

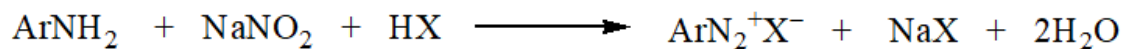
Notes on Diazonium salts



By
Dr. Gangutri Saikia

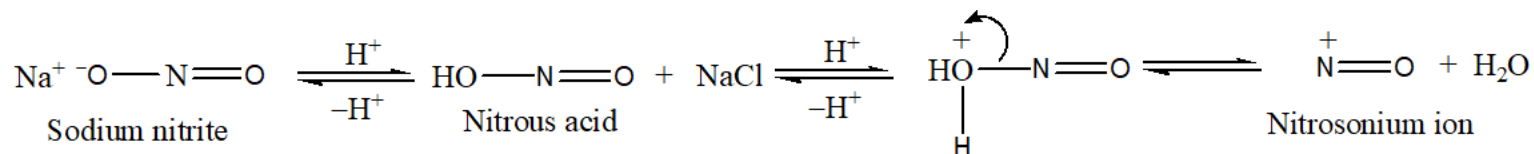
Preparation

When a primary aromatic amine in cold aqueous mineral acid is treated with sodium nitrite, a diazonium salt is formed.



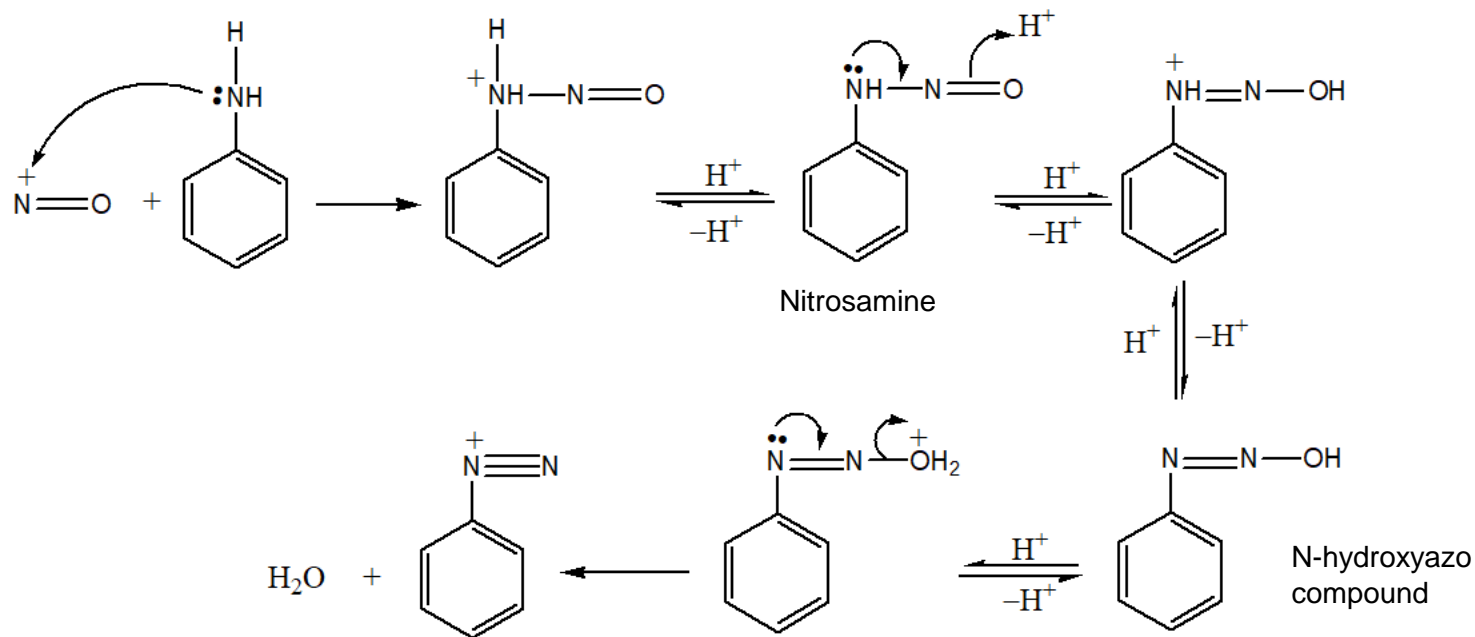
Mechanism:

1st step: The first step in this reaction is the formation of nitrous acid from sodium nitrite and HCl.



Loss of water from protonated nitrous acid generates the nitrosonium ion, which is the reactive species in the reaction of amines with nitrous acid.

2nd step:

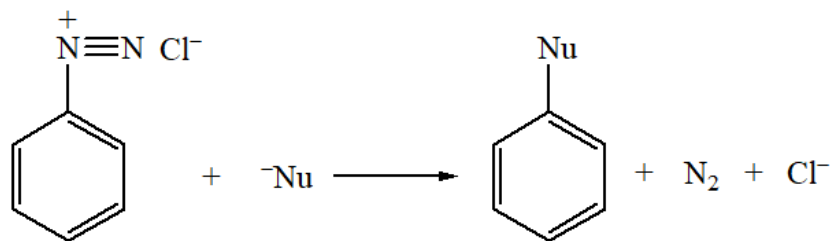


The nitrogen atom of the amine shares its lone pair electrons with the nitrosonium ion. Loss of a proton from nitrogen forms a nitrosamine. Delocalization of nitrogen's lone pair and electrons and protonation of oxygen form a protonated N-hydroxyazo compound. This compound is in equilibrium with its nonprotonated form, which can be reprotonated on nitrogen (reverse reaction) or protonated on oxygen (forward reaction). Elimination of water forms diazonium ion.

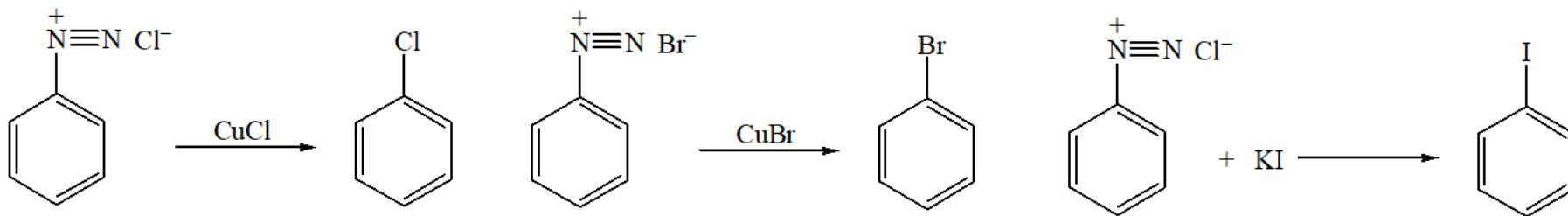
Reactions:

The large number of reactions undergone by diazonium salts may be divided into two classes: (i) replacement in which nitrogen is lost as N_2 , displaced by a wide variety of nucleophile, (ii) Coupling in which arenediazonium ion act as an electrophile and coupled with highly activated benzene ring. N_2 is retained in the product.

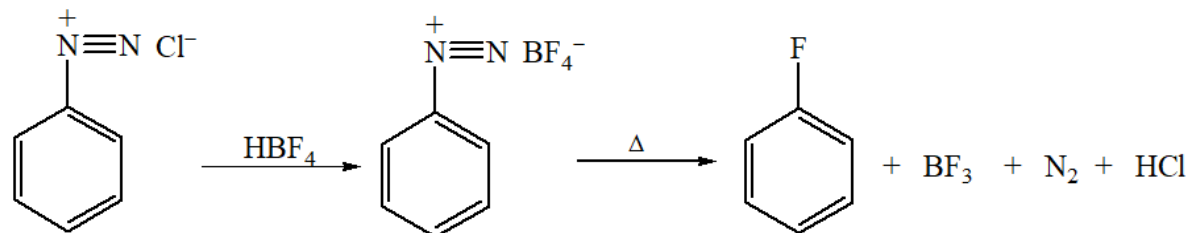
(i) Replacement: Replacement of the diazonium group is the best general way of introducing F, Cl, Br, I, CN, OH, Ar, NO_2 , -OR, -SH, -SR, -NCS, -NCO and H etc. into an aromatic ring.



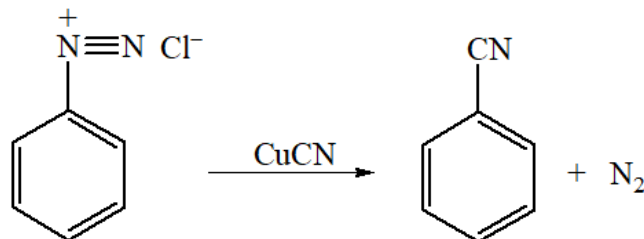
Replacement by halogen. Sandmeyer reaction: The reaction of an arenediazonium salt with a cuprous salt is known as a Sandmeyer reaction. The preparation of aryl halides from diazonium salt is more important than direct halogenation, because, aryl fluorides and iodides cannot generally be prepared by direct halogenation, aryl chlorides and bromides can be prepared by direct halogenation, but a mixture of o- and p-isomers is obtained.



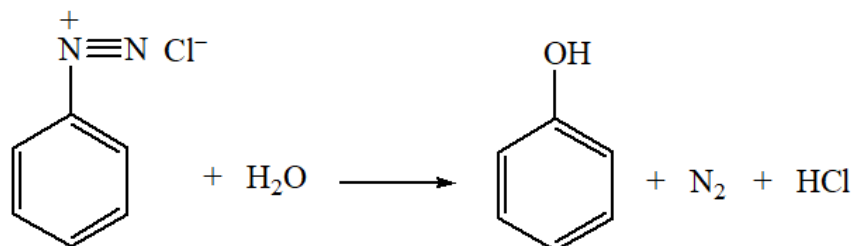
Fluoro substitution occurs if arenediazonium salt is heated with fluoroboric acid (HBF_4). The reaction is known as the **Schiemann reaction**.



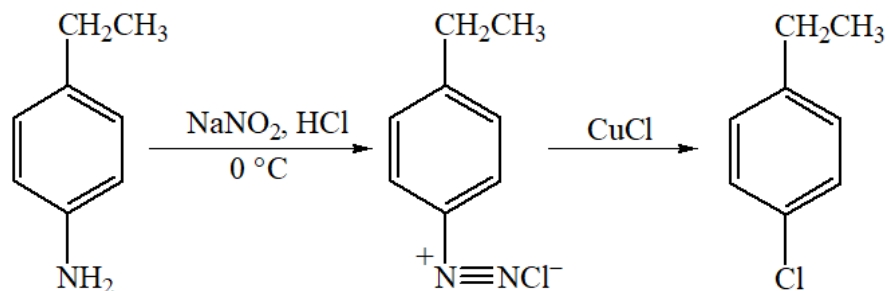
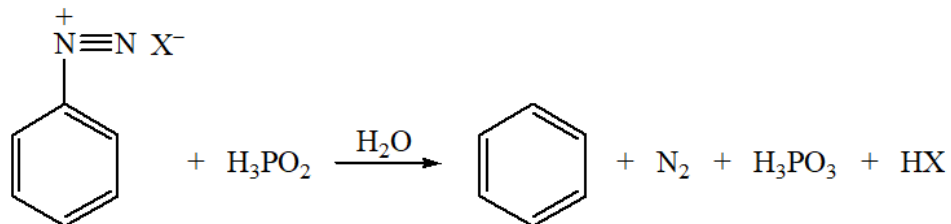
Replacement by $-\text{CN}$:



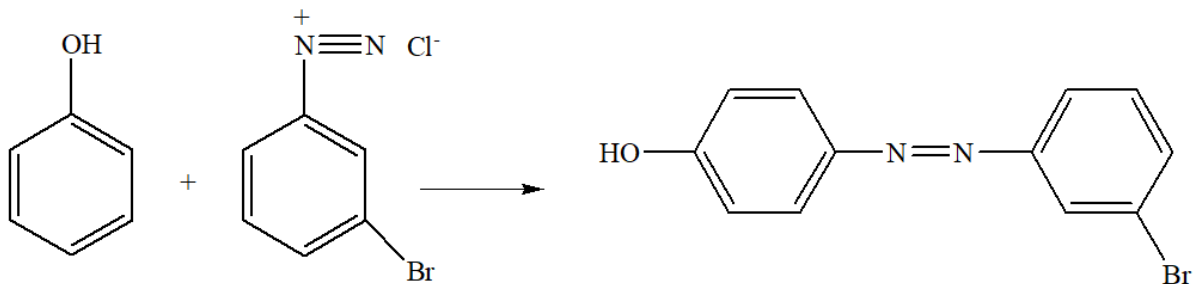
Replacement by $-\text{OH}$: If the aqueous solution in which diazonium salt has been synthesized is allowed to warm up to room temperature, an OH group will replace the diazonium group. This is a convenient way to synthesize phenols.



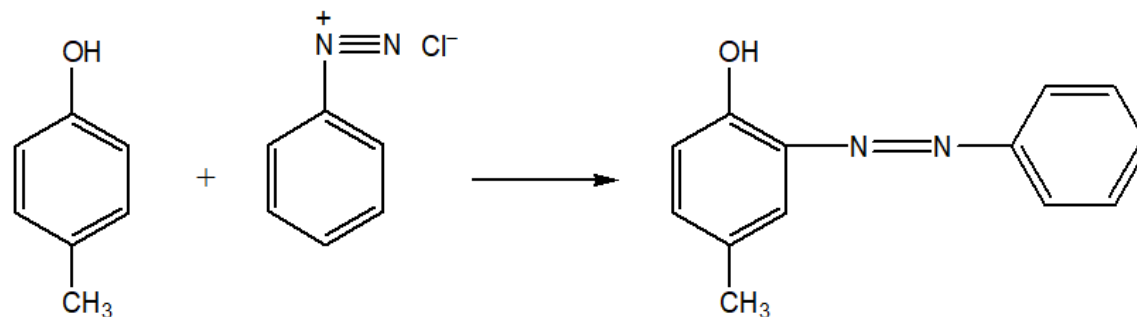
Replacement by -H: A hydrogen will replace a diazonium group if the diazonium salt is treated with hypophosphorus acid (H_3PO_2).



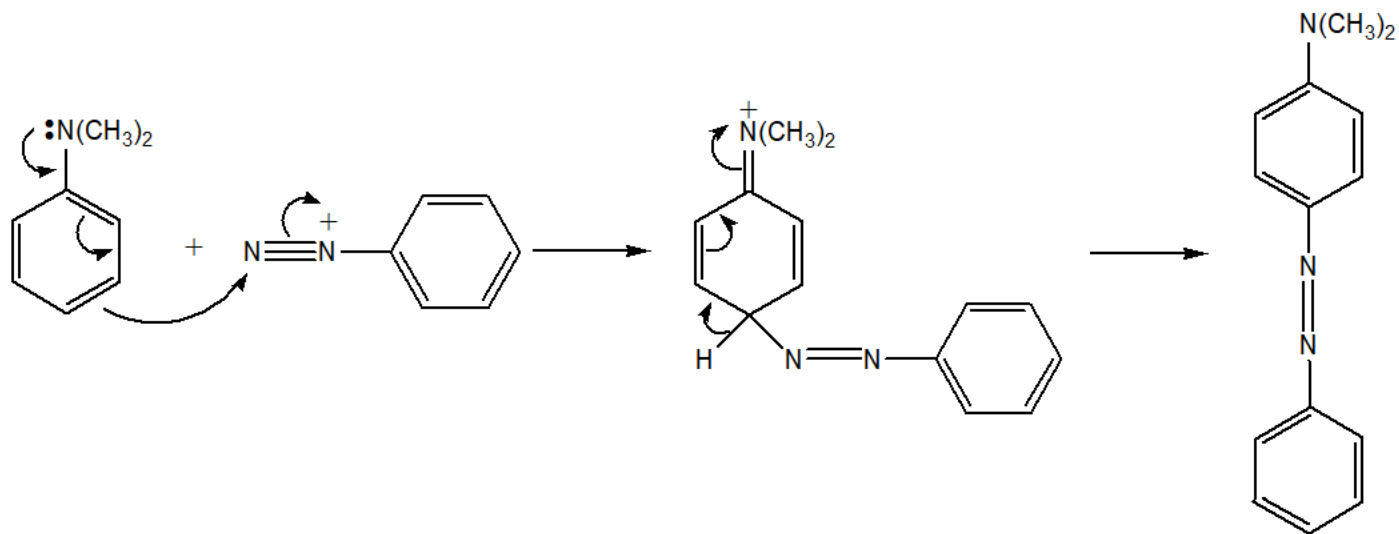
(ii) Coupling of diazonium salts. Synthesis of azo compounds: Diazonium salts react with certain aromatic compounds to yield products of general formula, Ar-N=N-Ar , called azo compounds. Arenediazonium ion acts as an electrophile in the electrophilic substitution reactions that can be carried out well below room temperature. The aromatic ring undergoing attack by the diazonium ion, must in general, contain a powerfully electron releasing groups, generally $-\text{OH}$, $-\text{NR}_2$, $-\text{NHR}$, $-\text{NHR}$ etc. Substitution preferentially occurs at the less sterically hindered para position.



If the para position is blocked, substitution will occur at an ortho position.



Mechanism for electrophilic substitution using an arenediazonium ion as electrophile:



Azobenzenes are colored compounds because of their extended conjugation and are used commercially as dyes.