Second Semester

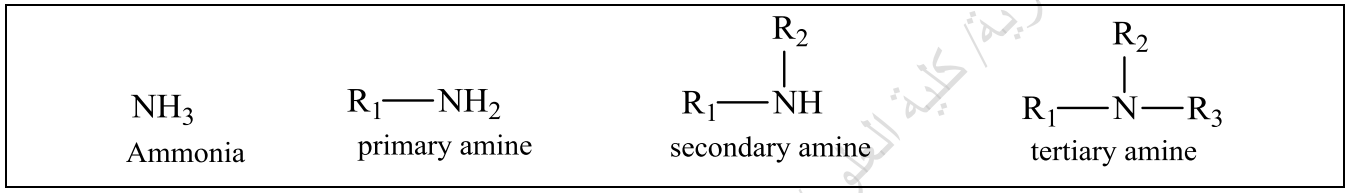
Experiment 1

Preparation of Azo dye from diazonium salt

Theoretical part:

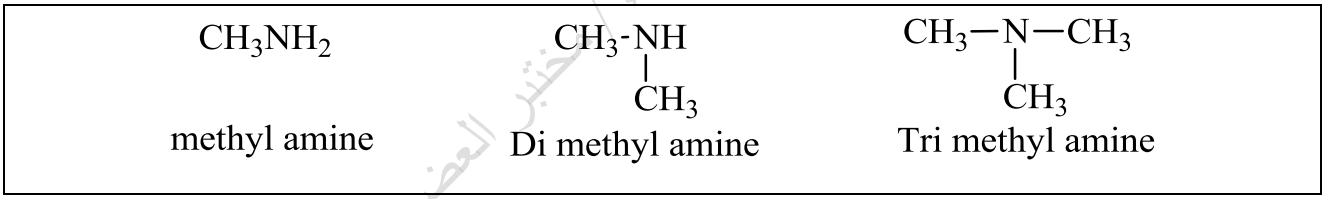
Amines : Are organic compounds that show appreciable basicity ,the general formula RNH_2 , R_2NH , or R_3N , where R is any alkyl or aryl group.

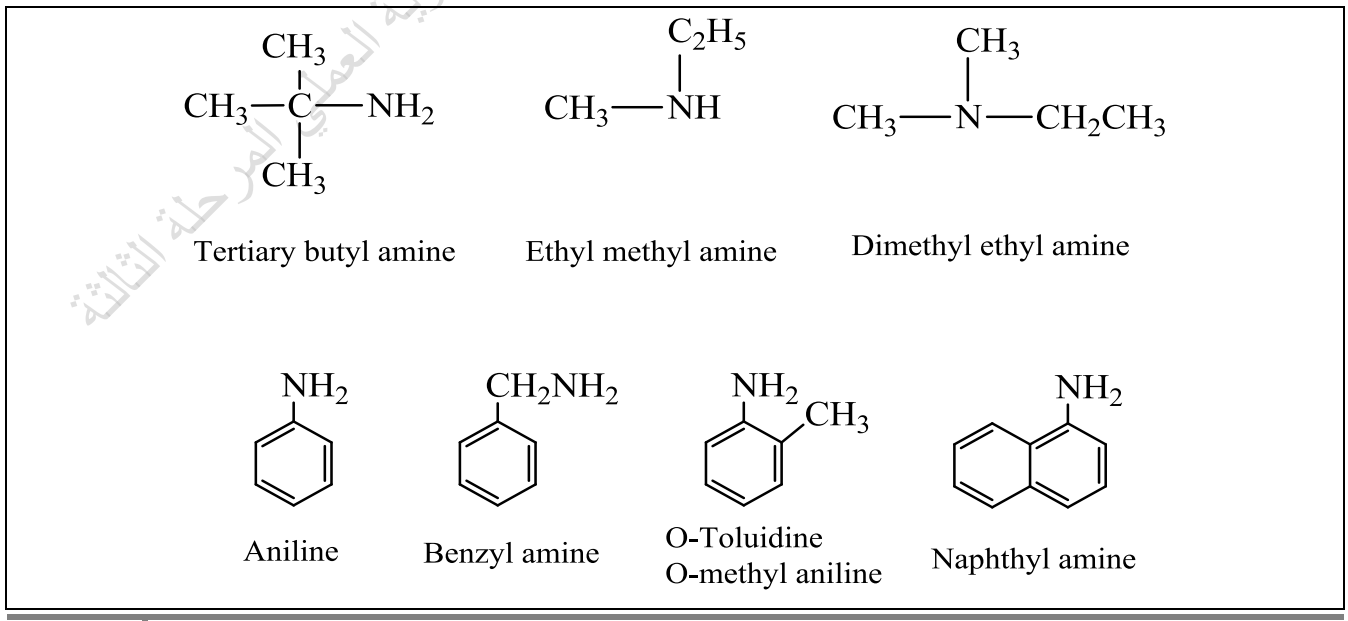
Amines are classified as primary, secondary, or tertiary according to the number of groups are attached to the nitrogen atom.



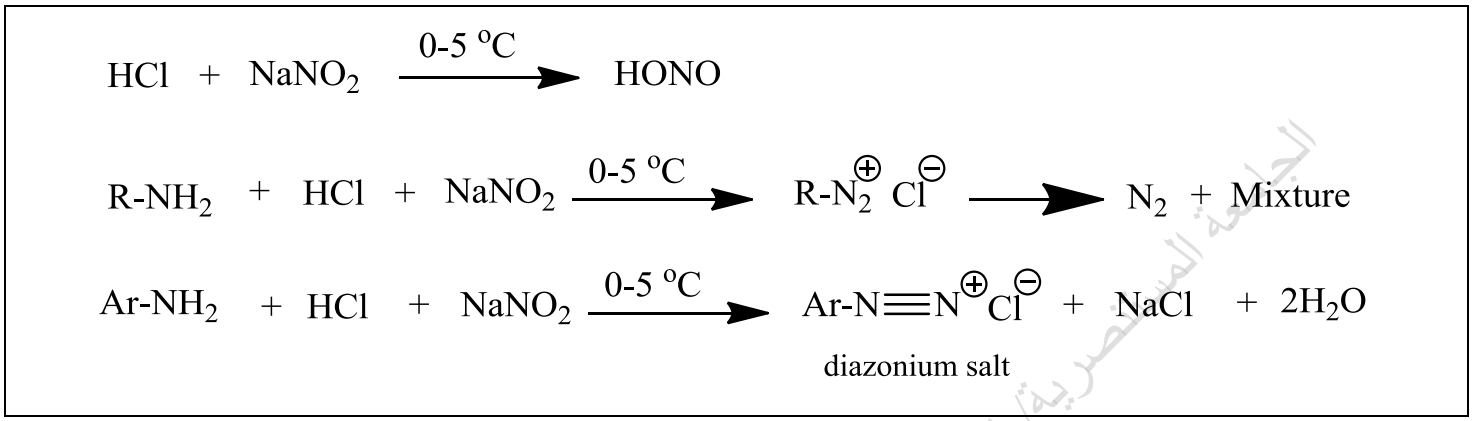
Nomenclature:

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

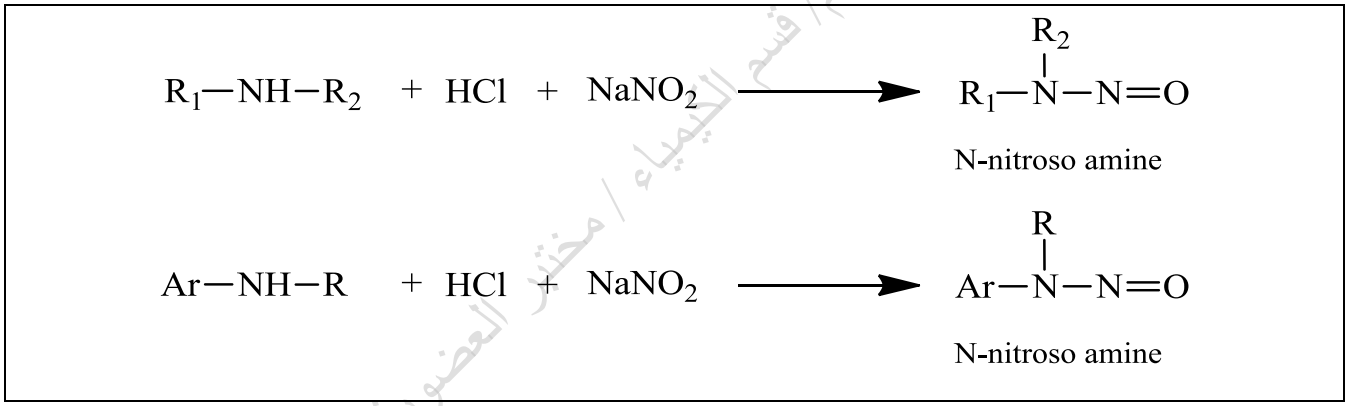




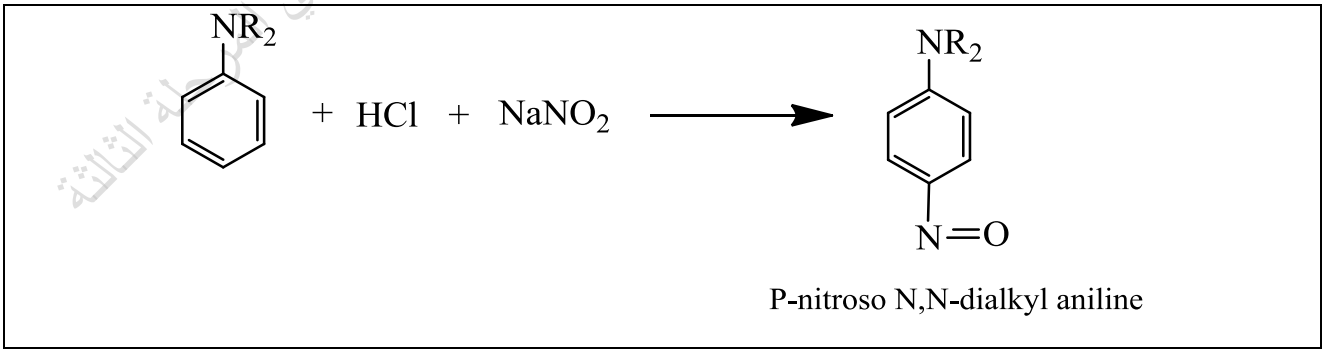
Amines are react with nitrous acid (HONO)to yields a different kind of product, HONO prepare by the action of mineral acid on sodium nitrite .Primary amines react with nitrous acid to yield diazonium salt .



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

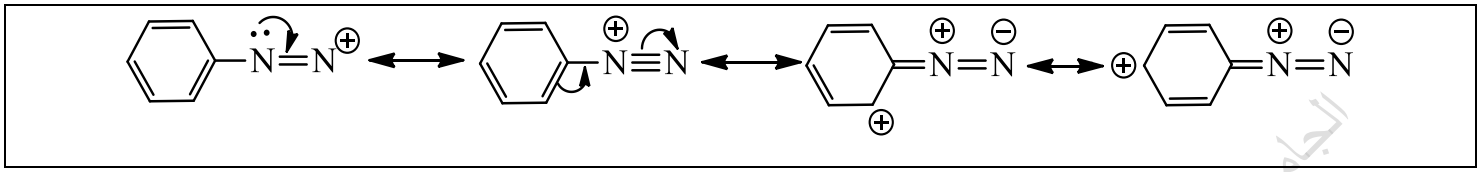


Tertiary aromatic amines undergo ring substitution, to yield compounds in which a nitroso group , -N=O is joined to carbon in *p*- position .



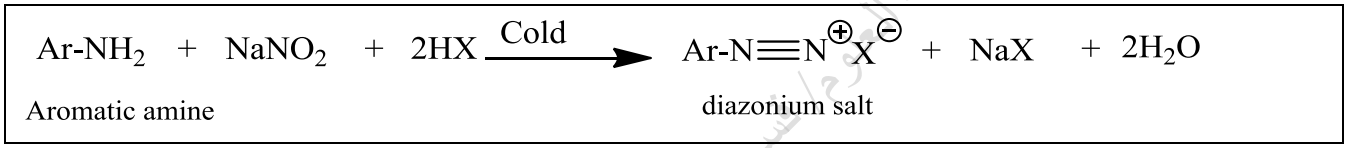
Primary aromatic amines react with nitrous acid to yield diazonium salt , this is one of the most important reactions in organic chemistry .

aromatic diazonium salt is more stable than aliphatic diazonium salt .



diazonium salt reaction :

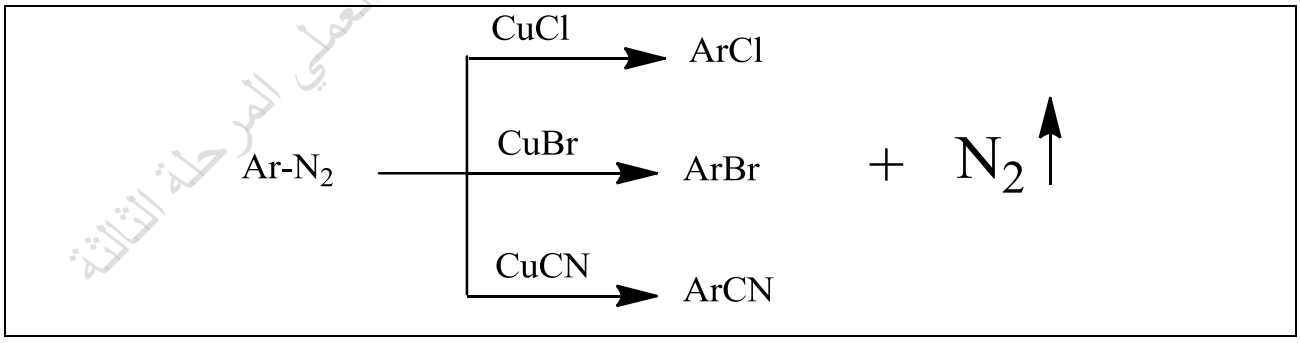
when primary aromatic amine is dissolved or suspend in cold aqueous mineral acid & treated with sodium nitrite , there is formed a diazonium salt



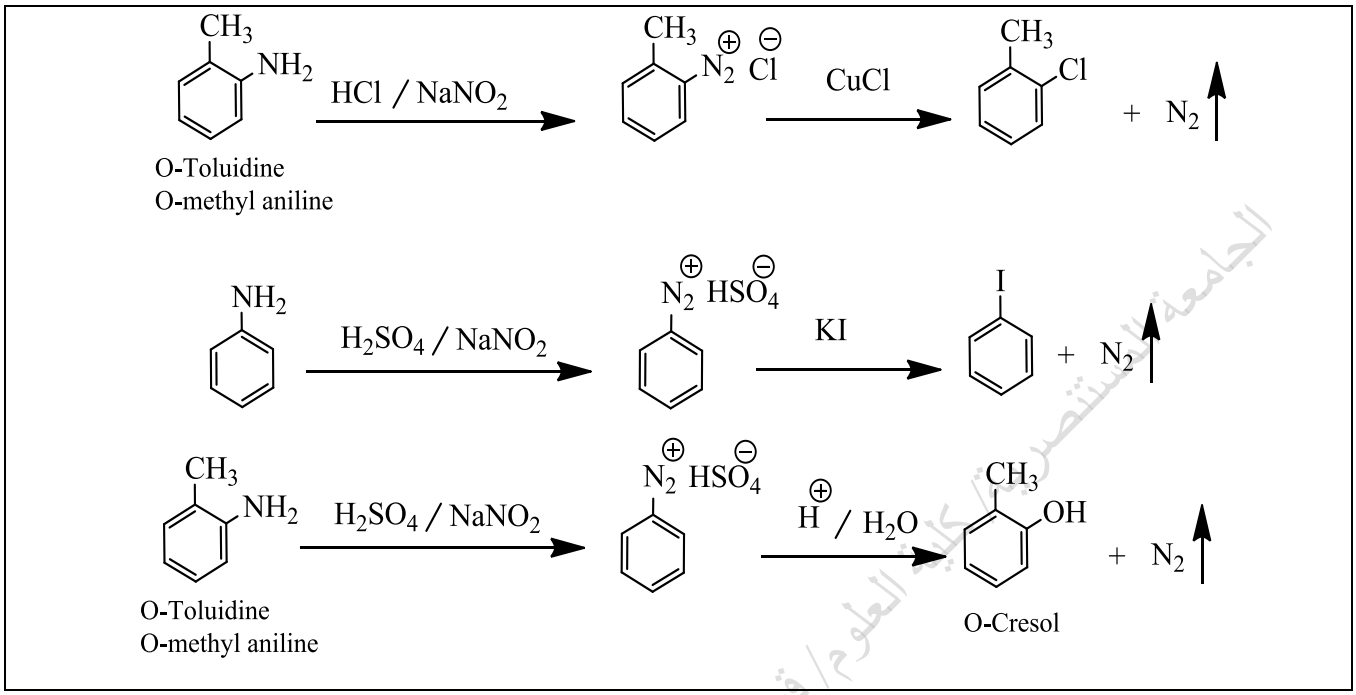
diazonium salt slowly decomposes even at ice-bath temperatures , the solution is used immediately after preparation .

There are large numbers of reaction undergo by diazonium salts may be divided in two types:

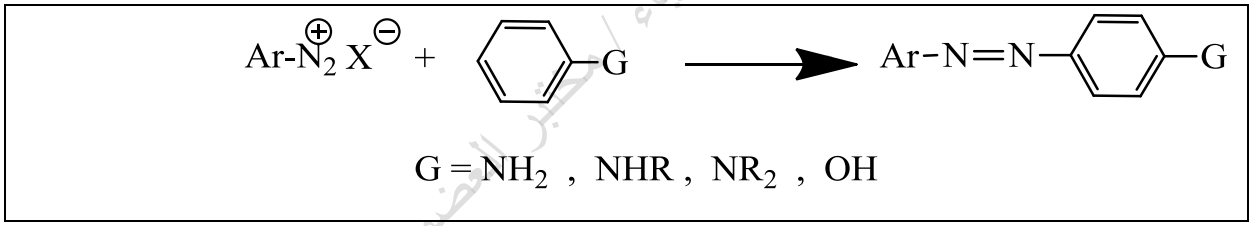
1- **Replacement reaction:** in which nitrogen is lost as N_2 , and some other atom or group becomes attached to the ring in its place .



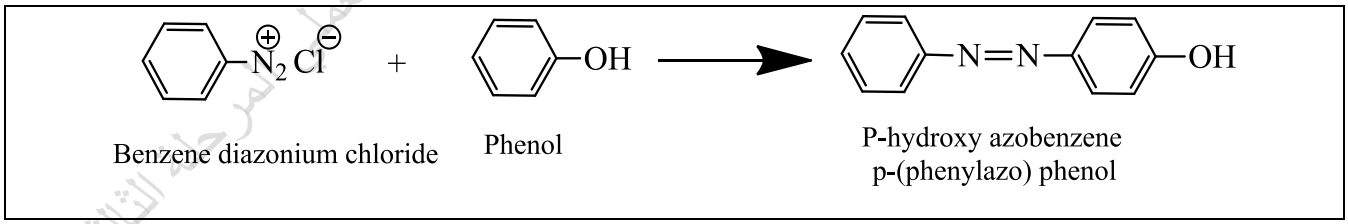
Examples:



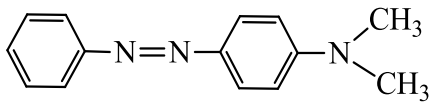
2- **Coupling reaction :** in which the nitrogen in diazonium salt is retained in the product .



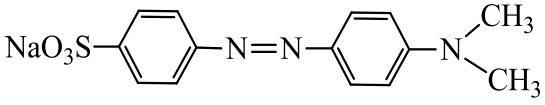
Example:



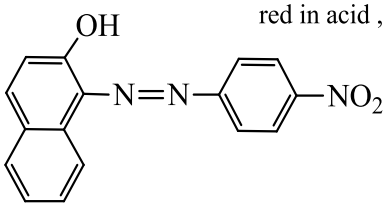
Examples for AZO dye :



p-di methylamino azobenzene

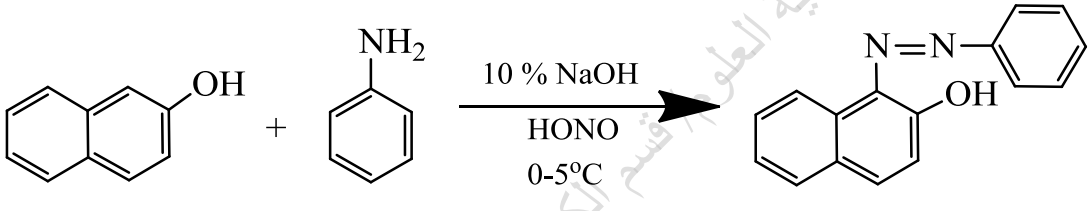


methyl Orange and acid base indicator
red in acid , yellow in base



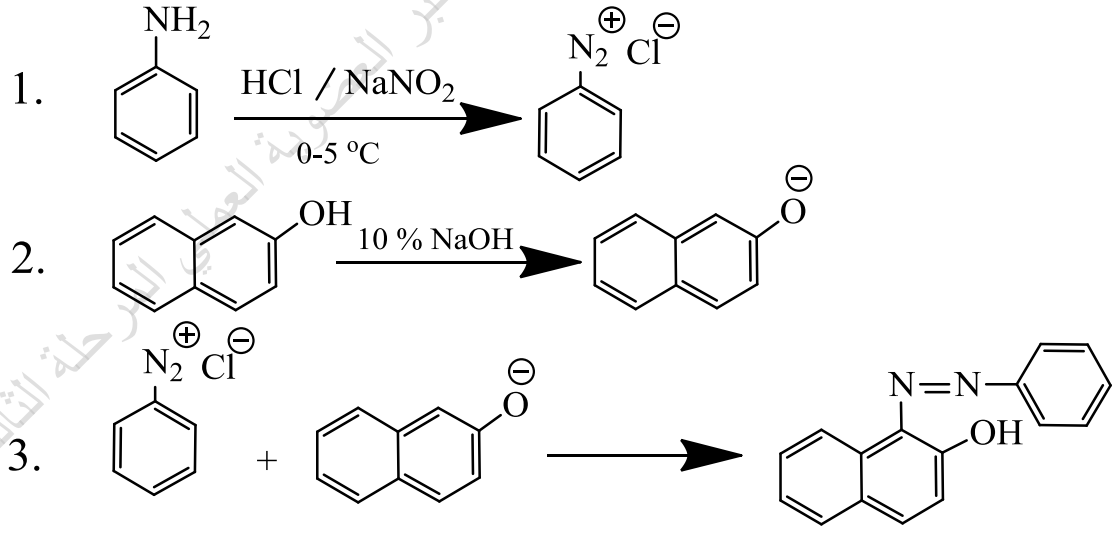
P-nitro azo-2-naphthol para red

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



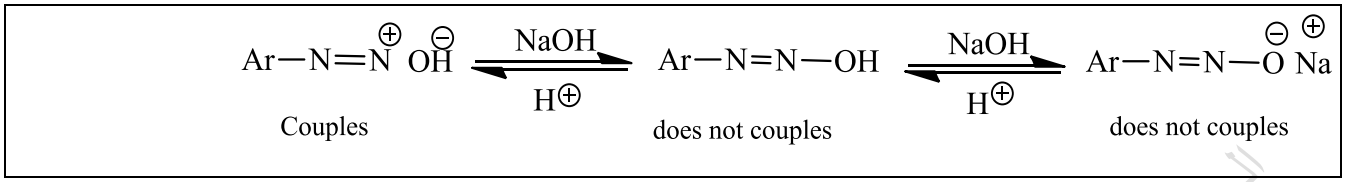
1-phenyl azo -2-naphthol

mechanism preparation of 1-phenylazo-2-naphthol:

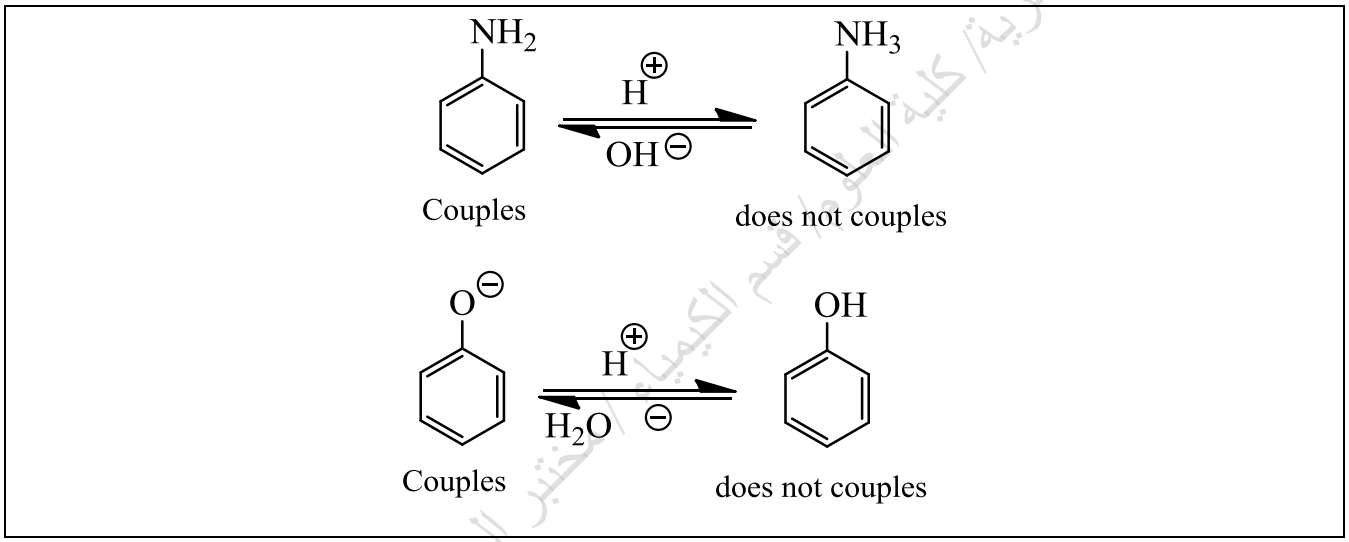


Conditions for preparation of AZO dye:

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 (0-5°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 –OH,-NR_2, -NHR, or -NH_2.

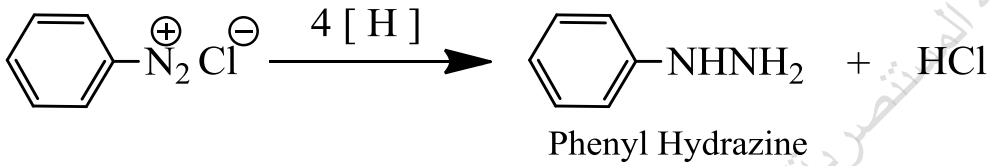
Experimental part:

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 mixturein step 1 .The mixture was kept in ice bath (0-5°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.

Experiment Eight
Reduction of Azo dye

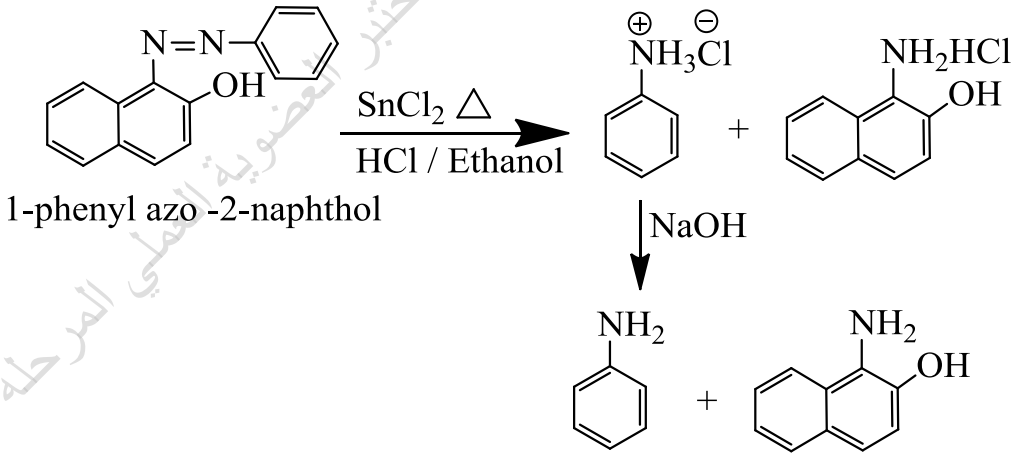
The aryl diazonium ion group is reduced by SnCl2/ Hcl or Na2SO3 to produce the phenyl hydrazine compound. Which is considered as important detector in the carbonyl chemistry and sugars. An azo compound is cleaved at the azo linkage by stannous chloride (SnCl2 / Hcl) to form two amines .



Phenyl Hydrazine

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 :



1-phenyl azo -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

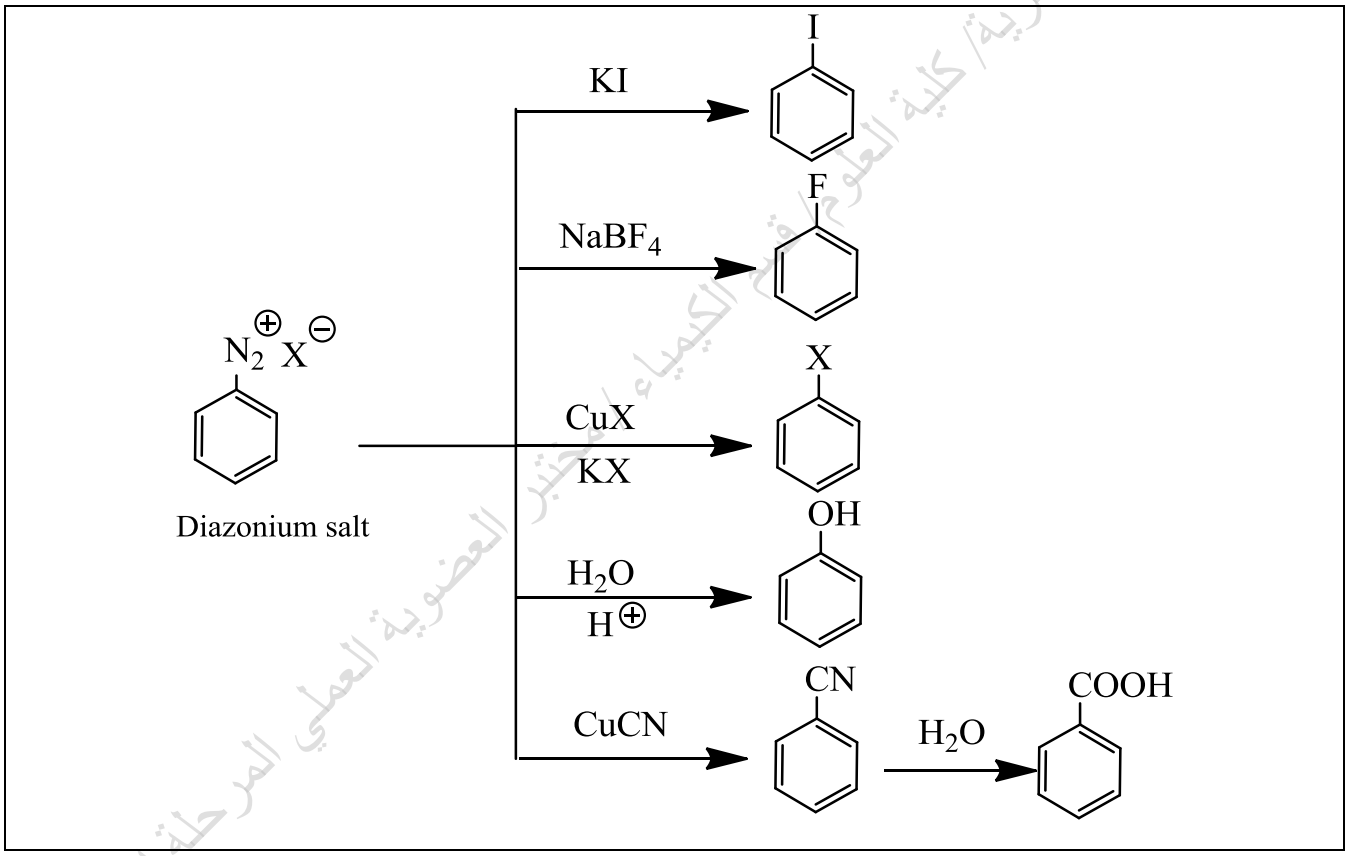
calculated.

Experiment Nine

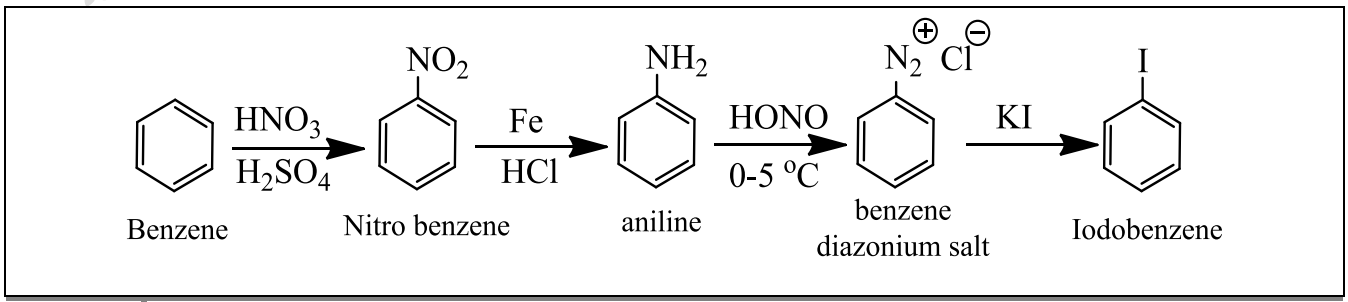
Preparation of Iodobenzene

Theoretical part:

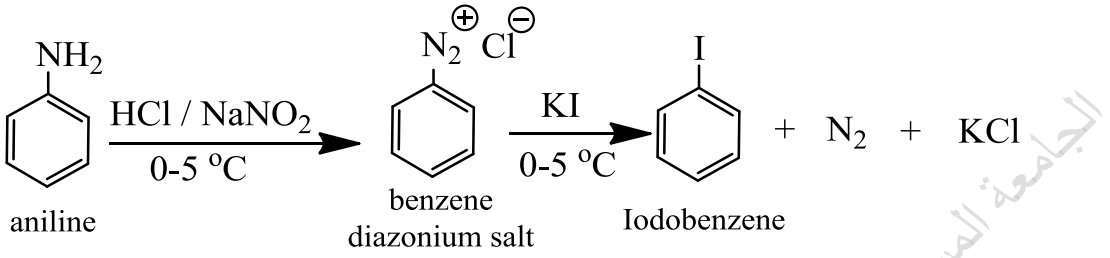
Aryl Iodides and fluorides cannot generally be prepared by direct halogenations. Replacement of diazonium group is the best general way of introducing (F,Cl,I,CN,OH, and H) into an aromatic ring . Diazonium salts are valuable in synthesis not only because they react to form so many classes of compounds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