Second Semester

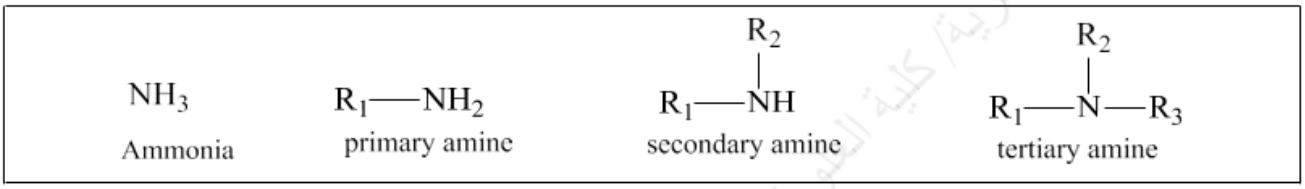
Experiment 1

Preparation of Azo dye from diazonium salt

Theoretical part:

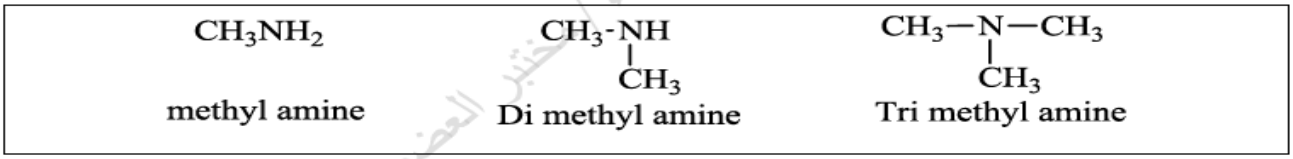
Amines: Are organic compounds that show appreciable basicity, the general formula RNH_2, R_2NH, or R_3N, where R is any alkyl or aryl group.

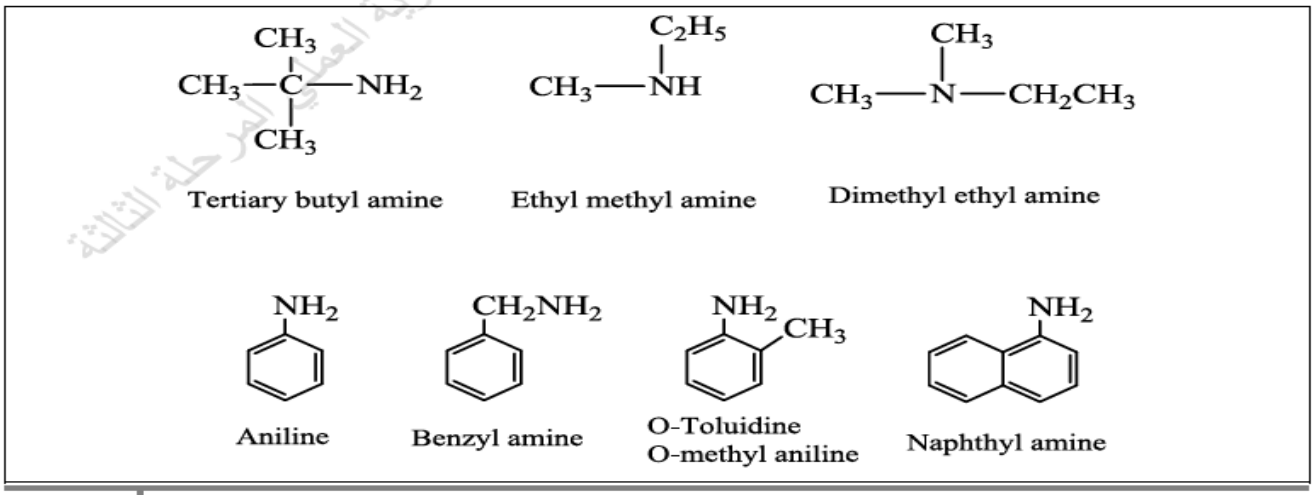
Amines are classified as primary, secondary, or tertiary according to the number of groups are attached to the nitrogen atom.



Nomenclature:

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





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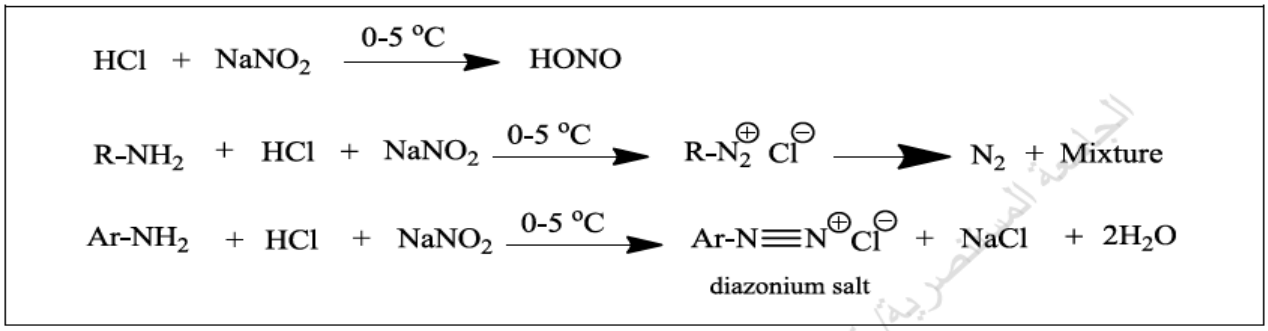
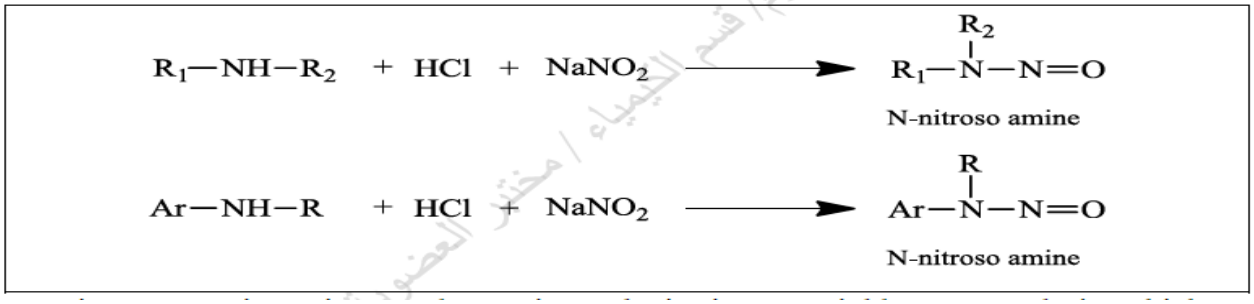
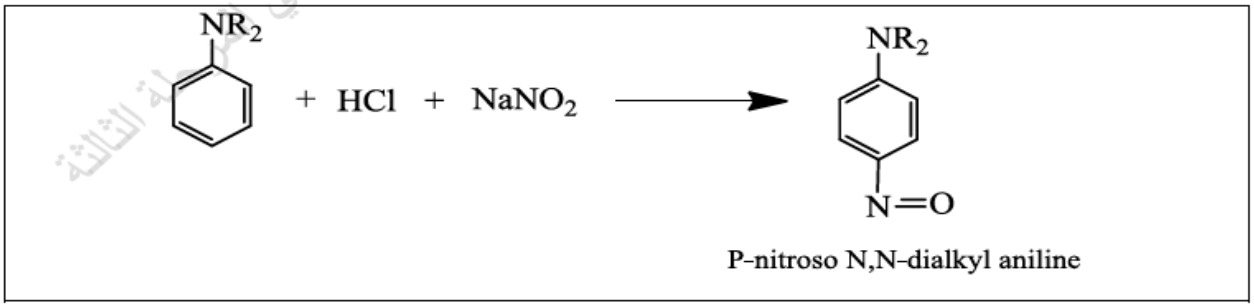
Amines react with nitrous acid (HONO) to yield a different kind of product, HONO prepare by the action of mineral acid on sodium nitrite. Primary amines react with nitrous acid to yield diazonium salt.



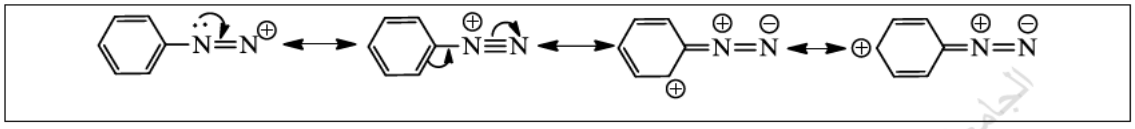
Secondary amines, both aliphatic and aromatic reacted with nitrous acid to yield *N*-nitrosamines.



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

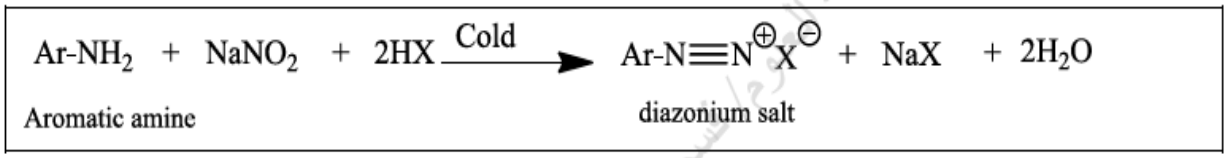


Primary aromatic amines react with nitrous acid to yield diazonium salt, this is one of the most important reactions in organic chemistry. Aromatic diazonium salt is more stable than aliphatic diazonium salt.



diazonium salt reaction:

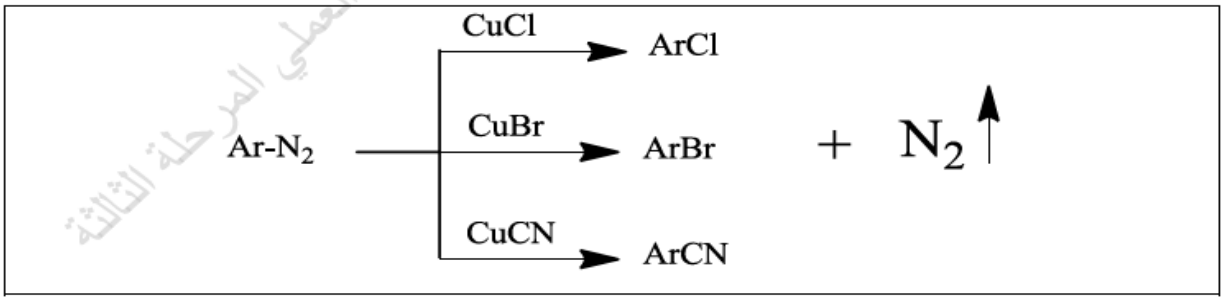
When primary aromatic amine is dissolved or suspend in cold aqueous mineral acid & treated with sodium nitrite , there is formed a diazonium salt



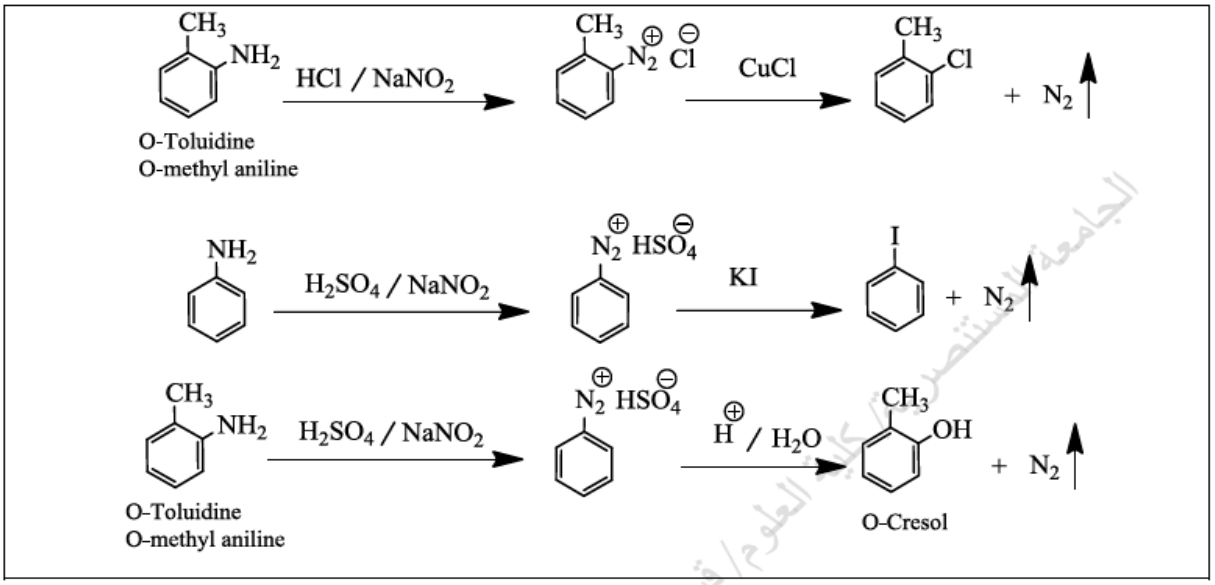
diazonium salt slowly decomposes even at an ice-bath temperatures, the solution are used immediately after preparation.

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

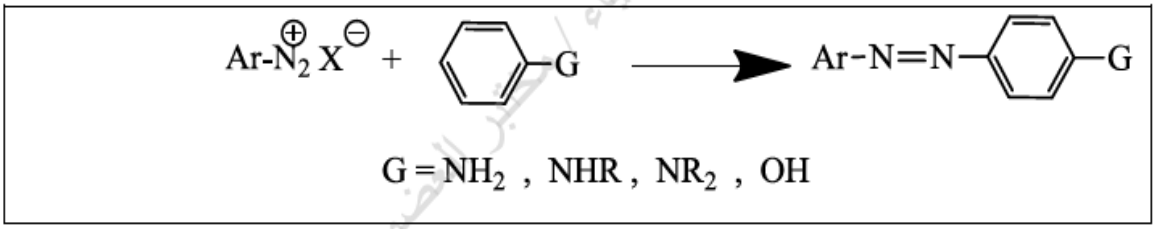
1- **Replacement reaction:** in which nitrogen is lost as N_2, and some other atom or group becomes attached to the ring in its place.



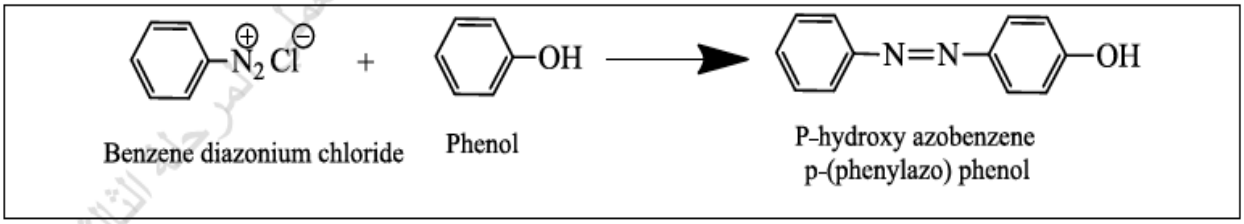
Examples:



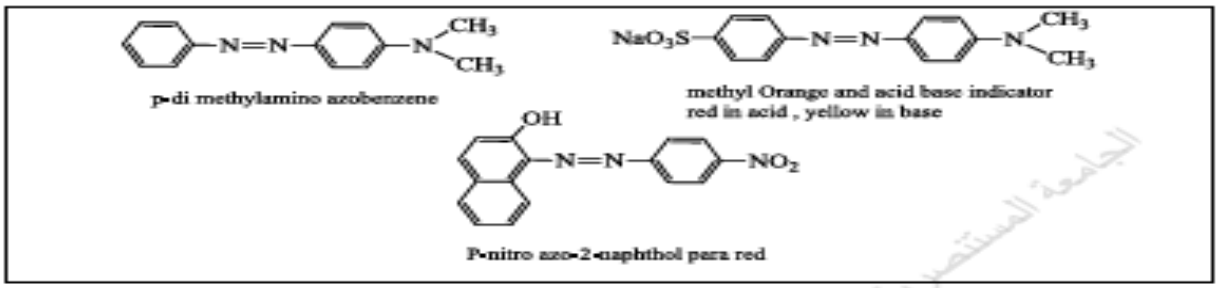
2- **Coupling reaction:** in which the nitrogen in diazonium salt is retained in the product.



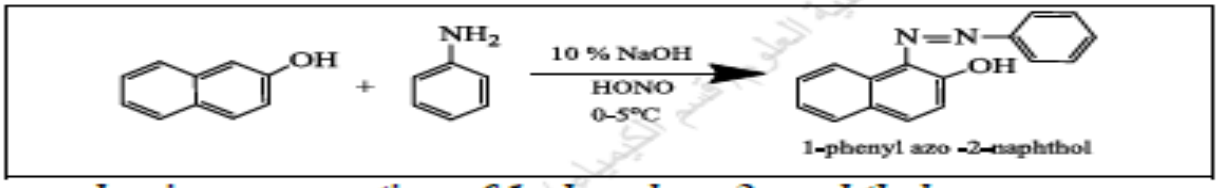
Example:



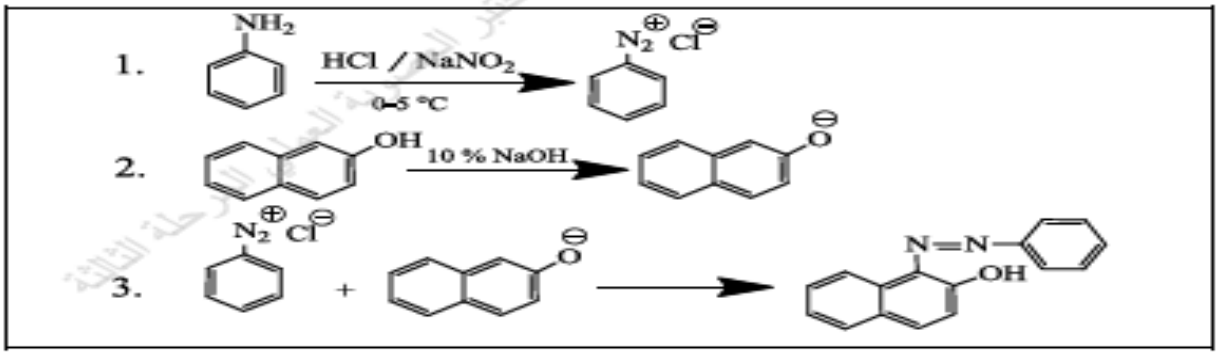
Examples for AZO dye :



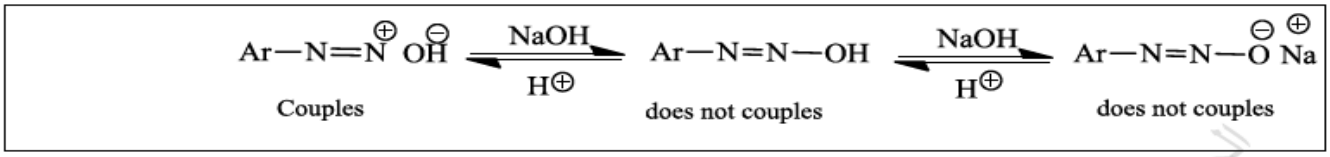
E.G. : preparation of 1-phenylazo-2-naphthol :



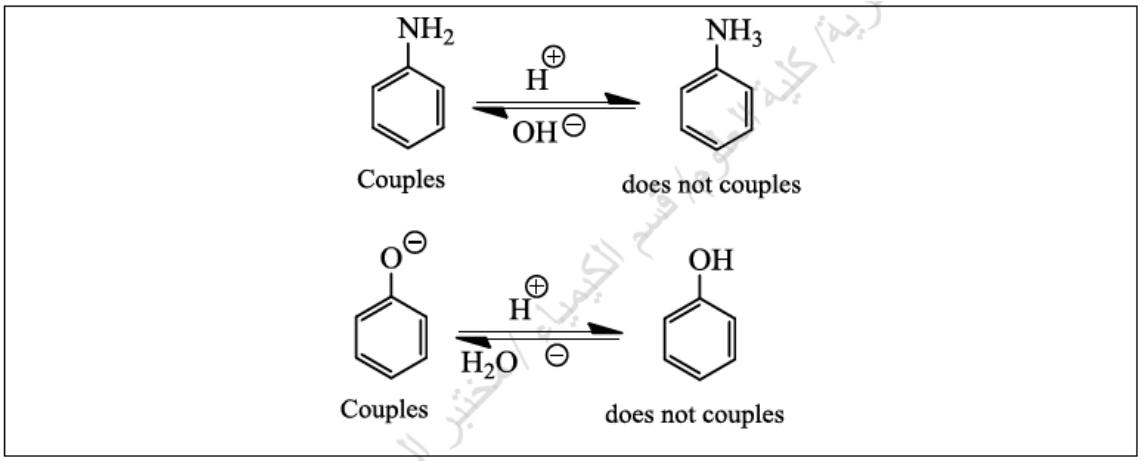
mechanism preparation of 1-phenylazo-2-naphthol:



1- It is most important that the coupling medium be adjusted to the right degree of acidity or alkalinity. This is accomplished by the 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 the addition the mixture was kept in ice bath for (30min) with occasional stirring

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

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