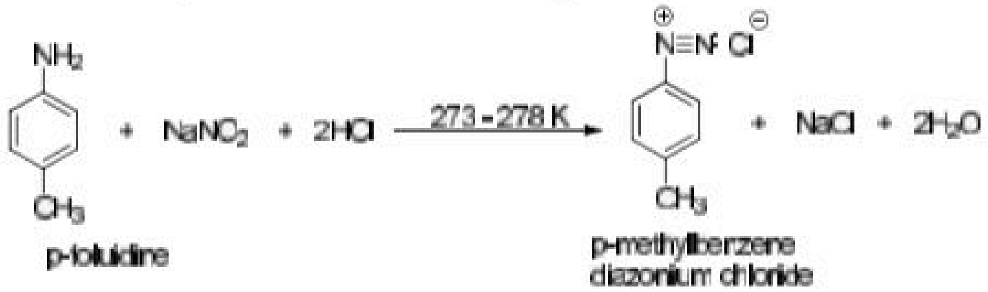
Synthesis of diazonium salts

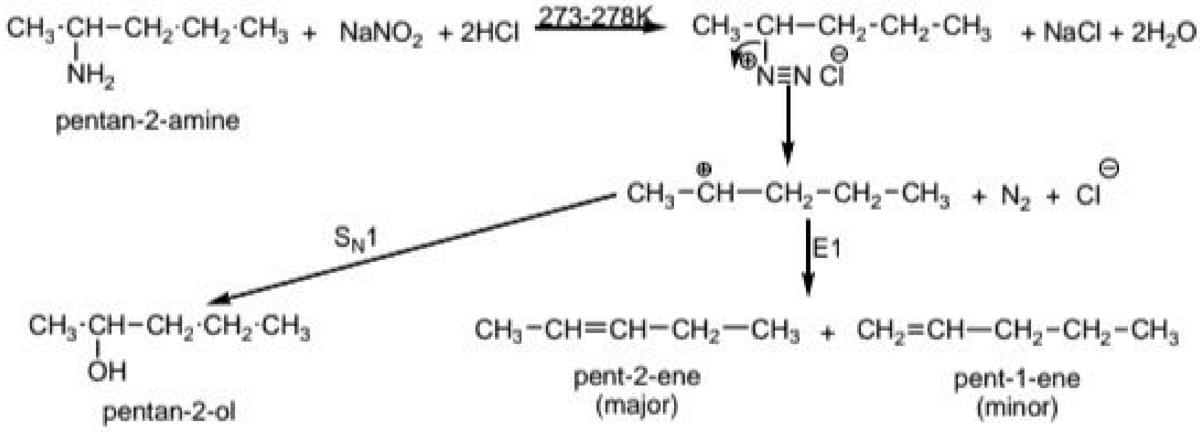
Treatment of primary amine with nitrous acid results in the formation of diazonium salt, a compound of the type Ar/R-N $N^+ X^-$, where X- is an anion like chloride, bromide, sulphate etc. But since nitrous acid is unstable, as a result it is generated in situ by treatment of sodium nitrite with strong acid such as HCl or H_2SO_4. This process of conversion of primary amine to its diazonium salt is known as **diazotization**.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$



$$CH_3\text{-}\underset{NH_2}{CH}-CH_2\text{-}CH_2\text{-}CH_3 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} CH_3\text{-}\underset{\overset{\oplus}{N}\equiv N\text{:}\overset{\ominus}{Cl}}{CH}-CH_2\text{-}CH_2\text{-}CH_3 + NaCl + 2H_2O$$

Diazonium salts of aliphatic primary amine are highly unstable even at lower temperatures, as a result as soon as they are formed they decompose, liberating nitrogen to form carbocation. The carbocation may undergo substitution and elimination reaction to give alcohol and alkene respectively. As a result diazotization of aliphatic primary amine is of little or no importance, and their reaction are also of no importance.

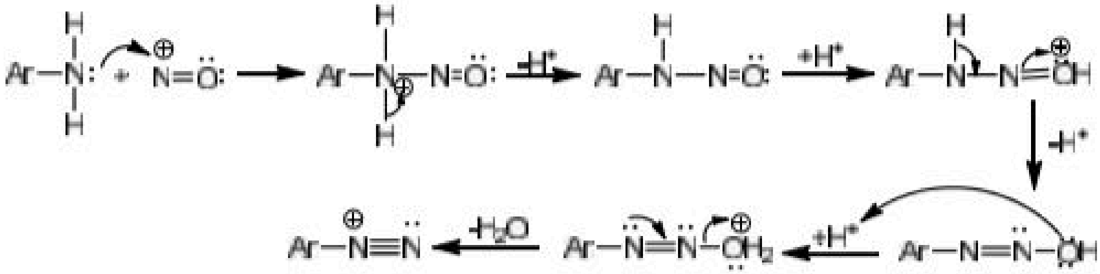


Though diazonium salts of primary aromatic amines are also unstable, but they are far more stable in comparison to diazonium salts of aliphatic primary amines and they do not decompose when the temperature of the reaction mixture is kept below 278K.

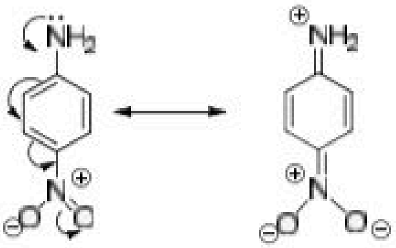
Mechanism: The reactive species in the diazotization is the nitrosonium cation, generated by the reaction of nitrous acid with acid. The electrophilic nitrosonium cation then nitrosates the nitrogen of the nucleophilic amine. After a series of protonic shifts, followed by loss of water, leads to the formation of diazonium salt.

$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$

$$HONO \underset{}{\overset{H^+}{\rightleftharpoons}} H_2\overset{\oplus}{O}{-}NO \overset{fast}{\rightleftharpoons} H_2O + \overset{\oplus}{N}O$$



From the above mechanism it can be seen that the reaction is dependent on the nucleophilicity of the amino-nitrogen. If an electron withdrawing group is bonded to the aromatic ring, the nucleophilicity of amino nitrogen is reduced, making it difficult for the diazotization reaction to take place. For example p-nitroaniline is a weaker base in comparison to aniline because of the mesomeric (-M) and inductive (-I) effect of the nitro group. Thus diazotization of p-nitroaniline is difficult in comparison to aniline.

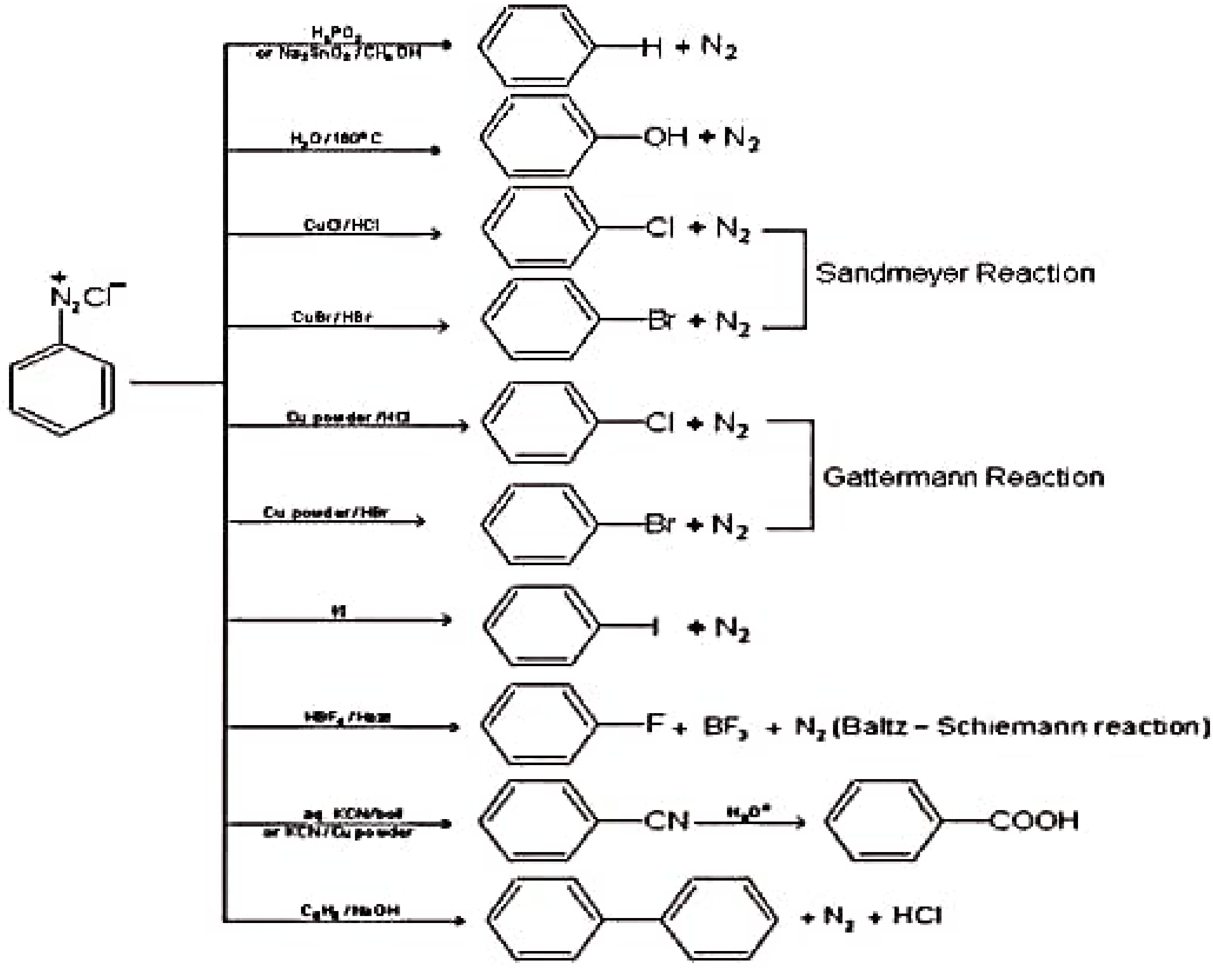


On the other hand electron donating groups present at ortho and para position to the amino group increases the nucleophilicity of amino nitrogen, thereby increasing the rate of diazotization process

II. Reactions of diazonium salts:

These salts give substitution reactions and coupling reactions as follows:

1. Substitution reactions:



2. COUPLING REACTIONS:

Coupling reactions are electrophilic substitution reactions. Some examples are as follows:

General reaction