

Second Semester

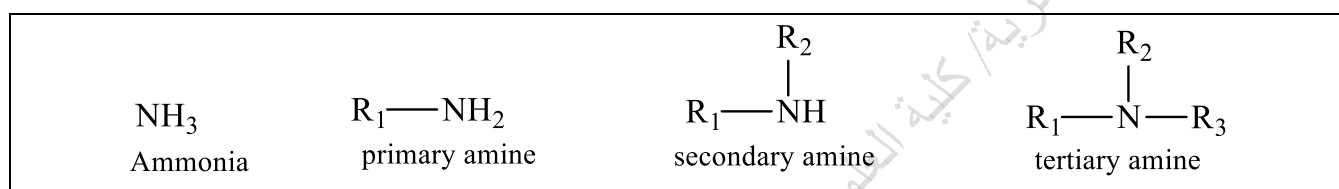
Experiment 1

Preparation of Azo dye from diazonium salt

Theoretical part:

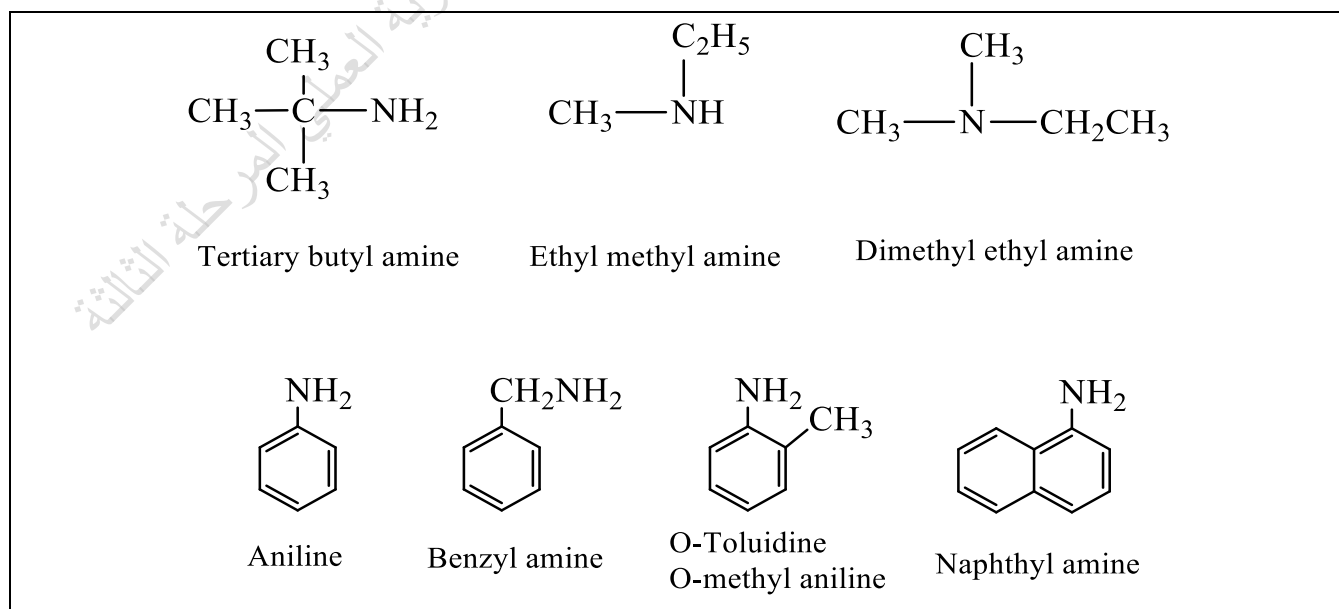
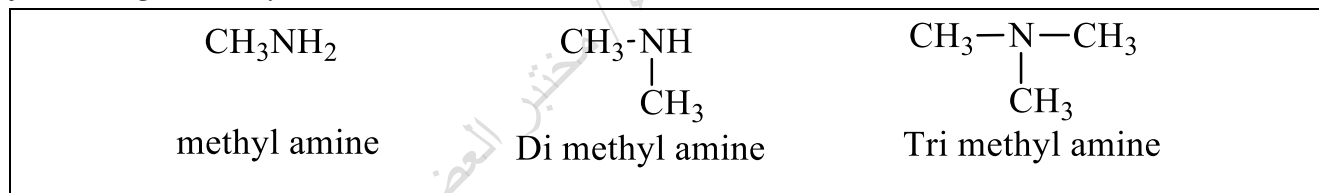
Amines : Are organic compounds that show appreciable basicity ,the general formula RNH_2 , R_2NH , or R_3N , where R is any alkyl or aryl group.

Amines are classified as primary, secondary, or tertiary according to the number of groups are attached to the nitrogen atom.

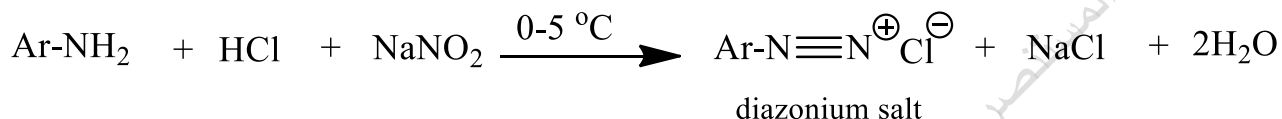
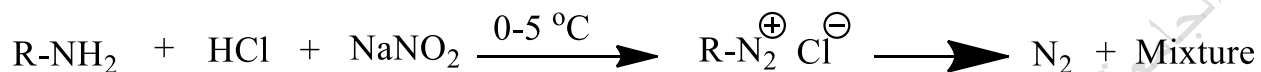
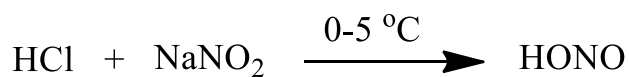


Nomenclature:

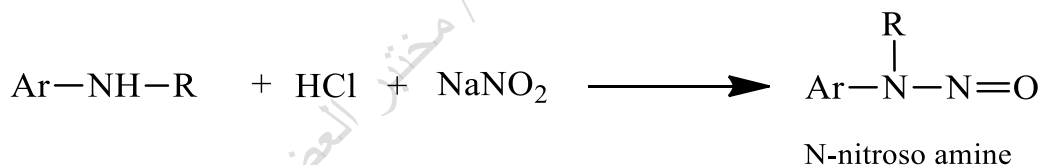
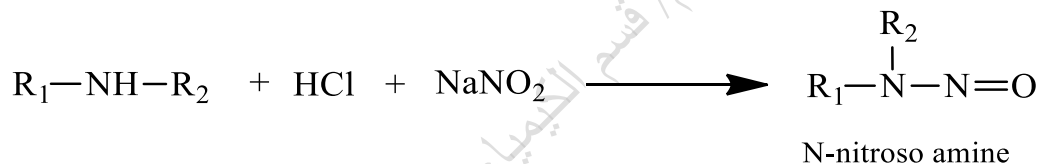
amines are named by naming the alkyl group or groups attached to nitrogen , and following these by the word –amine .



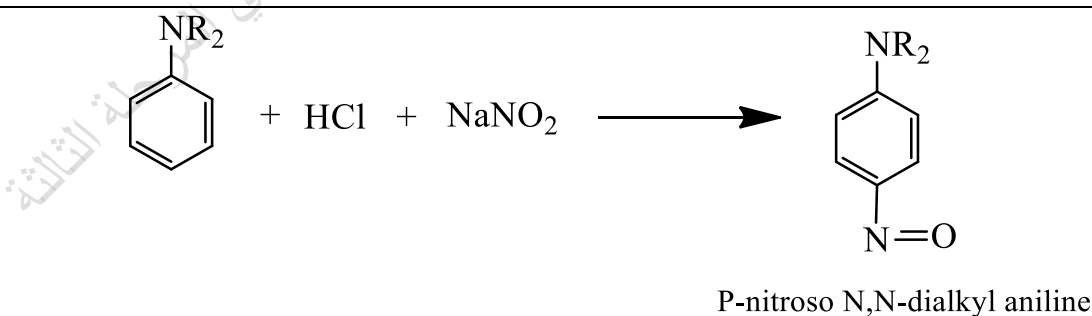
Amines react with nitrous acid (HONO) to yield a different kind of product, HONO prepared by the action of mineral acid on sodium nitrite. Primary amines react with nitrous acid to yield diazonium salt.



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

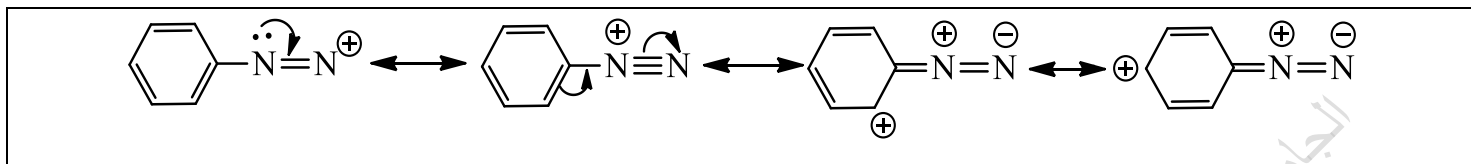


Tertiary aromatic amines undergo ring substitution, to yield compounds in which a nitroso group, -N=O, is joined to carbon in *p*-position.



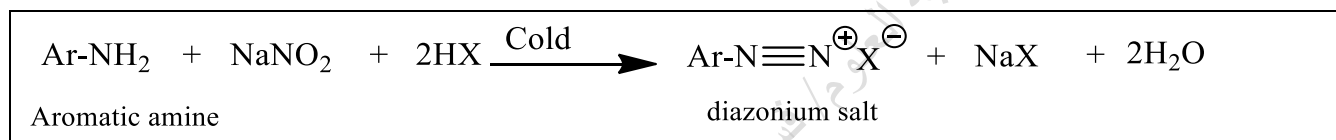
Primary aromatic amines react with nitrous acid to yield diazonium salt, this is one of the most important reactions in organic chemistry.

aromatic diazonium salt is more stable than aliphatic diazonium salt.



diazonium salt reaction :

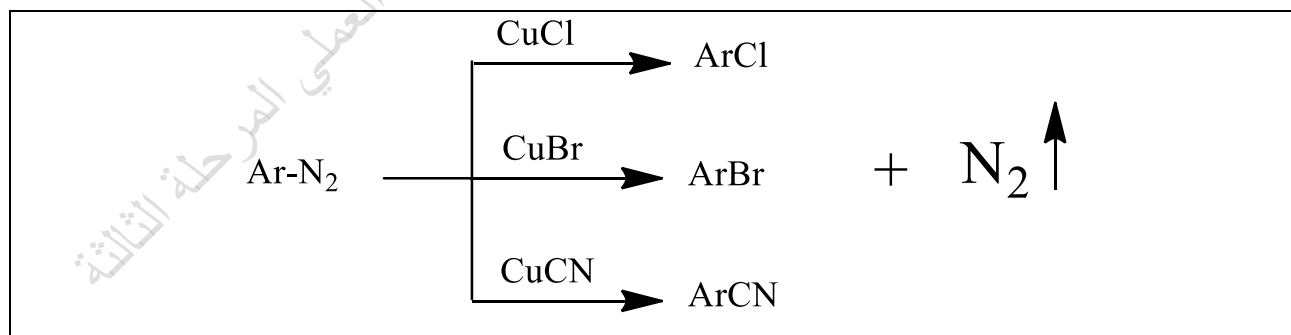
when primary aromatic amine is dissolved or suspended in cold aqueous mineral acid & treated with sodium nitrite, there is formed a diazonium salt



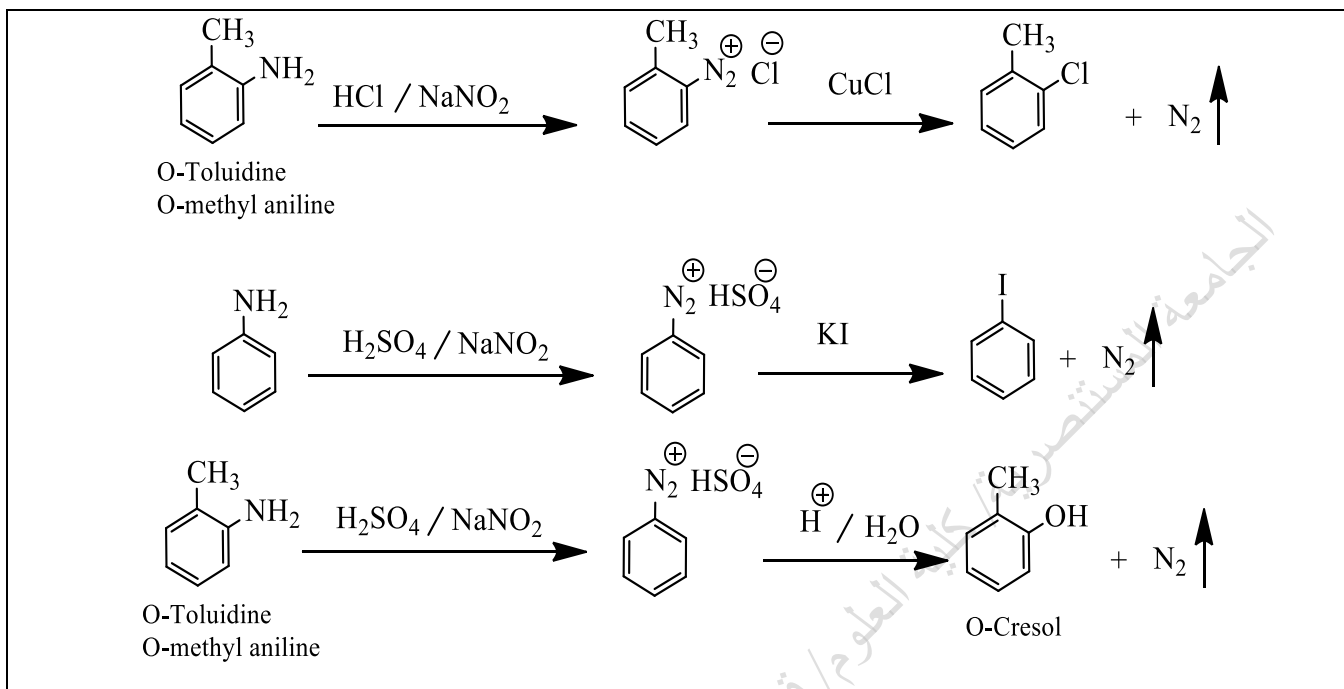
diazonium salt slowly decomposes even at ice-bath temperatures, the solution is used immediately after preparation.

There are large numbers of reactions undergone by diazonium salts that may be divided into two types:

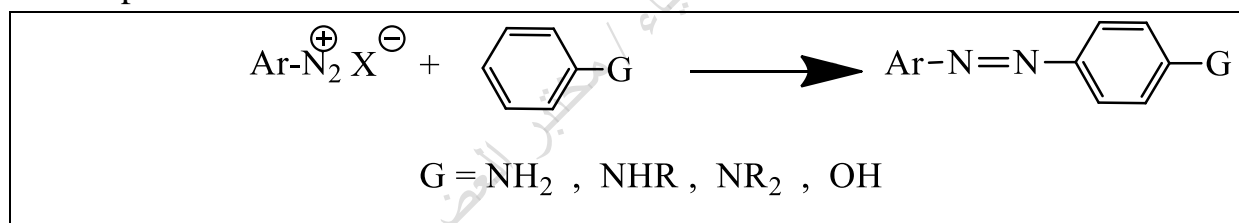
- 1- **Replacement reaction:** in which nitrogen is lost as N_2 , and some other atom or group becomes attached to the ring in its place.



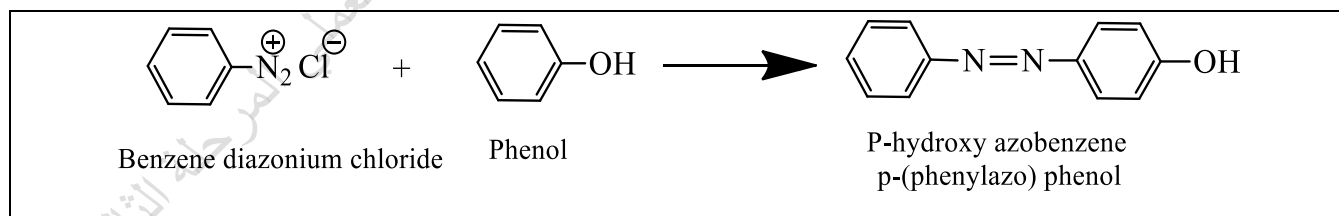
Examples:



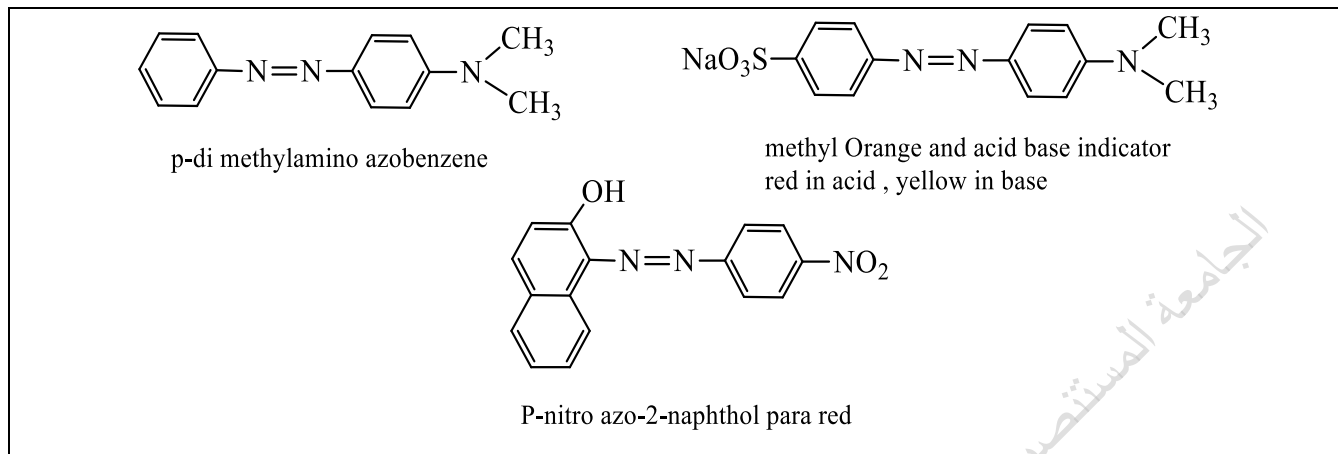
2- **Coupling reaction** : in which the nitrogen in diazonium salt is retained in the product .



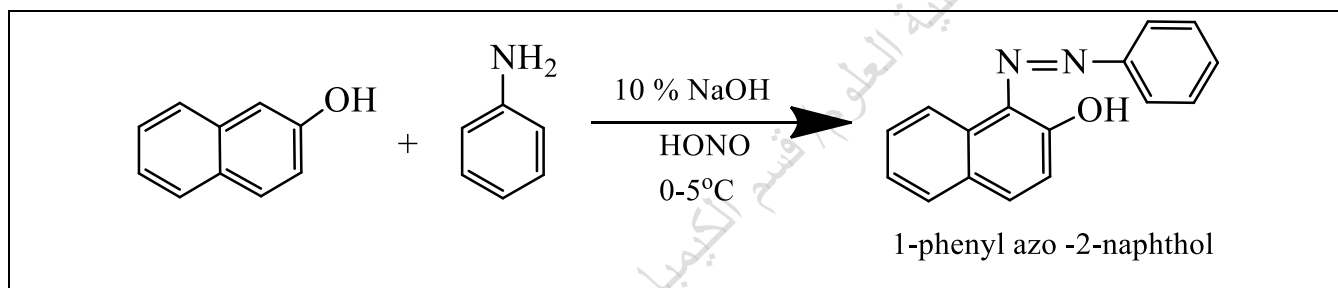
Example:



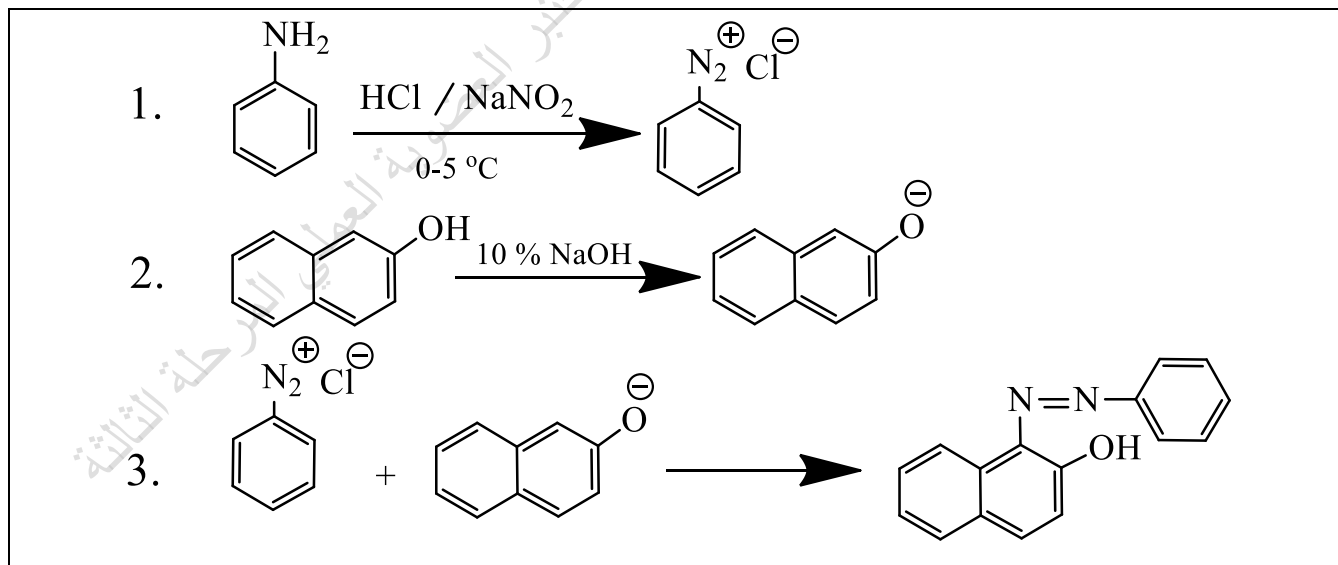
Examples for AZO dye :



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

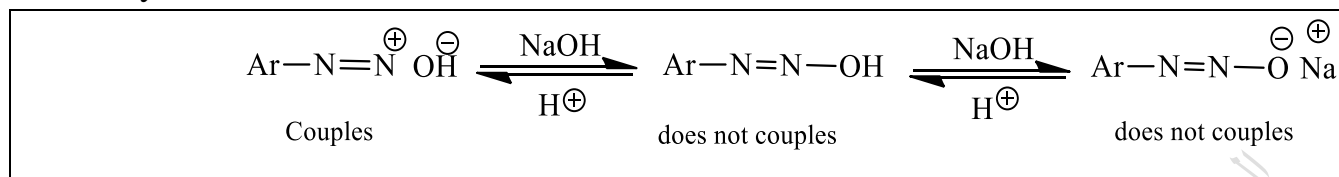


mechanism preparation of 1-phenylazo-2-naphthol:

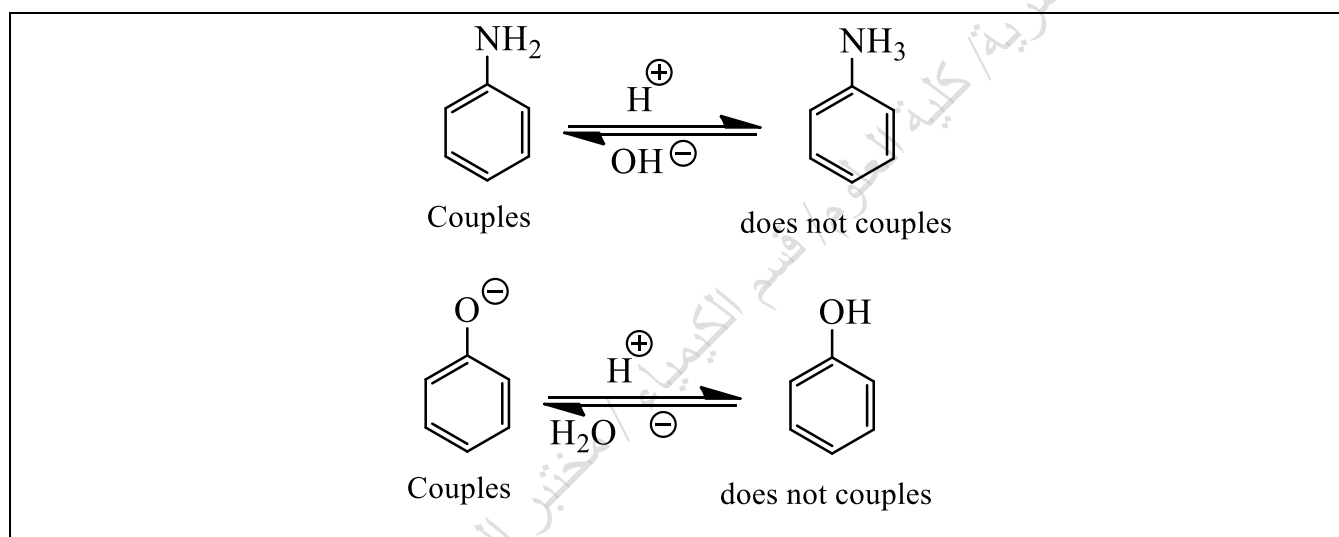


Conditions for preparation of AZO dye:

- 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, $\text{Ar}-\text{N}=\text{N}-\text{OH}$, and salts ($\text{Ar}-\text{N}=\text{N}-\text{O}^{\ominus}\text{Na}^{\oplus}$) derived from it :



- 2- The diazonium salt is reacted with aromatic amines in low temperature ($0-5^{\circ}\text{C}$), 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 $-\text{OH}$, $-\text{NR}_2$, $-\text{NHR}$, or $-\text{NH}_2$.

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 ($0-5^{\circ}\text{C}$).

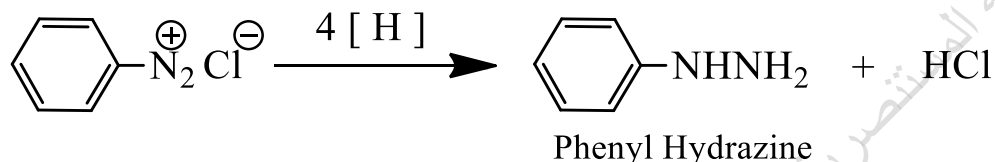
- 3- (1.6g) of 2-naphthol in (9ml) of (10%) percent sodium hydroxide (aq.), was kept in ice bath too.
- 4- The Coled mixture in step 2 was added slowly to Naphthol solution.
- 5- A red color. Develops and red crystals of 1-phenyl-azo-2-naphthol separated.
- 6- After the completion of addition the mixture 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.

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Experiment Eight

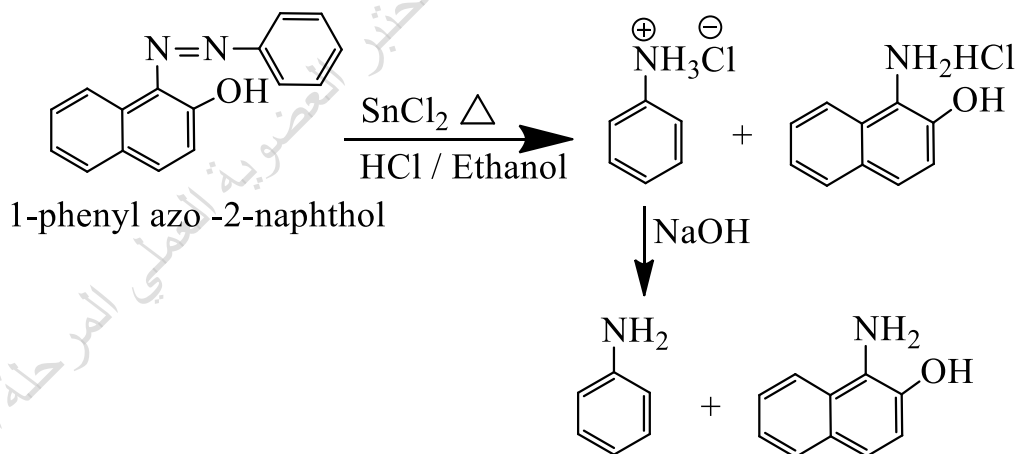
Reduction of Azo dye

The aryl diazonium ion group is reduced by SnCl_2/HCl or Na_2SO_3 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 ($\text{SnCl}_2 / \text{HCl}$) 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

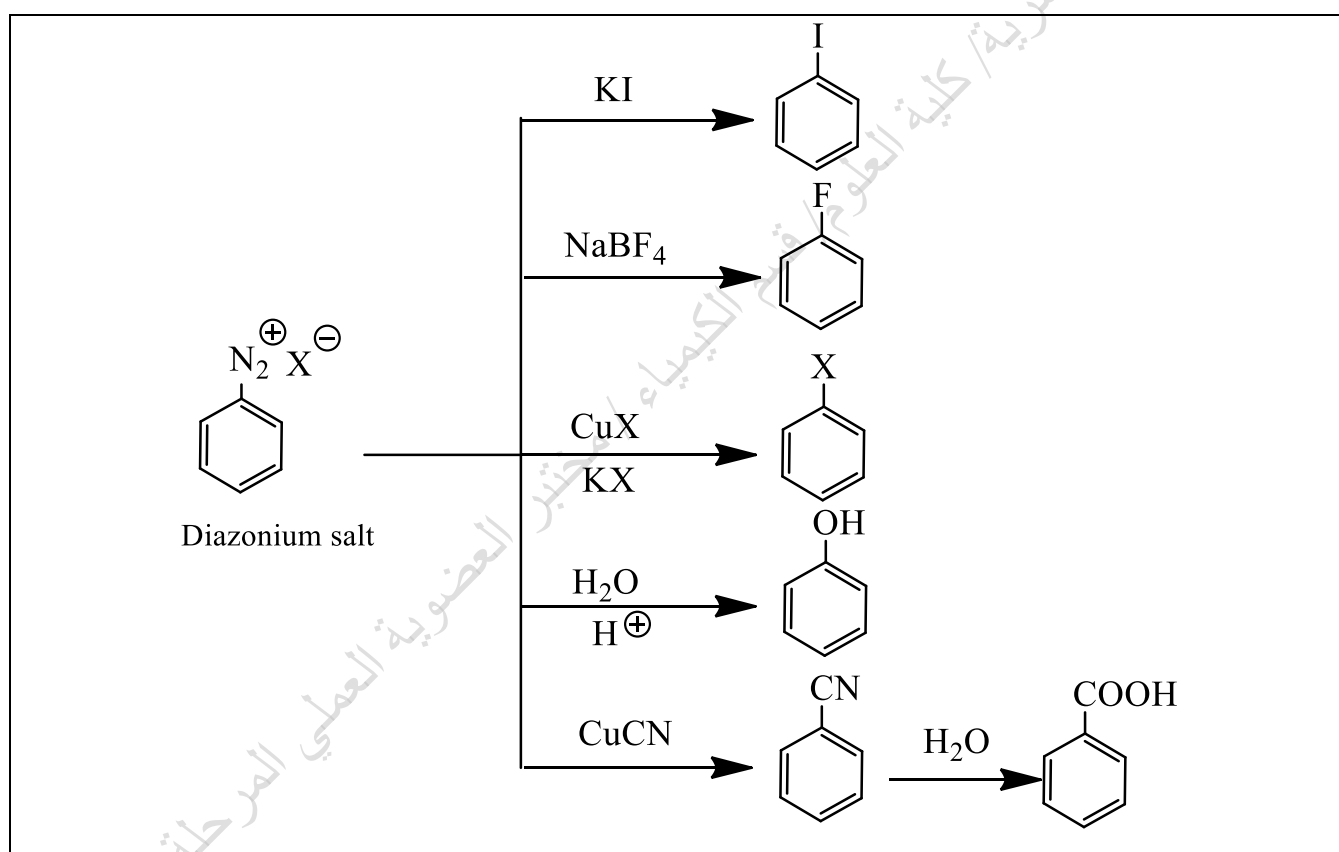
- 1- In a (100ml) round bottom flask (0.5g) of 1-phenylazo-2-naphthol is dissolved in (10ml) of ethanol absolute.
- 2- (1g) of SnCl_2 is dissolved in (3ml) of concentrated hydrochloric acid in a beaker and added to the content in the flask.
- 3- The mixture is refluxed gently for (30mins) with occasional 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 Nine

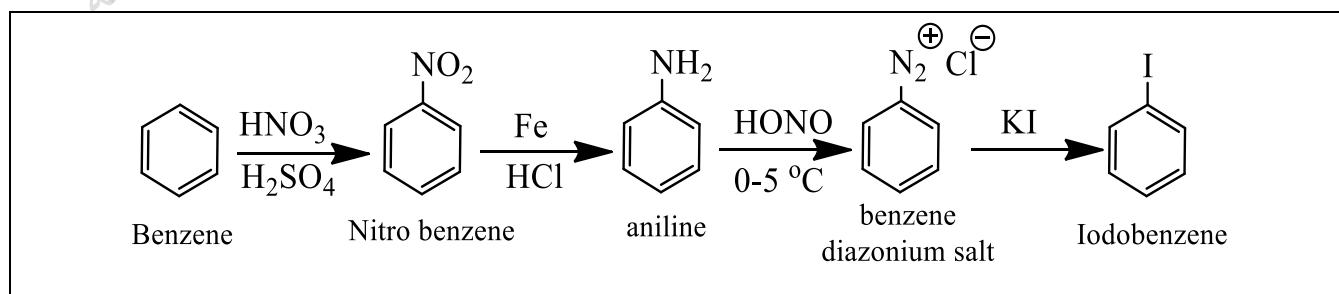
Preparation of Iodobenzene

Theoretical part:

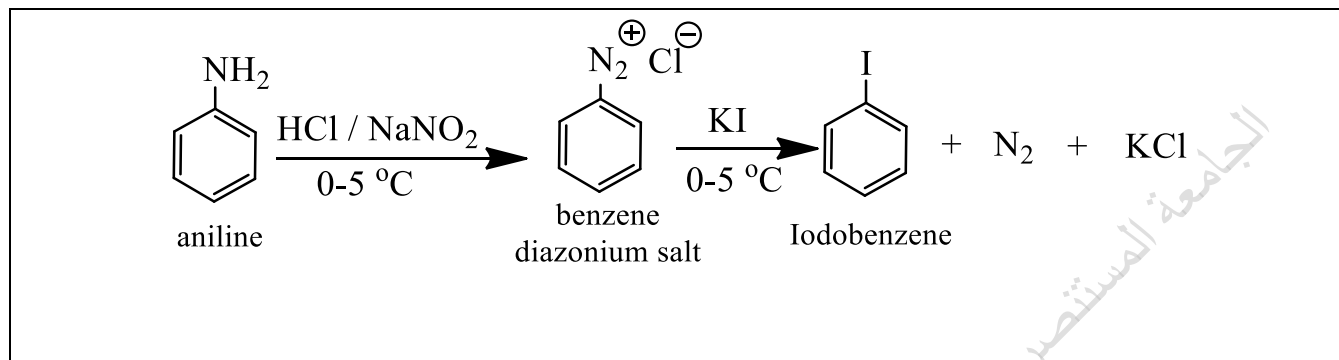
Aryl Iodides and fluorides cannot generally be prepared by direct halogenations. Replacement of diazonium group is the best general way of introducing (F,Cl,I,CN,OH, and H) into an aromatic ring. Diazonium salts are valuable in synthesis not only because they react to form so many classes of compounds,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

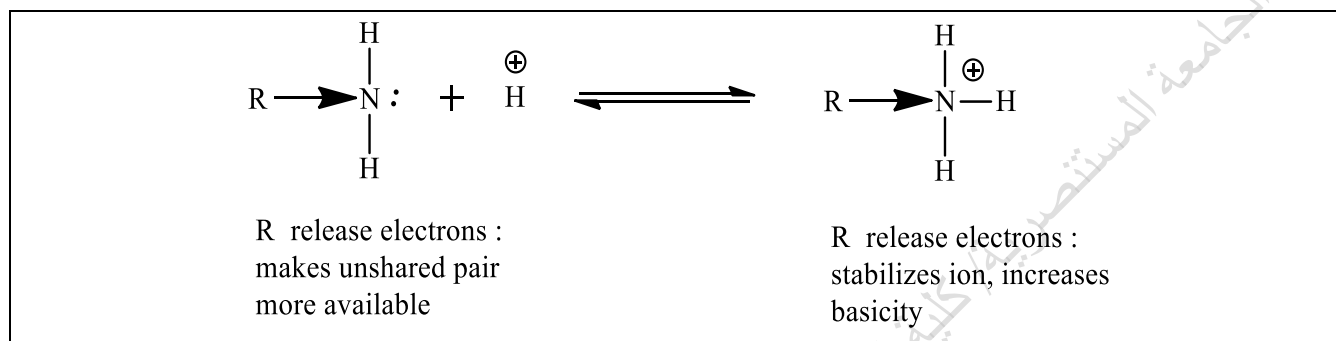
Experiment:

- 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 ice-bath.
- 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

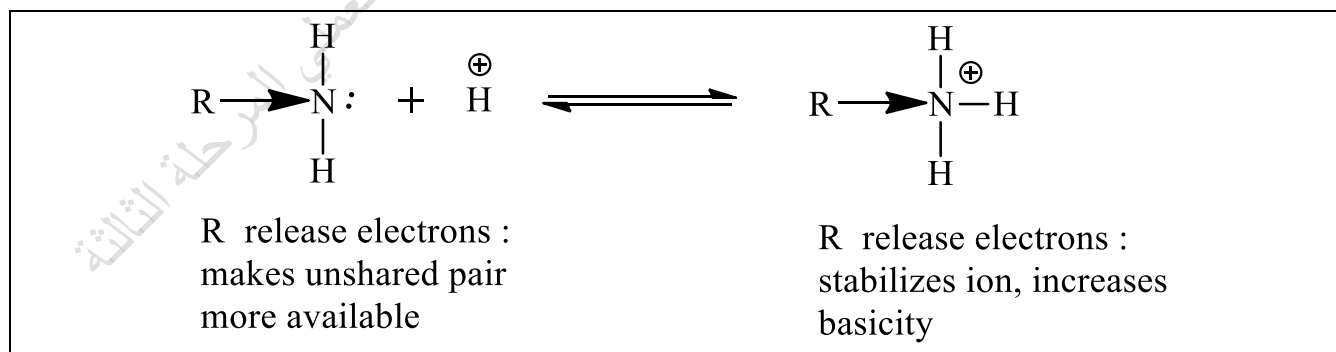
Amines are convenient to compare basicity's by measuring the extent to which they accept hydrogen ion from water; the equilibrium constant for this reaction we combine with $[H_2O]$ to obtain the basicity's constant, K_b .



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

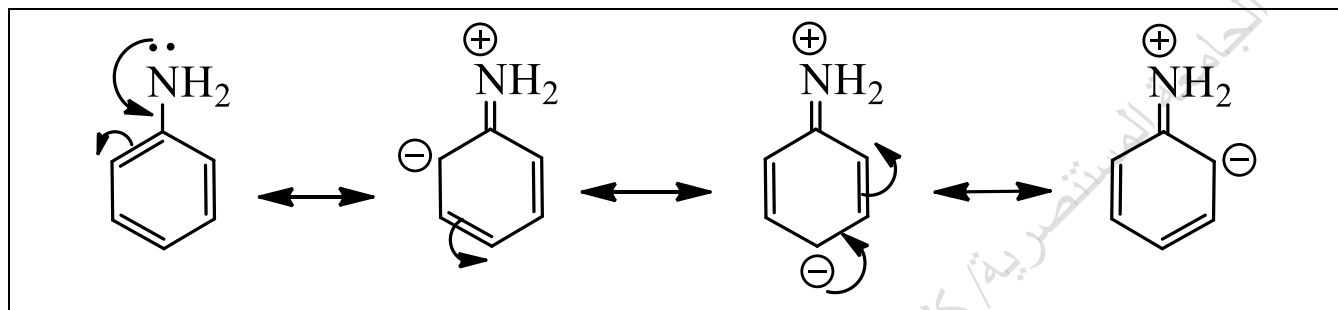
An aliphatic amine is more basic than ammonia ?

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.



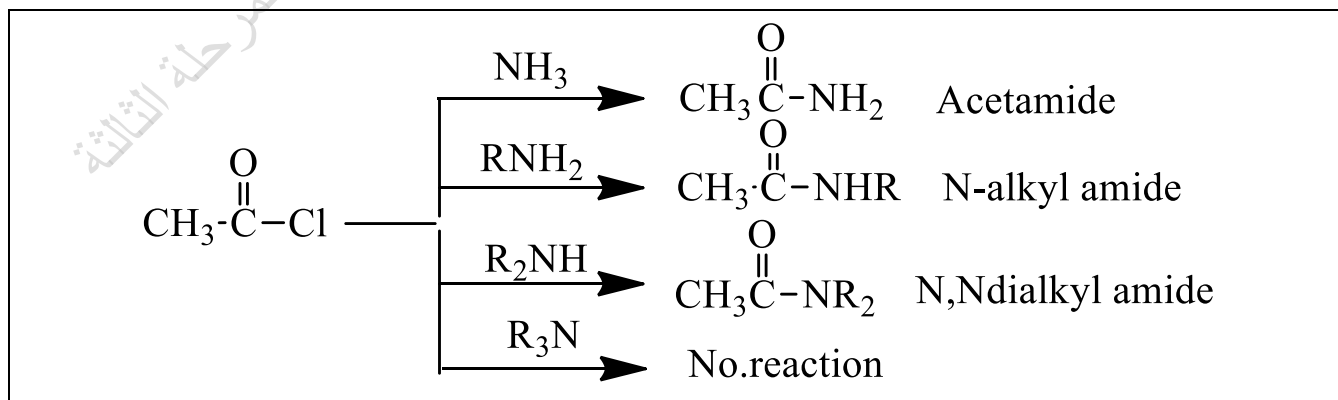
An aromatic amines are weaker bases than ammonia ?

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).

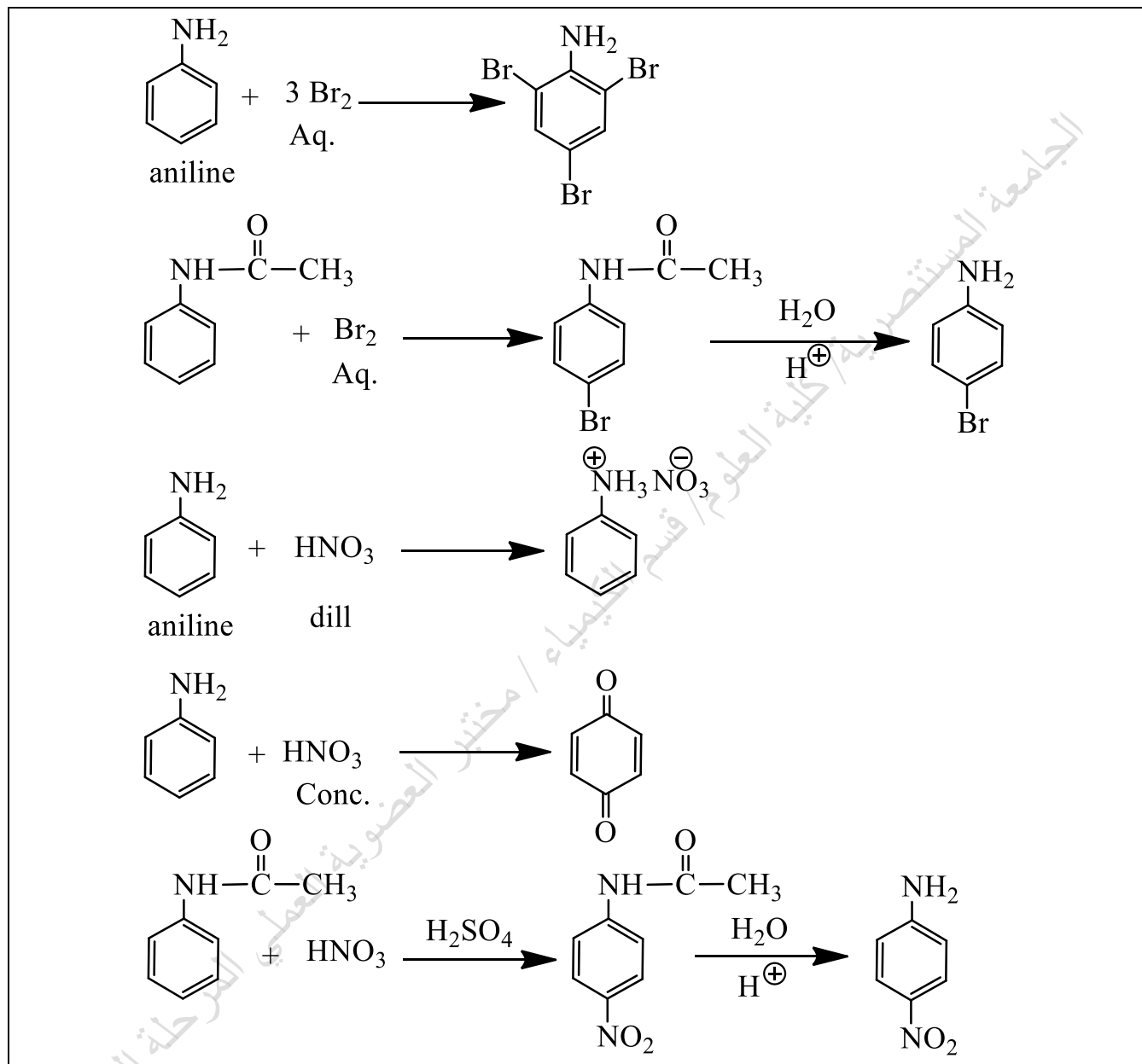


The low basicity of aromatic amines is thus due to the fact that the amine is stabilized by resonance to a greater extent than is the ion and the fourth pair if electrons is partly shared with the ring and is thus less available for sharing with hydrogen ion . The tendency (through resonance) for the –NH₂ group to release electrons to the aromatic ring more reaction toward necessarily makes the amine less basic. similar consideration apply to other aromatic amines .

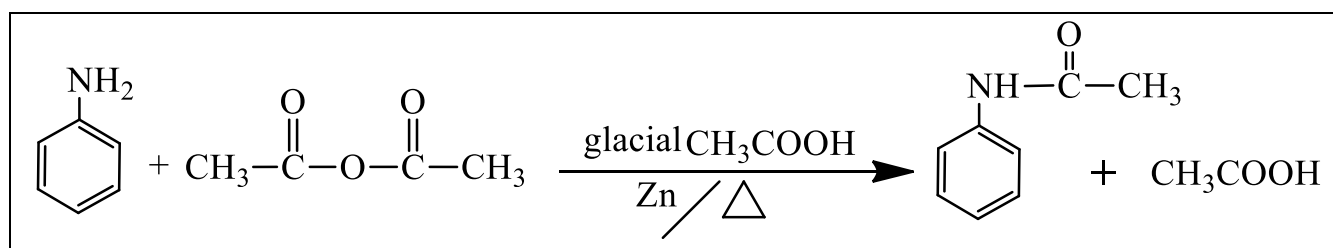
A similar way primary and secondary amines can react with derivatives of carboxylic acid to form substituted amides, compounds in which –Cl has been replaced by the -NHR or NR₂ group. Tertiary amines , although basic and hence nucleophilic, fail to yield amides.



Ring substitution aromatic ring :



The general question:



Experimental part:

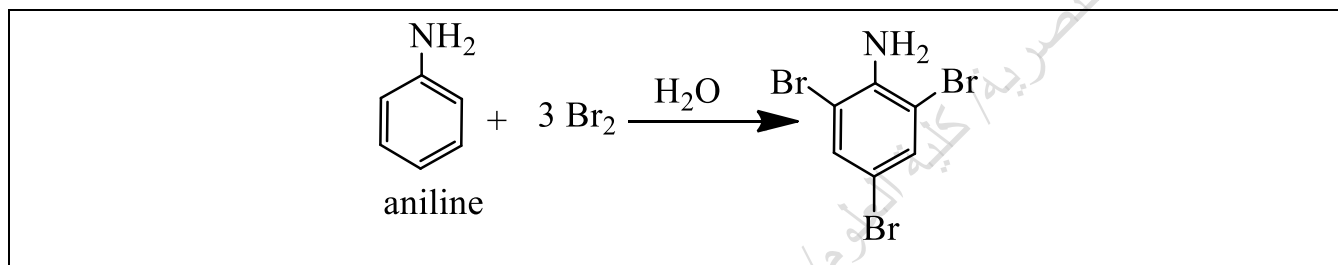
1. In (100ml) round bottom flask, a mixture of (4ml) of Aniline , (4ml) of Acetic Anhydride, (0.5g) of zinc and (4ml) of glacial acetic acid are added and stirred
2. The mixture is reflux gently for (30mins) with occasional shaking until a clear solution is formed.
3. The mixture is cooled after reflux and poured into (50ml) of ice-cold water and with shaking for (5mins) until a white 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 .

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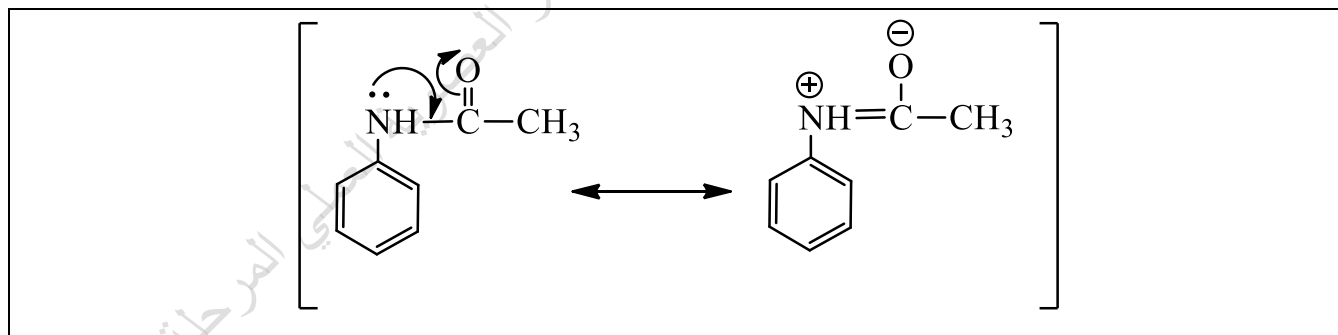
Expierment Eleven

Preparation of p-nitro acetanilide

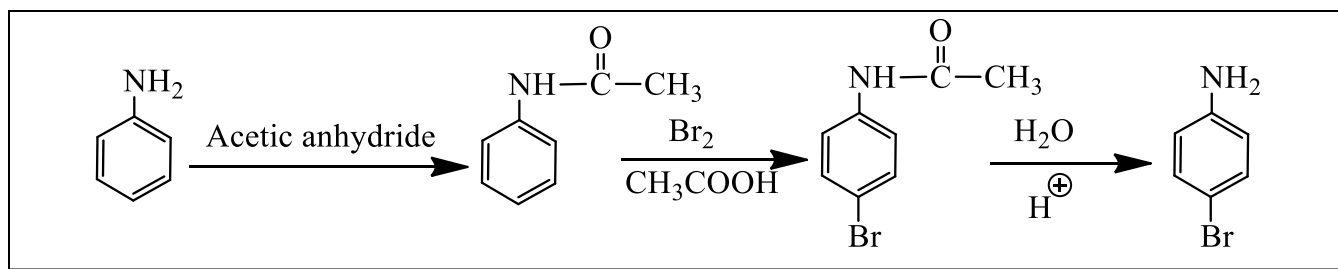
In electrophilic substitution the chief problem encountered with aromatic amines is that they are too reactive . In halogenation , substitution tends to occur at every available ortho or para position , for example the result of mixing the aniline with bromine water is (2,4,6-tribromoaniline).



The acetamide group , (-NHCOCH₃) , 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

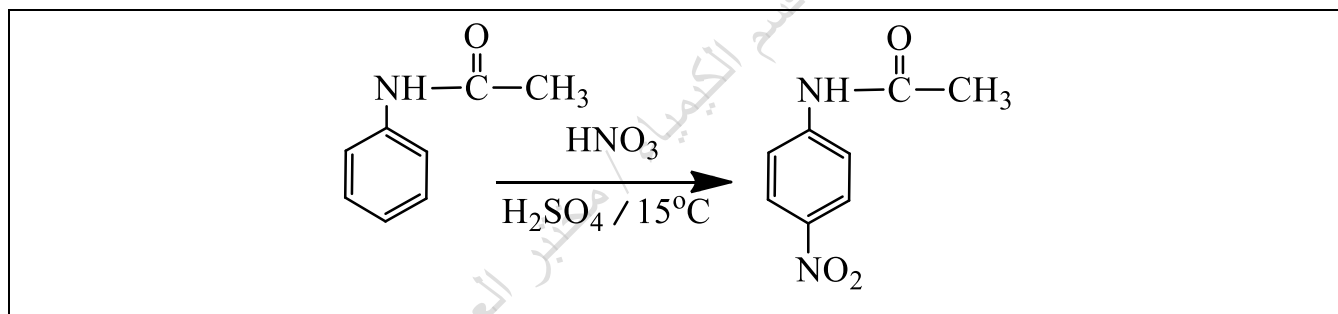


As example we can prepare P-Bromoaniline as shown below:



In nitration of amines , nitric acid not only nitrates , but oxidizes the highly reactive as well , with loss of much material as tar. Further more , 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 :



Expermental 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 $(0-5)^\circ\text{C}$.
4. The mixture is left at room temperature for 15 min.

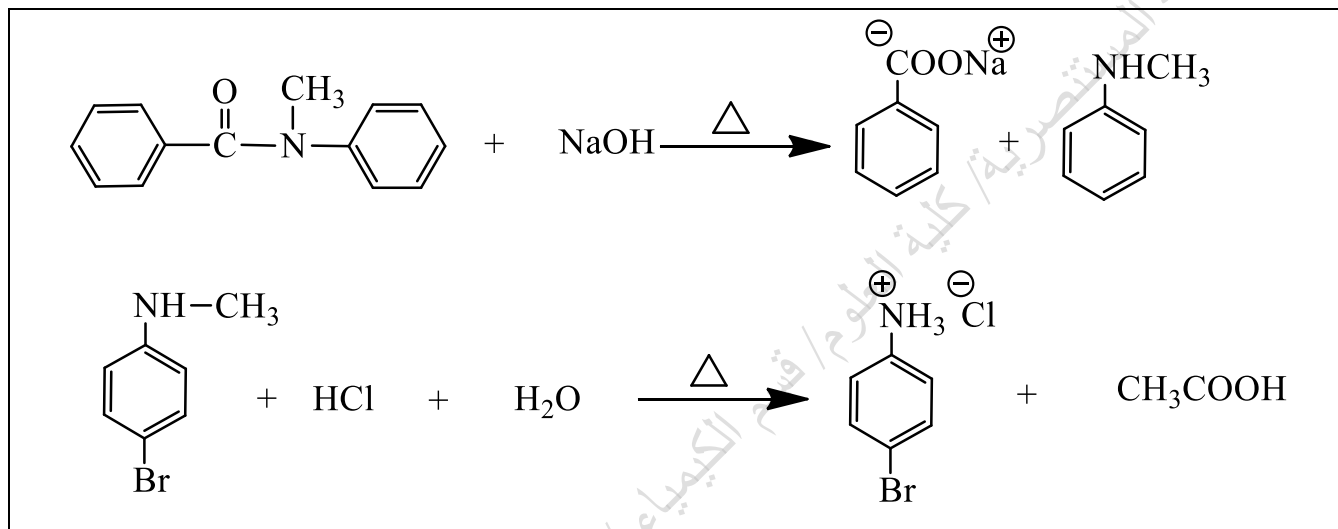
5. The mixture is poured onto 100 ml of ice cooled water ,the precipitate is fomed.
6. The precipitate is filtered and dried.
7. The product is weighed and the percentage of yield is calculated

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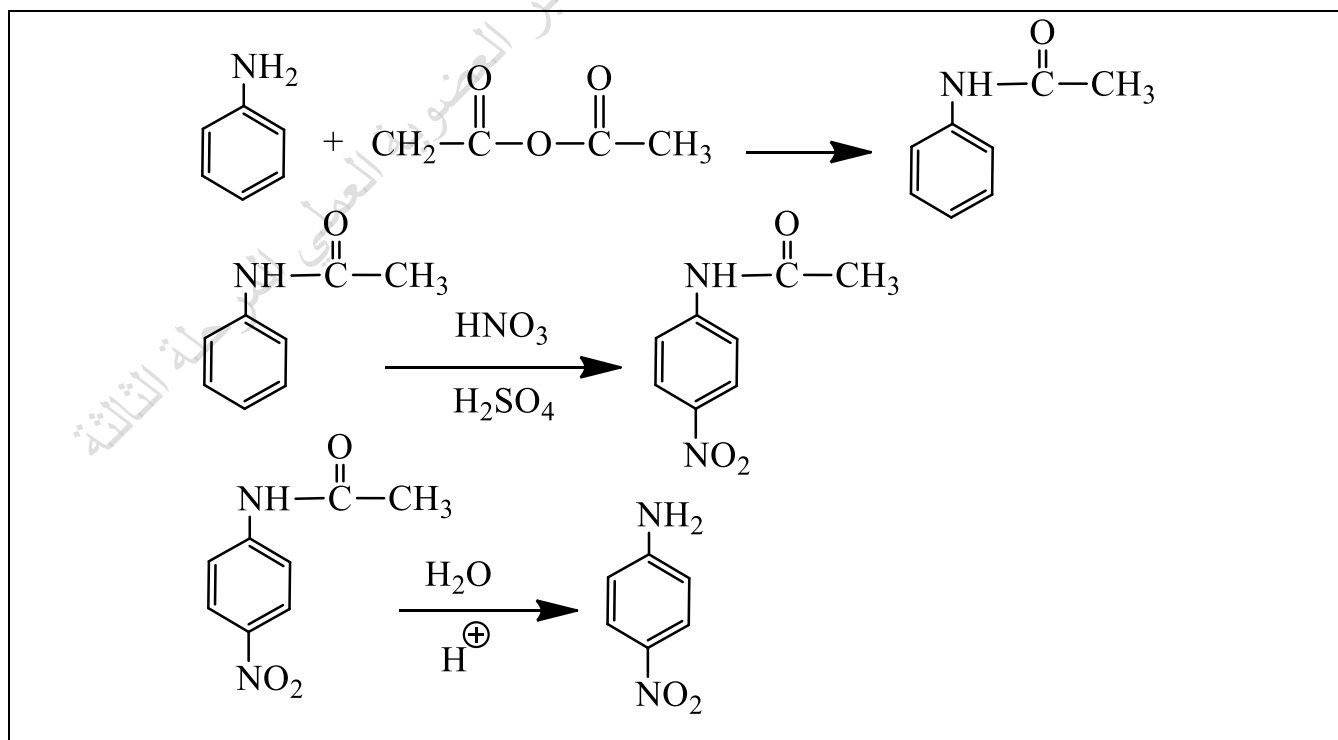
Experiment Twelve

Hydrolysis of *P*-nitroacetanilide

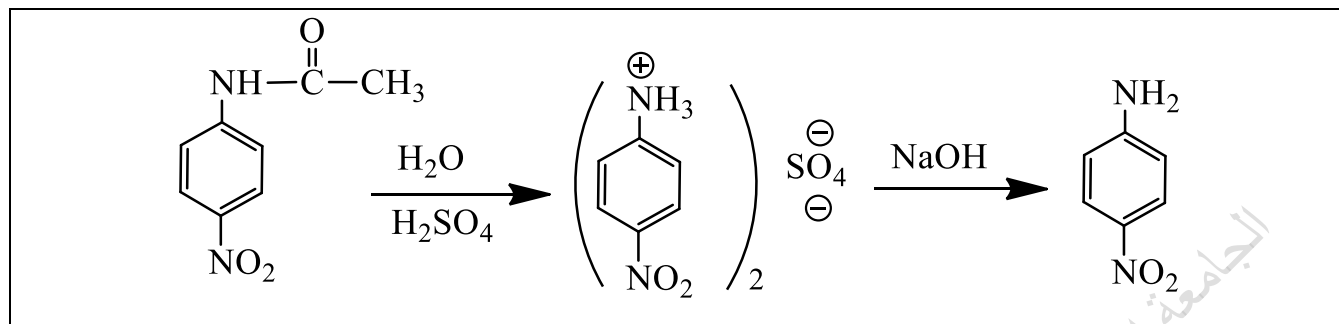
Like simple amides, substituted amides undergo hydrolysis, the products are the acid and the amine although one or the other is obtained as its salt, depending upon the acidity or alkalinity of the medium:



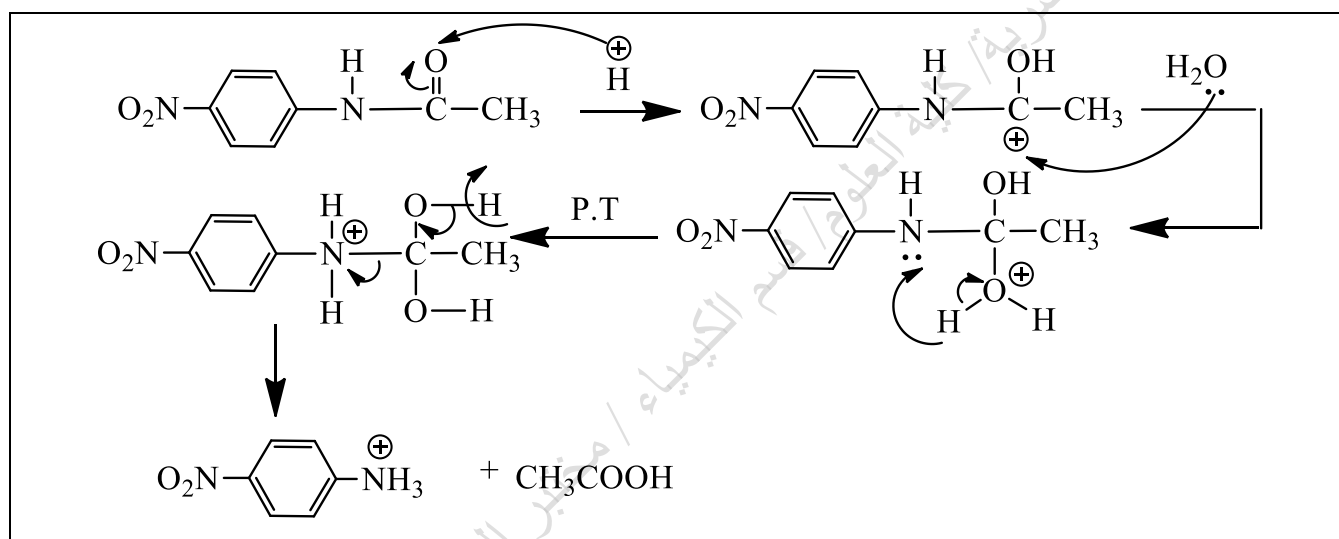
To prepare *P*-nitroaniline we should follow the steps as shown below:



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