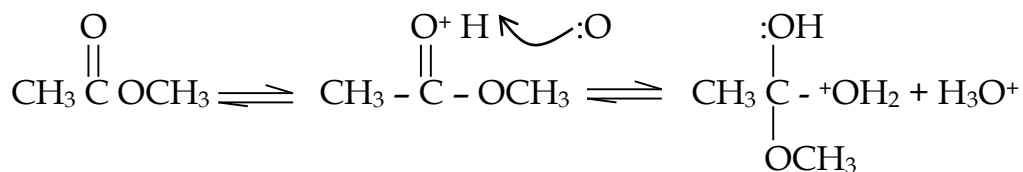
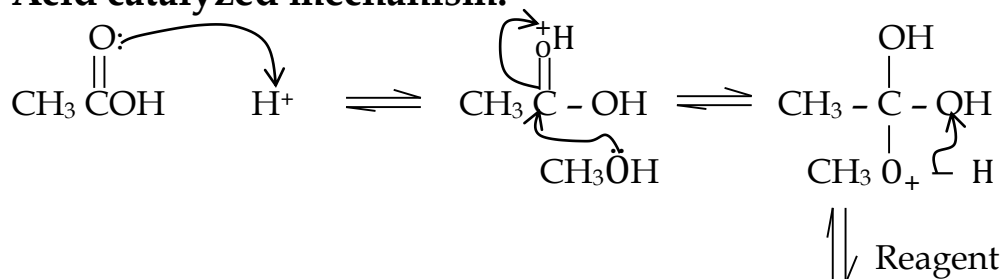
To complete the reaction, one of the components either an acid or an alcohol has to be in excess or to remove an ester at a certain interval once it is formed.





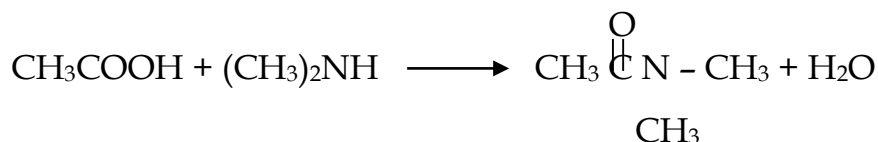
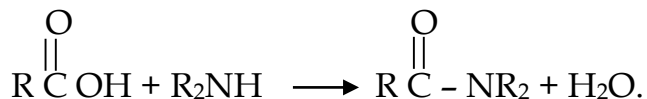
The mechanism for this reaction depends on the catalyst used/base catalysed or acid catalysed.

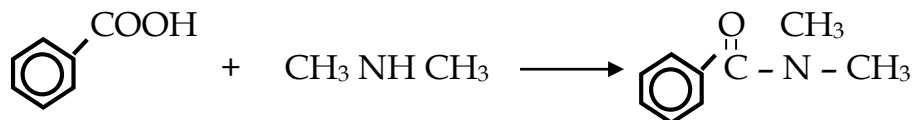
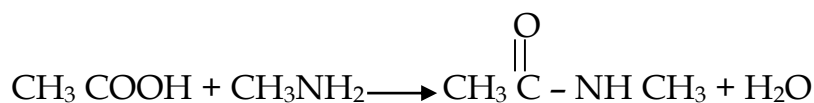
Acid catalyzed mechanism.



Reaction with amides:

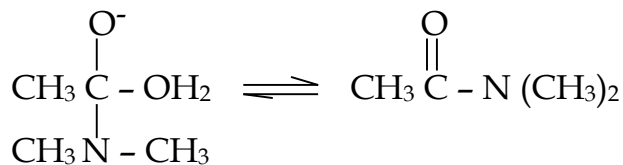
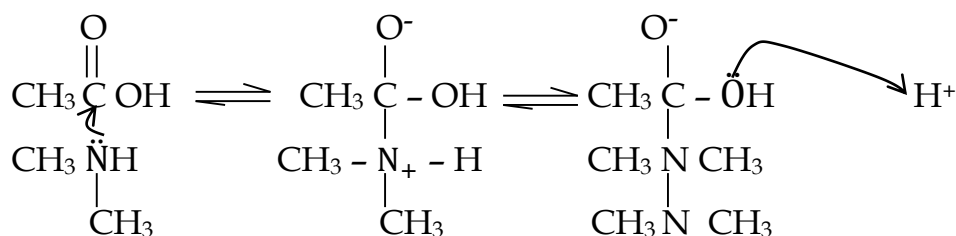
Carboxylic acids react with amides to form substituted amines. With amines, they form amides.





This reaction occurs because of the presence of a proton on the amine which are substituted by the carboxylate.

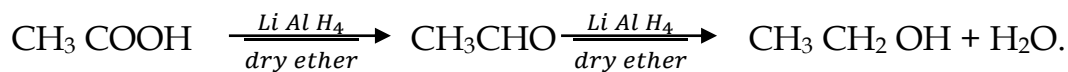
Mechanism:



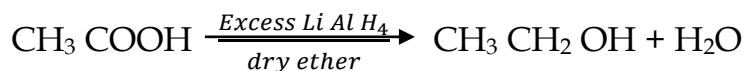
REDUCTION OF CARBOXYLIC ACIDS

Carboxylic acids are usually reduced by reducing agents e.g. LiAlH_4 /ether (THF) to form aldehydes and later alcohols (primary).

Note: NaBH_4 is not commonly used to decrease carboxylic acids because it is less reactive.

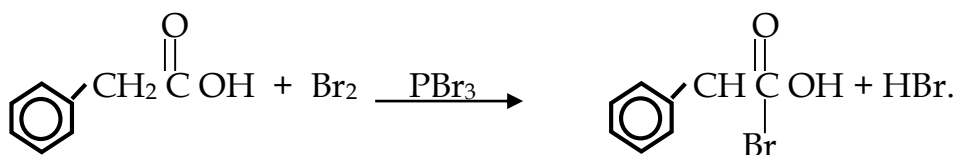
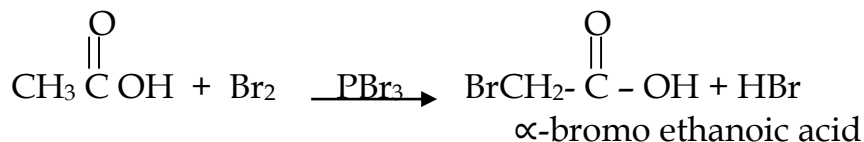


OR:



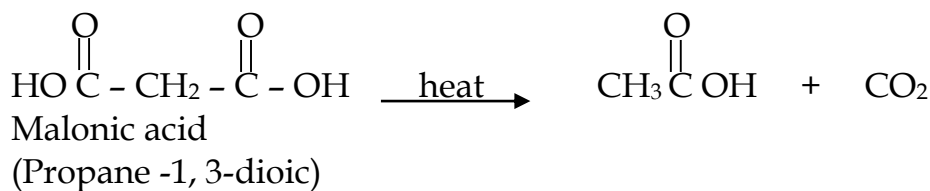
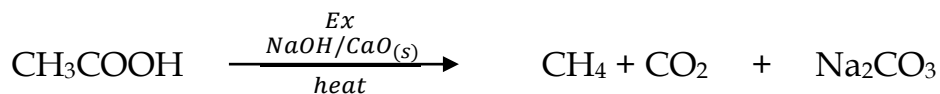
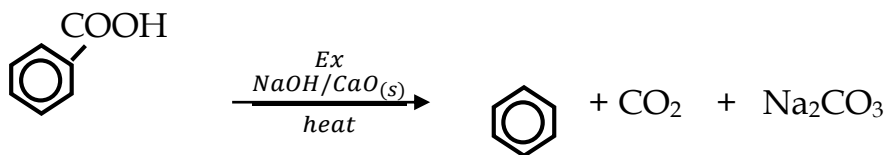
REACTIONS WITH HALOGENS (α -HALOGENATIONS)

Carboxylic acids can be halogenated at the carbon atom adjacent to the carboxylic group when reacted with reagents like Br_2 , PCl_5 . This reaction depends on the character of the carbonyl compound where the product of the reaction known as α -bromo carboxylic acid, is converted to α -hydroxy or α -amino carboxylic acid.



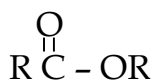
DECARBOXYLATION

Carboxylic acids with a carbonyl group at the third position readily undergoes thermal decarboxylation where CO_2 is lost to form a simple alkane when heated in the presence of dry soda lime.



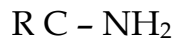
Carboxylic acid derivatives

Esters



Amides

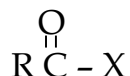




Anhydrides

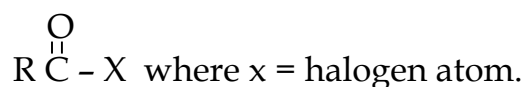


Acid halides



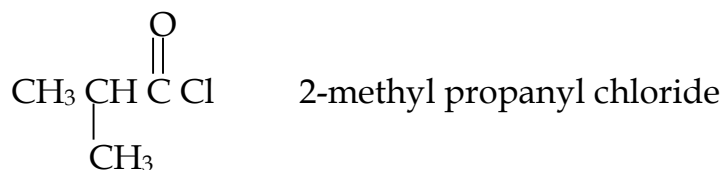
ACID HALIDES

These are compounds derived from carboxylic acids by reacting an acid with a halogen. The commonest examples are acid chlorides.



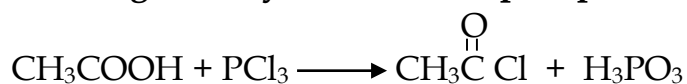
Nomenclature:

Acid chlorides are named by replacing the suffix -ic in acids with -oyl.



PREPARATION

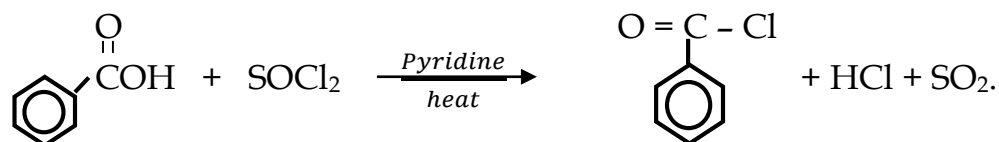
i) **Reacting carboxylic acids with phosphorous halides.**





ii) **Reaction of carboxylic acid with thionyl chloride**

This reaction should occur in a fume cupboard due to evolution of toxic acids or should occur in the presence of pyridine which absorbs.



PROPERTIES OF ACID HALIDES

Physical:

They are colourless volatile liquids with irritating smells. They fume easily in moist air due to evolution of HCl gas.

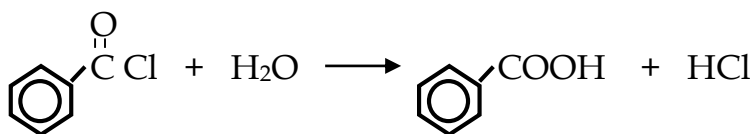
Have low boiling points than the corresponding acids.

Chemical properties:

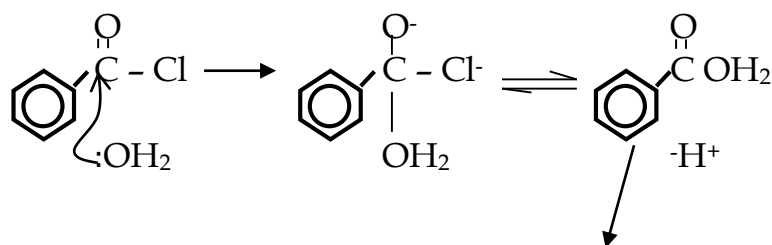
They undergo a number of reactions making them suitable for organic synthesis.

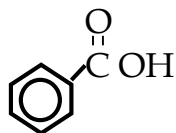
Hydrolysis using H₂O.

Acid halides react with H₂O to form their parent carboxylic acids.



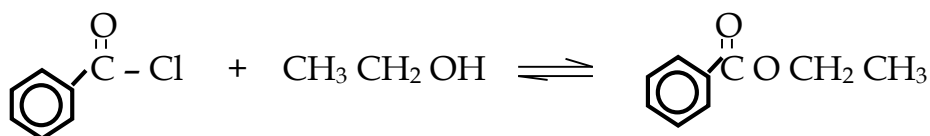
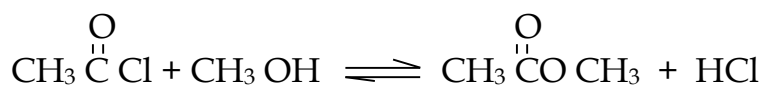
Mechanism:



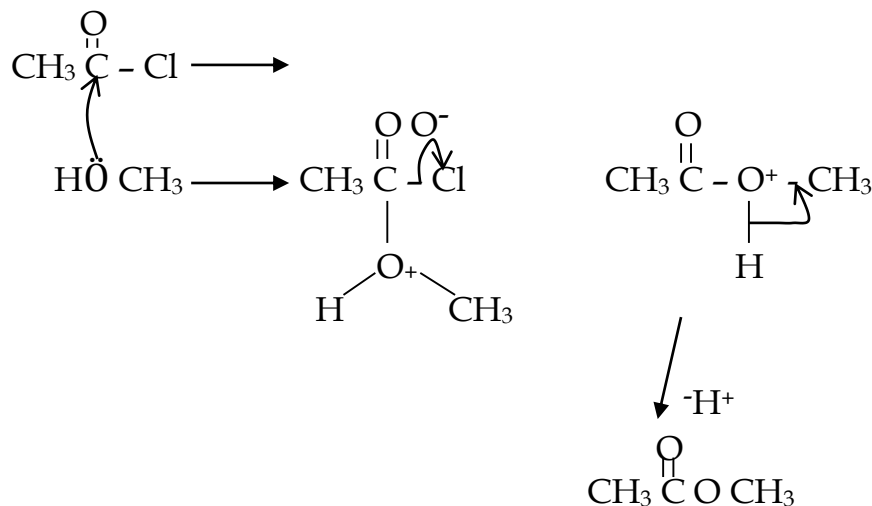


Reaction with alcohols:

Acid chlorides react with alcohols to form esters.

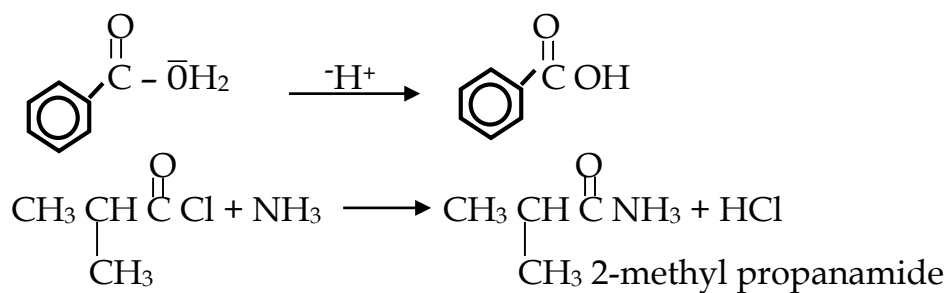


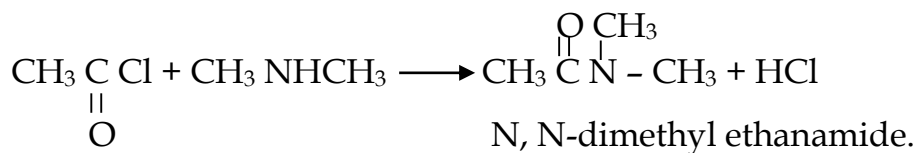
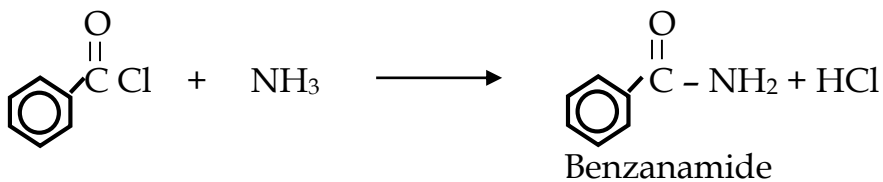
Mechanism:



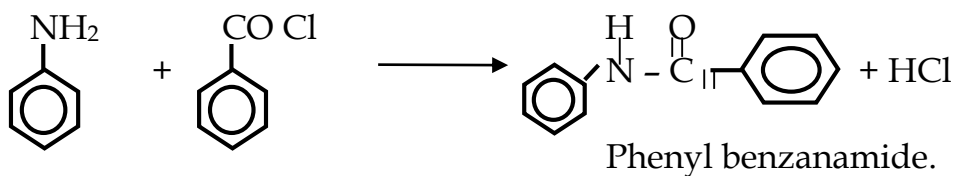
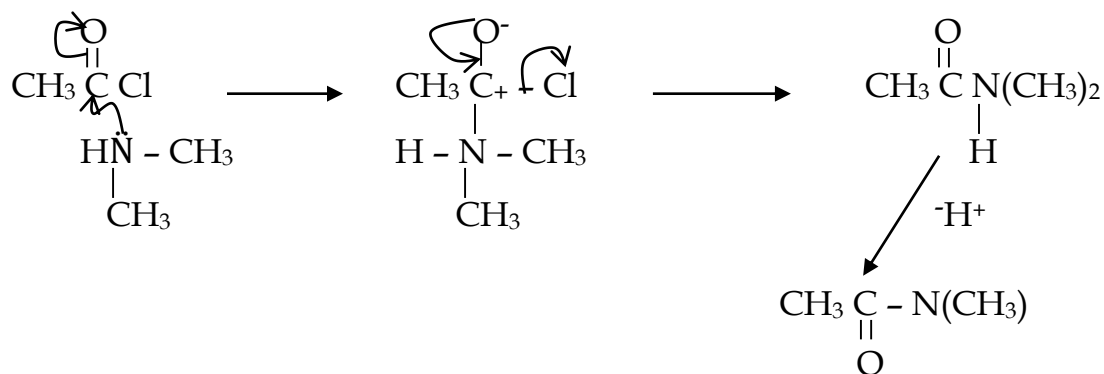
Reaction with NH_3 and amines:

Acid chlorides react with NH_3 to form amides. This reaction is responsible with primary/secondary amines to form amides.



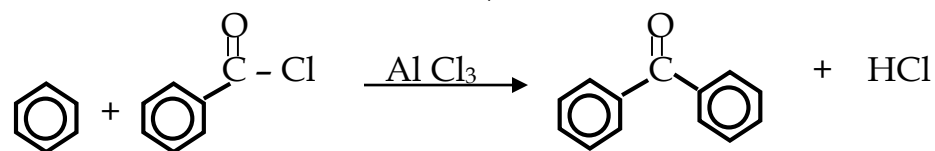
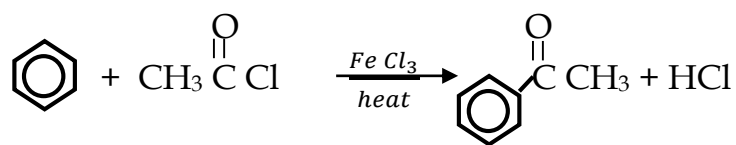


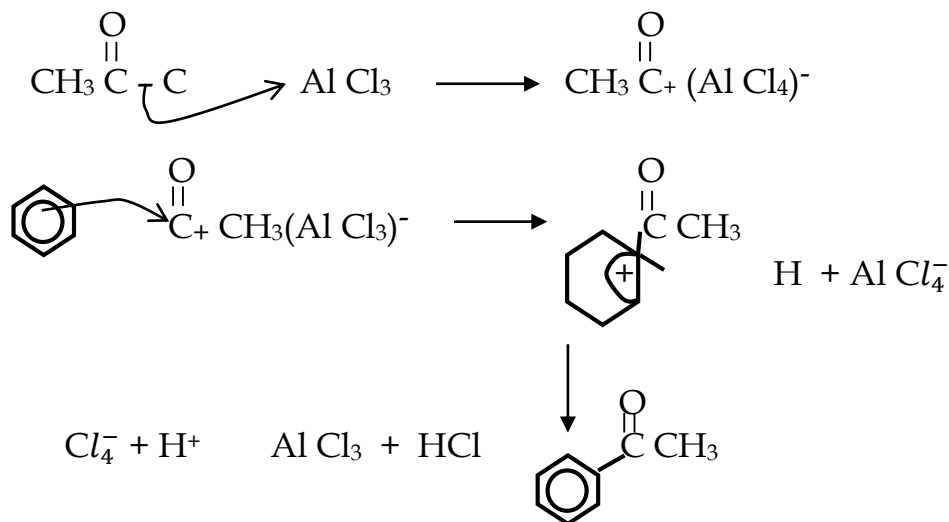
Mechanism:



Reaction with benzene:

Acid halides react with benzene in presence of a hydrogen carrier.



Mechanism:**AMIDES**

Amides are compounds derived from carboxylic acid and nitrogen containing compound like amine or NH_3 with a general formula



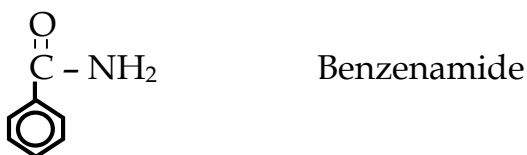
Unlike amines, they contain a carbonyl carbon directly attached to the nitrogen.

Naturally, such compounds are found in proteins.

Nomenclature:

Amides are named as derivatives of parent hydrocarbons alkane, replacing -e- amide.

E.g.



$\text{CH}_3\text{CONH}(\text{CH}_3)_2$ N, N-dimethyl ethanamide

$\text{CH}_3\text{CH}_2\overset{\text{O}}{\underset{\text{CH}_3}{\text{C}}}-\overset{\text{CH}_3}{\text{N}}-\text{CH}_3$ N, N, N - trimethyl propanamide.

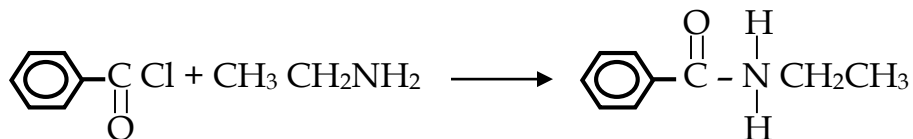
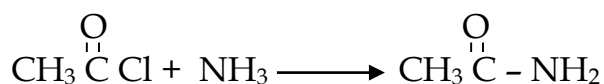
PROPERTIES OF AMIDES

Physical:

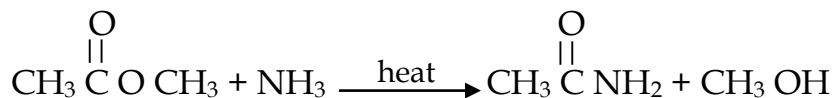
All amides are colourless crystalline solids except ethanamide. They have got higher boiling points than corresponding carboxylic acids due to the formation of H_2 bonding.

PREPARATION

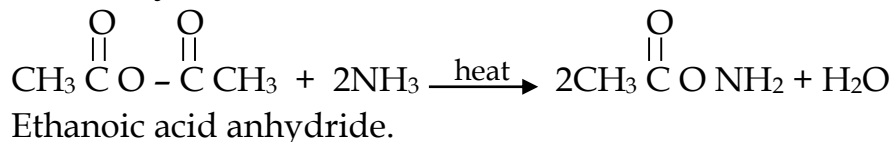
Reaction between acid halides and NH_3 or amines.



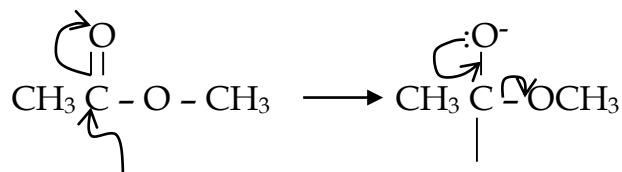
Esters and ammonia

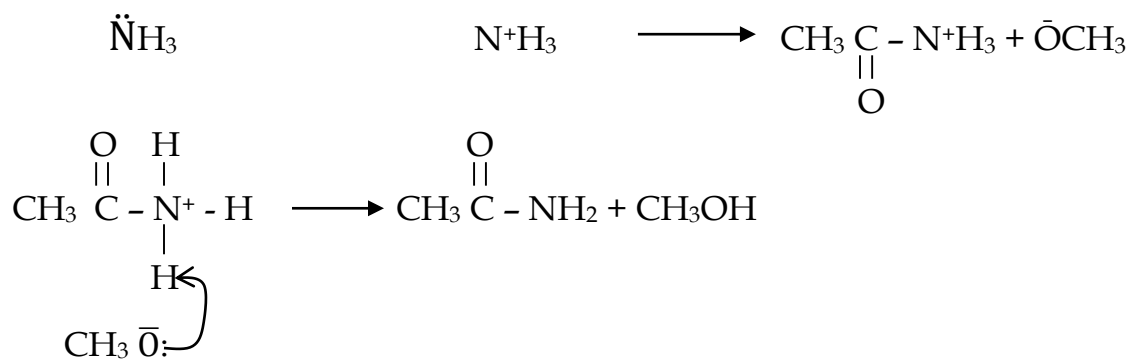


Acid anhydrides and ammonia

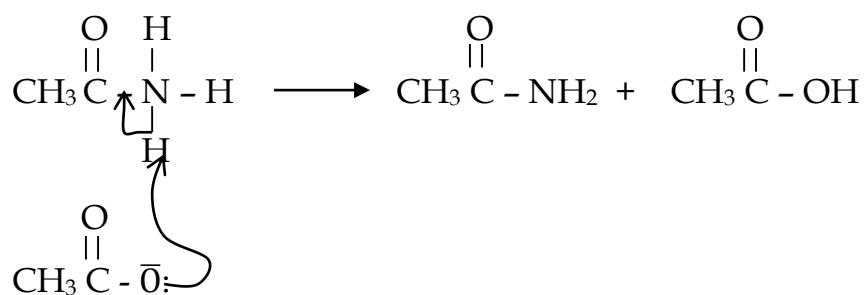
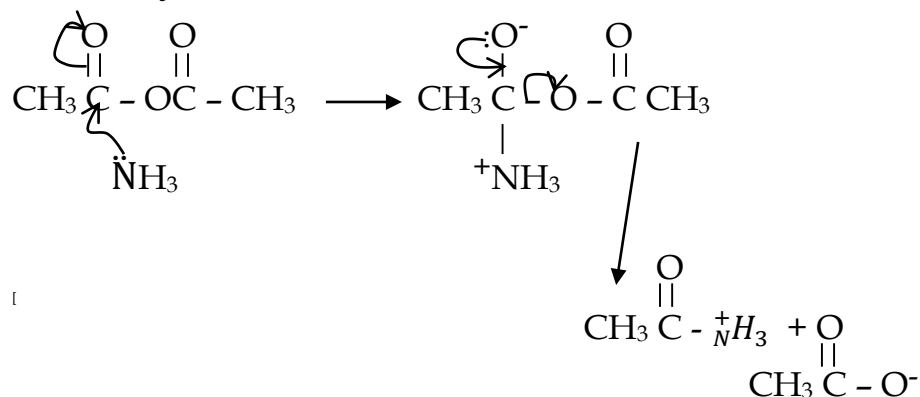


Mechanism:

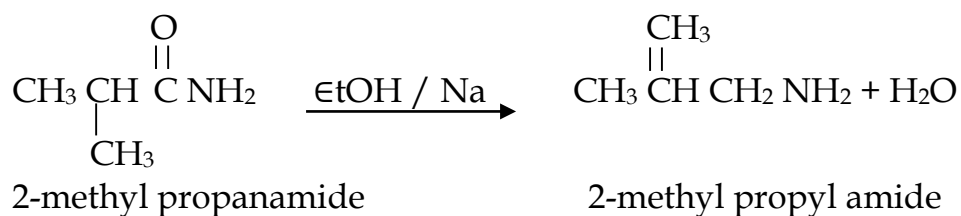




With anhydrides



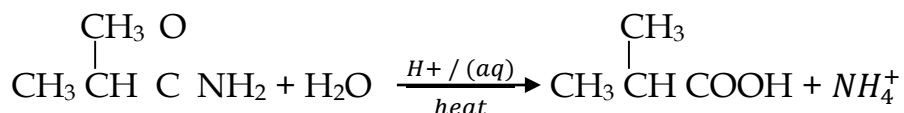
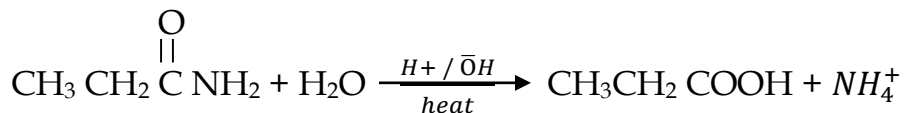
Amides are reduced by reducing agents such as sodium tetrahydride borate, LiAlH_4 .



Hydrolysis

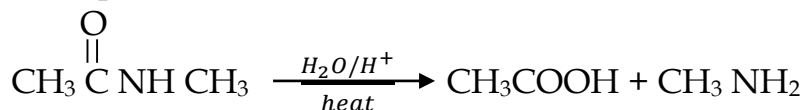
Amides are hydrolysed in presence of a mineral acid or an alkali to form a carboxylic acid.

For example:



For distributed amides, hydrolysis produces a carboxylic acid and an amine.

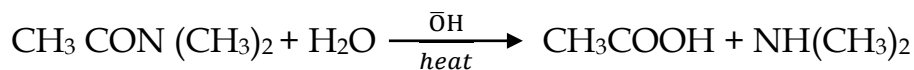
Example:



N-methyl ethanamide

Primary amine

For trisubstituted.

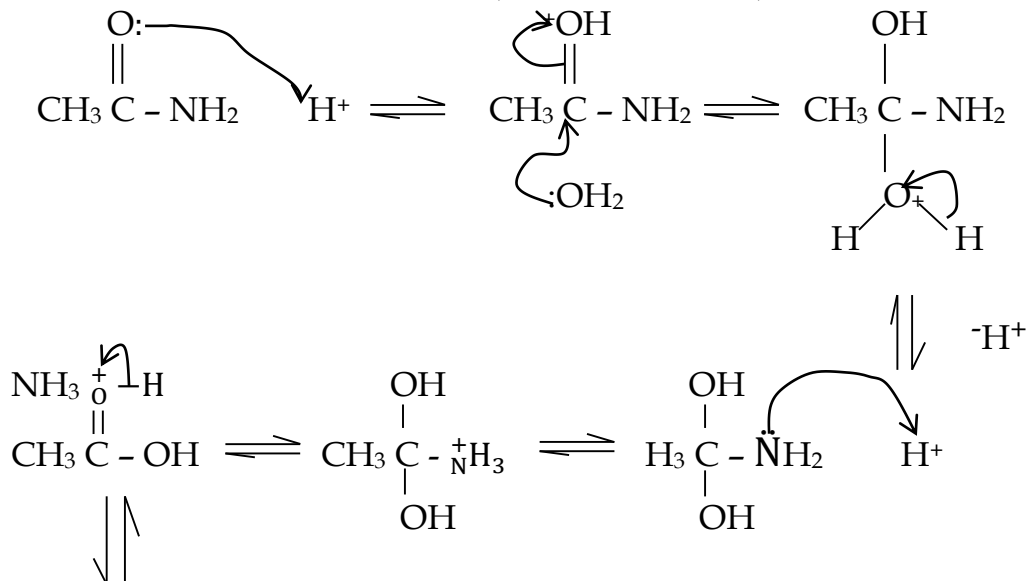


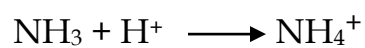
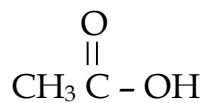
N-N-dimethylethanamide

Secondary amine.

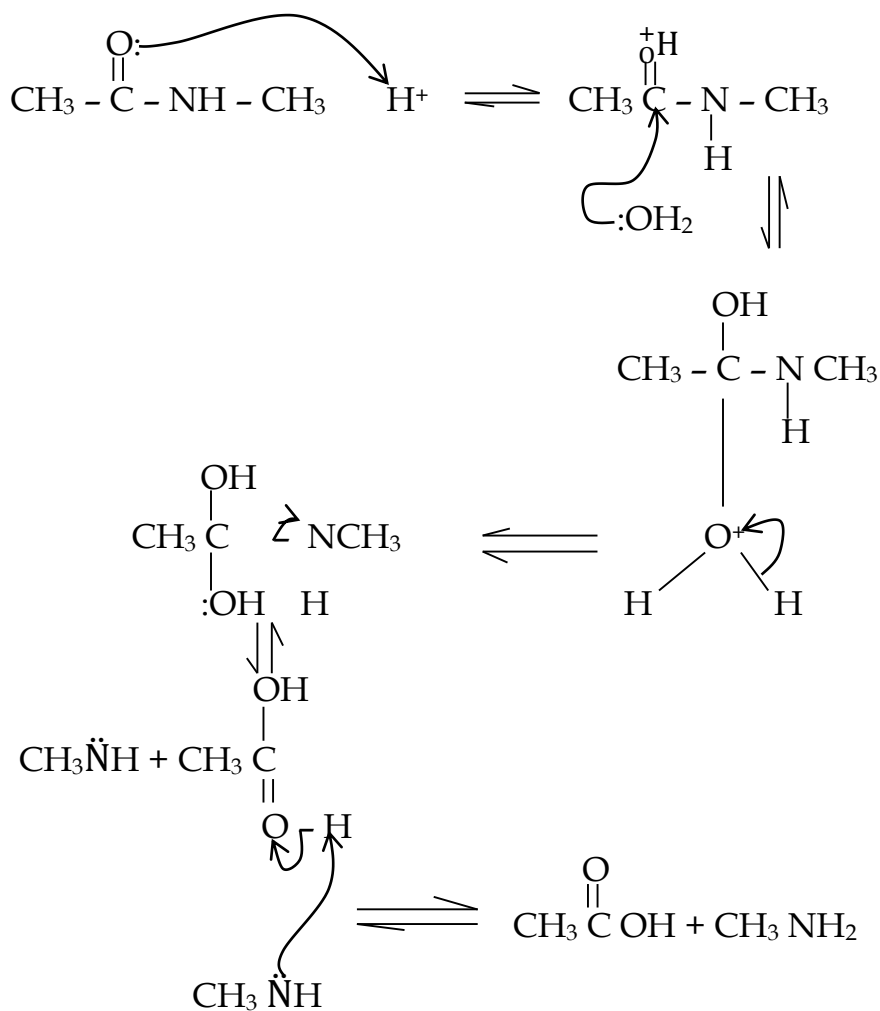
ACID CATALYZED HYDROLYSIS (MECHANISMS)

1.





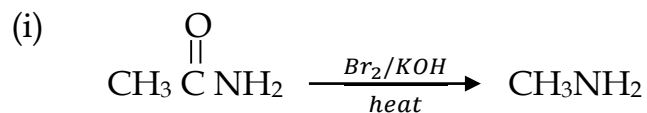
2.



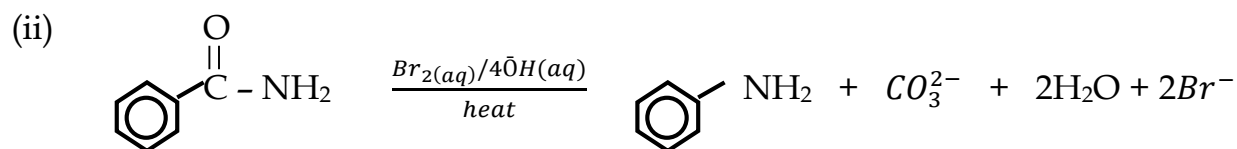
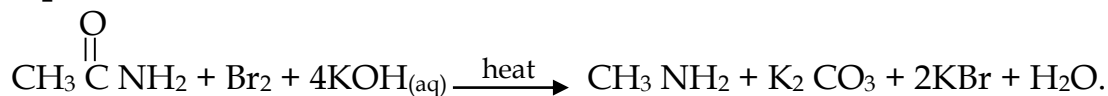
HOFFMAN'S DEGRADATION

When an amide is heated with Br₂ and an alkali, a primary amine is produced which is less than one carbon from the original amide; this reaction is known as

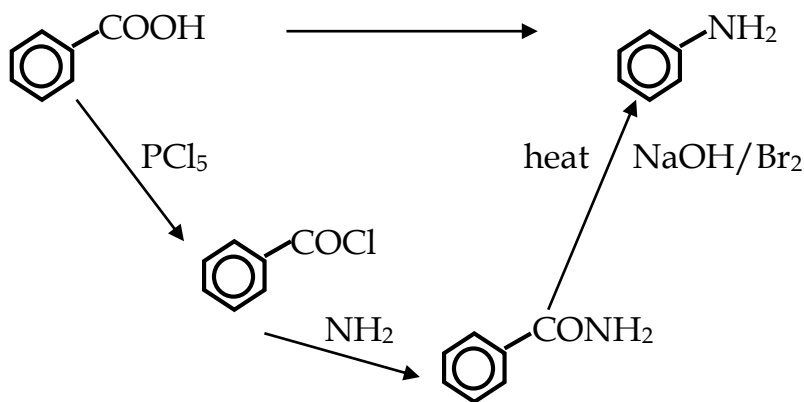
Hoffman's degradation because it involves reduction of the carbon chain by one carbon atom.



Equation:

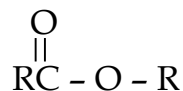


Convert  to 



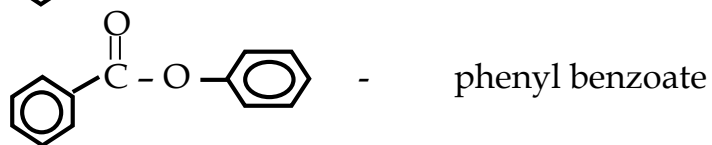
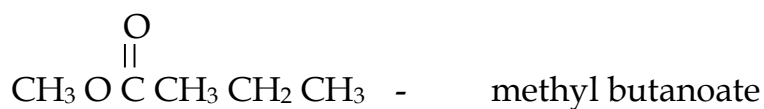
ESTERS

Esters are derivatives of carboxylic acids. Are highly volatile compounds with a fruity smell. They conform to a general formula:



NOMENCLATURE

Esters are named using their parent acid name but adding the suffix -ate.



Isomerism

Esters show structural isomerism and functional isomerism.

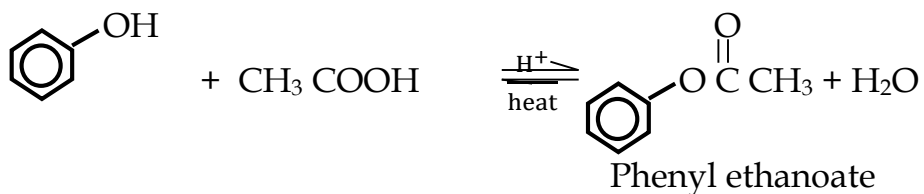
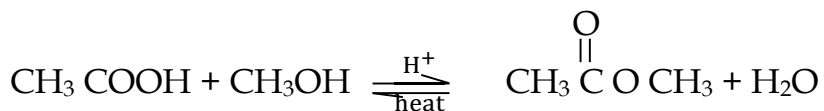
Functionally esters are isomeric with carboxylic acids.



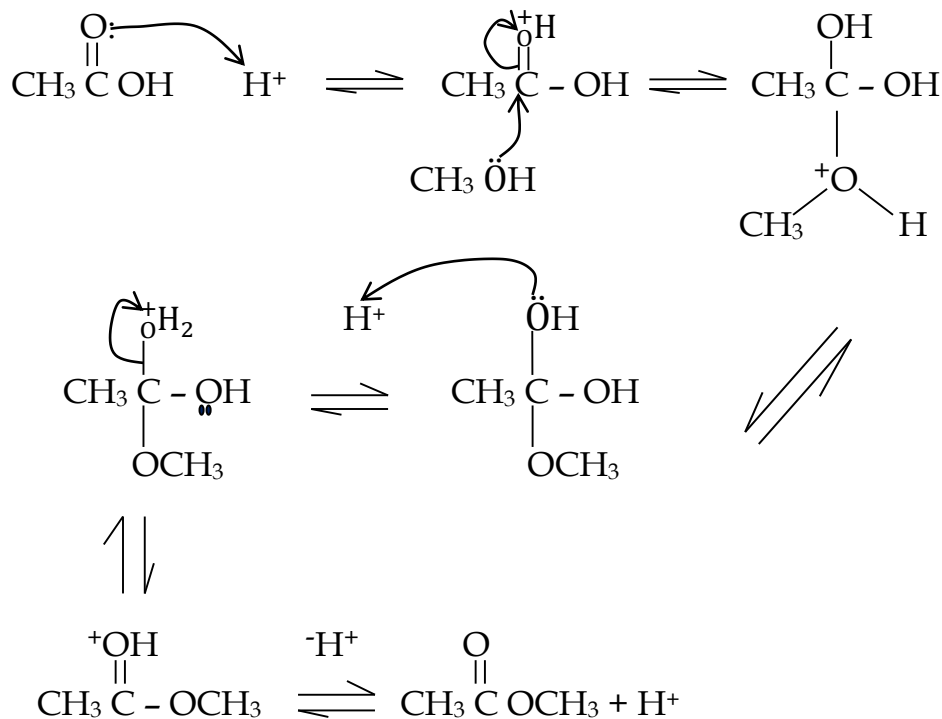
PREPARATION OF ESTERS

(i) **Esterification:**

From carboxylic acids and an alcohol. This reaction is catalyzed by a mineral acid or an alkali.

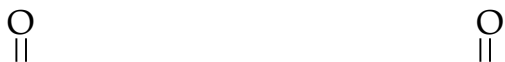


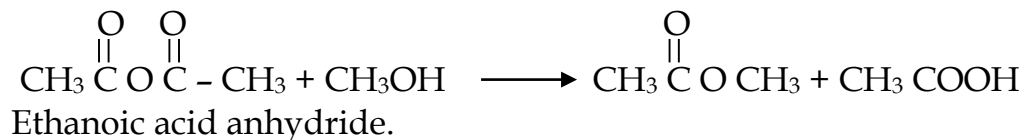
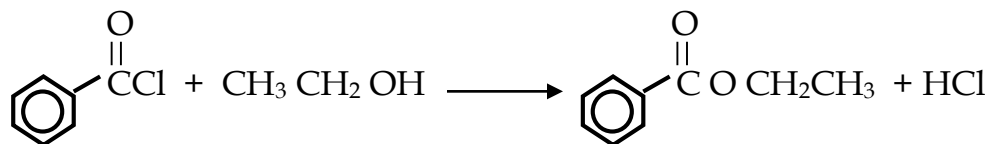
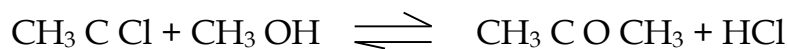
Mechanism:



From acid chlorides and acid anhydrides

When alcohols are reacted with acid chlorides or acid anhydrides, an ester is formed.



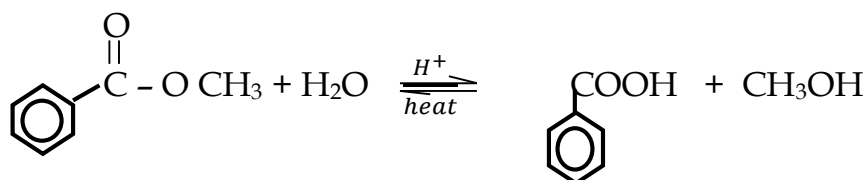
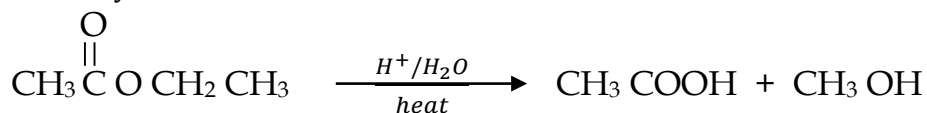


REACTIONS OF ESTERS

Esters undergo the following reactions:

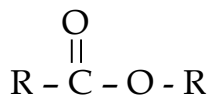
i) Hydrolysis

Esters are hydrolyzed in presence of a mineral acid to a corresponding carboxylic acid and alcohol.



NOTE:

Hydrolysis involves cleavage at



The position of this cleavage is useful in radiolabelling to trace for the reaction mechanisms.

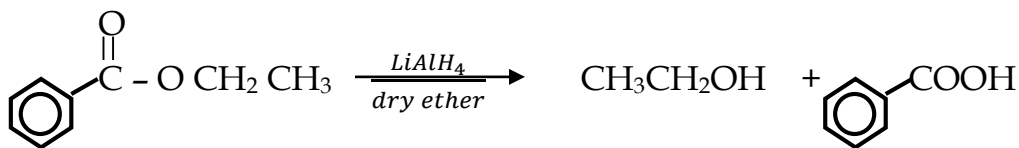
Example:



ii) Reduction

Esters are reduced with LiAlH_4 in presence of ether to carboxylic acid and the alcohol.

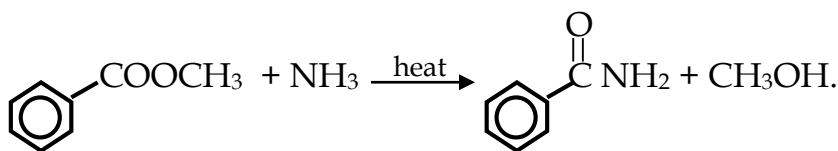
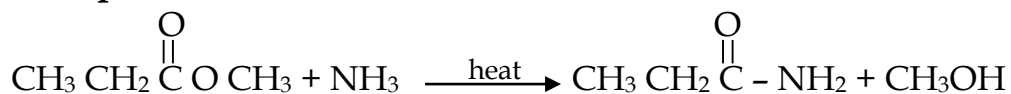
Example:



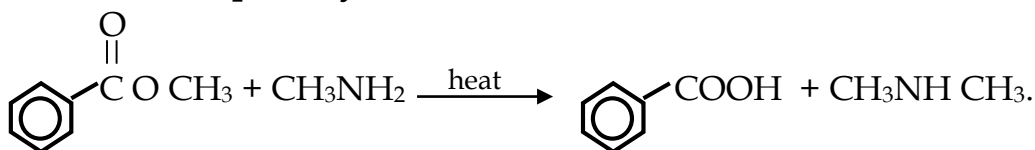
iii) **Reaction with NH₃**

Esters react with NH₃ to give amides and alcohols.

Example:



iv) **Reaction with primary amines**



AMINES

These are compounds that are derived from ammonia base by replacing one hydrogen with an amino group. They therefore have a general formula.
RCH₂ - NH₂.

The functional group of amines is - NH₂ (amino group).

NOMENCLATURE

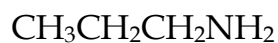
Amines are named as derivatives of alkanes by adding amine suffix to the stem name.



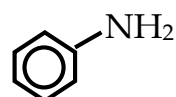
methyl amine



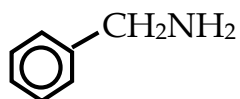
ethyl amine



propyl amine



phenyl-amine (aniline)



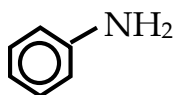
phenyl methyl amine

CLASSES OF AMINES

Amines are classified into four groups or four classes.

i) **Primary amines**

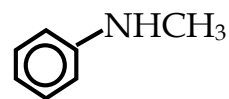
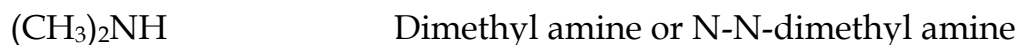
Is formed when only one hydrogen is replaced from the NH_3 .



Phenyl amine (primary aromatic)

ii) **Secondary amines**

Is formed when two hydrogens of NH_3 are replaced by alkyl or anyl groups.



Phenyl methyl amine

iii) **Tertiary amines**

Are formed when all the hydrogens in the NH_3 are replaced by the alkyl group.



iv) **Quartenary amines**

Are salts formed when the lone pair on the Nitrogen is donated to an alkyl group.



Isomerism

Amines exhibit all the three types of isomerism, chain, positional and functional.

Write all isomers of $C_4H_{11}N$.

- $CH_3 CH_2 CH_2 CH_2 NH_2$ n-butylamine
- $CH_3 \begin{array}{c} CH \\ | \\ CH_3 \end{array} CH_2 NH_2$ 2-methyl propylamine
- $CH_3 - \begin{array}{c} CH_3 \\ | \\ C - NH_2 \\ | \\ CH_3 \end{array}$ 2-amino-2-methyl propane.
- $CH_3 CH_2 CH CH_3$ 2-amino butane

1 and 2 are chain isomers.
3 and 4 are position isomers.

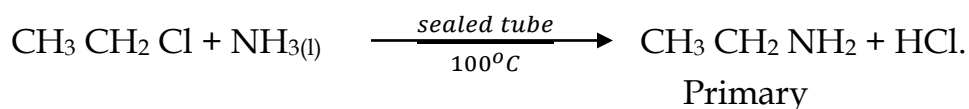
- $CH_3 CH_2 \begin{array}{c} H \\ | \\ N \\ | \\ CH_2 CH_3 \end{array}$ N-diethyl amine (functional)
- $CH_3 \begin{array}{c} CH_3 \\ | \\ CH_3 N \\ | \\ CH_2 CH_3 \end{array}$ (Functional)

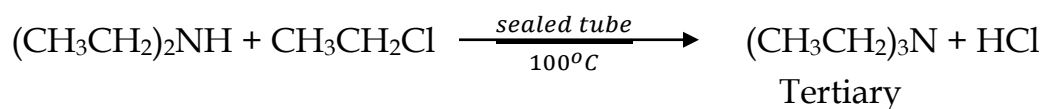
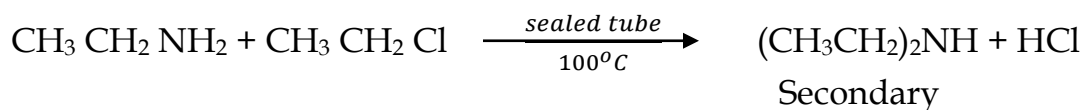
METHODS OF PREPARATION

From alkyl halides

When alkyl halides are heated with NH_3 in a sealed tube at a temperature of $100^\circ C$, the reaction gives a mixture of amines. This method is not suitable for producing a specific amine because of a mixture of amines.

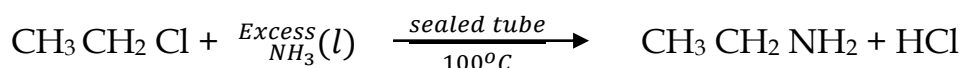
Although the products produced may be controlled by using excess NH_3 and at the same time separating each product by functional distillation.





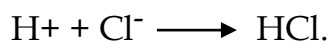
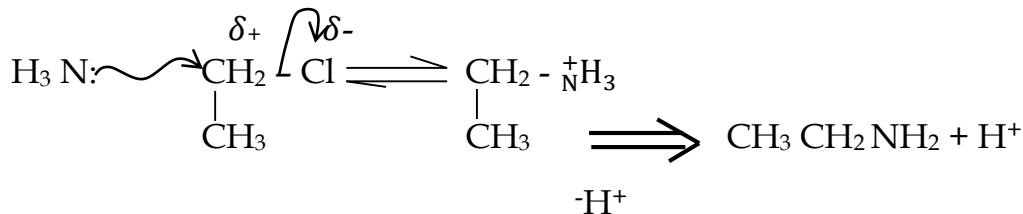
NOTE:

When excess NH_3 is used,



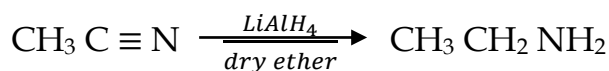
Mechanism:

Excess NH_3

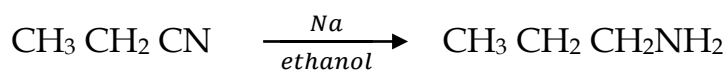


From alkyl cyanides

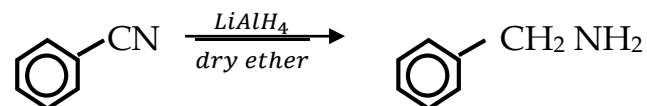
When an alkyl cyanide also known as a nitrile is reduced with reducing agents such as LiAlH_4 or NaBH_4 . Or simply sodium in an alcohol, dry ether a primary amine is formed.



Ethanitrile



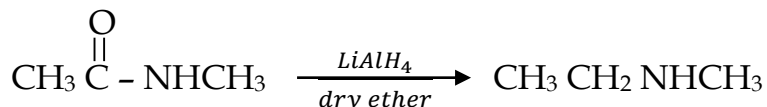
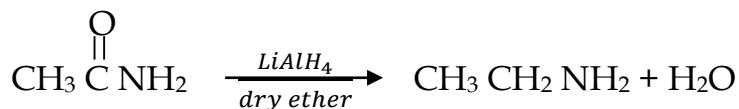
Propanitrile



Benzenitrile

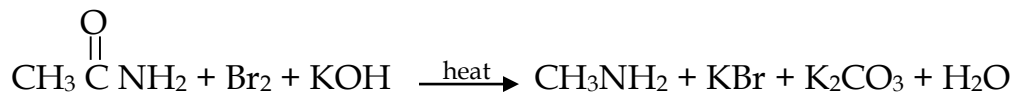
From acid amides

When an acid amide is reduced using reducing agents like LiAlH_4 /dry ether, primary amines are formed.



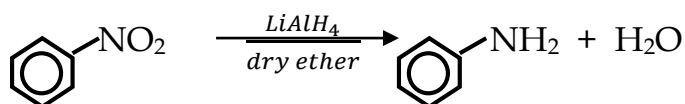
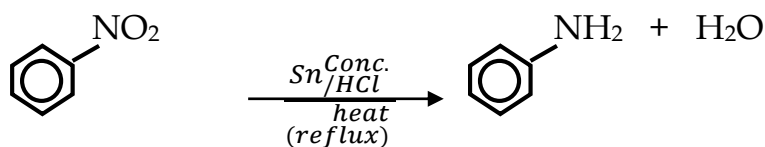
HOFFMAN'S DEGRADATION

When amines are reacted with Br_2 in a solution of KOH or NaOH , a primary amine is formed which is one carbonless from the parent amide. This reaction shortens the chain by one carbon and it is known as Hoffman's degradation.



From nitro compounds

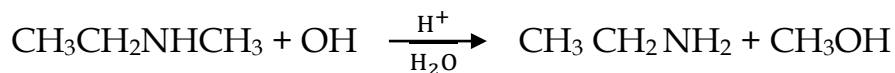
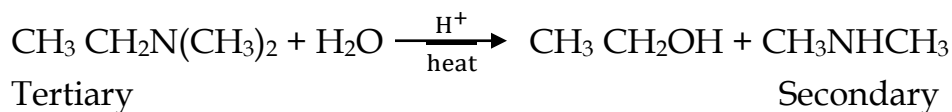
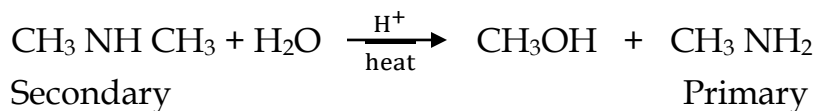
When a nitro compound preferably aromatic nitro compound is reacted with tin in conc. HCl or LiAlH_4 /ether, aromatic amine is formed.



This method is suitable for preparing aromatic amines.

HYDROLYSIS OF TERTIARY AND SECONDARY AMINES

This produces primary and secondary amines respectively. When they are heated with mineralized acid H_2O or a base.



Mechanism: (Base catalysed)

PHYSICAL PROPERTIES OF AMINES

- i. Lower amines up to C₂ are gases while those with C₃ = C₁₁ are liquids, higher amines are solids at room temperature.
- ii. Lower amines have got a fishy ammoniacal smell or odour.
- iii. Boiling points of amines are higher than those of corresponding alkanes.
- iv. Lower members are soluble in H₂O but the solubility decreases with increase in molecular weight.

Explanations for boiling points and solubility

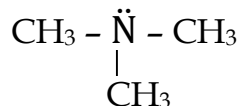
Question:

Methyl amine CH ₃ NH ₂	Molecular weight	Boiling point °C
	31	-7
CH ₃ CH ₃	30	-89

Methyl amine boils at a high temperature than ethane because of the presence of intramolecular hydrogen bonding which holds methylamine molecules together in the liquid phase and difficult to escape to vapour phase during boiling and more heat required to boil while in ethane, the weak Van der Waal's forces are easily broken and less heat required to boil.

Comparing three classes of amines, primary amine boils at a higher temperature than the secondary followed by tertiary.

Amine	Molecular weight	Boiling point °C
CH ₃ CH ₂ CH ₂ NH ₂	59	49
CH ₃ CH ₂ NHCH ₃	59	35



Primary amine forms atleast two intramolecular hydrogen bonding due to the presence of more hydrogen atoms on the nitrogen and hence boiling at a higher temperature.

The secondary amine forms only one hydrogen bond since it has only one hydrogen in the nitrogen while the tertiary amine has not hydrogen on the nitrogen and therefore forming no hydrogen bonding and ends boiling at the lowest temperature.

Assignment (Research work)

Carboxylic acids boil at higher temperatures than alcohols which also boils at a higher temperature than an amine and an alkane has the least boiling point. Explain.

BASICITY OF AMINES

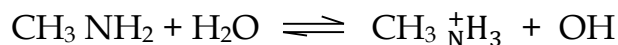
Amines are bases which form weak alkaline solutions when dissolved in H₂O. Such solutions turn litmus paper to blue.

The basic strength of an amine is determined by the extent of ionization denoted as K_b. The greater the K_b value, the more basic the amine. The basic character of an amine can be explained by the presence of lone pair of electrons on the nitrogen atom which are always donated.

The more available these lone pair of electrons are, the more basic an amine is.

The availability of electrons on the nitrogen atom is determined by the atoms that are bonded onto it.

Groups of atoms that have got positive inductive effect will push electrons towards nitrogen making them available while those with negative inductive effect will lower the electron density on the nitrogen atom making them less available.



$$K_b = \frac{[\text{CH}_3\text{N}^+\text{H}_3][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

Questions:

1. Methylamine is a more stronger base than ammonia.
2. Phenylamine is a weaker base than methylamine.
3. Ethylmethylamine is a stronger bases than trimethyl amine.

Trend:

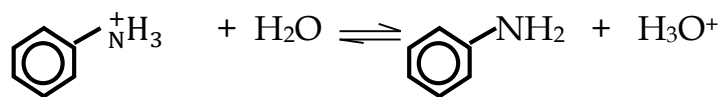
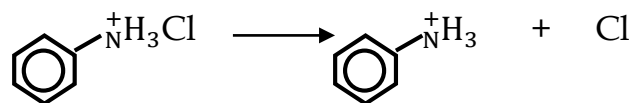
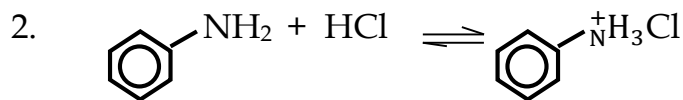
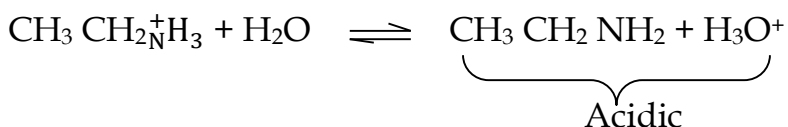
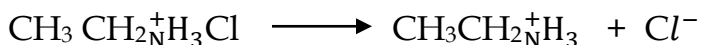
Secondary amine > Primary > Tertiary > ammonia

4. Amino benzene is a weaker base than aliphatic primary amine. Explain.

The final of Basicity will be;

Secondary > Primary > Tertiary > Ammonia > Aromatic

Being basic amines, they react with mineral acids to produce salts. These salts are strong electrolytes because they fully get ionized and their pH is slightly less than 7.



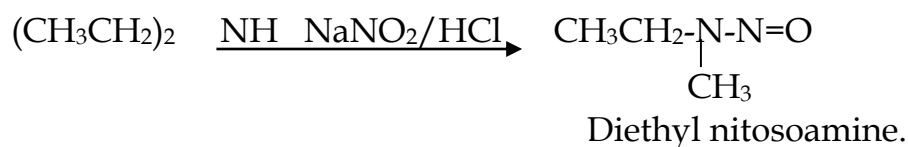
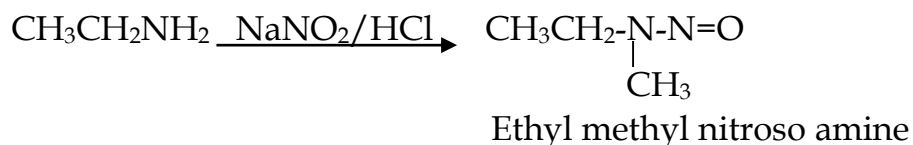
REACTIONS OF AMINES

1. With nitrous acid:

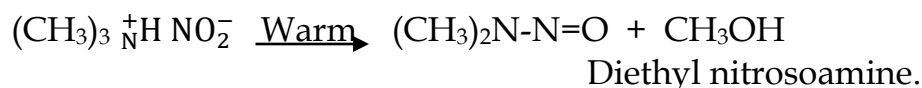
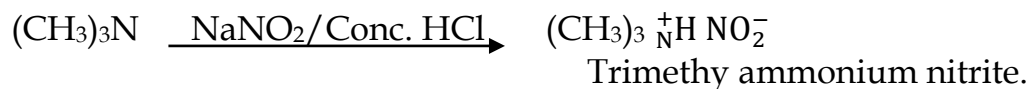
Nitrous acid being liable is generated insitu. Primary amines react with nitrous acid to form a colourless solution of alcohol and a colourless gas of nitrogen.



Secondary amines will produce a yellow oily substances known as nitroso amines.

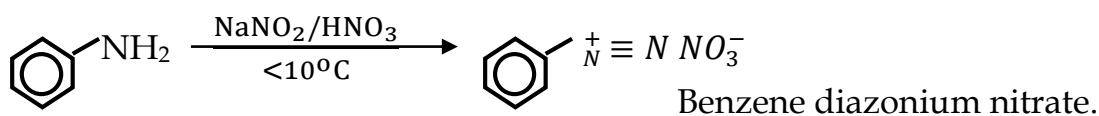
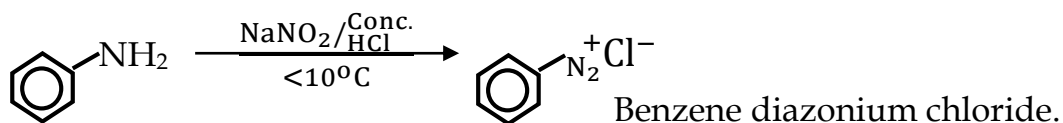


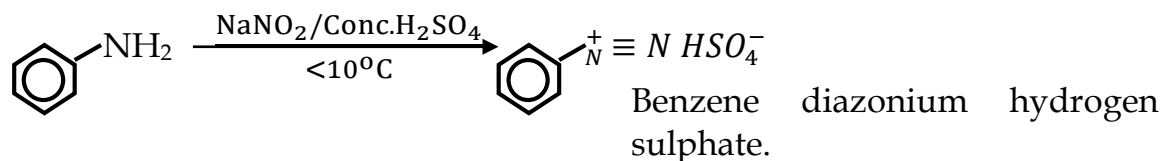
Tertiary amines when dissolved in HNO acid to form NH_4NO_2 which when warmed forms a nitrosoamine and an alcohol by decomposition.



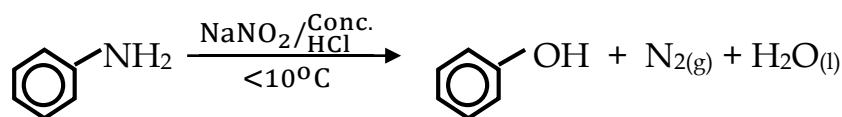
Aromatic primary amines react with nitrous acid giving different products depending on the temperatures.

At temperatures below 10°C , aromatic primary amines with nitrous acid to form diazonium salts.






At temperatures above ten ($>10^\circ\text{C}$), the major product formed is a phenol.



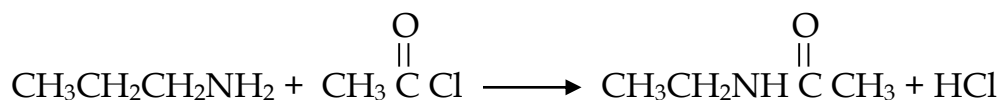
The above reaction is of practical importance in distinguishing the classes of amines.

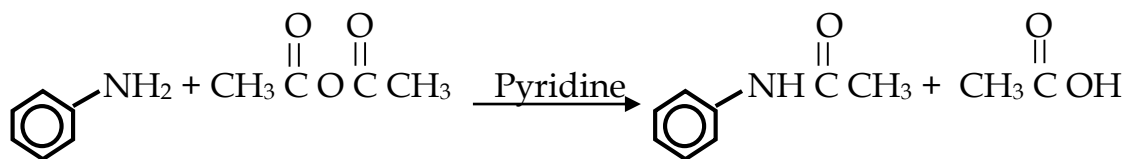
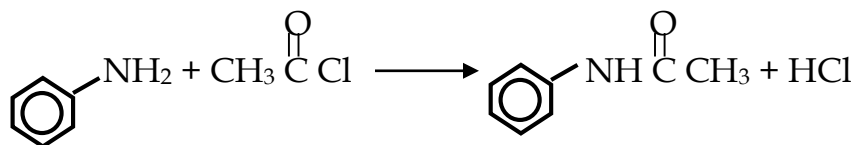
In summary:

- i) 1° amines : Yield a colourless solution and effervescence of a colourless gas.
- ii) 2° amines : Yield a yellow oily substance which when phenol and conc. H_2SO_4 is added and the mixture made alkaline. This yields an *intense blue colour*.
- iii) 3° amines : A yellow oily substance persists.
- iv) Aromatic amine : A brightly coloured compound known as an azo dye is produced when 2-naphthol () is added.

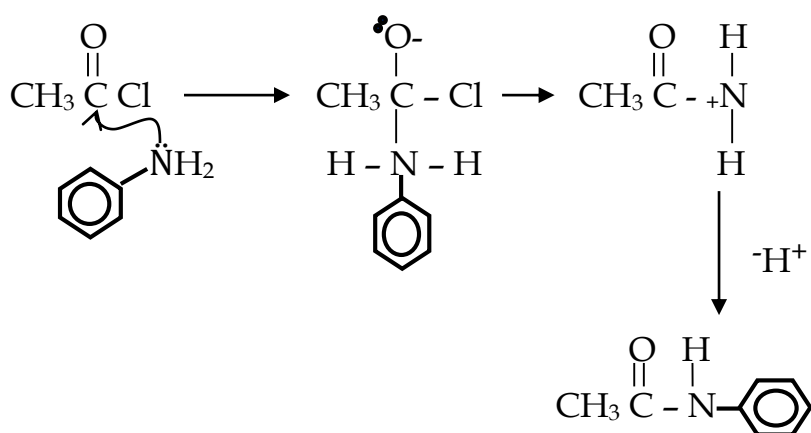
2. Reactions with acid chlorides and acid anhydrides.

1° and 2° amines react with acid chlorides and acid anhydrides to form amides.



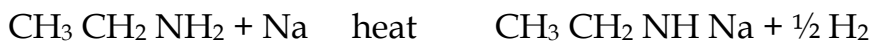


Mechanism:



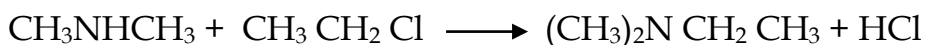
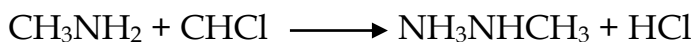
3. **Reactions with sodium metal**

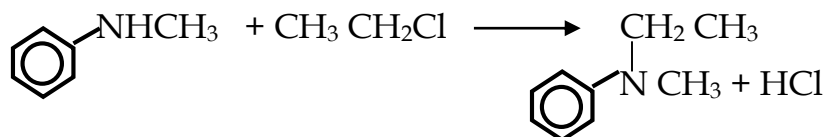
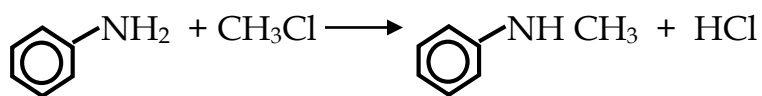
Amines react with Na when heated to produce H_2 . This reaction is only possible with 1° and 2° amines which do have H_2 . The tertiary ones without H_2 do not.



4. **Reactions with alkyl halides**

Aromatic and alkyl amines react with alkyl halides to form higher amines.

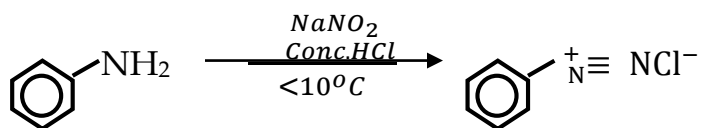
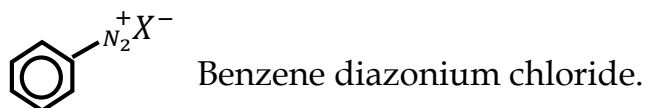




DIAZONIUM SALTS

These are salts formed from primary aromatic amine when reacted with an inorganic mineral acid. The process of forming these salts is diazotization.

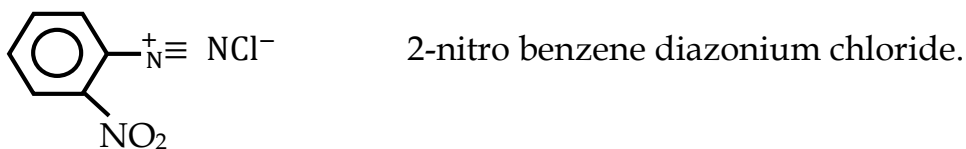
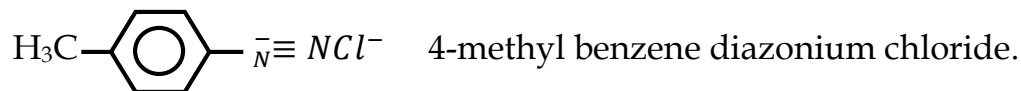
Temperature is critical in the formation of a diazonium salt and the temperature always has to be $<10^\circ\text{C}$. Where X is the halogen or NO_3^- , HSO_4^- .

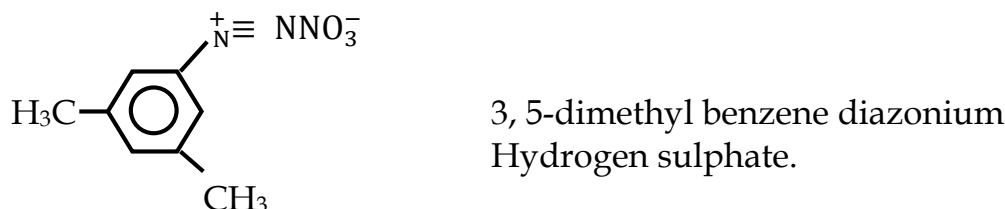
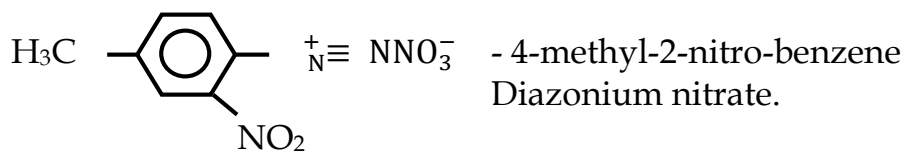


What determines the anion is the acid used.

Nomenclature

Diazonium salts are named as benzene diazonium.





Physical properties of diazonium salts

Are a colourless crystalline solids which turn brown on exposure to air.

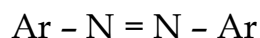
Their solutions are neutral to litmus but very soluble in H_2O to give an ionic solution that has got good electrolytic conductivity.

Chemical reactions

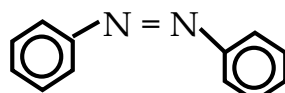
Diazonium salts are very useful in organic synthesis reacting with different substances to form different products.

Coupling reaction

Benzene diazonium salts react with phenols to form brightly coloured compounds known as azo compounds by adding an aromatic ring to the nitronium ion a reaction known as coupling.



or

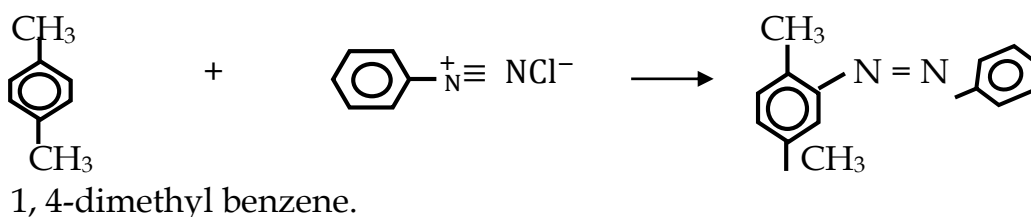
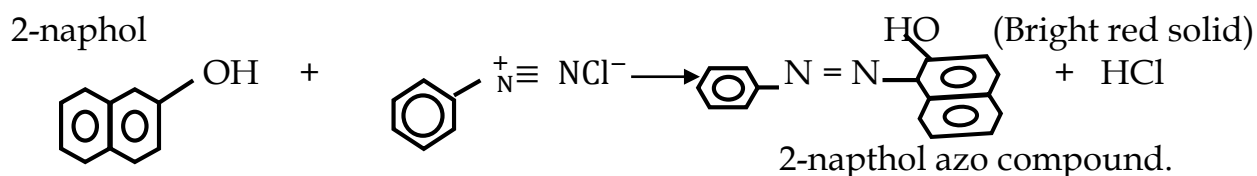
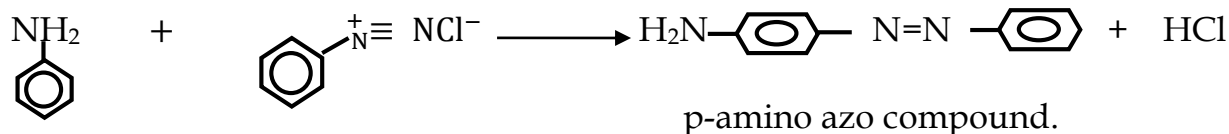
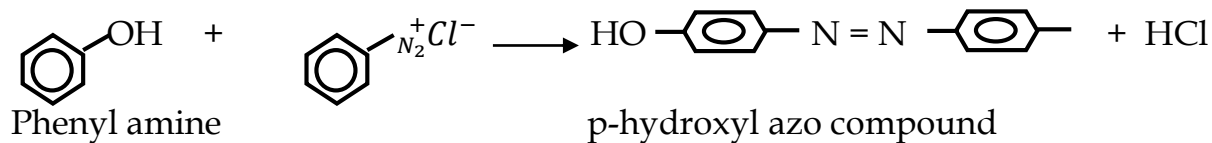


Azo compounds.

For coupling to occur, the aromatic ring must have a strong electron releasing groups such as hydroxyl, NH_2 - (amino), OR group and NHR group.

These groups will activate the ring making the electrons available at the para position for diazotization.

If the para position is already occupied, then diazoti-phenol.

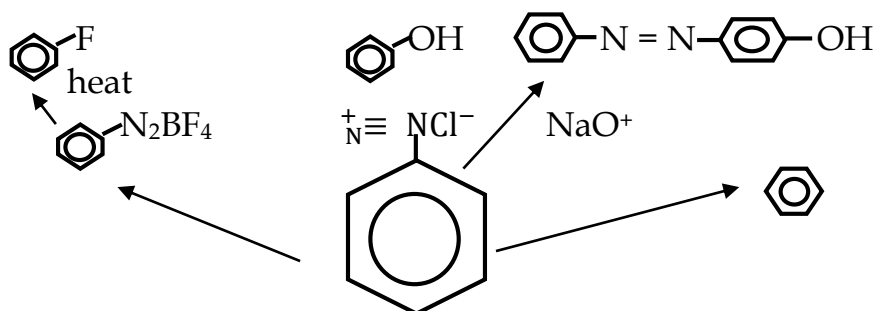
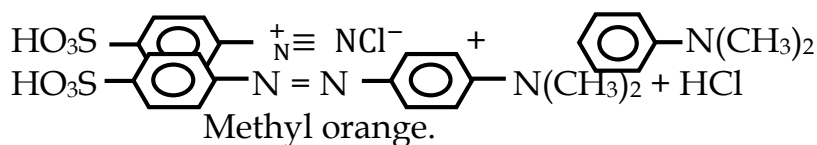


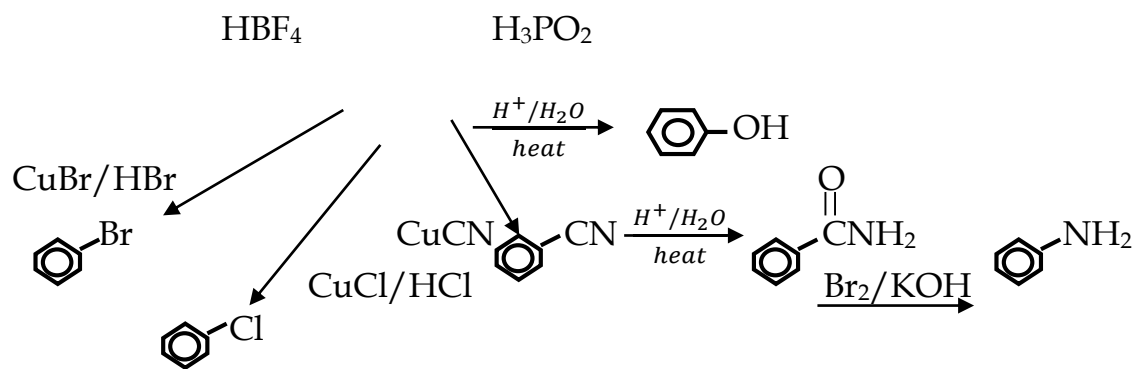
The importance of coupling

i) **Test for primary aromatic amines:**

If a primary aromatic amine is treated with a mixture of NaNO_2 and HCl , 2-naphthol, a bright red solid is formed due to the reaction of diazonium salt with 2-naphthol at a temperature below 10°C .

ii) It is used in preparation of dyes (coloured compounds) e.g. methyl orange indicator is prepared by coupling 4-hydrogen sulphite benzene, diazonium chloride and dimethyl phenyl amine.





Convert Nitro benzene to chloro benzene

