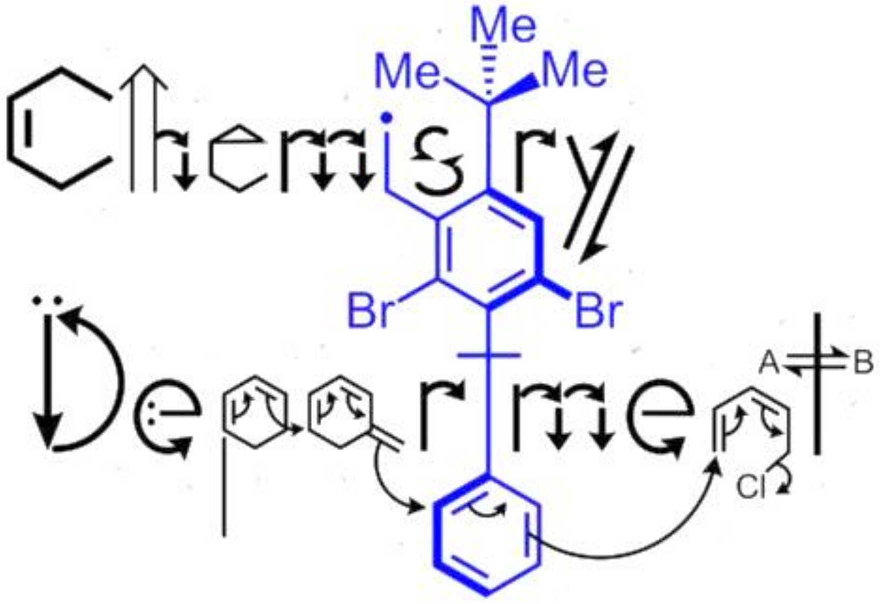
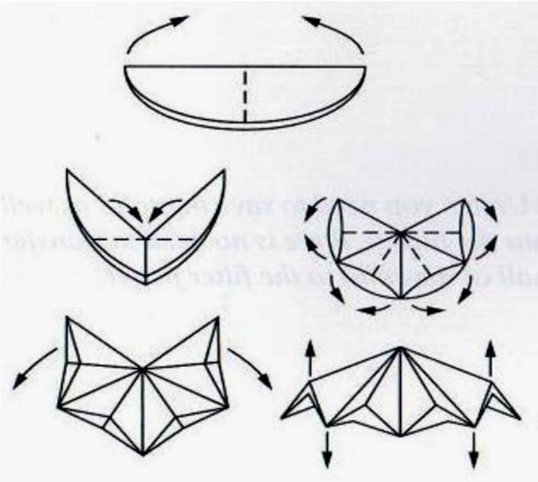


Practical Organic Chemistry

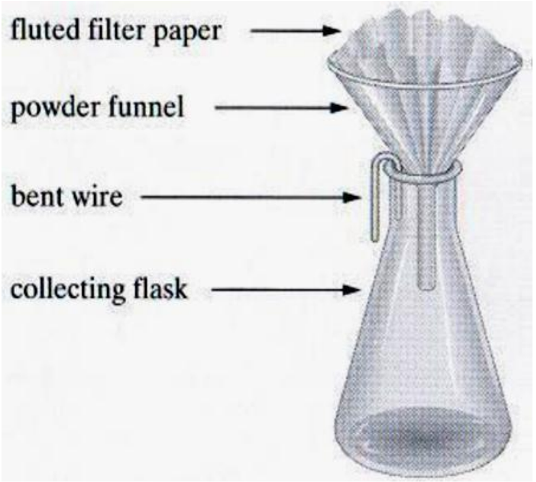
Stage 3

Dr. Hashim Jaafar

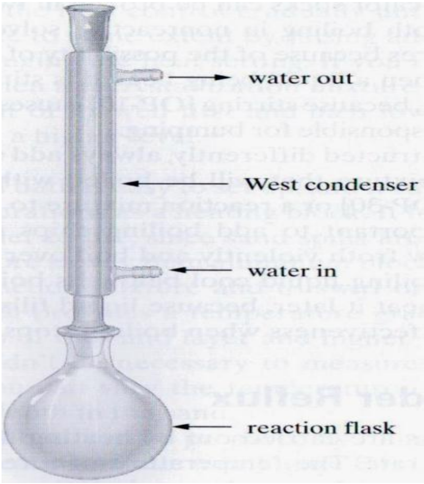
January 12, 2025



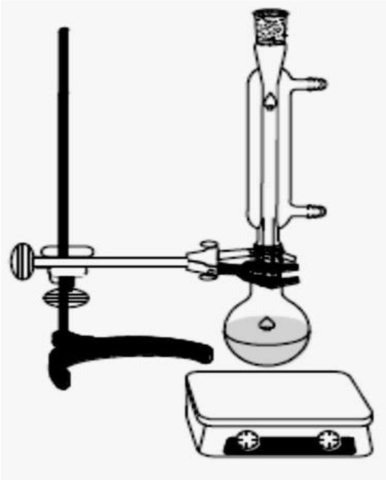
Making a fluted filter paper



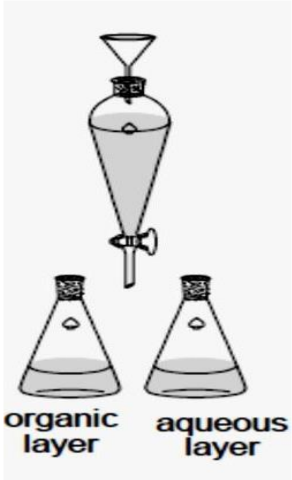
Apparatus for gravity filtration



Reflux appliance

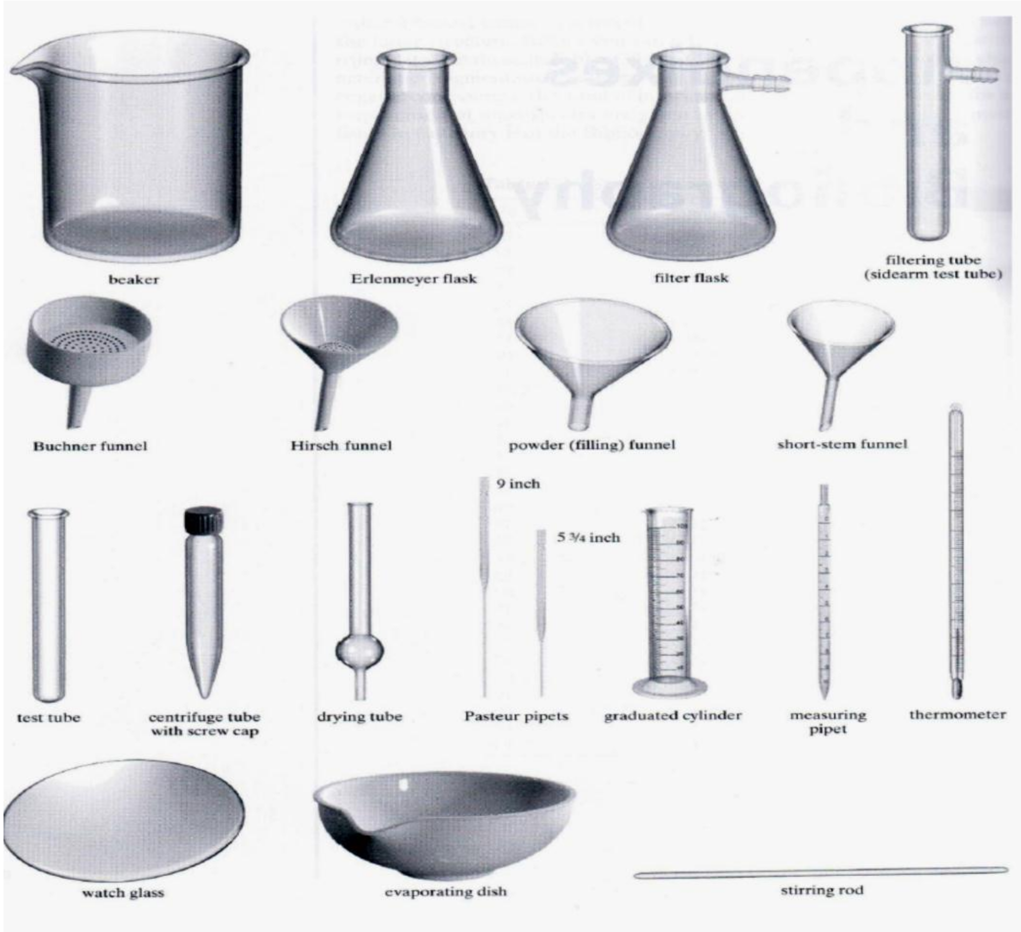


Apparatus for heating under reflux

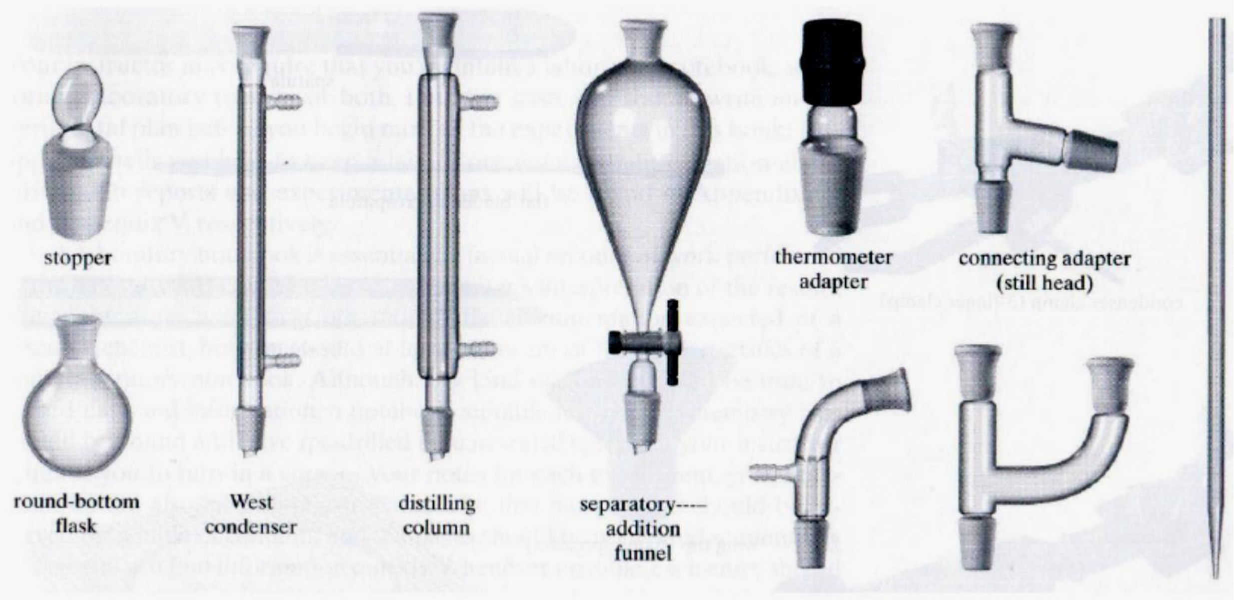


Separating funnel

Hardware



Chemical glassware



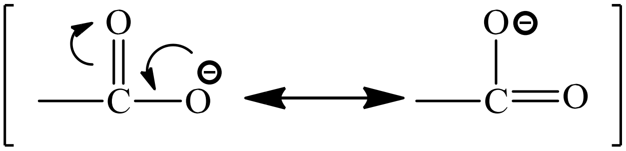
Lab kit component

Experiment 1

Preparation carboxylic acid by cannizzaro reaction

Theoretical part:

Carboxylic acid: is an organic compound that contains a carboxyl group, and show appreciable acidity. The general formula of a carboxylic acid is R–COOH, with R referring to an alkyl group or to an aryl group. The acidity of a carboxylic acid is thus due to the powerful resonance stabilization of its anions. This stabilization and the resulting acidity are possible only because of the presence of the carbonyl group. According to the resonance theory, then, a carboxylate ion is a hybrid of two structures which, being of equal stability, contribute equally. Carbon is joined to each oxygen by "one-and-a-half" bond. The negative charge is evenly distributed over both oxygen atoms.



Names of carboxylic acids:

1- The common names: That refer to their sources rather than to their chemical structure, such as formic acid, adds the sting to the bite of an ant (Latin: formica, ant), Butyric acid gives rancid butter its typical smell (Latin: butyrum, butter).

2- The International Union of Pure and Applied Chemistry (IUPAC) system: Follow the usual pattern. The longest chain carrying the carboxyl group is considered the parent structure, and is named by replacing the –e of corresponding alkane with –oic acid.

Examples:

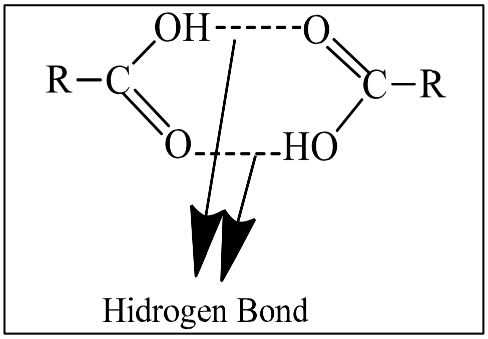
Alkane → Alkanoic acid

Compound formula	Opposite alkane name	Acids name (IUPAC) system	Acids name common names
CH3COOH	Ethane	Ethanoic acid	Acetic acid
CH3CH2COOH	Propane	Propanoic acid	Propionic acid

Physical Properties of carboxylic acids:

1- As we would expect from their structure, carboxylic acid molecules are polar, and like alcohol molecules can form hydrogen bonds with each other and with other kinds of molecules. The aliphatic acid therefor shows very much the same solubility behavior as the alcohol: the first four are miscible with water, the five –carbon acid is partly soluble, and the higher acids are virtually insoluble. Water solubility undoubtedly arises from hydrogen bonding between the carboxylic acid and water. The simplest aromatic acid, benzoic acid, contains too many carbon atoms to show appreciable solubility in water.

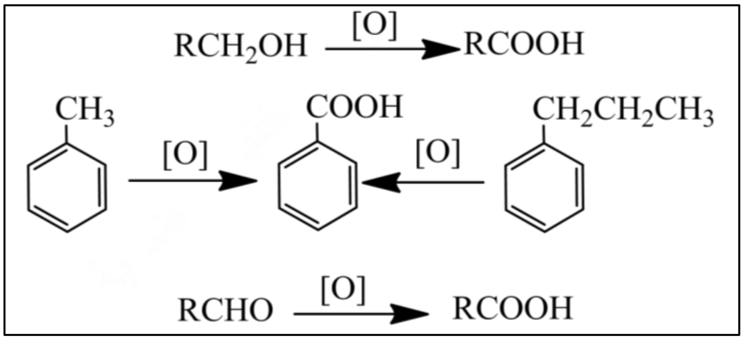
2- The carboxylic acid is even higher boiling than alcohols, this very high boiling points are due to the fact that a pair of carboxylic acid molecules are held together not by one but two hydrogen bonds.



3- The odors of the lower aliphatic acid progress from the sharp, irritating odors of formic and acetic acids to the distinctly unpleasant odors of butyric, valeric and caporic acids: the higher acids have little odor because of their low volatility.

Preparation of carboxylic acids:

1-Oxidation:

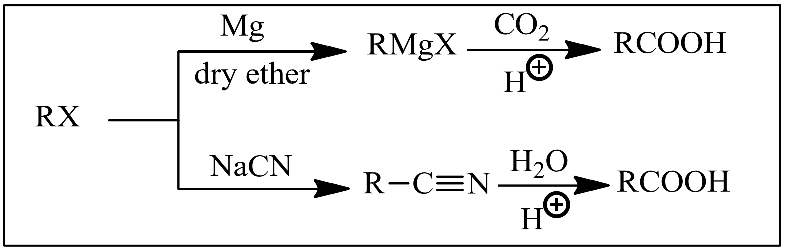


$$RCH_2OH \xrightarrow{[O]} RCOOH$$

$$RCHO \xrightarrow{[O]} RCOOH$$

$$CH_3CHO \xrightarrow[MnO]{air} CH_3COOH$$

2- The carbonation of Grignard reagents:



$$RX \xrightarrow[\text{dry ether}]{Mg} RMgX \xrightarrow[H^{\oplus}]{CO_2} RCOOH$$

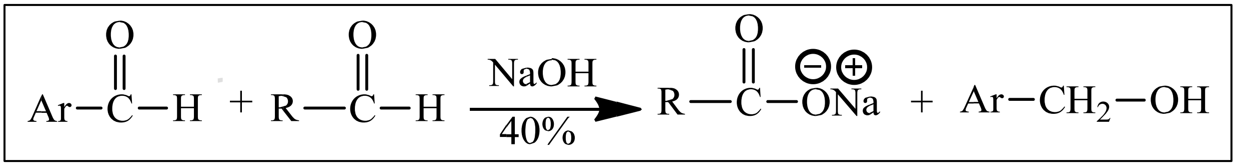
$$RX \xrightarrow{NaCN} R-C\equiv N \xrightarrow[H^{\oplus}]{H_2O} RCOOH$$

3- Hydrolysis of nitriles

$$RX \longrightarrow R-C\equiv N \xrightarrow[H^{\oplus}]{H_2O} RCOOH + NH_4^{\oplus}$$

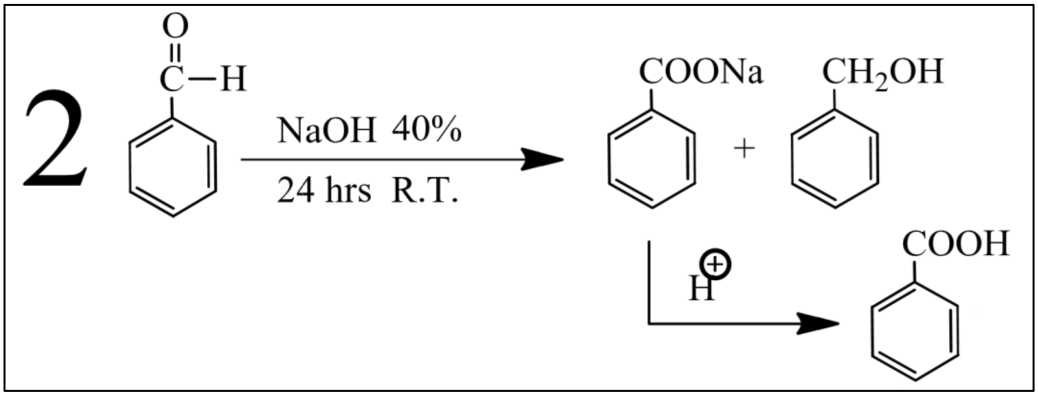
4- Cannizzaro reaction:

Aromatic aldehyde (and other aldehydes in which α-hydrogen atoms are absent, e.g. formaldehyde and trimethylacetaldehyde) under the influence of strong aqueous or alcoholic alkali undergo simultaneous oxidation and reduction yielding the alcohol and corresponding carboxylate salt. Thus:

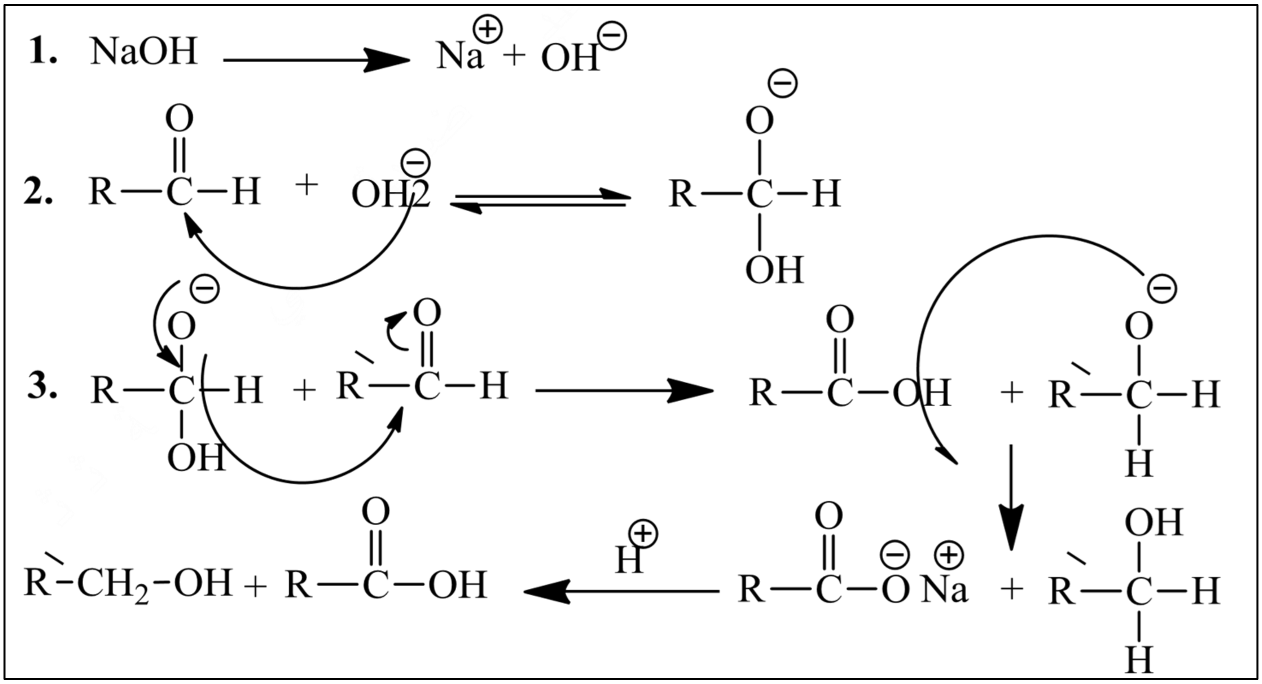


$$Ar-\overset{\overset{O}{\|}}{C}-H + R-\overset{\overset{O}{\|}}{C}-H \xrightarrow[40\%]{NaOH} R-\overset{\overset{O}{\|}}{C}-\overset{\ominus\oplus}{ONa} + Ar-CH_2-OH$$

E.G.: preparation benzoic acid:



The mechanism for the reaction involves the production of anion which may transfer a hybrid ion to a carbonyl carbon atom in another aldehyde molecule. The reaction sequence is completed by a proton transfer to yield the carboxylate anion and the alcohol.



Uses of benzoic acids:

1- dye intermediates, installation of paint, antiseptic steel and plastic intense.

2- Benzoic acid pharmaceutical grade: used as preservatives, antimicrobial agent. It is found in toothpastes and mouthwashes.

Experiment:

1- Pour 3 ml pure Benzaldehyde and 9 ml of sodium hydroxide (40%) into 250-ml conical flask and cork the conical securely with rubbery stopper.

2- Shake the mixture vigorously until it has been converted into a thick emulsion.

3- Allow the mixture to stand overnight or for 24 hrs. in the stoppered conical.

4- Add just 10 ml water to the mixture and pour the liquid into separator funnel.

5- Rinse out the bottle with about few milliliters of ether and add this ether to the solution in the funnel.

6- Shake the solution with 10 ml of ether several times.

7- Separate the lower aqueous solution and save it.

8- Pour the aqueous solution remaining with stirring into a mixture of 8 ml of concentrated hydrochloric acid, 8 ml of water and about 10 gm. of crushed ice.

9- Filter the precipitated benzoic acid, wash it with a little cold water, drain and recrystallize from boiling water. (m.p.=120-121).

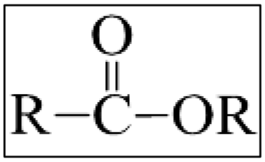
10- Weigh the product and calculate the percentage range.

Experiment 2

Preparation of Esters

Theoretical Part

Closely related to the carboxylic acids and to each other are a number of chemical families known as **functional derivatives of carboxylic acids:** acid chloride, anhydrides, amides, and esters. These derivatives are compounds in which the -**OH** of a carboxylic group has been replaced by**-Cl, -OOCR, -NH2, or –OR.**



$$R-\overset{\overset{O}{\|}}{C}-OR$$

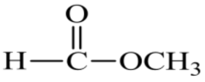
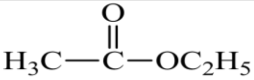
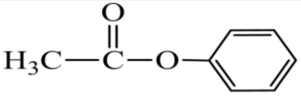
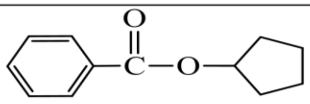
R, R¯ may be alkyl or aryl group

Like the acid to which it is related, an acid derivative may be aliphatic or aromatic, substituted or un substituted; whatever the structure of the rest of the molecule, the properties of the functional group remain essentially the same.

Nomenclature:

The names of acid derivatives are taken in simple ways from either Common name or the IUPAC name of the corresponding carboxylic acid for ester ic acid is replaced to –ate, proceeded by the name of alcohol or phenol group.

Examples:

Formula	Common name	IUPAC name
 $H-\overset{\overset{O}{\|}}{C}-OCH_3$	Methyl formate	Methyl Methanoate
 $H_3C-\overset{\overset{O}{\|}}{C}-OC_2H_5$	Ethyl Acetate	Ethyl Ethanoate
	Phenyl Acetate	Phenyl Ethanoate
	Cyclo pentyl Benzoate	Cyclo pentyl Benzoate

Physical Properties of esters:

1- The presence of the C=O group makes the acid derivatives polar compounds.

2- Esters have boiling points that are about the same as those of aldehydes or ketones of comparable molecular weight.

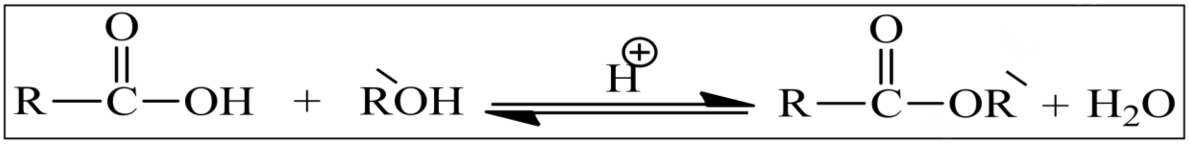
3- The borderline for solubility in water ranges from three to five carbons but solubility decrease with a long chain.

4- The acid derivatives are soluble in the usual organic solvents.

5- Volatile esters have pleasant, rather characteristic odors; they are often used in the preparation of perfumes and artificial flavorings.

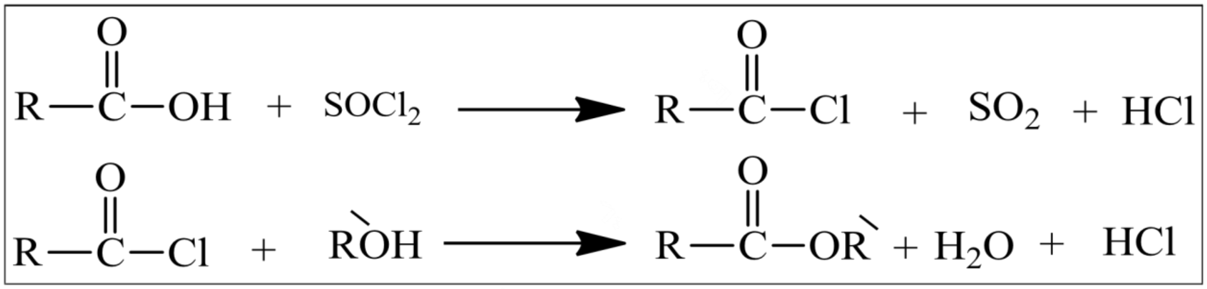
Preparation of esters:

1. *Fisher method:*



$$R-\overset{\overset{O}{\|}}{C}-OH + R'OH \xrightleftharpoons{H^{\oplus}} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

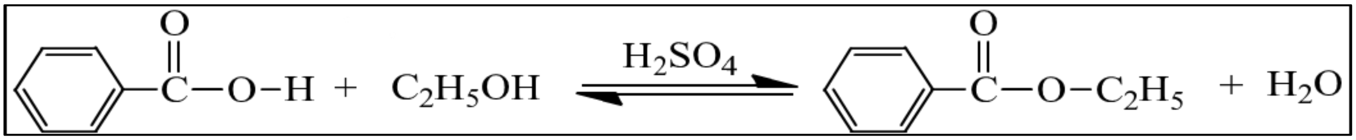
2-*Scotten – Baumann technique:*



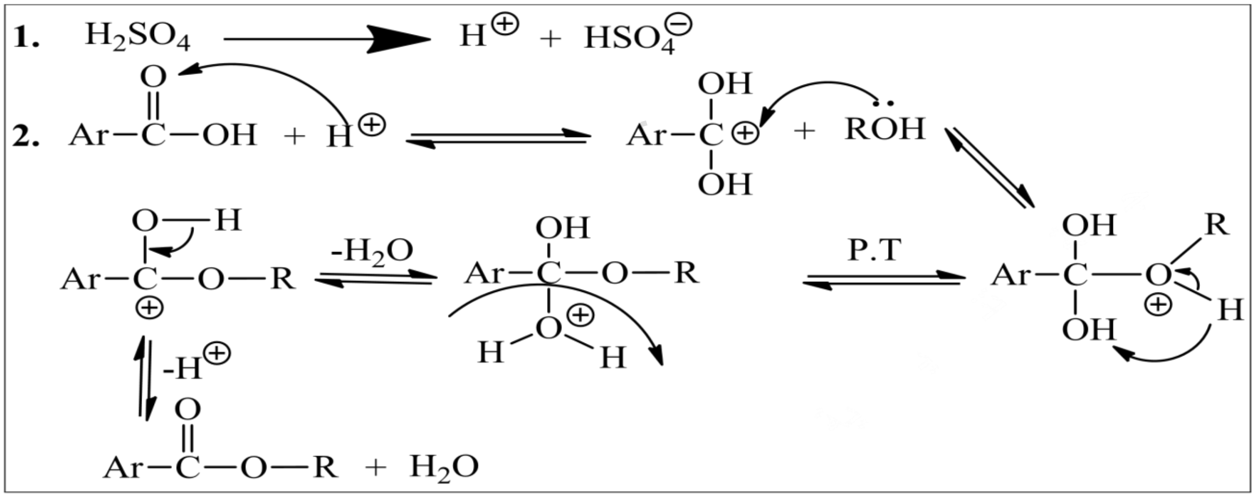
$$R-\overset{\overset{O}{\|}}{C}-OH + SOCl_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-Cl + SO_2 + HCl$$

$$R-\overset{\overset{O}{\|}}{C}-Cl + R'OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OR' + H_2O + HCl$$

The general equation:



The mechanism for the reaction:



Uses of Esters:

The esters have pleasant odor. It is commonly used as a flavoring agent in various substances. This ester is present in alcoholic beverages, fruits, milk, butter and black tea. For the most part, ethyl benzoate originates from food and is considered a nutrient.

Experimental part:

1- In a (100ml) round bottomed flask a mixture of (1.25g) of benzoic acid, (8ml) absolute ethanol and (5drops) of concentrated sulfuric acid is placed

2- Reflux the mixture gently for (30min) with occasional shaking until a clear solution is formed.

3- The mixture is Poured into a separating funnel then (10ml, 2%) of sodium carbonate with (10ml) of ether are added after cooling.

4- The separating funnel Shacked vigorously several times

5- The organic layer is run off carefully and the aqueous layer rejected.

6- The organic layer is left to dry to get the product.

7- The percentage range of the product is calculated.

Experiment 3

Preparation of Aspirin

Theoretical part:

Salicylic acid: is a mono hydroxyl benzoic acid, a type of phenolic acid, it is derived from the metabolism of salicin. In addition to serving as an important active metabolite of **aspirin** (acetylsalicylic acid or ASA) in which the phenol group turned to acetyl group.

Properties of Aspirin:

1- Have white color.

2- Crystalline.

3- Weakly acidic substance.

4- Melting point of 136 °C.

5- Its acid dissociation constant (pKa) is 3.5 at 25 °C.

6- Aspirin decomposes rapidly in solutions of ammonium acetate, acetates, carbonates, citrates, or hydroxides of the alkali metals.

7- It is stable in dry air, but gradually hydrolyses in contact with moisture to acetic and salicylic acids.

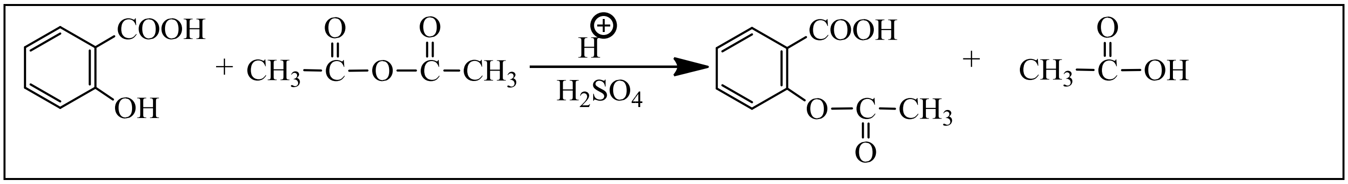
Uses of Aspirin:

1- Used to prevent heart attacks and prevent stroke, by preventing blood clotting.

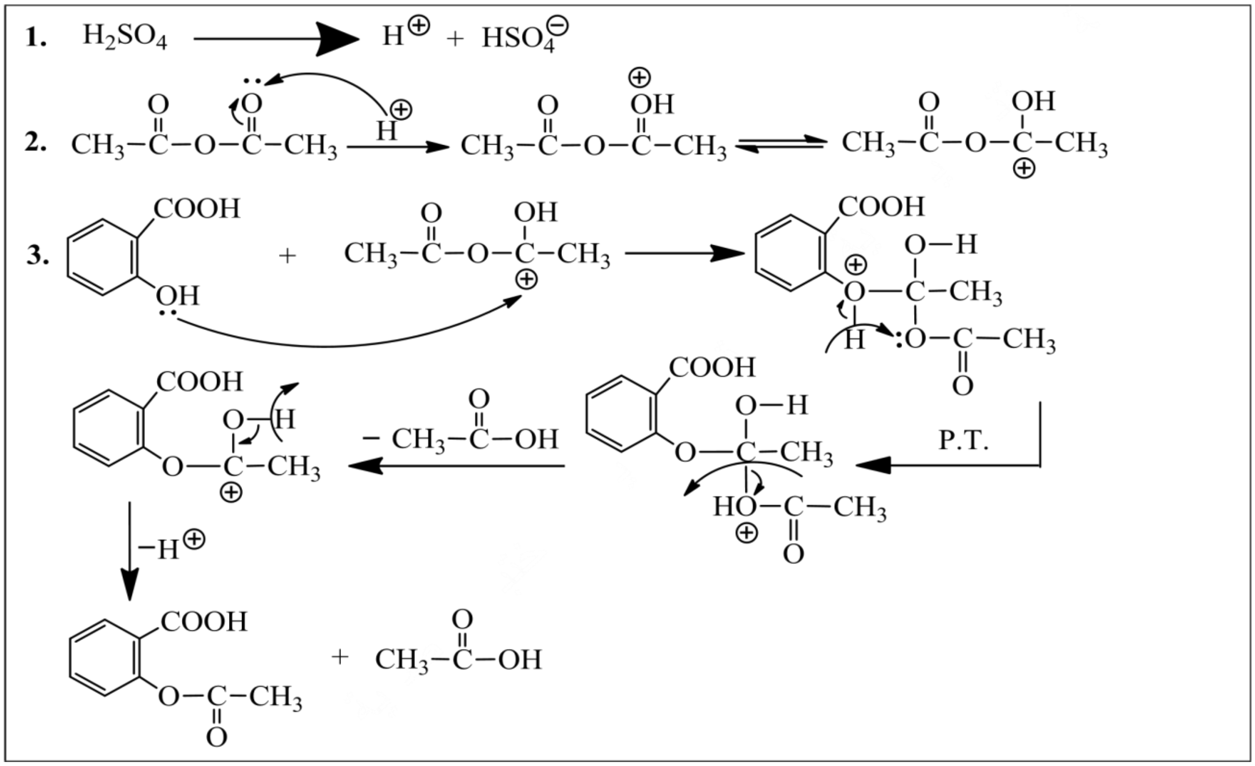
2- Used to relieve severe pain, inflammation and fever.

3- Used to treat *Rheumatoid Arthritis*.

The general equation:



The mechanism for the reaction:



Experimental part:

1- In a (100ml) round bottomed flask, A mixture of salicylic acid (1g) and acetic anhydride (2ml), and (3drops) of concentrated sulfuric acid are added and stirred.

2- The mixture is refluxed on water bath for (15mins) with constant stirring.

3- The mixture is cooled after reflux and added on ice-cold water and with shaking for (5mins) until a white precipitate is formed.

4- The precipitate is washed several times with cold water.

5- The precipitate is filtered and recrystallized from methanol or ethanol (M.p=$136C^0$).

6- After recrystallization, the solid is filtered and dried.

7- The product is weighted and the percentage of yield is calculated.

Experiment 4

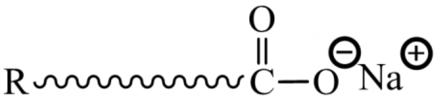
Preparation of soap

Theoretical part:

Soap: It is salt of a fatty acid with some additions such as fillers, perfumes, dyes and other, are obtained by treating vegetable or animal oils and fats with a strong base, such as sodium hydroxide or potassium hydroxide in an aqueous solution.

Saponification: A process by which triglycerides are reacted with sodium or potassium hydroxide to produce glycerol and a fatty acid salt.

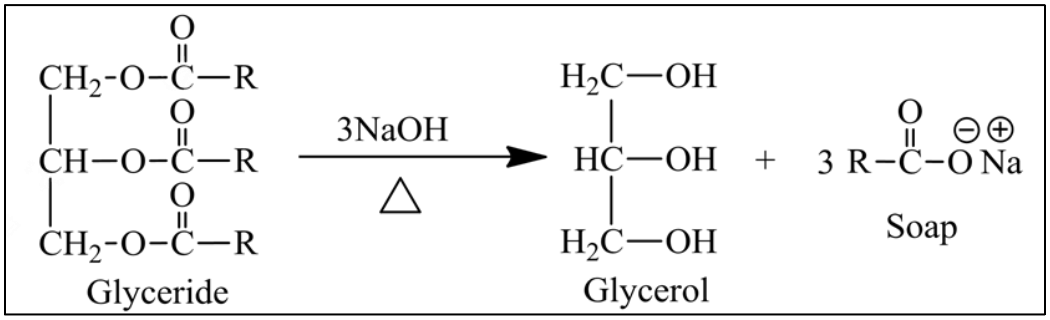
*Usually, when sodium hydroxide is used, a hard soap is produced, Using potassium hydroxide results in a soft soap



Soap molecule

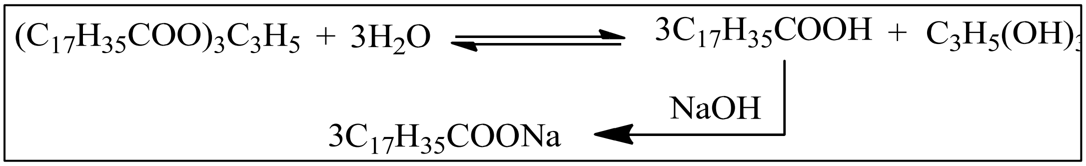
Preparation of soap:

1- **Heating Method:** The long chain of glyceride (ester) with Strong Base are heated for the preparation of soap.



2- **Cold Process Method:** The same of above method without heating.

3- **Continuous method:** This is an industrial process which ester continue hydrolysis into carboxylic acid then react with base to produce soap.

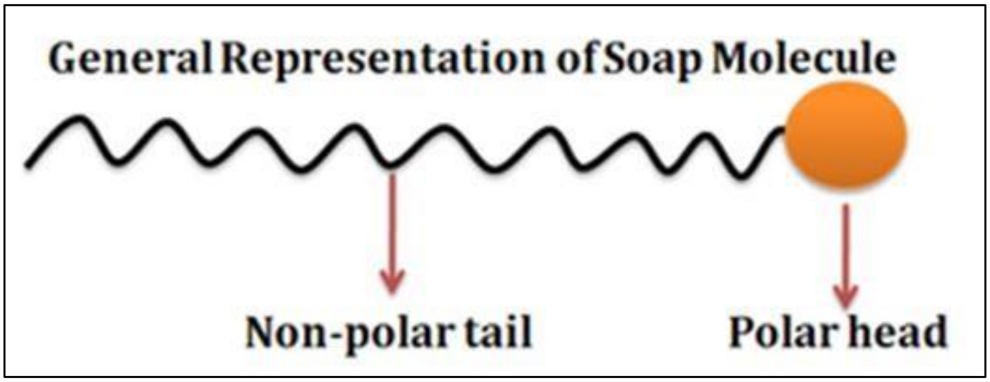


$$(C_{17}H_{35}COO)_3C_3H_5 + 3H_2O \rightleftharpoons 3C_{17}H_{35}COOH + C_3H_5(OH)$$

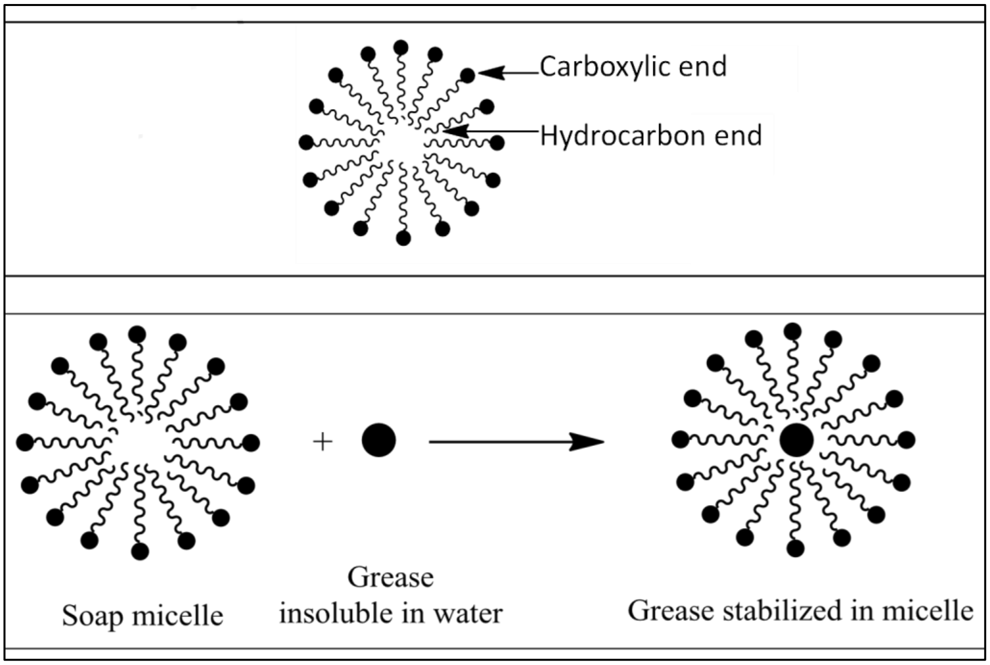
$$3C_{17}H_{35}COOH \xrightarrow{NaOH} 3C_{17}H_{35}COONa$$

Mechanism of cleaning by Soap:

Molecules of soaps (micelles) contain a non-polar (hydrophobic) hydrocarbon end, and a polar (hydrophilic) end that is usually ionic. The non-polar ends of the molecule surround the tiny oil droplets or dirt and are partially dissolved in them (resemble dissolves resemble). The polar ends of the molecules, which are extremely soluble in water, soluble s or emulsify the entire droplet.



Typical micelle formation



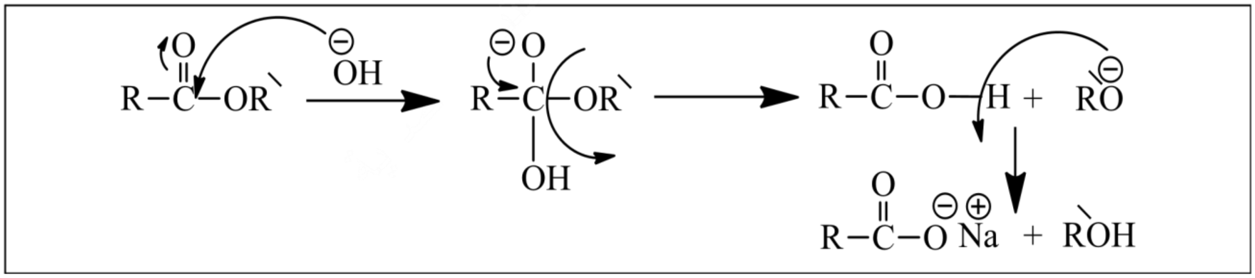
Uses of soap: Function soap is to remove the fat from the clothes and dirty objects.

Interaction equation:

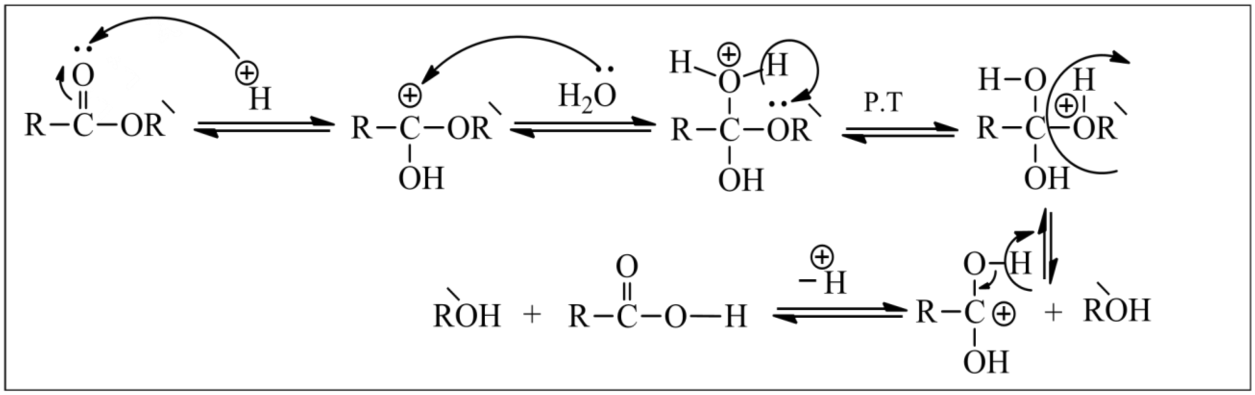
$$\boxed{(C_{17}H_{35}COO)_3C_3H_5 \xrightarrow[\triangle]{3\ NaOH} 3C_{17}H_{35}COONa + C_3H_5(OH)_3}$$

mechanism hydrolysis of the ester:

1- alkaline medium:



2- acidity medium:



Experimental part:

1- In a (250ml) round bottomed flask, a mixture of fat or oil (2.5g) and (ethanol + water) (9ml) (1:1), (2.5gm) of NaOH are added and stirred.

2- The mixture is refluxed on heating for (30 mins.) with constant stirring.

3- A saturated NaCl solution (by mixing (12.5g) of solid NaCl with (40ml) of distilled water is prepared.

4- The soap solution is poured into the salt solution and stirred by glass rod until the soap is put out.

5- The soap curds Collected by vacuum filtration with a Pickle pressure device and dried for several days.

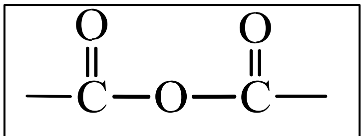
6- The product is weighted and the percentage of yield is calculated.

Experiment 5

Preparation of N-substitution Imides

Theoretical part:

Anhydrides: are organic compounds, General formula is

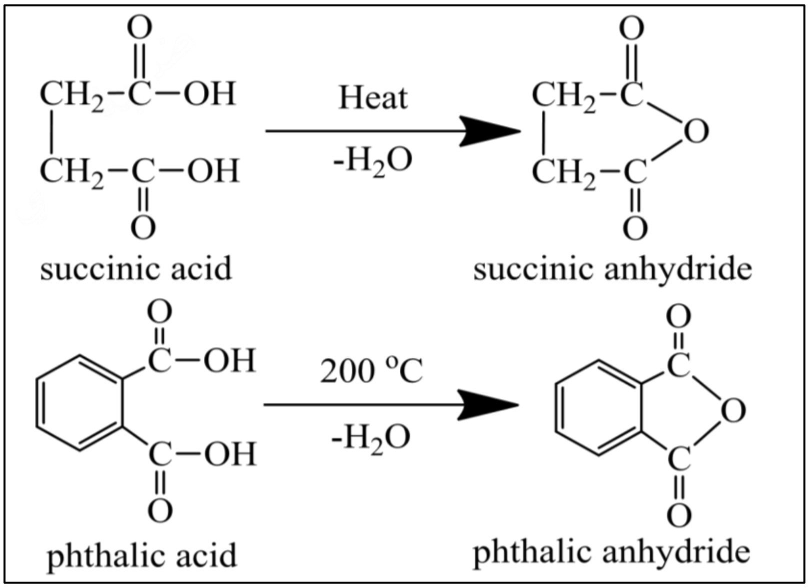


$$-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$$

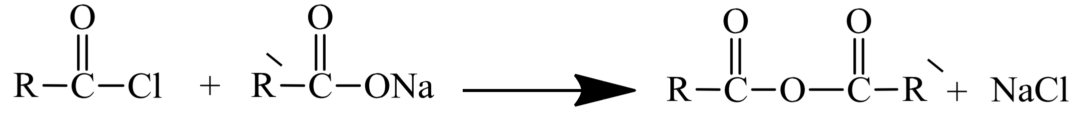
Anhydride

Preparation of anhydrides:

Anhydrides are a derivative of carboxylic acids by removing the water molecule from carboxylic acids.



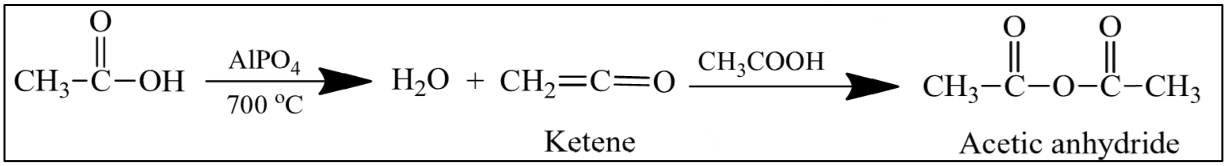
Can be prepared in the laboratory from the interaction between acetyl chloride with sodium acetate:



$$R-\overset{O}{\overset{\|}{C}}-Cl + R'-\overset{O}{\overset{\|}{C}}-ONa \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R' + NaCl$$

Acid Chloride Acid Salt Anhydride

Industrially the preparation is by of the dehydration reaction of acetic acid at temperature up to 800 °C:

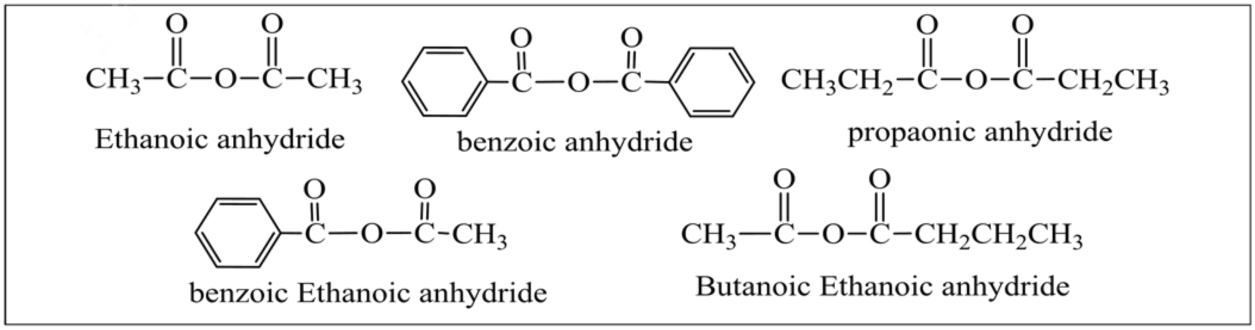


$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[700\ ^oC]{AlPO_4} H_2O + CH_2{=}C{=}O \xrightarrow{CH_3COOH} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

Nomenclature:

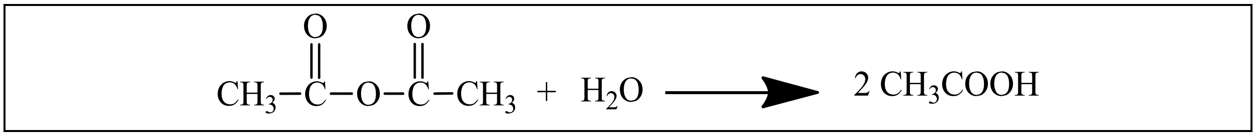
Symmetrical acid anhydrides are named by replacing the word acid in the name of the parent carboxylic acid by the word anhydride. **Unsymmetrical acid** anhydrides are named by first naming each component of carboxylic acid alphabetically arranged (without the word acid) followed by the word anhydride.

Examples:



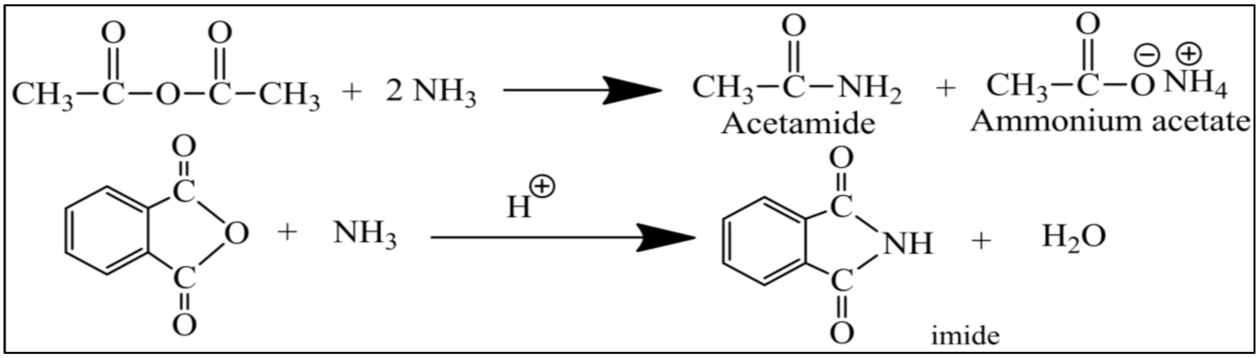
Reaction of anhydrides:

1- The reaction with water

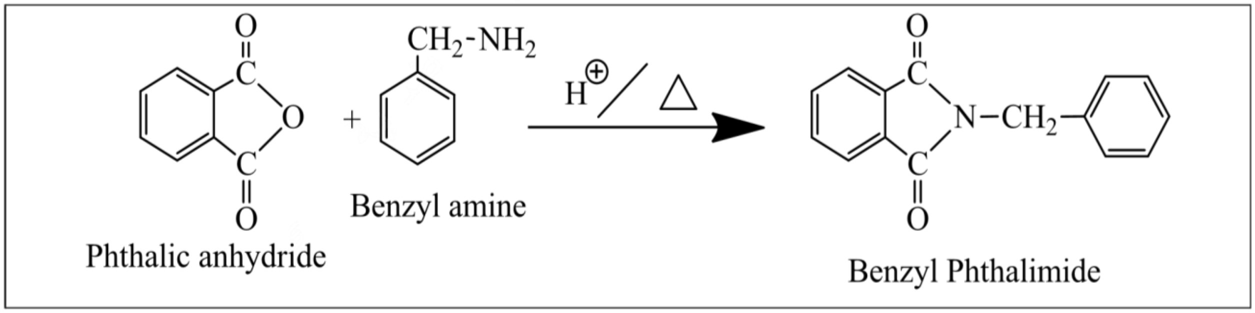


$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \longrightarrow 2\ CH_3COOH$$

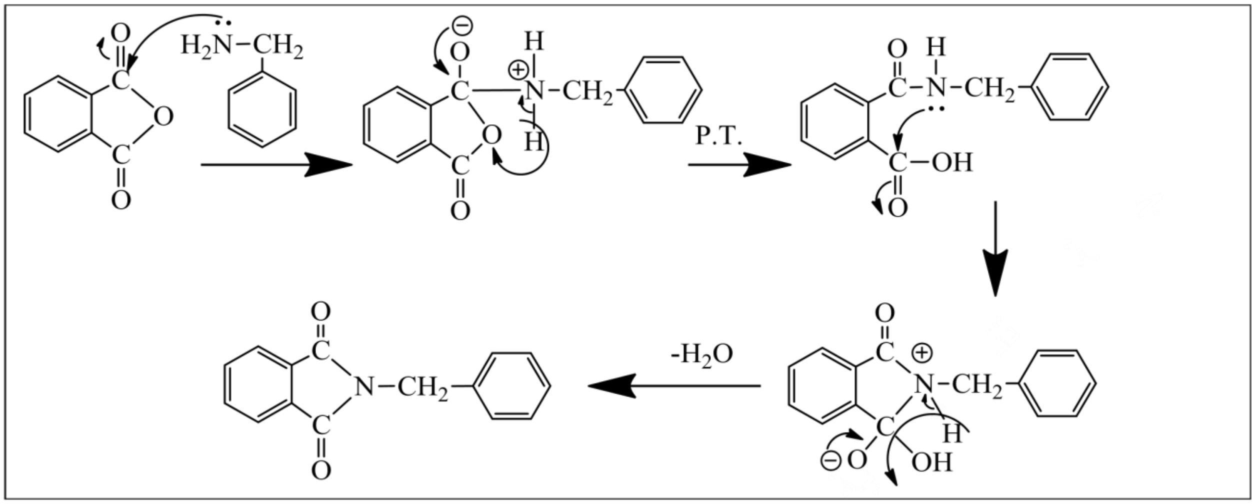
2- The reaction with ammonia or amines formed amide, while imides are formed by reaction of cyclic anhydride and amines:



Interaction equation:



The mechanism for the reaction:



Experimental part:

1- In (100ml) round bottomed flask, dissolve phthalic anhydride (0.5g) and benzyl amine (0.5ml) in (5ml) of glacial acetic acid and stirred the mixture.

2- The mixture reflux for (30mins) while stirring continually.

3- The mixture is Cooled after reflux finish and added on ice-cold water with shacking for (5 mins) until a white precipitate is formed.

4- The solid product is filtered and dried.

5- The N-benzyl phthalimide is Recrystallized from ethanol.

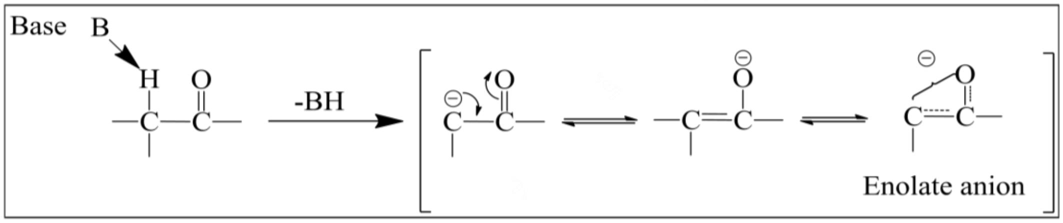
6- The product is Weighted and the percentage of yield is calculated.

Experimental 6

Aldol Condensation Theoretical part: Acidity of α hydrogens.

The carbonyl group strengthens is acidity of the hydrogen atoms attached to the α-carbon and by doing this, gives rise to a whole set of
chemical reactions.

Ionization of an α-hydrogen



Resonance that is possible only through participation by the carbonyl group. Resonance of this kind is not possible for carbanions formed by ionization of β-hydrogens, γ-hydrogens. The susceptibility of the carbonyl group to nucleophilic attack is due to the ability of oxygen to accommodate the negative charge that develops as a result of the attack.

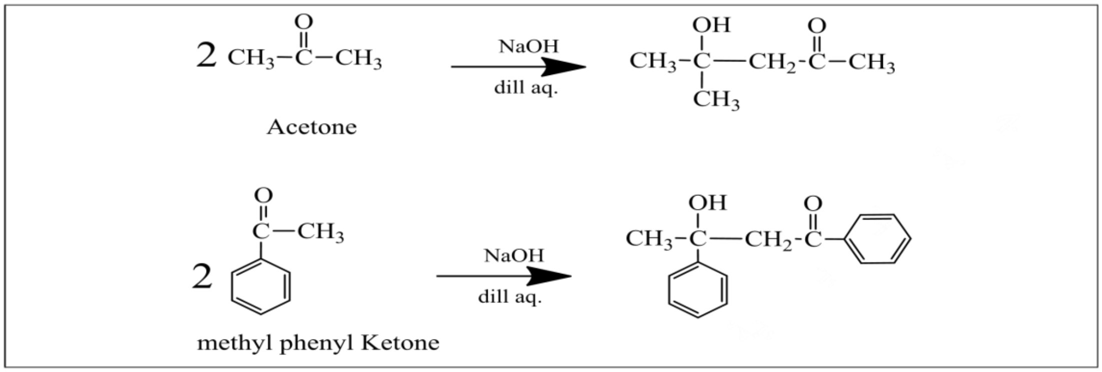
Conditions of aldol condensation:

1- Two molecules of an aldehyde or a ketone may combine to form a β-hydroxy aldehyde or β-hydroxyl ketone.

2- Under the influence of dilute base NaOH 10%.

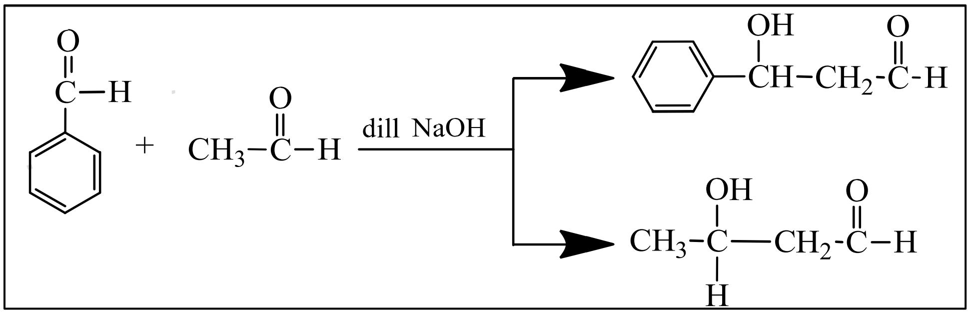
3- One molecule of aldehyde or ketone must be containing an α−hydrogen.

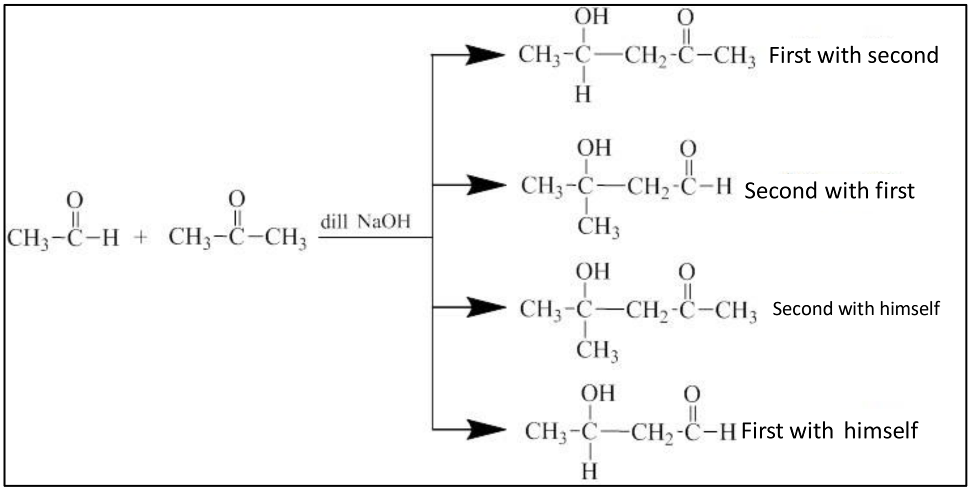
Examples:



Crossed aldol condensation

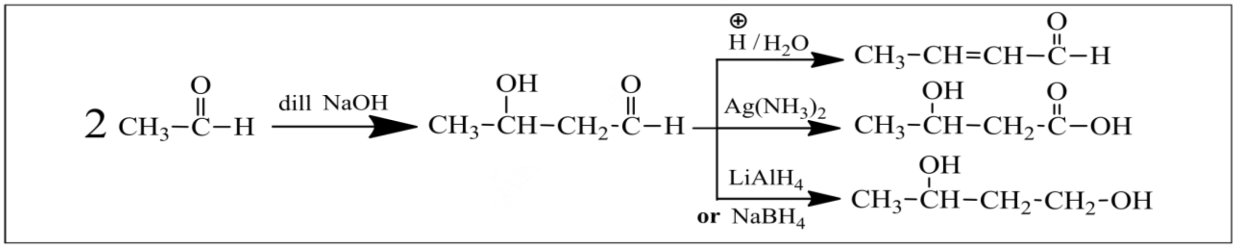
An aldol condensation between two different carbonyl compounds is called crossed aldol condensation, it is not always feasible in the laboratory, since a mixture of the four possible products may be obtained. On a commercial scale, however, such a synthesis may be worthwhile if the mixture can be separated and the compound marketed.



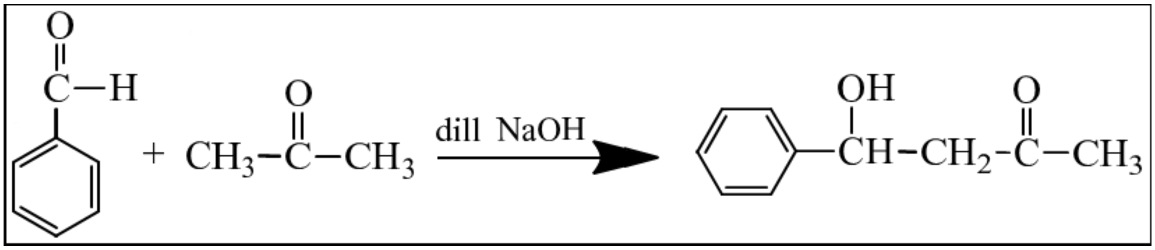


Uses of Aldol Condensation in synthesis:

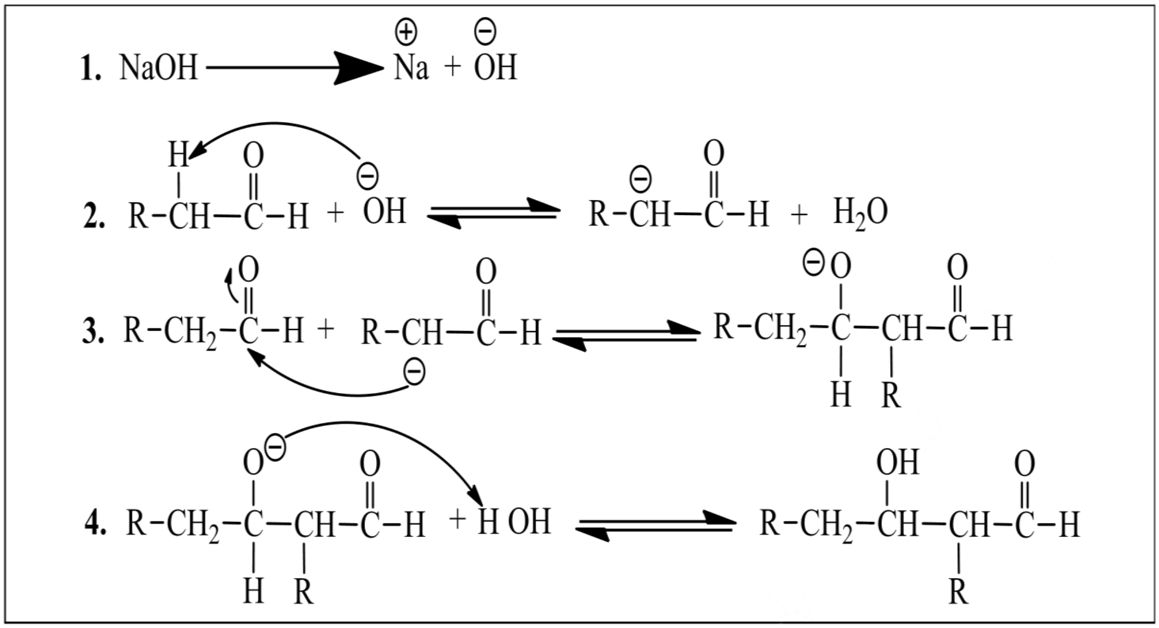
It gives many different products.



Interaction equation : preparation of (4-hydroxy-4-phenylbutan-2-one)



The mechanism for the reaction:



Experimental part:

1- In a (100ml) beaker is added (1ml) acetone and (0.5ml) of benzaldehyde.

2- In a (100ml) beaker is added a mixture of (0.5g) sodium hydroxide, (3.5ml) of ethanol and (4ml) of water.

3- Half of Contents of the first beaker is poured into the second beaker and stirring the mixture is left for (5mins).

4- The rest of mixture is added and left for (15mins).

5- The solid formed is filtered and dried.

6- The product is weighed and the percentage of yield is calculated.

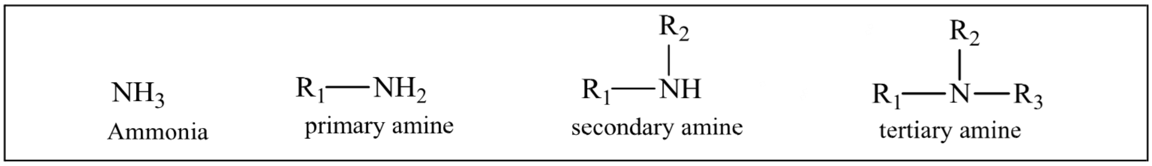
Second Semester

Experiment 1

Preparation of Azo dye from diazonium salt

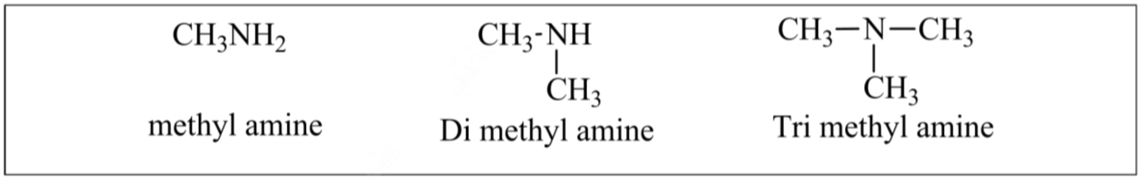
Theoretical part:

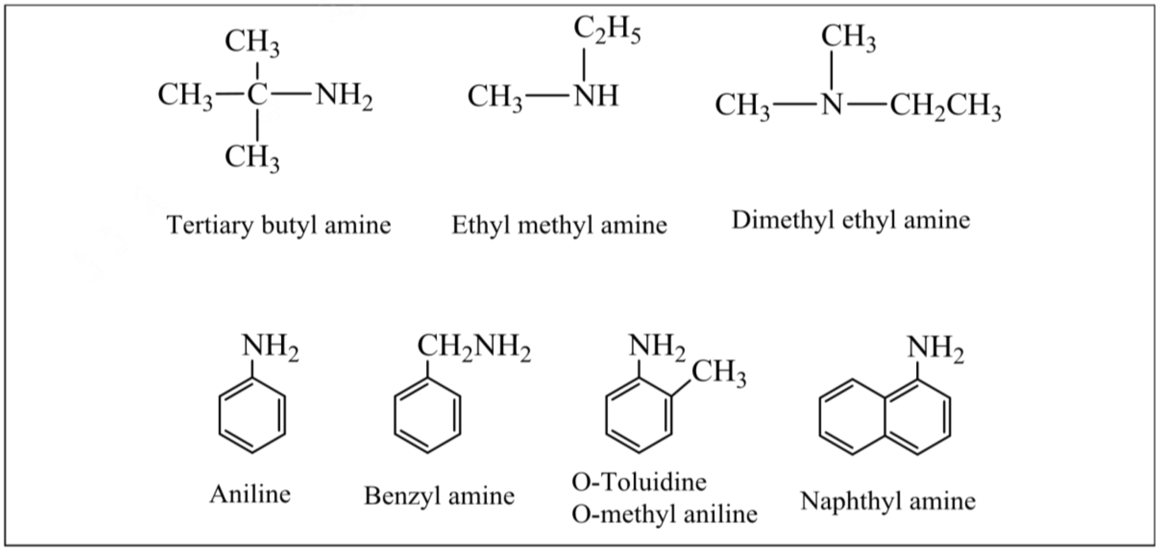
Amines: Are organic compounds that show appreciable basicity, the general formula RNH_2, R_2NH, or R_3N, where R is any alkyl or aryl group. Amines are classified as primary, secondary, or tertiary according to the number of groups are attached to the nitrogen atom.



Nomenclature:

amines are named by naming the alkyl group or groups attached to nitrogen, and following these by the word –amine.





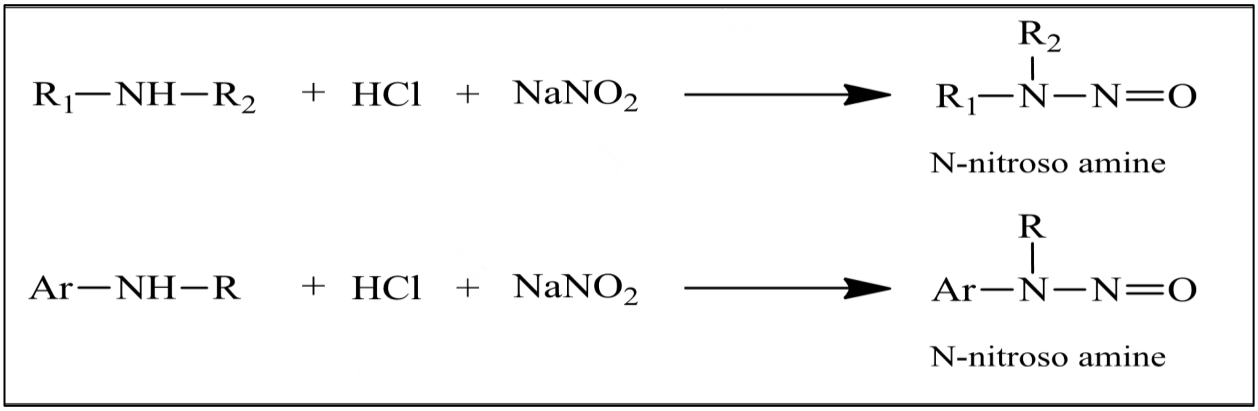
Amines are reacted with nitrous acid (HONO)to yields a different kind of product, HONO prepare by the action of mineral acid on sodium nitrite. Primary amines react with nitrous acid to yield diazonium salt.

$$HCl + NaNO_2 \xrightarrow{0\text{-}5\ ^{o}C} HONO$$

$$R\text{-}NH_2 + HCl + NaNO_2 \xrightarrow{0\text{-}5\ ^{o}C} R\text{-}\overset{\oplus}{N_2}\ \overset{\ominus}{Cl} \longrightarrow N_2 + \text{Mixture}$$

$$Ar\text{-}NH_2 + HCl + NaNO_2 \xrightarrow{0\text{-}5\ ^{o}C} \underset{\text{diazonium salt}}{Ar\text{-}N{\equiv}\overset{\oplus}{N}\ \overset{\ominus}{Cl}} + NaCl + 2H_2O$$

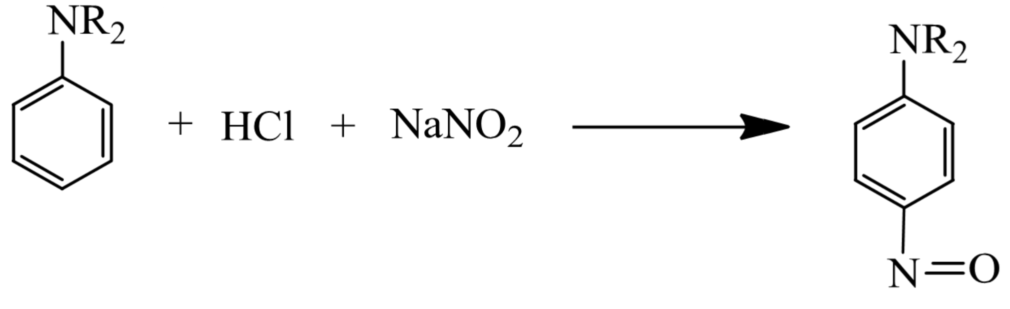
Secondary amines, both aliphatic and aromatic reacted with nitrous acid to yield *N*-nitrosoamines.



$$R_1-NH-R_2 + HCl + NaNO_2 \longrightarrow \underset{\text{N-nitroso amine}}{R_1-\overset{\overset{\displaystyle R_2}{|}}{N}-N=O}$$

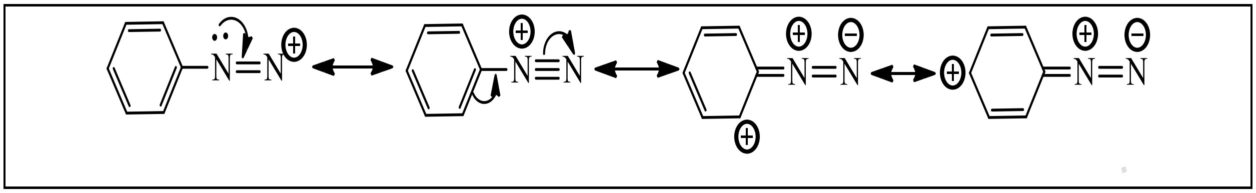
$$Ar-NH-R + HCl + NaNO_2 \longrightarrow \underset{\text{N-nitroso amine}}{Ar-\overset{\overset{\displaystyle R}{|}}{N}-N=O}$$

Tertiary aromatic amines undergo ring substitution, to yield compounds in which a nitroso group, -N=O is joined to carbon in *p*- position.



P-nitroso N,N-dialkyl aniline

Primary aromatic amines react with nitrous acid to yield diazonium salt, this is one of the most important reactions in organic chemistry. aromatic diazonium salt is more stable than aliphatic diazonium salt.



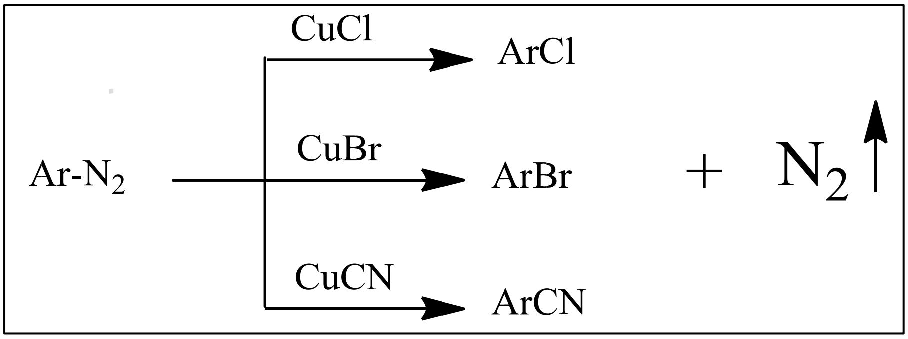
Diazonium Salt Reaction:

when primary aromatic amine is dissolved or suspend in cold aqueous mineral acid & treated with sodium nitrite, there is formed a diazonium salt

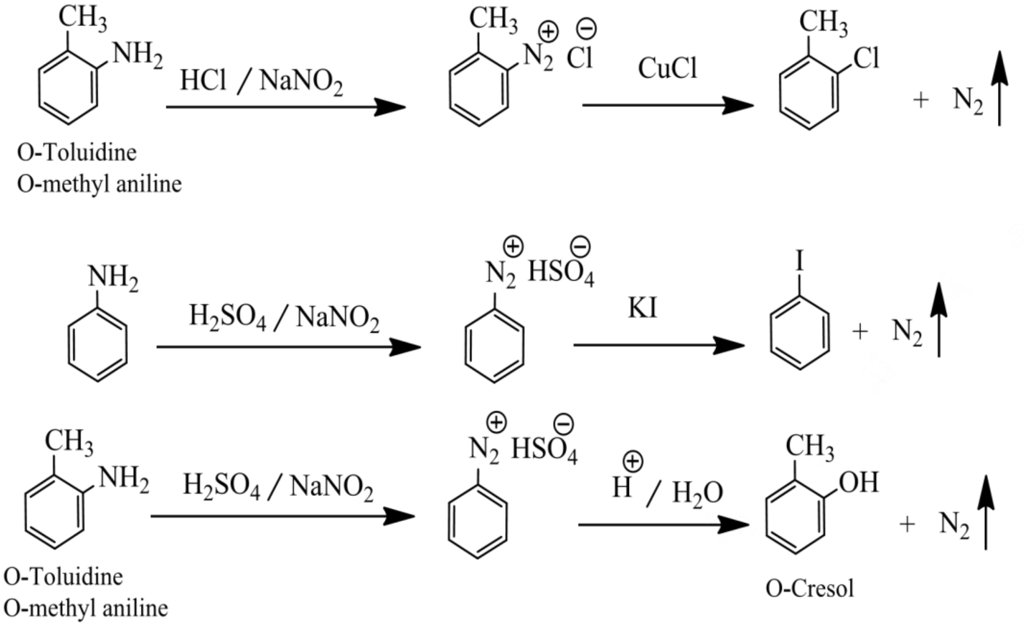
$$\underset{\text{Aromatic amine}}{Ar\text{-}NH_2} + NaNO_2 + 2HX \xrightarrow{\text{Cold}} \underset{\text{diazonium salt}}{Ar\text{-}N\equiv N^{\oplus}X^{\ominus}} + NaX + 2H_2O$$

diazonium salt slowly decomposes even at ice-bath temperatures, the solution is used immediately after preparation. There are large numbers of reaction undergo by diazonium salts may be divided in two types:

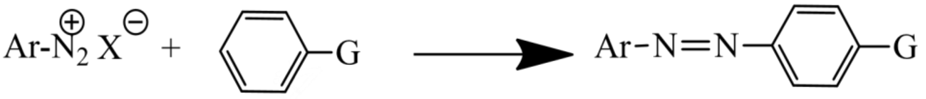
1- **Replacement reaction:** in which nitrogen is lost as N_2, and some other atom or group becomes attached to the ring in its place.



Examples:

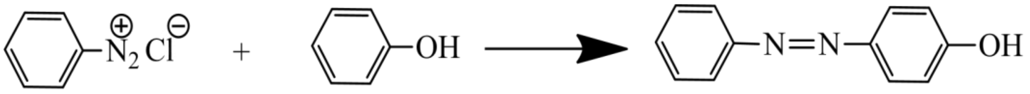


2- **Coupling reaction:** in which the nitrogen in diazonium salt is retained in the product.



$G = NH_2$, NHR , NR_2 , OH

Example:

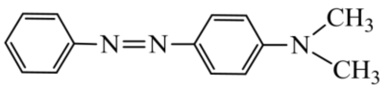


Benzene diazonium chloride

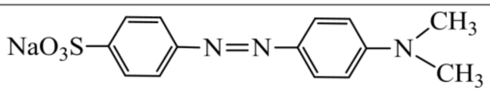
Phenol

P-hydroxy azobenzene
p-(phenylazo) phenol

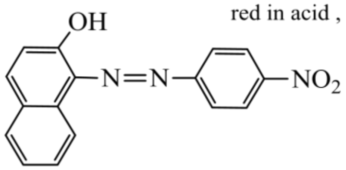
Examples for AZO dye :



p-di methylamino azobenzene

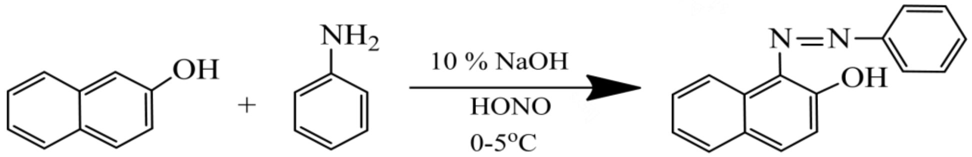


methyl Orange and acid base indicator
red in acid , yellow in base



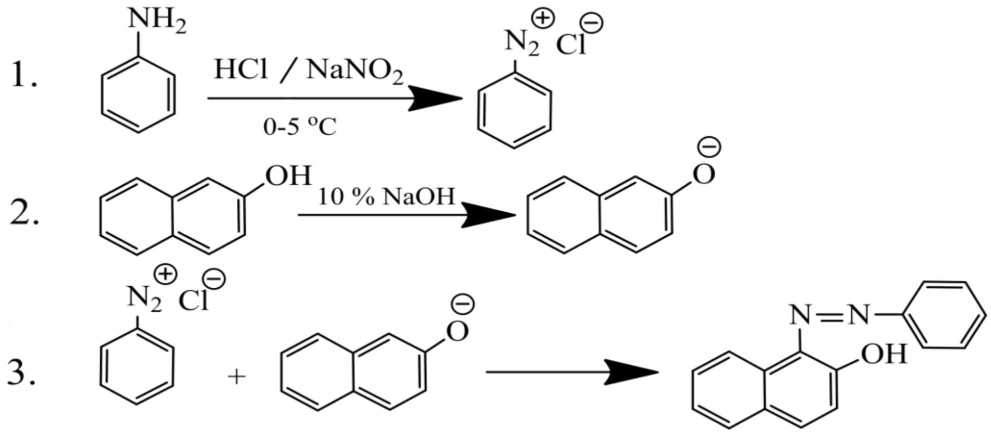
P-nitro azo-2-naphthol para red

E.G. : preparation of 1-phenylazo-2-naphthol :



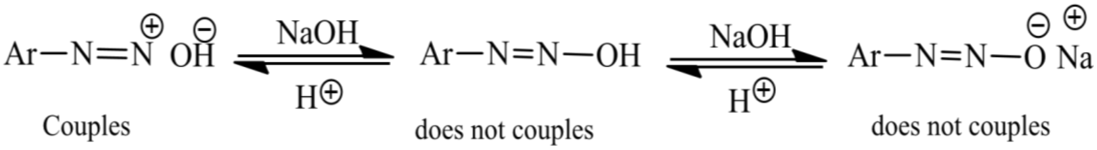
1-phenyl azo -2-naphthol

mechanism preparation of 1-phenylazo-2-naphthol:

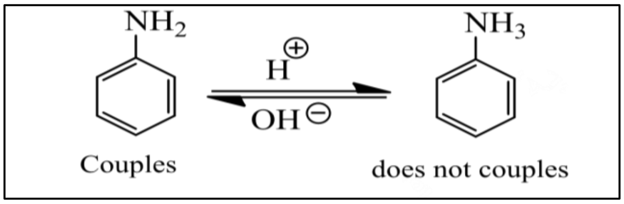


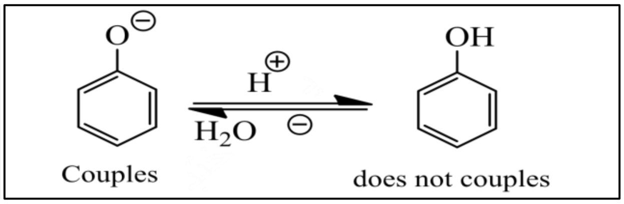
Conditions for preparation of AZO dye:

1- It is most important that the coupling medium be adjusted to the right degree of acidity or alkalinity. This is accomplished by addition of the proper amount of hydroxide or salts like sodium acetate or sodium carbonate.



The electrophilic reagent is the diazonium ion, ArN_2+. In the presence of hydroxide ion, the diazonium ion exists in equilibrium with an un-ionized compound, Ar-N=N-OH, and salts (Ar-N=N-O-Na+) derived from it:





2- The diazonium salt is reacted with aromatic amines in low temperature (0-5ºC), because diazonium salt is unstable reagent.

3- The aromatic ring (ArH) undergoing attack by the diazonium ion must, in general, contain a powerfully electron-releasing group, generally –OH, $-NR_2$, NHR, or $-NH_2$.

Experimental part:

1- (1ml) of aniline was dissolved in (5ml) of concentrated hydrochloric acid and (5ml) of water, in a small beaker.

2- (0.8g) of sodium nitrite in (4ml) of water was added to the mixture in step 1. The mixture was kept in ice bath (0-5ºC).

3- (1.6g) of 2-naphthol in (9ml) of (10%) percent sodium hydroxide (aq.), was kept in ice bath too.

4- The Cooled mixture in step 2 was added slowly to Naphthol solution.

5- A red color. Develops and red crystals of 1-phenyl-azo-2-naphthol separated.

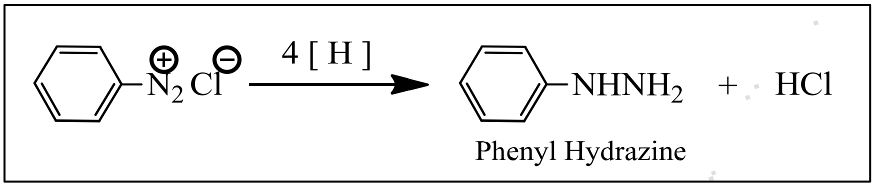
6- After the completion of addition, the mixture was kept in ice bath for (30min) with occasional stirring

7- The precipitate was filtered through Buchner funnel washed with water and dried.

8- The precipitated dye was weighed to calculate the percentage yield.

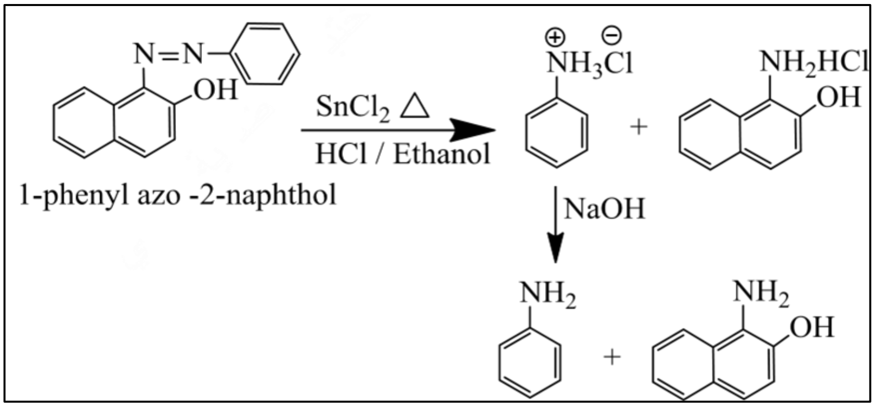
Experiment Eight Reduction of Azo dye

The aryl diazonium ion group is reduced by SnCl2/ HCl or Na2SO3 to produce the phenyl hydrazine compound. Which is considered as important detector in the carbonyl chemistry and sugars. An azo compound is cleaved at the azo linkage by stannous chloride (SnCl2 / HCl) to form two amines.



The azo dye′s reduction is indicated by the changing of the red color to a very pale brown. There are other reductive reagents as Zn/ HCl, Fe/ HCl.

E.G: preparation of 1-amino-2-naphthol:



Experimental part

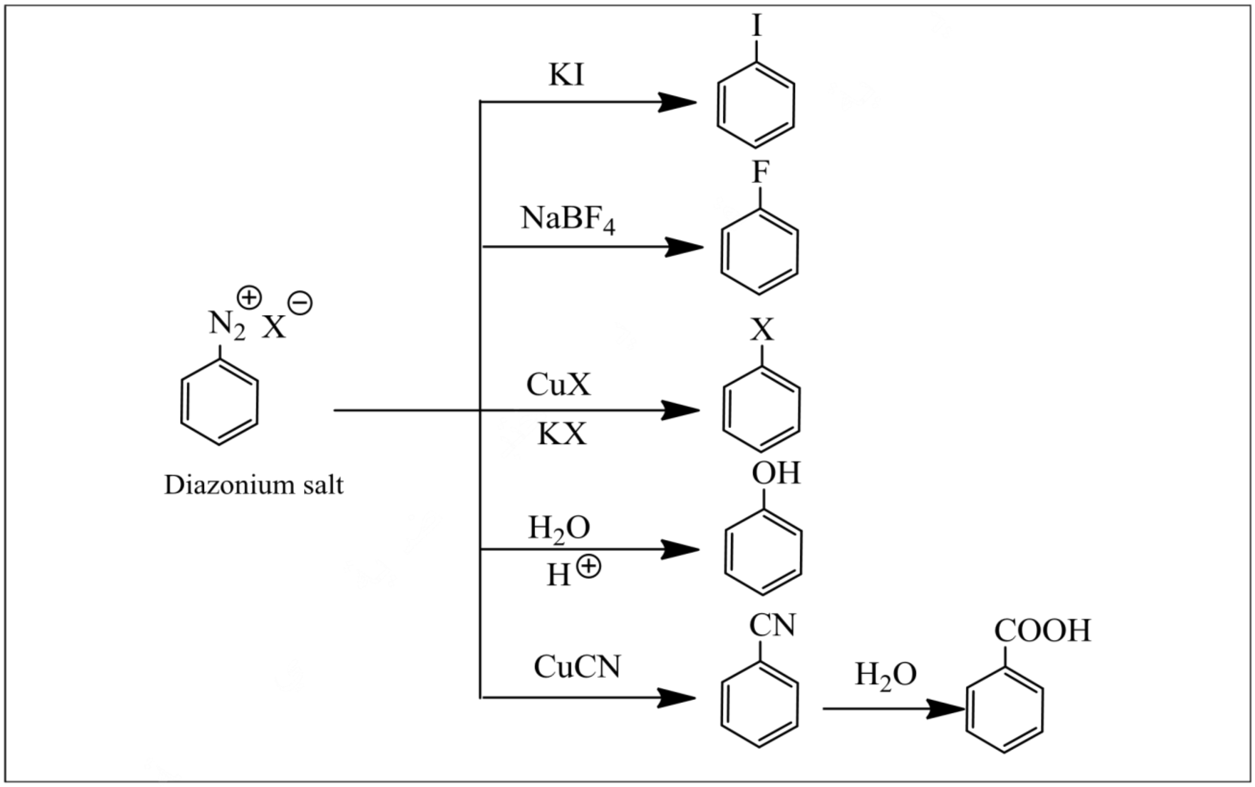
1- In a (100ml) round bottom flask (0.5g) of 1-phenylazo-2-naphthol is dissolved in (10ml) of ethanol absolute.
2- (1g) of Sncl2 is dissolved in (3ml) of concentrated hydrochloric acid in a beaker and added to the content in the flask.
3- The mixture is refluxed gently for (30mins) with occasional shaking until a clear solution is formed.
4- The solution is filtered hot and left for (10 mins).
5- (10%) of NaOH is added to the solution drop wise until the precipitate is formed.
6- The precipitate is filtered and dried.
7- The product is weighed and the percentage of yield is calculated.

Experiment 9

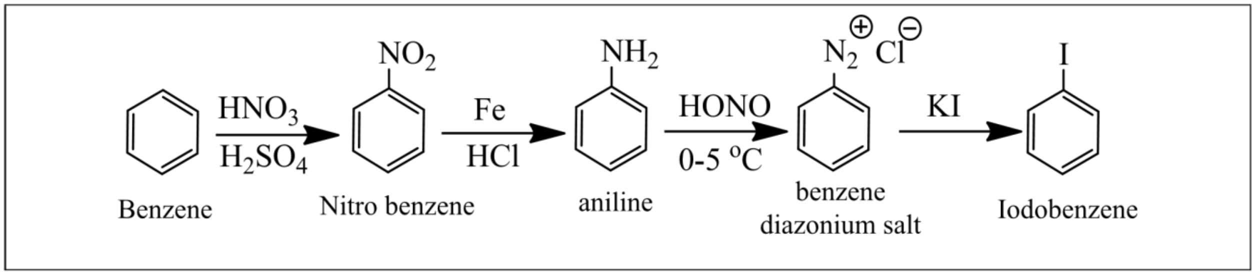
Preparation of Iodobenzene

Theoretical part:

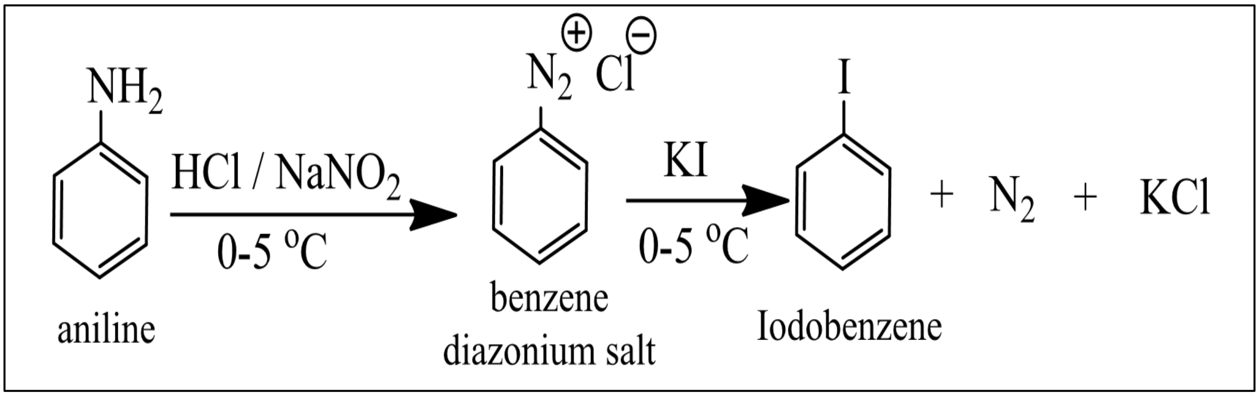
Aryl Iodides and fluorides cannot generally be prepared by direct halogenations. Replacement of diazonium group is the best general way of introducing (F,Cl,I,CN,OH, and H) into an aromatic ring. Diazonium salts are valuable in synthesis not only because they react to form so many classes of compounds, but also because they can be prepared from nearly all primary aromatic amines.



Example:



The general equation



Uses of iodobenzene:

Iodine Compounds; Pharmaceutical Intermediate; it is useful as a synthetic intermediate in organic chemistry.

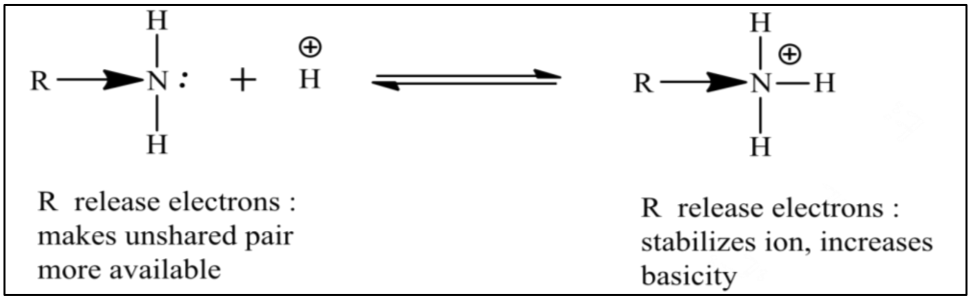
Experiment:

1- (1.25ml) of aniline was dissolved in (3.5ml) of concentrated hydrochloric acid, (3.5ml) of water in a small beaker.
2- The diazonium salt is prepared by the addition of a solution of (1g) of sodium nitrite in (5ml) of water to the solution in step 1 and left in ice bath (0-5°C).
3- (2.25g) of potassium iodide was dissolved in (5ml) of water and cooled in icebath.
4- The Cold solution of potassium iodide is added slowly to the mixture in step 2.
5- The solution is allowed to stand in an ice bath for (15 min.) with occasional stirring.
6- The precipitate formed is filtered through a Buchner funnel washed and dried
7- The dry product is weighed to get the percentage yield.

Experiment ten

Acetanilide

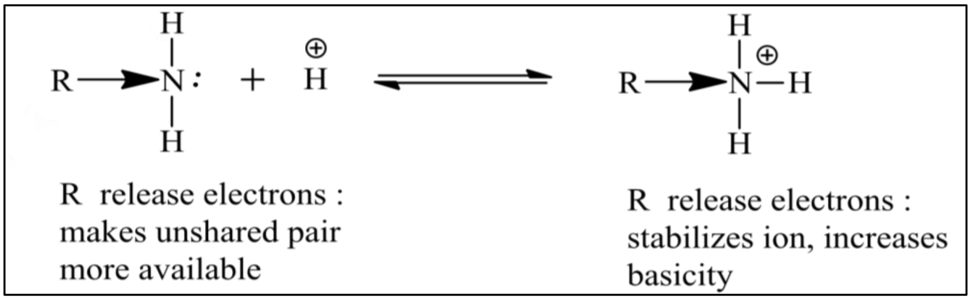
Amines are convenient to compare basicity's by measuring the extent to which they accept hydrogen ion from water; the equilibrium constant for this reaction we combine with $[H_2O]$ to obtain the basicity's constant, Kb.



Each amine has its characteristic Kb; the larger the Kb, the stronger the base. Measurement of [OH]is simply a convenient way to compare basicities.

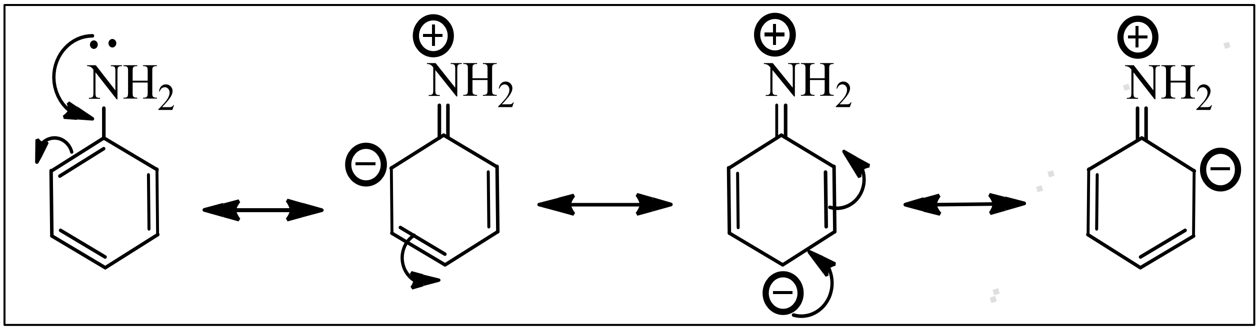
An aliphatic amine is more basic than ammonia?

Because the electron-releasing alkyl groups tend to disperse the positive charge of the substituted ammonium ion, and therefore stabilize it in a way that is not possible for the substituted ammonium ion. Thus, an ammonium ion is stabilized.

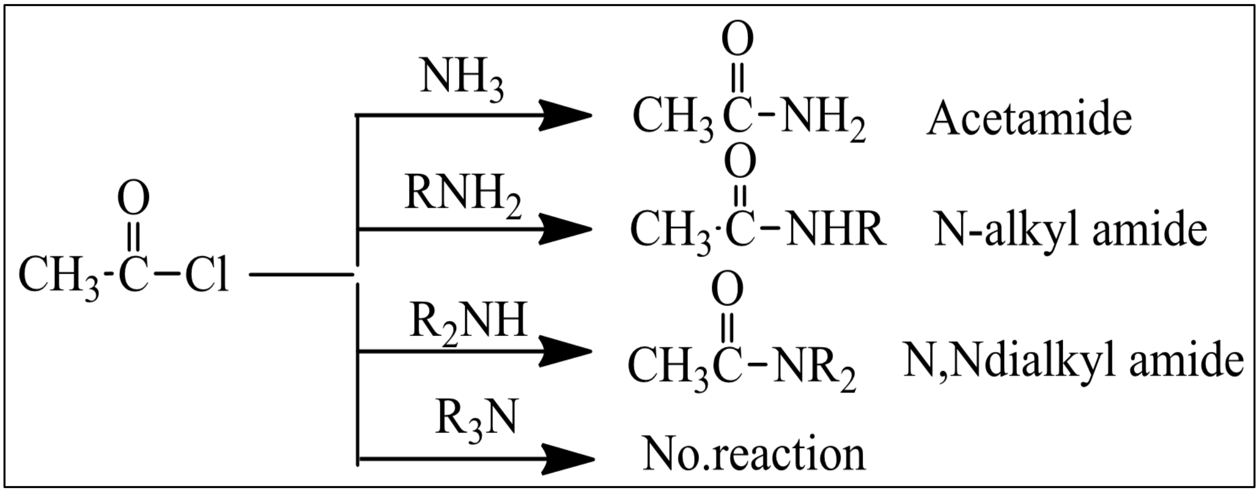


Aromatic amines are weaker bases than ammonia?

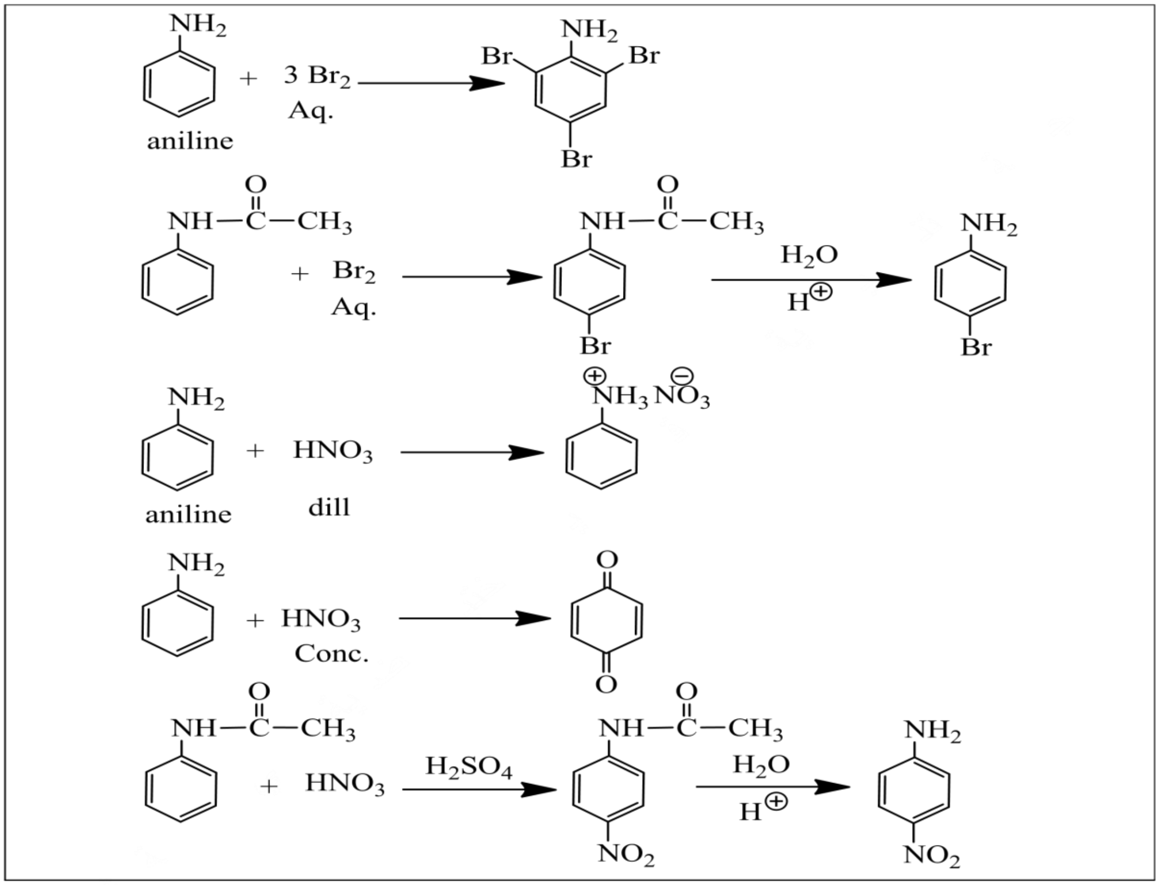
Because electron release in the same way as carbocation. From another point view, we can consider that an alkyl group pushes electrons toward nitrogen, and thus makes the fourth pair more available for sharing with an acid. (The differences in basicity among primary, secondary, and tertiary aliphatic amines are due to a combination of solvation and polar factors).



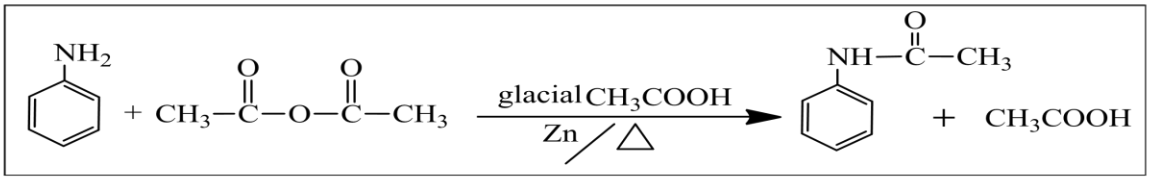
The low basicity of aromatic amines is thus due to the fact that the amine is stabilized by resonance to a greater extent than is the ion and the fourth pair if electrons is partly shared with the ring and is thus less available for sharing with hydrogen ion. The tendency (through resonance) for the –NH2 group to release electrons to the aromatic ring more reaction toward necessarily makes the amine less basic. similar consideration applies to other aromatic amines. A similar way primary and secondary amines can react with derivatives of carboxylic acid to form substituted amides, compounds in which –Cl has been replaced by the -NHR or NR2 group. Tertiary amines, although basic and hence nucleophilic, fail to yield amides.



Ring substitution aromatic ring:



The general question:



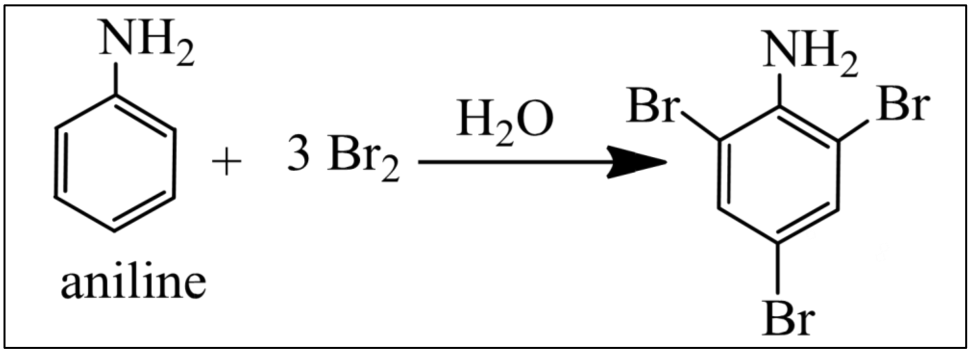
Experimental part:

1. In (100ml) round bottom flask, a mixture of (4ml) of Aniline, (4ml) of Acetic Anhydride, (0.5g) of zinc and (4ml) of glacial acetic acid are added and stirred
2. The mixture is reflux gently for (30mins) with occasional shaking until a clear solution is formed.
3. The mixture is cooled after reflux and poured into (50ml) of ice-cold water and with shaking for (5mins) until a while precipitate is formed.
4. The precipitate is washed several times with cold water.
5. The precipitate is filtered and dried.
6. The product is weighed and the percentage of yield is calculated.

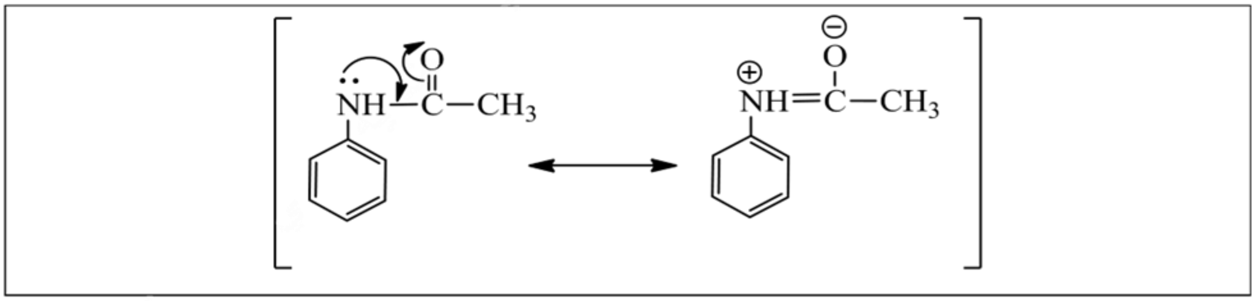
Experiment Eleven

Preparation of p-nitro acetanilide

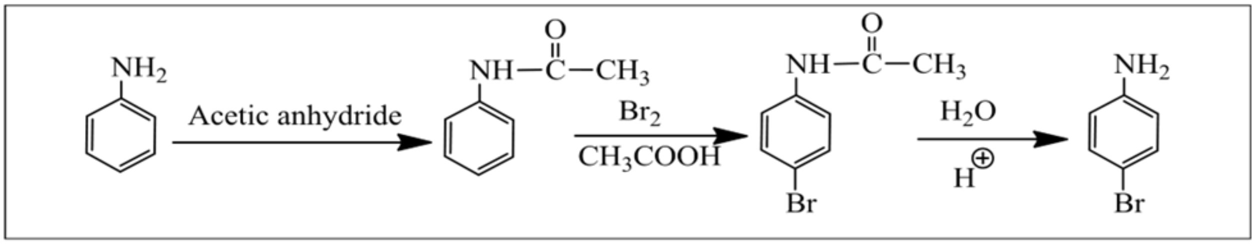
In electrophilic substitution the chief problem encountered with aromatic amines is that they are too reactive. In halogenation, substitution tends to occur at every available ortho or para position, for example the result of mixing the aniline with bromine water is (2,4,6-tribromoaniline).



The acetamide group, (-NHCOCH$_3$), is also activating and ortho , para ,directing , but less powerfully so than free amino group . electron withdrawer by oxegen of the carbonyl group mix the nitrogen of an amide a much porer source of electrons than the nitrogen of an amine.

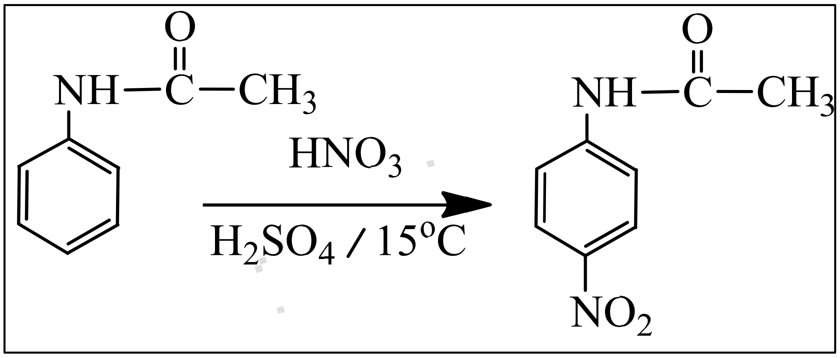


As example we can prepare P-Bromoaniline as shown below:



In nitration of amines, nitric acid not only nitrates, but oxidizes the highly reactive as well, with loss of much material as tar. Furthermore, in strongly acidic nitration medium, the amine is converted into the anilinium ion, substitution is thus controlled not by the amino group but by the NH_3^+ group which, because of its positive charge, directs much of the substitution to the meta position. there is fortunately, a assemble way out of these difficulties. we protect the amino group, we acetalate the amine, then carry out the substitution, and finally hydrolyze amide to the desired substituted amine.

General Equation



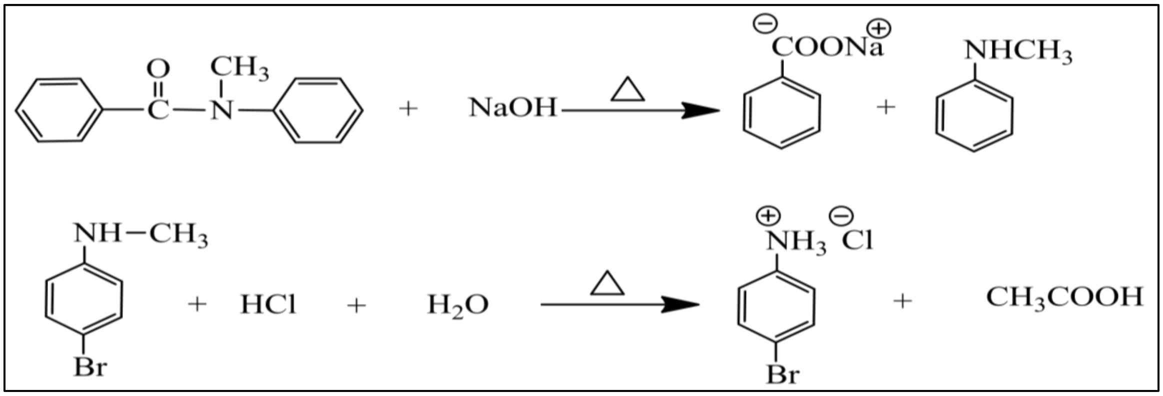
Experimental Part

1. (2.5 gm.) of acetanilide is added to 2.5 ml of glacial acetic acid in a beaker with continuous stirring
2. .2.5 ml of concentrated sulfuric acid is added to the mixture in step 1,with cooling in ice bath.
3. A mixture of 1.5 ml of nitric acid and 1 ml of sulfuric acid is added to the mixture in step 2 drop wise with continuous stirring in ice bath keeping the temperature (0-5) C°.
4. The mixture is left at room temperature for 15 min.
5. The mixture is poured onto 100 ml of ice cooled water, the precipitate is fomed.
6. The precipitate is filtered and dried.
7. The product is weighed and the percentage of yield is calculated

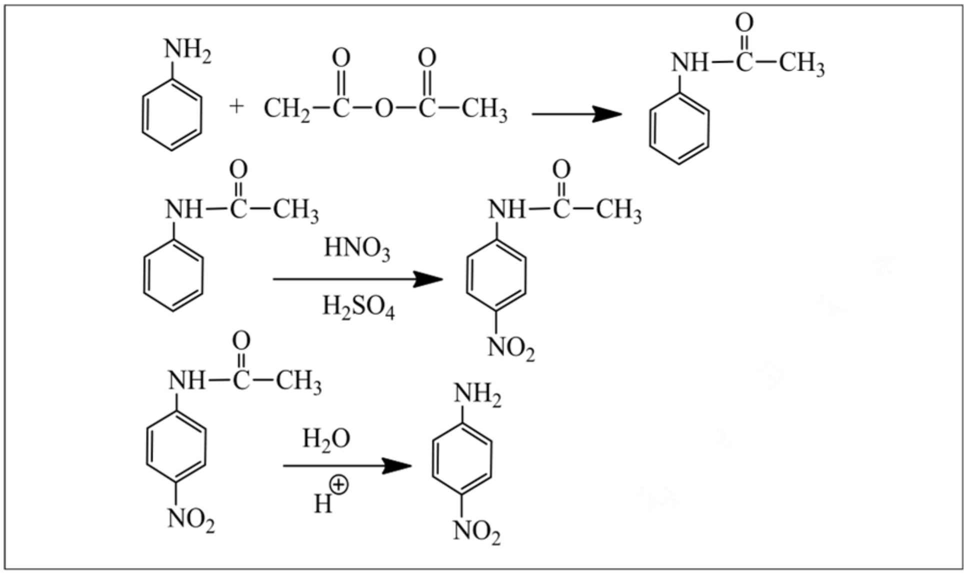
Experiment Twelve

Hydrolysis of *p*-nitroacetanilide

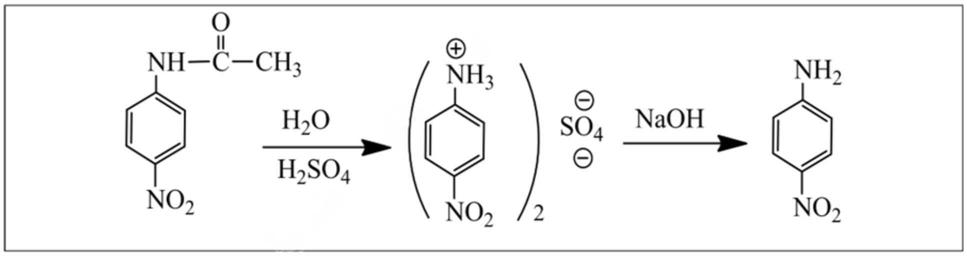
Like simple amides, substituted amides undergo hydrolysis, the product are the acid and the amine although one or the other is obtained as its salt, depending upon the acidity or alkalinity of the medium:



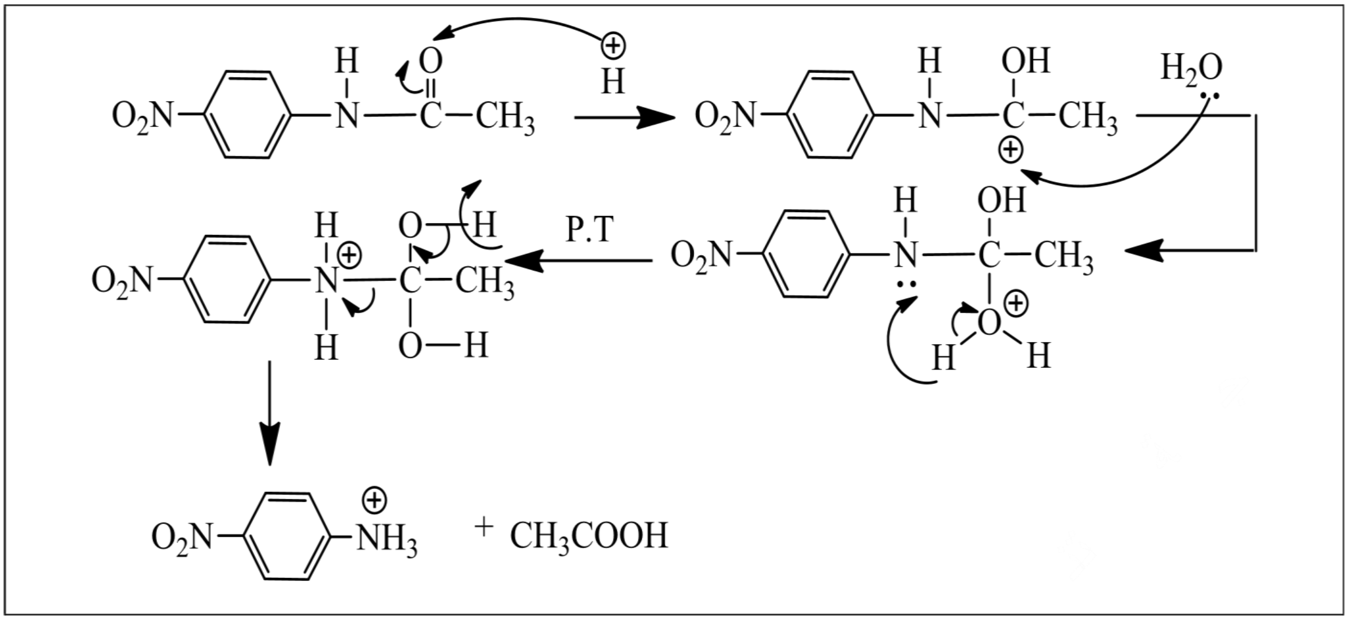
To prepare P-nitroaniline we should follow the steps as shown below:



General Equation



Mechanism



Experimental part :

1. In (100ml) round bottomed flask, a mixture of (0.75 gm.) of *p*-nitroacetanilide, (3.5 ml) of sulfuric acid (30 %) refluxed with stirring for half hour until the mixture become clear.
2. The mixture is poured onto 100 ml ice cooled water and justified with (10 % NaOH) until the precipitate is formed
3. The precipitate is filtered and dried.
4. The product is weighed and the percentage of yield is calculated