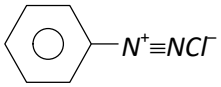
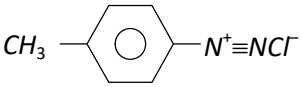
Diazonium salts

The diazonium salts have the general formula $ArN_2^+X^-$, where X^- may be an anion like Cl^-, Br^- etc. and the group $N_2^+(-N \equiv N^+)$ is called diazonium ion group.

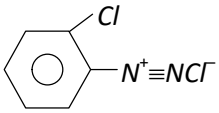
(1)**Nomenclature:** The diazonium salts are named by adding the word diazonium to the name of the parent aromatic compound to which they are related followed by the name of the anion. For example,



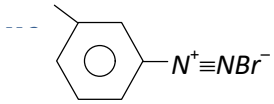
Benzenediazonium chloride



p-Toluenediazonium chloride

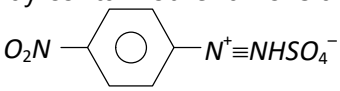


o-chlorobenzenediazonium chloride



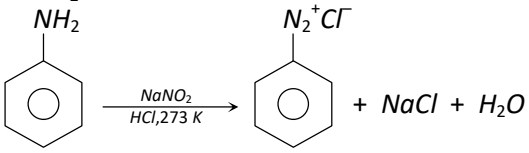
m-Hydroxybenzenediazonium bromide

The diazonium salt may contain other anions also such as NO_3^-, HSO_4^-, BF_4 etc.



p-Nitrobenzenediazonium hydrogen sulphate

(2) **Preparation of diazonium salts:** $NaNO_2 + HCl \rightarrow NaCl + HONO$



Aniline Benzene diazonium

The reaction of converting aromatic primary amine to diazonium salt is called **diazotisation.**

(3) **Physical properties of diazonium salts**

(i) Diazonium salts are generally colorless, crystalline solids.

(ii) These are readily soluble in water but less soluble in alcohol.

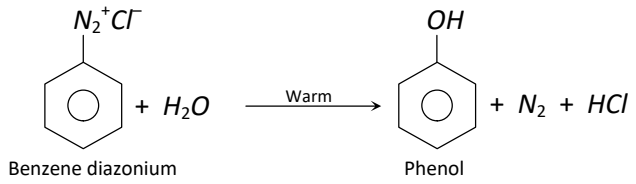
(iii) They are unstable and explode in dry state. Therefore, they are generally used in solution state.

(iv) Their aqueous solutions are neutral to litmus and conduct electricity due to the presence of ions.

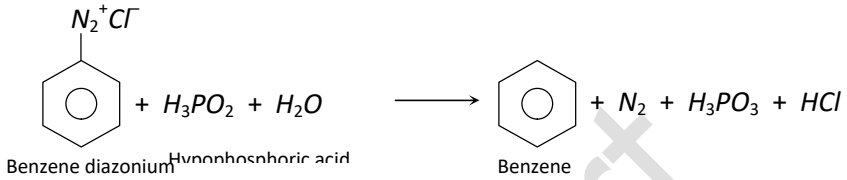
(4) **Chemical properties of diazonium salts**

(i) **Substitution reaction:** In substitution or replacement reactions, nitrogen of diazonium salts is lost as N_2 and different groups are introduced in its place.

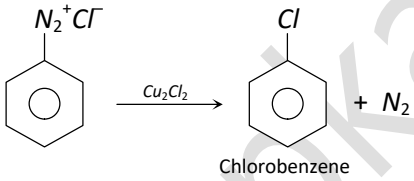
(a) Replacement by –OH group



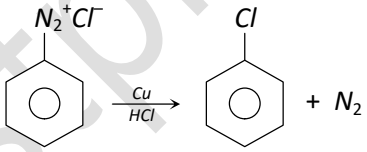
(b) Replacement by hydrogen



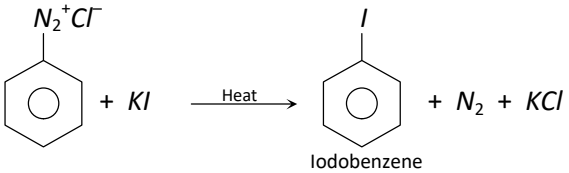
(c) Replacement by–Cl group



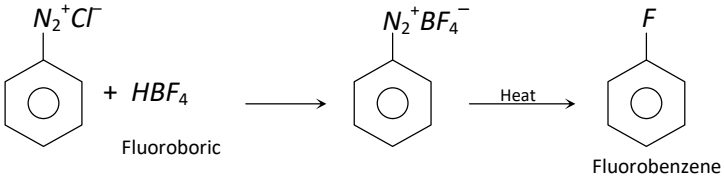
This reaction is called **Sandmeyer reaction.**
When the diazonium salt solution is warmed with copper powder and the corresponding halogen acid, the respective halogen is introduced. The reaction is a modified form of Sandmeyer reaction and is known as **Gattermann reaction.**



(d) Replacement by iodo (–I) group

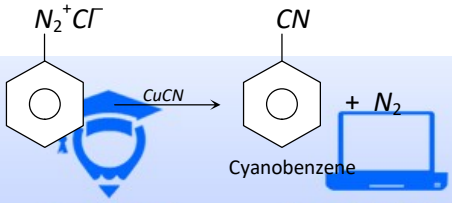


(e) Replacement by – F group

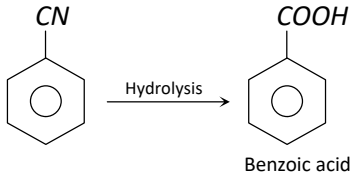


This reaction is called **Schiemann reaction.**

(f) Replacement by Cyano (– CN) group

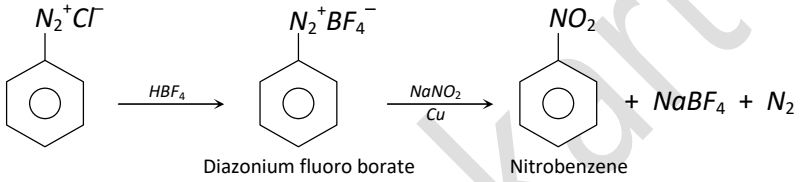


The nitrites can be hydrolysed to acids.

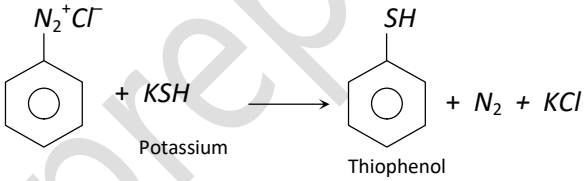


This method of preparing carboxylic acids is more useful than carbonation of Grignard reagents.

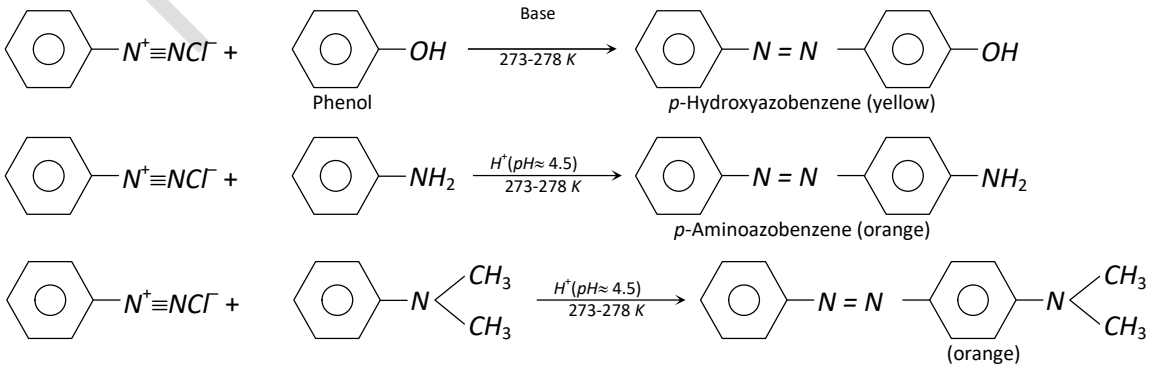
(g) Replacement by – NO_2 group



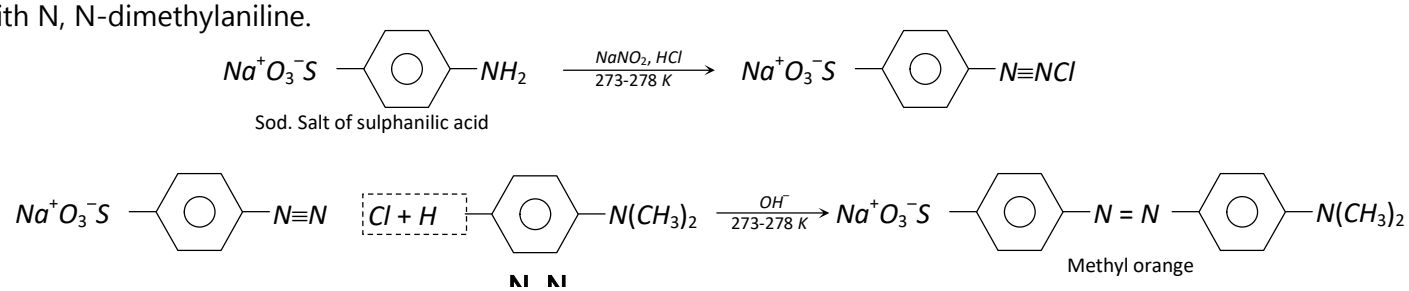
(h) Replacement by thio (–SH) group



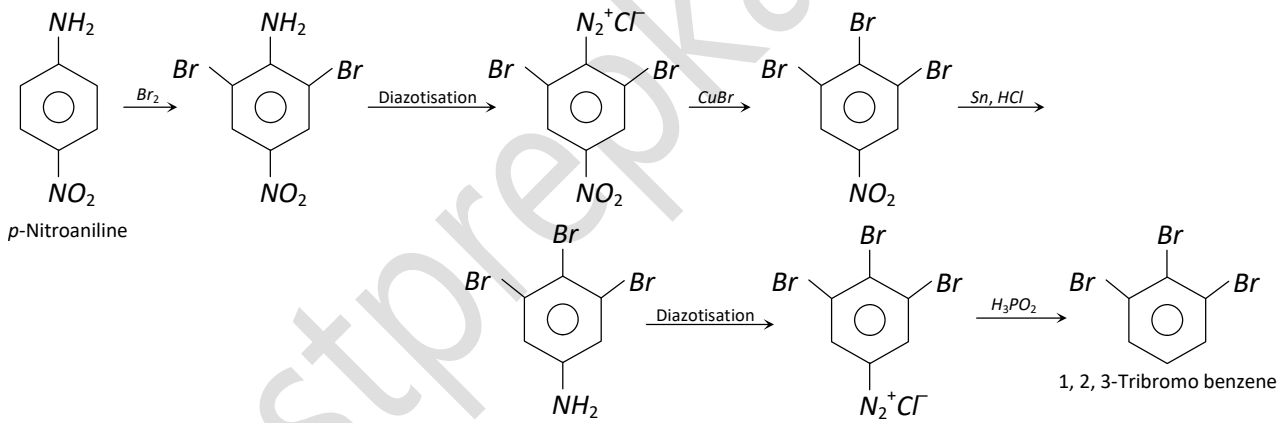
(ii) **Coupling reactions:** The diazonum ion acts as an electrophile because there is positive charge on terminal nitrogen. It can react with nucleophilic aromatic compounds (Ar–H) activated by electron donating groups (– OH and – NH_2), which as strong nucleophiles react with aromatic diazonium salts. Therefore, benzene diazonium chloride couples with electron rich aromatic compounds like phenols and anilines to give azo compounds. The azo compounds contain –N = N– bond and the reaction is called **coupling reaction.**



Coupling occurs para to hydroxy or amino group. All azo compounds are strongly coloured and are used as dyes. Methyl orange is an important dye obtained by coupling the diazonium salt of sulphanilic acid with N, N-dimethylaniline.



Note: Diazonium salts are highly **useful intermediates** in the synthesis of large variety of aromatic compounds. These can be used to prepare many classes of organic compounds especially aryl halides in pure state. For example,. 1, 2, 3-tribromo benzene is not formed in the pure state by direct bromination of benzene. However, it can be prepared by the following sequence of reaction starting from p-nitroaniline through the formation of diazonium salts as:



(5) **Uses of diazonium salts**

(i) For the manufacture of azo dyes.

(ii) For the industrial preparation of important organic compounds like m-bromotoluene, m-bromophenol, etc.

(iii) For the preparation of a variety of useful halogen substituted arenes.