VIVEKANANDA COLLEGE THAKURPUKUR KOLKATA-700063

NAAC ACCREDITED ‘A’ GRADE

Topic: Amines and Diazonium Salts

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Name of the Department: Chemistry

CONTENTS

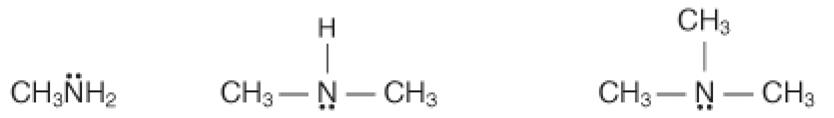
Amines and Diazonium Salts

Amines (aliphatic and aromatic): strength of organic bases; Preparation: from alkyl halides, Hofmann degradation;

Reactions: with HNO2 (distinction of 1°-, 2°- and 3°- amines), Schotten – Baumann reaction , Diazo coupling reaction (with mechanism).

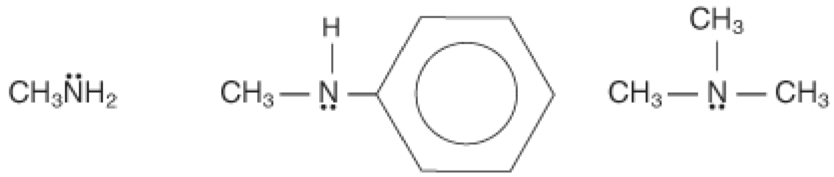
Diazonium salts: Preparation: from aromatic amines; Reactions: conversion to benzene, phenol, benzoic acid and nitrobenzene.

Amines are classified as primary, secondary, or tertiary based upon the number of carbon-containing groups that are attached to the nitrogen atom. Those amine compounds that have only one group attached to the nitrogen atom are primary, while those with two or three groups attached to the nitrogen atom are secondary and tertiary, respectively.



1°	2°	3°
methanamine (methylamine)	N-methylmethanamine (dimethylamine)	N, N-dimethylmethanamine (trimethylamine)

In the common system, you name amines by naming the group or groups attached to the nitrogen atom and adding the word amine.



methyl amine　　methyl phenyl amine　　trimethyl amine

Basicity of amines

Amines are aliphatic and aromatic derivatives of ammonia. Amines, like ammonia, are weak bases ($K_b = 10^{-4}$ to 10^{-6}). This basicity is due to the unshared electron pair on the nitrogen atom.

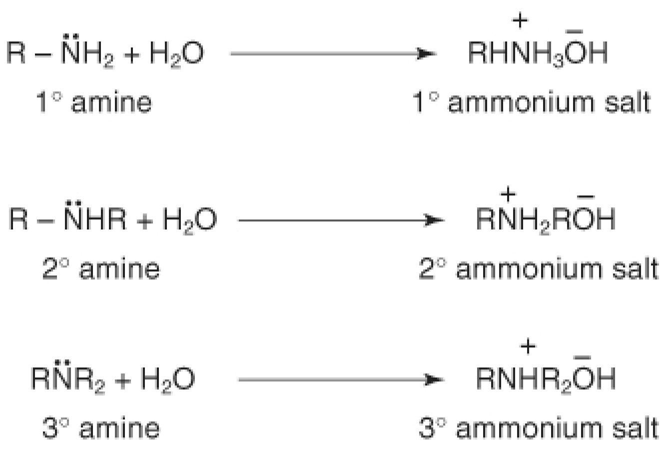
Amines are basic because they possess a pair of unshared electrons, which they can share with other atoms. These unshared electrons create an electron density around the nitrogen atom. The greater the electron density, the more basic the molecule. Groups that donate or supply electrons will increase the basicity of amines while groups that decrease the electron density around the nitrogen decrease the basicity of the molecule. For alkyl amines in the gas phase, the order of base strength is given below:

$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

However, in aqueous solutions, the order of basicity changes.

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

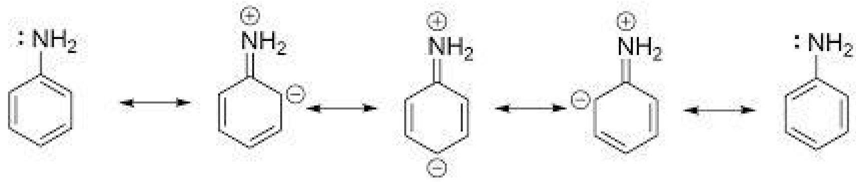
The differences in the basicity order in the gas phase and aqueous solutions are the result of solvation effects. Amines in water solution exist as ammonium ions.



In water, the ammonium salts of primary and secondary amines undergo solvation effects (due to hydrogen bonding) to a much greater degree than ammonium salts of tertiary amines. These solvation effects increase the electron density on the amine nitrogen to a greater degree than the inductive effect of alkyl groups.

Aryl amines are weaker bases than cyclohexylamines because of resonance. Aniline, a typical arylamine, exhibits the resonance structures shown below.

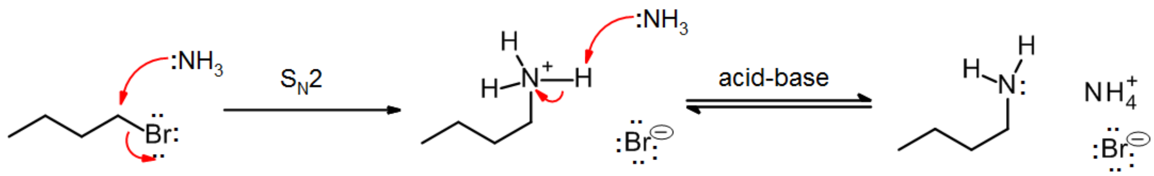
Resonating structures of aniline



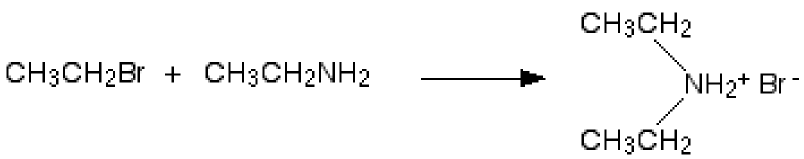
Resonating structures show delocalization of the unshared electron pair occurs throughout the ring, making these electrons less available for reaction. As a result of this electron delocalization, the molecule becomes less basic.

Preparation of Amines

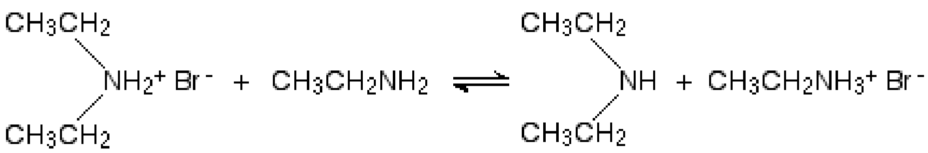
The reaction of ammonia with an alkyl halide leads to the formation of a primary amine. The primary amine that is formed can also react with the alkyl halide, which leads to a disubstituted amine that can further react to form a trisubstituted amine. Therefore, the alkylation of ammonia leads to a mixture of products.



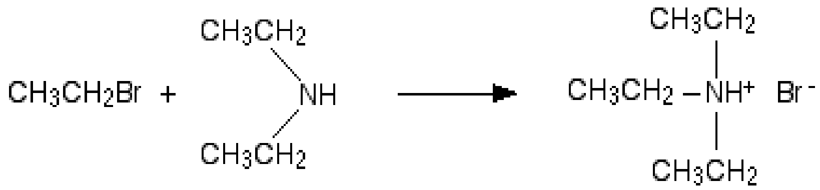
Making secondary amines and their salts



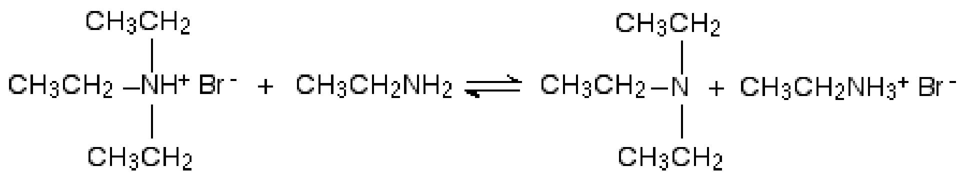
In the presence of excess ethylamine in the mixture, there is the possibility of a reversible reaction. The ethylamine removes a hydrogen from the diethylammonium ion to give free diethylamine – a secondary amine.



Making tertiary amines and their salts

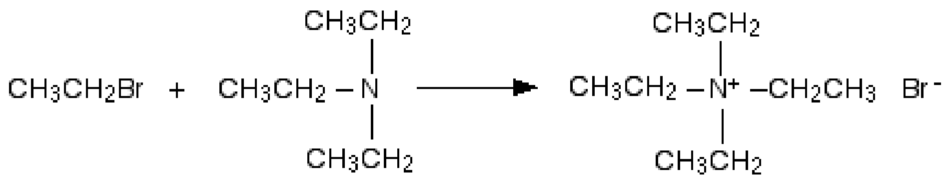


There is again the possibility of a reversible reaction between this salt and excess ethylamine in the mixture.



The ethylamine removes a hydrogen ion from the triethylammonium ion to leave a tertiary amine – triethylamine.

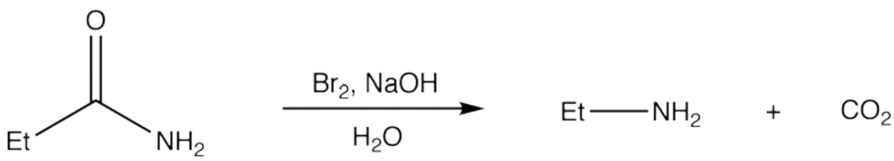
Making a quaternary ammonium salt



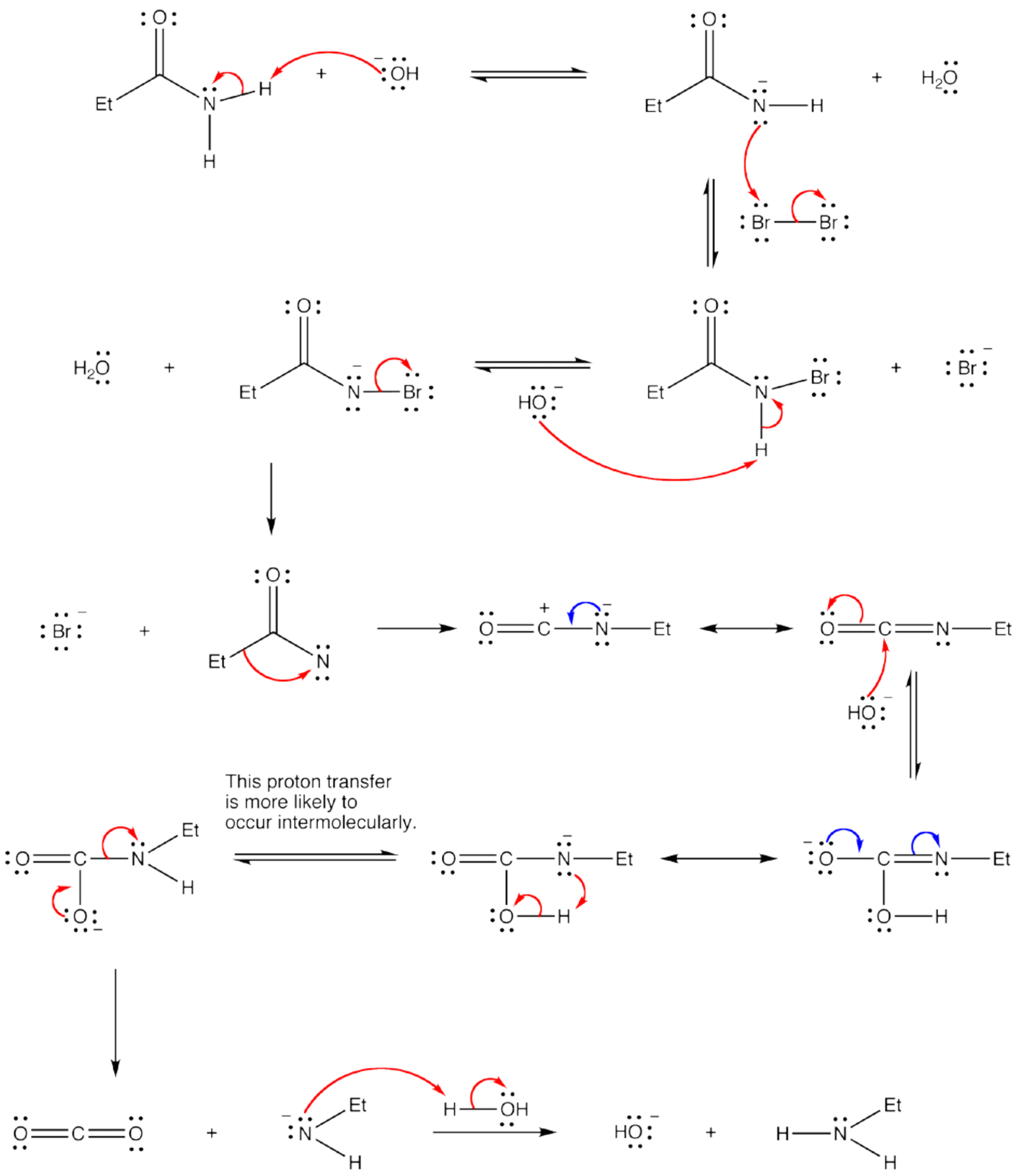
This time there isn't any hydrogen left on the nitrogen to be removed. The reaction stops here.

Hofmann Degradation

Hofmann rearrangement, also known as Hofmann degradation and not to be confused with Hofmann elimination, is the reaction of a primary amide with a halogen (chlorine or bromine) in strongly basic (sodium or potassium hydroxide) aqueous medium, which converts the amide to a primary amine. eg:



Mechanism



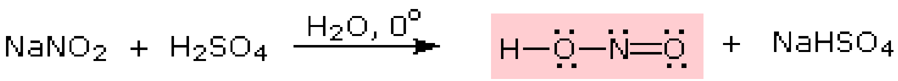
This proton transfer
is more likely to
occur intermolecularly.

How will you distinguish between primary, secondary and tertiary amines by Hinsberg's test?

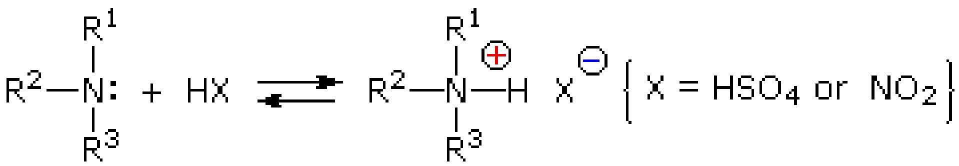
Nitrous acid (HNO2 or HONO) reacts with aliphatic amines in a fashion that provides a useful test for distinguishing primary, secondary and tertiary amines.

- 1°-Amines + HONO (cold acidic solution) →Nitrogen Gas Evolution from a Clear Solution
- 2°-Amines + HONO (cold acidic solution) → An Insoluble Oil (N-Nitrosamine)
- 3°-Amines + HONO (cold acidic solution) → A Clear Solution (Ammonium Salt Formation)

Nitrous acid is a Brønsted acid of moderate strength (pK_a = 3.3). Because it is unstable, it is prepared immediately before use in the following manner:

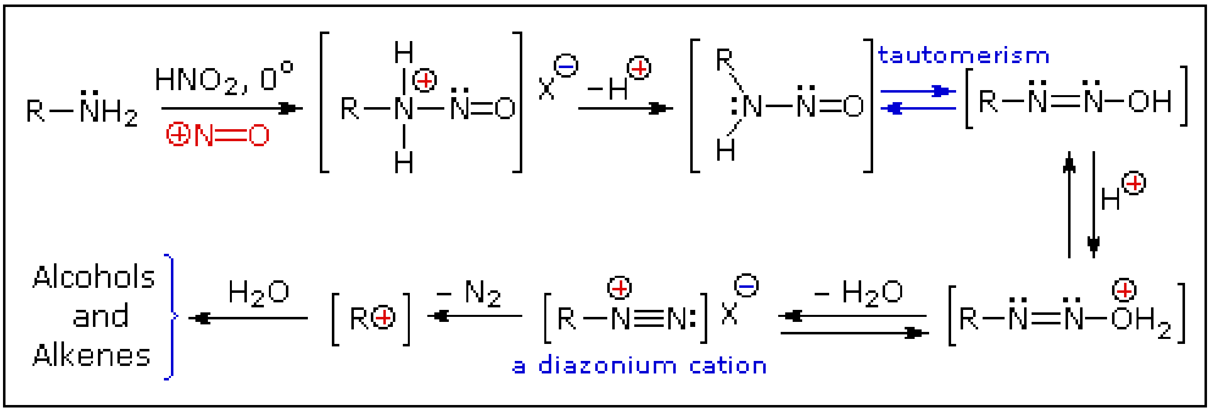


Under the acidic conditions of this reaction, all amines undergo reversible salt formation:

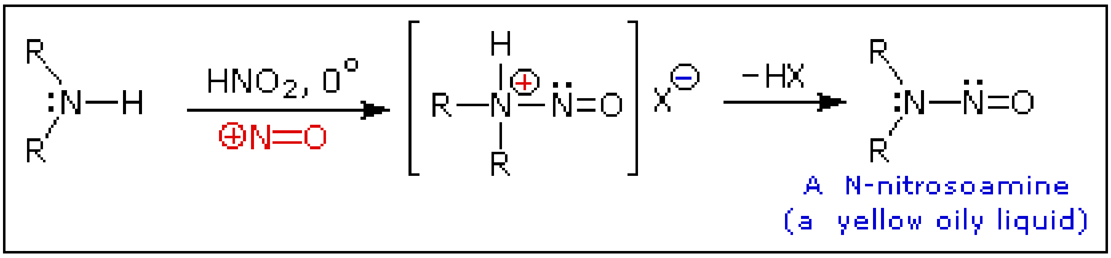


This happens with 3º-amines, and the salts are usually soluble in water. The reactions of nitrous acid with 1°- and 2°- aliphatic amines may be explained by considering their behavior with the nitrosonium cation, $NO^{(+)}$, an electrophilic species present in acidic nitrous acid solutions.

Primary Amines

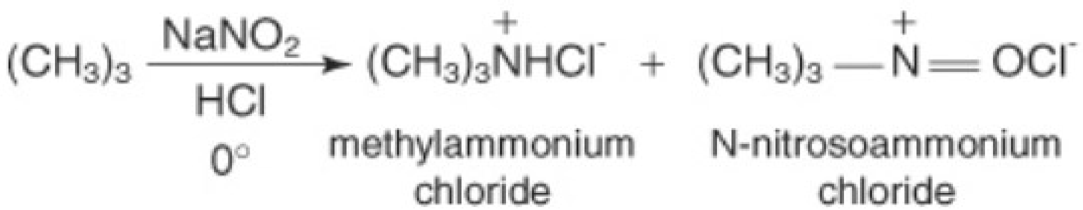


Secondary Amines



Tertiary Amines

Tertiary amines react with nitrous acid to form N-nitrosoammonium compounds (ammonium salts).



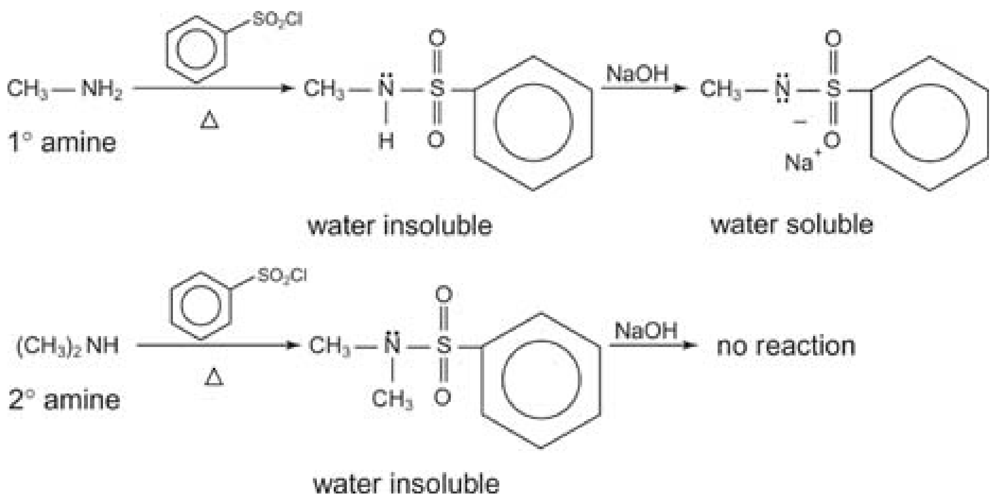
Hinsberg test

Hinsberg test is a chemical reaction that is used to distinguish between primary, secondary, tertiary amines. This reaction was described first in 1890 by the German chemist Oscar Heinrich Daniel Hinsberg.

In the Hinsberg Test, the amines act as nucleophiles and attack the electrophile (sulfonyl chloride). This leads to the displacement of the chloride and the generation of the sulfonamides.

The reaction of the benzene sulfonyl chloride with primary amines gives a sulfonamide product that is soluble in alkali.

The reaction of the benzene sulfonyl chloride with secondary amines gives a sulfonamide product that is NOT soluble in alkali.



No such reaction occurs between a tertiary amine and the benzene sulfonyl chloride reagent.

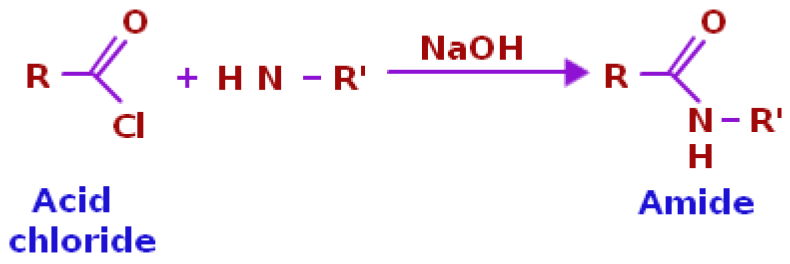
Schotten-Baumann Reaction

Schotten Baumann reaction refers to the method of chemically synthesizing amides from acyl chlorides and amines. This organic chemical reaction is named after the German chemists Carl Schotten and Eugen Baumann, who discovered this method of synthesizing amides.

Features of Schotten Baumann Reaction

The Schotten Baumann reaction can also refer to the benzoylation of active hydrogen-containing compounds with the help of benzyl chloride and aqueous sodium hydroxide. Pyridine can also be used as an alternative to the sodium hydroxide base.

This reaction can be generalized as follows.



Some key features of the Schotten Baumann Reaction are:

- It is a base-catalyzed reaction. The base is necessary to encourage an equilibrium shift towards the formation of amides.
- The base also neutralizes the hydrochloric acid which is formed in the process, thereby preventing the further protonation of the amide product formed.
- Usually, aqueous sodium hydroxide is used as the base catalyst, but pyridine also can be used in this reaction.
- It is generally observed that the acyl chlorides are converted into acylating agents of superior power when pyridine is used as the base catalyst.

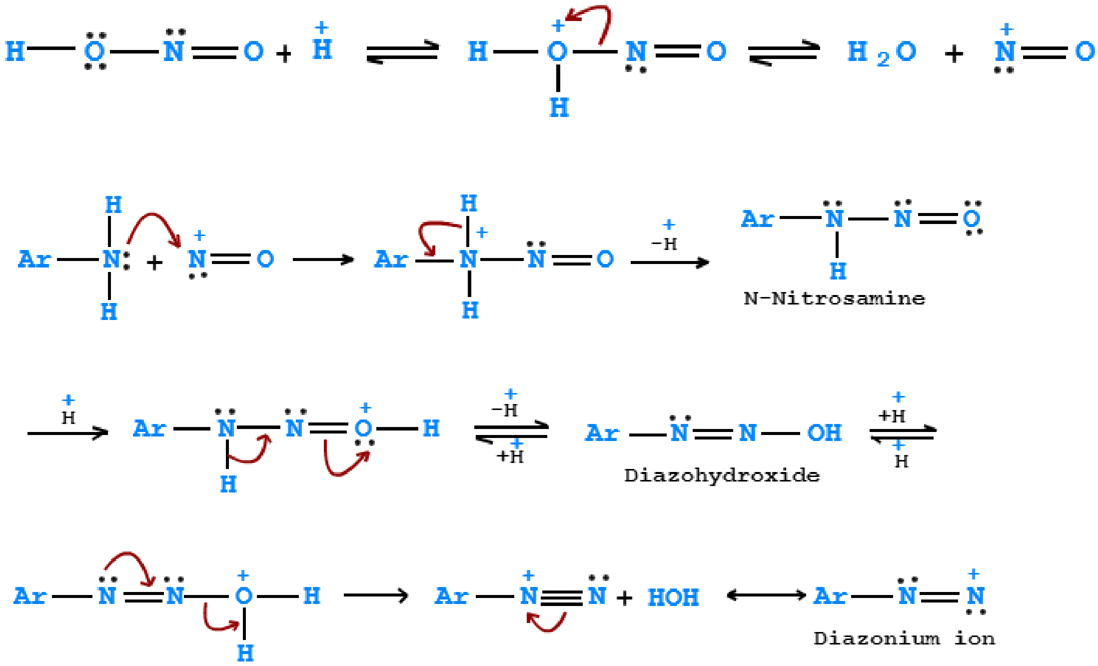
The 'Schotten Baumann conditions' maintained in this reaction refer to the aqueous basic environment which is biphasic in nature.

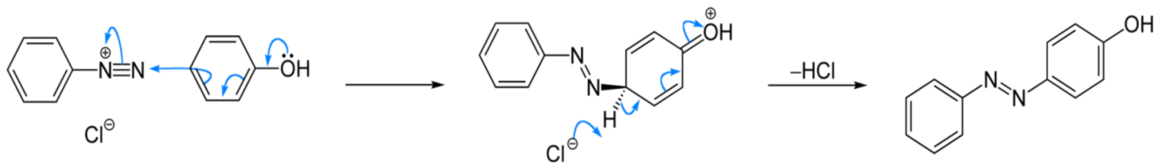
Diazonium Coupling (Diazo Coupling, Azo Coupling) Reaction

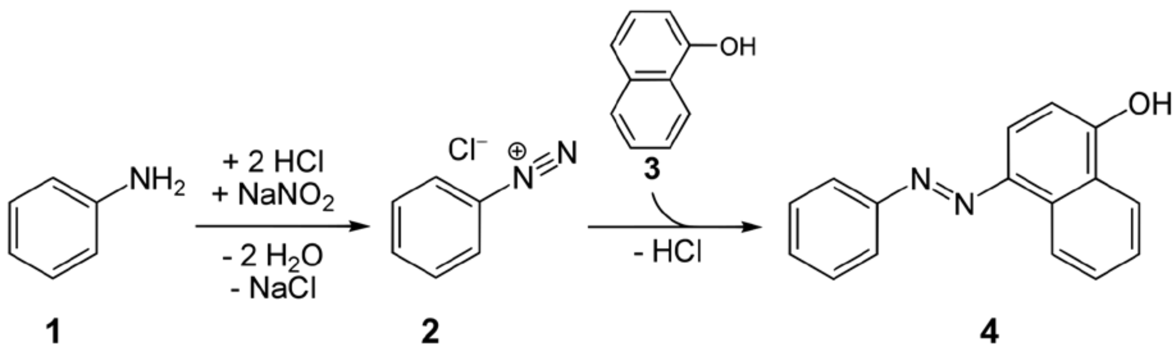
The chemical process used in converting a primary aromatic amine into the corresponding diazonium salt of the amine is commonly referred to as diazotization. This process is also known as 'diazotation' .

The German industrial chemist Peter Griess was the first person to report such a reaction in 1858.

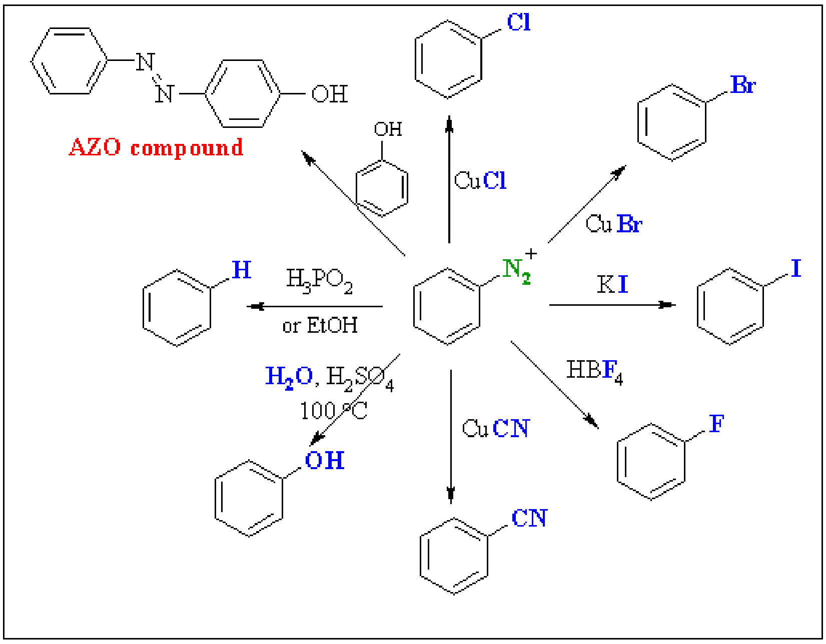
Aryl diazocation (ArN_2^+) may attack the highly activated aromatic rings of phenoxide ion (PhO^-), N,N-dialkyl aromatic amines or pyrrole to give the corresponding substitution products. This reaction is referred to as diazo-coupling. The electrophile (ArN_2^+) is generated by the reaction of aniline with HNO_2($NaNO_2/HCl$) at 0-5^{0}C.

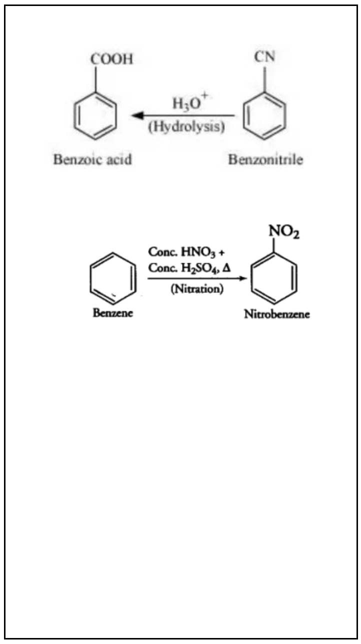

N-Nitrosamine
Diazohydroxide
Diazonium ion


–HCl


+ 2 HCl
+ NaNO2
- 2 H2O
- NaCl
- HCl
1
2
3
4

Reactions: conversion to benzene, phenol, benzoic acid and nitrobenzene.





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