4. Nitrogen Containing Organic Compounds

Content

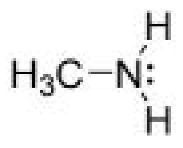
Introduction

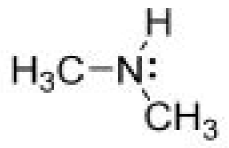
Common organic compounds containing N includes amines and amides. Reactions of amides have been discussed under derivatives of carboxylic acids because of the presence of acyl group which are common to all derivatives of carboxylic acids. In this unit properties and reactions of amines in relation to their structures will be discussed. Amines can be defined as compounds where alkyl or aryl groups are attached to nitrogen in place of hydrogen atoms in ammonia.

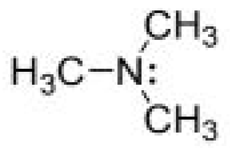
4.1 Structure, properties and reactions of primary amines and aniline

4.1.1 Classification of amines

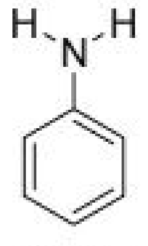
Unlike in alkyl halides and alcohols, amines are classified as primary, secondary and tertiary according to the number of alkyl or aryl groups attached to the hetero atom (N in amines). The compounds in which an alkyl or an aryl group is attached in place of one of the three hydrogen atoms in ammonia are called primary amines. The compounds in which two groups, each of which could be an alkyl or aryl group are attached in place of two atoms of hydrogen in ammonia are called secondary amines and the compounds in which three such groups are attached in place of the three atoms of hydrogen are called tertiary amines.

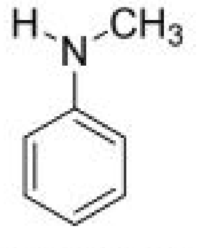

methylamine
(primary amine)


dimethylamine
(secondary amine)


trimethylamine
(tertiary amine)

The compounds in which at least one aryl group (aromatic ring) is attached to the nitrogen atom are called aromatic amines.

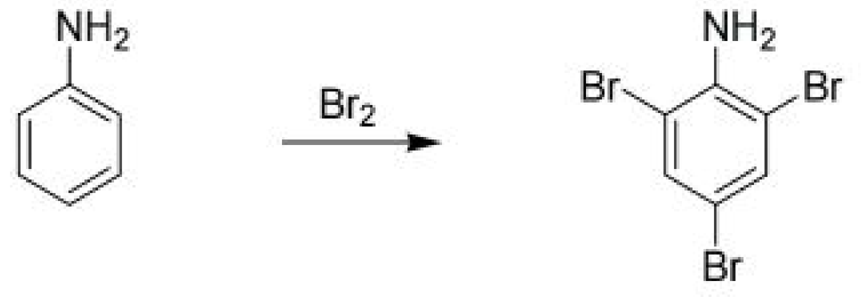

aniline
(primary aromatic amine)


N-methylaniline
secondary aromatic amine

The simplest aromatic amine is the one with NH_2 attached to a benzene ring (aniline)

4.1.2 Reactivity of the benzene ring of aniline

Similar to phenol, aniline readily reacts with bromine to give 2,4,6-tribromoaniline because the $-NH_2$ group activates the benzene ring towards electrophilic substitution.



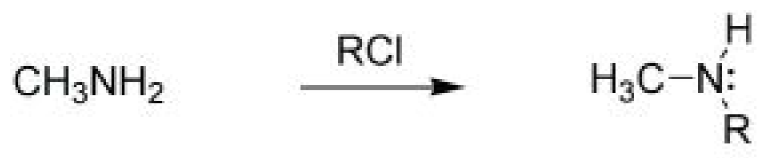
When this reaction is carried out with bromine water 2,4,6-tribromoaniline is observed as a white precipitate.

4.1.3 Reactions of primary amines

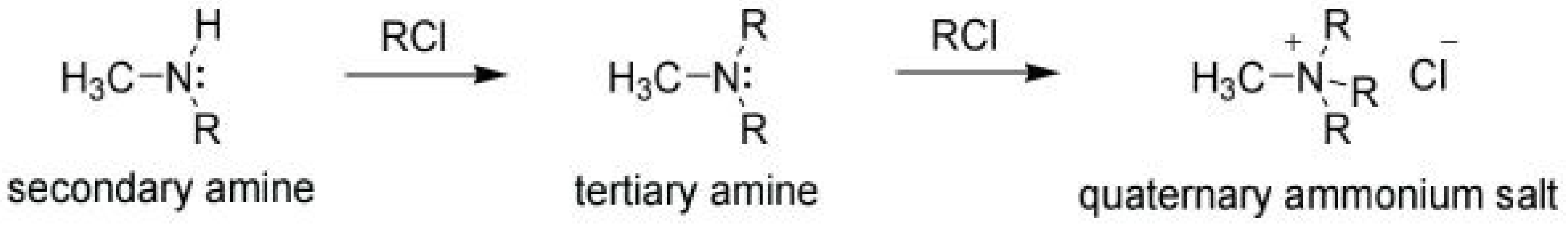
Amines can act as nucleophiles as the N atom contains a lone pair of electrons. The following are some of the reactions of primary amines with various reagents where the amine acts as a nucleophile.

4.1.3.1 Reaction of amines with alkyl halides

Primary amines react with alkyl halides to give secondary amines.



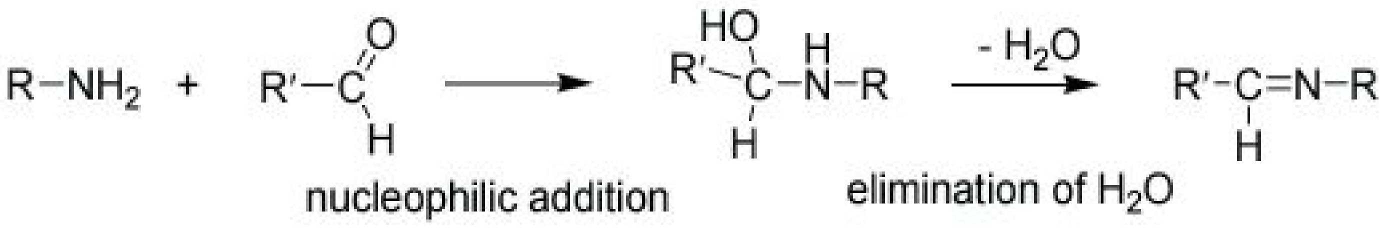
These secondary amines too have a lone pair of electrons on N atom and hence can further react with alkyl halide to form tertiary amines. Thus formed tertiary amine can react with alkyl halide further, because it also has a lone pair of electrons, to give a quaternary ammonium salt.



Therefore the reaction between primary amine and alkyl halides give a mixture of products.

4.1.3.2 Reaction of amines with aldehydes and ketones

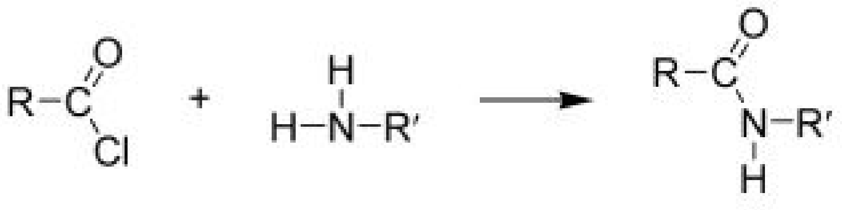
Amines show nucleophilic addition followed by elimination with aldehydes and ketones. The products are called imines.



This reaction corresponds to the reaction of aldehydes and ketones with the 2,4-dinitrophenylhydrazine (Brady reagent).

4.1.3.3 Reaction of amines with acid chlorides

Primary amines react with acid chlorides to give secondary amides.



4.1.3.4 Reaction of amines with nitrous acid ($NaNO_2/HCl$)

Primary amines react with nitrous acid to form diazonium salts. As alkyl diazonium salts are unstable they rapidly convert to alcohols with the evolution of nitrogen gas.

$$R{-}NH_2 \xrightarrow{NaNO_2/\text{dil. } HCl} \underset{\text{alkyl diazonium chloride}}{R{-}\overset{+}{N}{\equiv}N\overset{-}{Cl}} \xrightarrow{H_2O} R{-}OH + N_2 + HCl$$

Aromatic diazonium salts formed from aromatic amines are more stable than alkyl diazonium salts.Therefore solutions of aromatic diazonium salts may be obtained at low temperatures.

4.2 Basicity of amines

Aliphatic amines are basic and the basicity is comparable to that of ammonia. Aqueous mineral acids or carboxylic acids convert amines into their salts. These salts react readily with hydroxide ions to regenerate the amine.

$$R{-}NH_2 + H_3O^{+} \longrightarrow R{-}\overset{+}{N}H_3 + H_2O$$

$$R{-}\overset{+}{N}H_3 + {}^{-}OH \longrightarrow R{-}NH_2 + H_2O$$

4.2.1 Basicity of amines versus alcohols

Nitrogen is less electronegative than oxygen. Therefore it has a higher tendency to donate lone pair of electrons than oxygen. On the other hand, nitrogen atom can bear a positive charge more easily than oxygen due to its lower electronegativity when compared to oxygen. Therefore the stability of the alkyl ammonium ion relative to the amine is more than the stability of the alkyl oxonium ion relative to the alcohol. Hence, amines are more basic than alcohols.

4.2.2 Basicity of primary aliphatic amines and aniline

Aliphatic primary amines are more basic than aniline. In aniline the lone pair of electrons on the nitrogen is delocalized on to the aromatic ring by resonance **(Figure 4.1)**. Therefore it is not easily available to a proton. Due to this reason aniline show lower basicity than primary aliphatic amines.

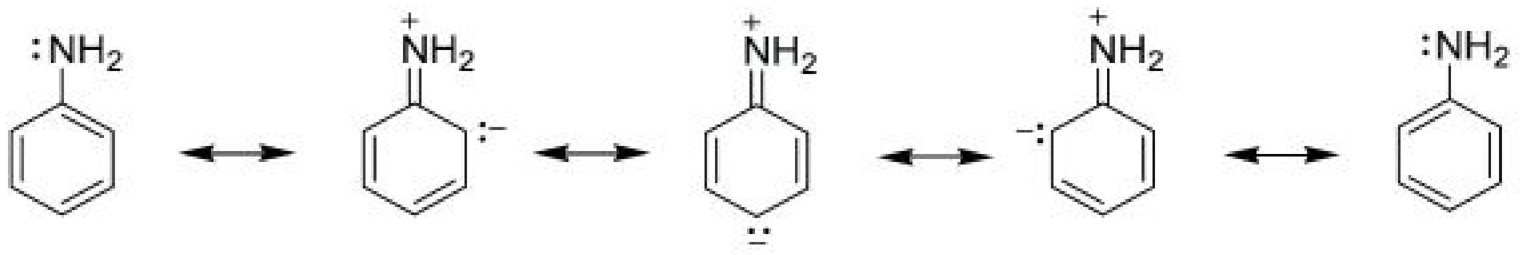


Figure 4.1 Resonance structures of aniline

4.2.3 Basicity of amines compared to amides

Amides are less basic than amines. It is because the pair of electrons on the nitrogen of the amide group is delocalized on to the carbonyl group by resonance **(Figure 4.2)** making them less available to a proton than is the lone pair of electrons on the N atom of amines.

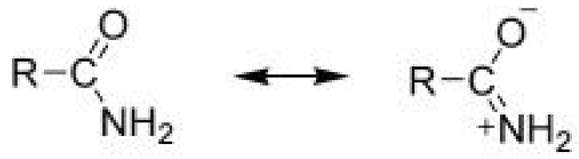
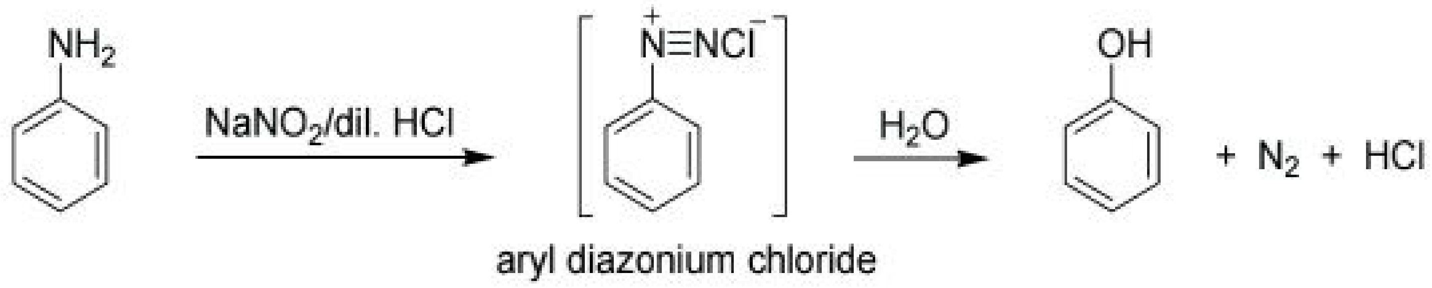


Figure 4.2 Resonance structures of amides

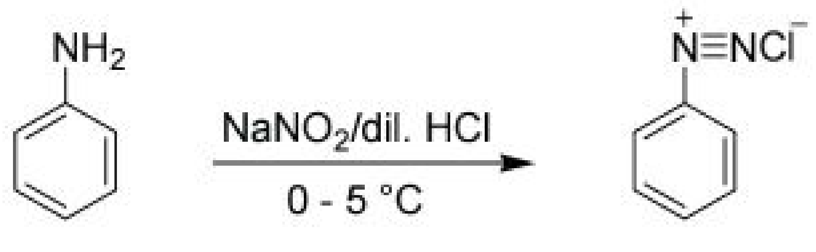
4.3 Reactions of aromatic diazonium salts

Aromatic amines such as aniline when reacted with nitrous acid ($NaNO_2$/HCl) give aromatic diazonium salts which undergo decomposition at room temperature to give phenols.



Aromatic diazonium salts are more stable than aliphatic diazonium salts. Therefore, when this reaction is carried out at low temperatures, the conversion of the aromatic diazonium salt to the phenol can be slowed down, and the diazonium salt can be isolated.

Therefore aromatic diazonium salts are prepared by the treatment of aromatic primary amines with an aqueous solution of $NaNO_2$ in the presence of dilute mineral acid such as dil. HCl or dil. H_2SO_4 at low temperature (0 – 5 °C). Since diazonium salts slowly decompose even at these temperatures, the solutions of diazonium salts are used immediately after preparation for any desired reaction.

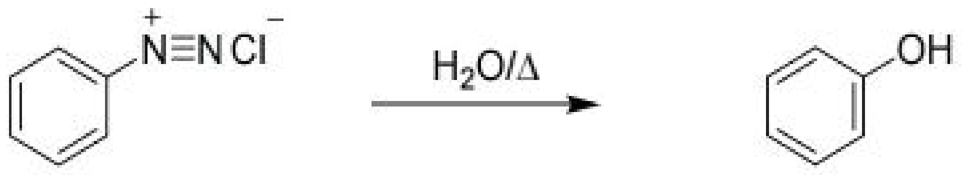


Diazonium salts undergo a large number of reactions. They can be divided into two classes: **replacement** of the diazonium group by another atom or a group; and **coupling** in which diazonium ion act as an electrophile and the nitrogen atoms are retained in the product.

4.3.1 Reactions in which the diazonium group is replaced by another atom or a group

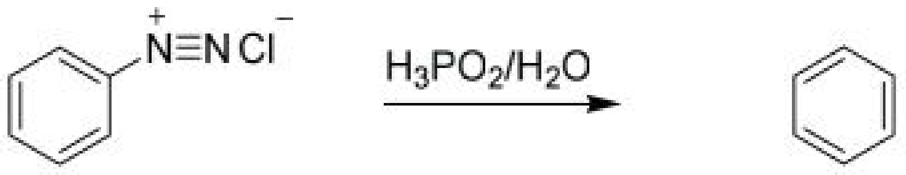
4.3.1.1 Reaction of diazonium salts with water

When aqueous solutions of diazonium salts are heated, phenols are formed.



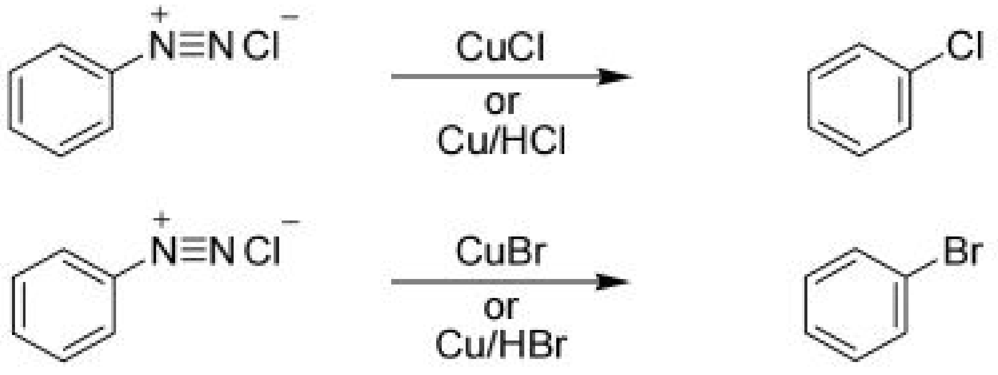
4.3.1.2 Reaction of diazonium salts with hypophosphorous acid (H_3PO_2)

When diazonium salts are treated with hypophosphorous acid (H_3PO_2), the diazonium group is replaced by an H atom.



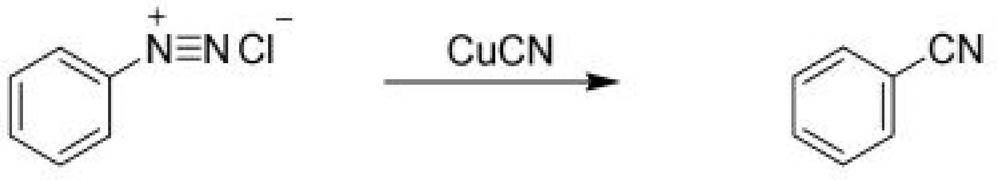
4.3.1.3 Reaction of diazonium salts with CuCl and CuBr

When diazonium salts are reacted with CuCl or CuBr, the corresponding aromatic halide is formed. This reaction can also be carried out with copper powder and hydrogen halide (Cu/HCl or HBr) instead of copper(I) halide.



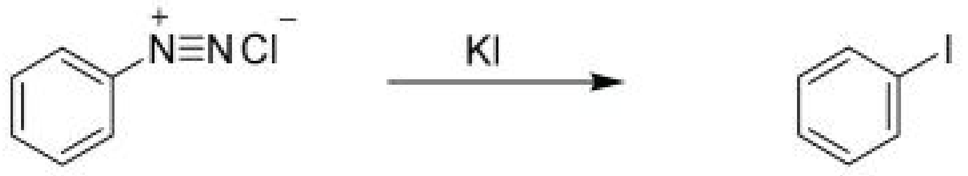
4.3.1.4 Reaction of diazonium salts with CuCN

When diazonium salts are reacted with CuCN, the diazonium group is replaced by CN group.



4.3.1.5 Reaction of diazonium salts with KI

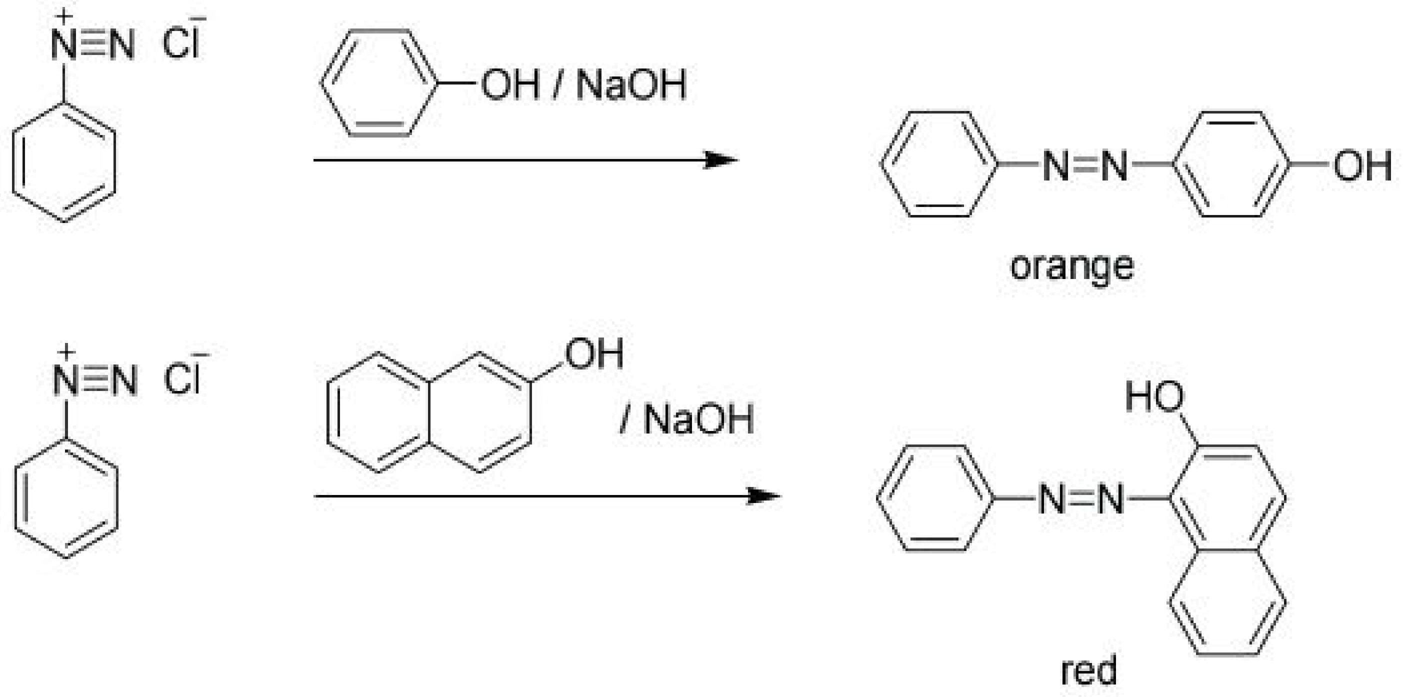
When diazonium salts are reacted with KI, the diazonium group is replaced by I.



4.3.2 Reactions in which the diazonium ion acts as an electrophile

Aryl diazonium ions can participate as electrophiles as it contains a positive charge on N. They react with phenols under alkaline conditions.

Benzene diazonium chloride reacts with phenol in the presence of aqueous NaOH to give an orange coloured compound, and with β-naphthol (2-naphthol) in the presence of aqueous NaOH to give a red coloured compound.



Reference:

Morrison, R. T. and Boyd, R. N. (2010) *Organic Chemistry*: Pearson.

Solomons, T. W. G. and Fryhle C. B. (2011) *Organic Chemistry*: John Wiley and Sons Inc.