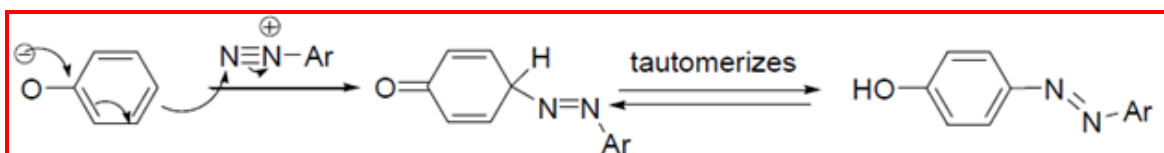


## Diazonium Salts

### ❖ Reaction

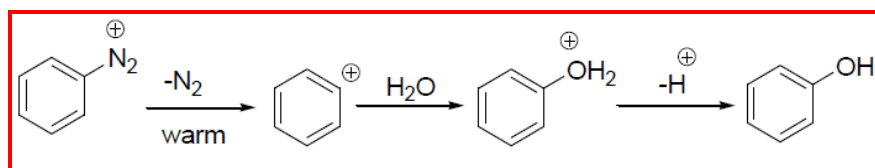
#### A. Reactions of nucleophiles at nitrogen:

Diazonium ions are attacked by nucleophiles at N atom to give covalent diazo-compounds. For example, phenol via phenoxide ion couples with diazonium salt at pH 9-10 to afford para-azophenols in good yield.



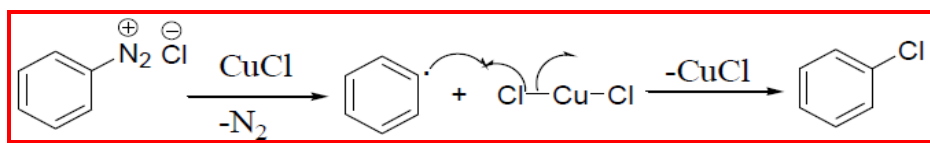
#### B. S<sub>N</sub>1 Reaction:

Diazonium salts are decomposed on warming into nitrogen and aryl cation which is highly reactive and could be attacked by any nucleophile in its vicinity.



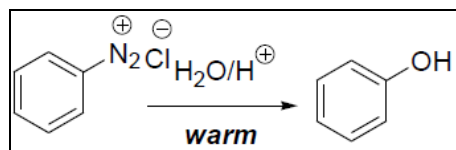
#### C. One Electron Reduction:

Diazonium ions can be reduced by single electron transfer to give an aryl radical and nitrogen. Copper (I) is frequently used for this purpose.



#### D. Replacement by Hydroxyl:

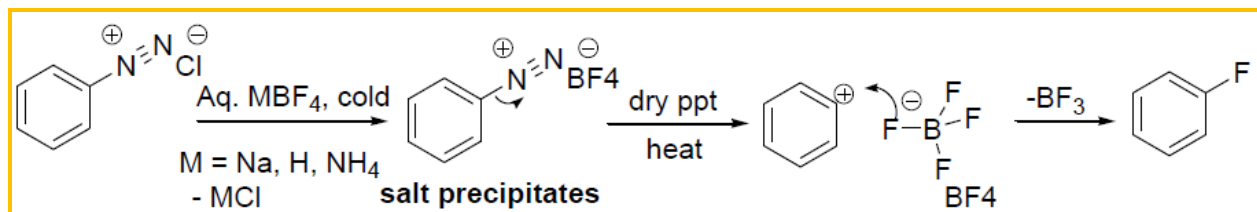
Diazonium salt gives phenol on warming in water. The reaction follows S<sub>N</sub>1 pathway. The reaction is generally performed in acidic solution to preserve phenol in its unionized form.



## E. Replacement by Halogen:

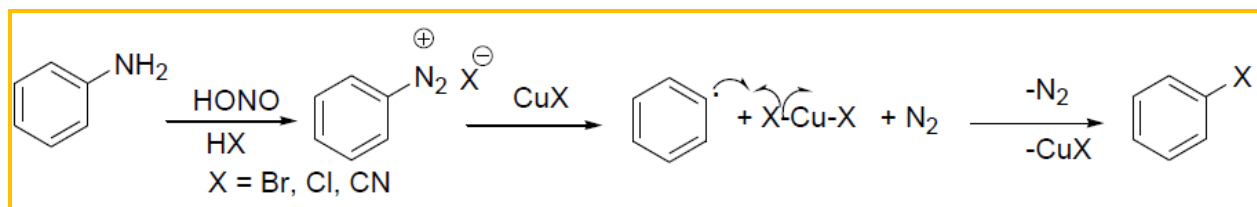
### 1] Schiemann Reaction:

Reaction of an aqueous solution of diazonium salt with fluoroboric acid under cold conditions gives diazonium fluoroborate as precipitate, which gives fluorobenzene on heating. The reaction involves  $S_N1$  mechanism.



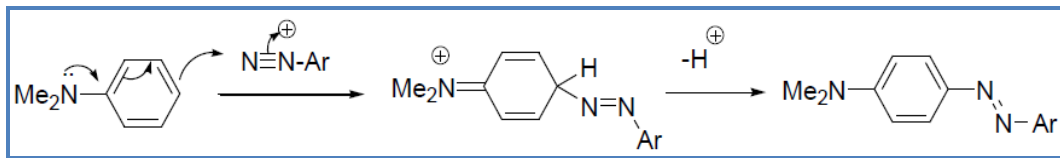
### 2] Sandmeyer Reaction:

This method is very useful for the preparation of aromatic bromides and chlorides. Addition of cold aqueous solution of diazonium chloride to a solution of  $CuCl$  in  $HCl$  medium gives a sparingly soluble complex which is separated and heated to give aryl chloride or bromide by decomposition.

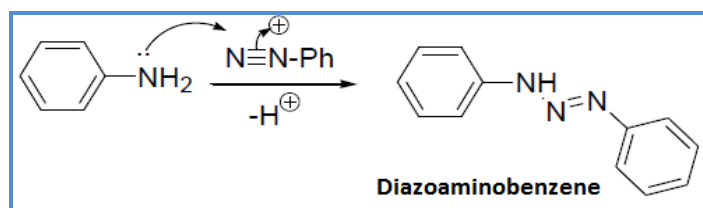


## F. Coupling Reaction:

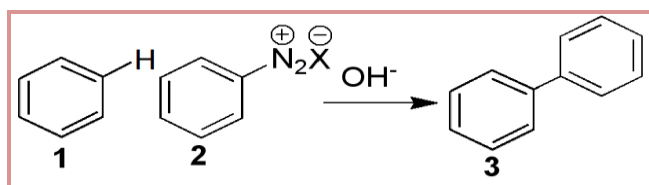
Diazonium ions undergo coupling with activated aromatic nuclei such as aryl amines, phenols and aromatic heterocyclic compounds. For example,  $N,N$ -dimethylaniline reacts with diazonium ion almost at the para-position. However, for the success of the process, the pH of the reaction medium is carefully controlled.



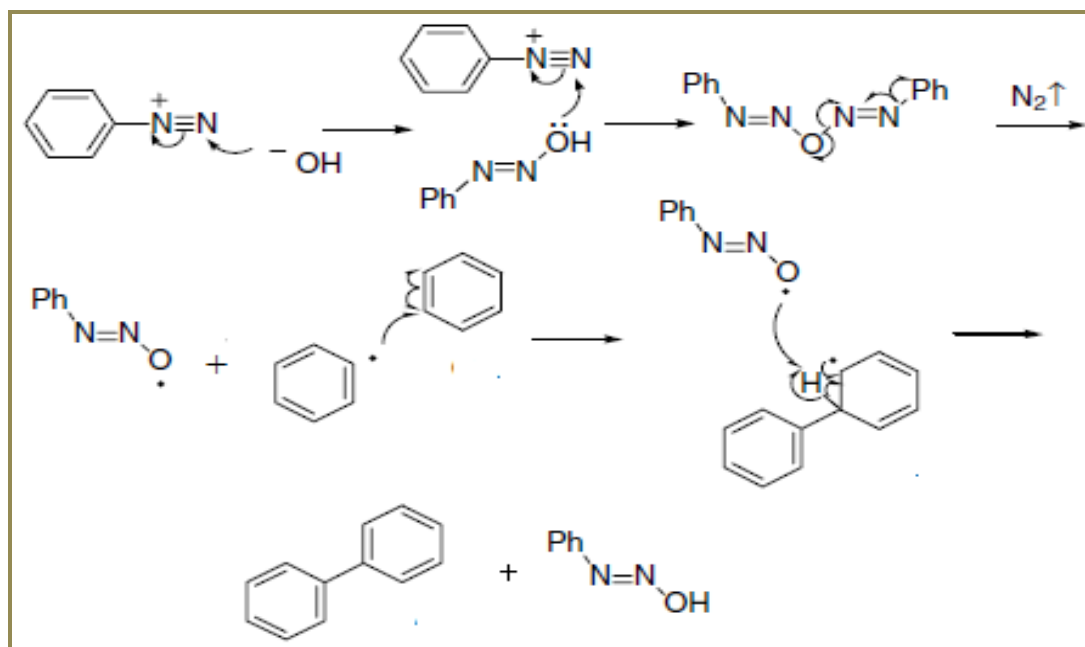
In case of primary and secondary aromatic amines, the reaction preferentially takes place at the nitrogen atoms of the diazonium ions. For example, aniline adds to the aromatic diazonium salt to give diazoaminobenzene.



### G. Gomberg reaction:

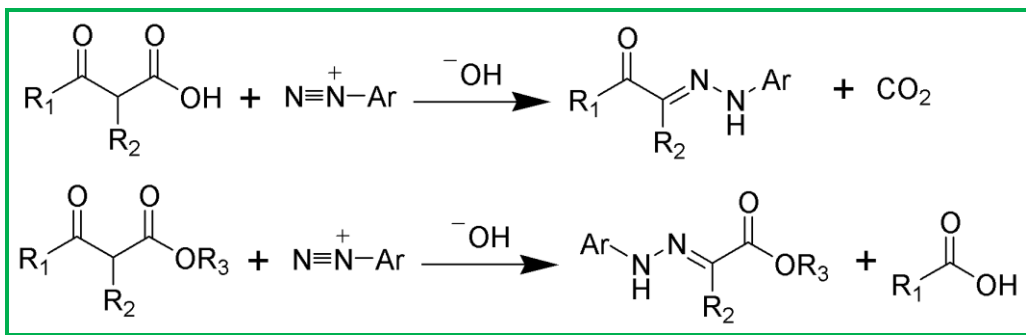


### Mechanism:



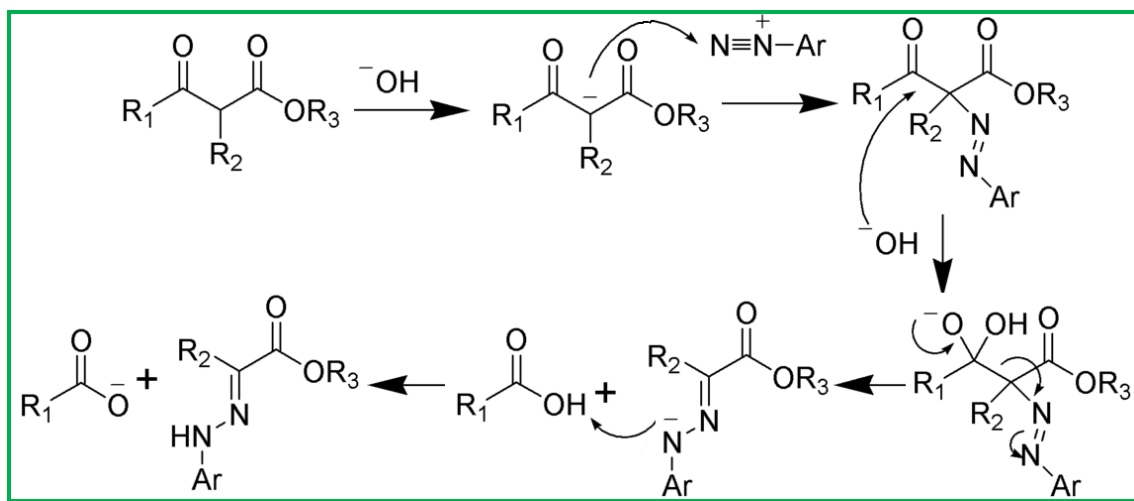
## H. Japp–Klingemann reaction:

The Japp–Klingemann reaction is a chemical reaction used to synthesize hydrazones from  $\beta$ -keto-acids (or  $\beta$ -keto-esters) and aryl diazonium salts.



### Mechanism:

Firstly the  $\beta$ -keto-ester is deprotonated to form enolate anion which attacks the diazonium salt to produce the azo compound. However, in most cases, the hydrolysis of azo compound produces a tetrahedral intermediate, which quickly decomposes to release the carboxylic acid. After hydrogen exchange, the final hydrazone is produced.



## I. Meerwein Reaction:

The Meerwein reaction means arylation in which the addition of an aryl diazonium salt ( $\text{ArN}_2\text{X}$ ) to an electron-poor alkene usually supported by a metal salt. The reaction product is an alkylated arene compound.

