# Revision Notes

# Class - 12 Chemistry

# Chapter 13 – Amines

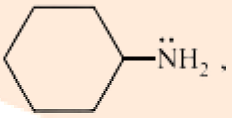
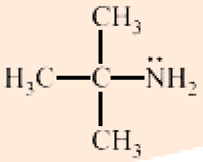
## Introduction

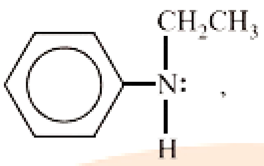
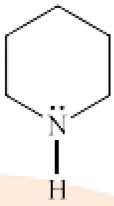
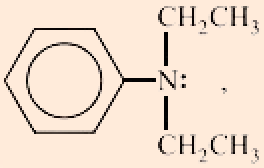
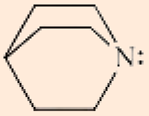
Amines are ammonia-based organic compounds that have one or more alkyl or aryl groups attached to the nitrogen atom. Amines play a variety of roles in living creatures, including bioregulation, neurotransmission, and predator protection. Many amines are employed as pharmaceuticals and treatments because of their great biological activity.

Alkaloids are a class of physiologically active amines that are primarily produced by plants to protect them from insects and other animals. Although some alkaloids are used medicinally (as pain relievers), they are all poisonous and can lead to death if consumed in high amounts.

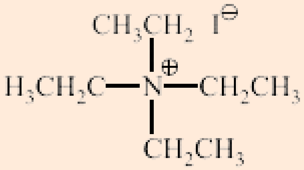
## Classification

Primary, secondary, and tertiary amines have one, two, or three alkyl or aryl groups linked to nitrogen, respectively.

| Type | Examples |
|---|---|
| Primary $(1^{\circ})$<br>$R-NH_2$ |  <br>Cyclohexylamine (1°) Tert-Butylamine (1°) |

| | |
|---|---|
| Secondary $(2^{\circ})$<br>$R_2NH$ |  N-Ethylaniline (2°)  Piperidine (2°) |
| Tertiary $(3^{\circ})$<br>$R_3N$ |  N, N-Diethylaniline (3°)  Quinuclidine (3°) |

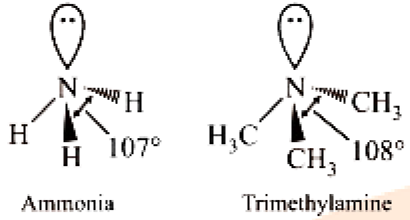
Four alkyl or aryl bonds connect a nitrogen atom in quaternary ammonium ions. Just like in simple ammonium salts like ammonium chloride, the nitrogen atom has a positive charge. An example of quaternary ammonium salt is as follows:



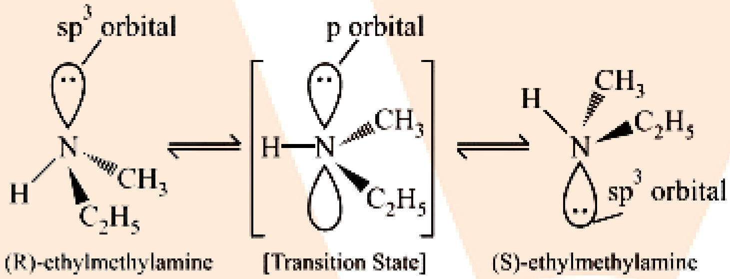
Tetraethylammonium Iodide

## Structure of Amines

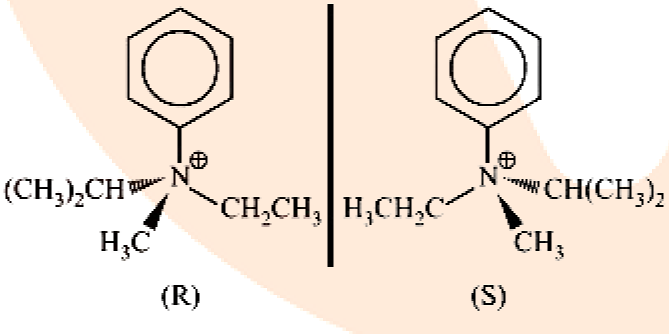
The tetrahedral geometry of ammonia is slightly deformed. One of the tetrahedral sites is occupied by a single pair of nonbonding electrons. The bulky lone pair compresses the $H-N-H$ bond angles to $107^{\circ}$ from the "ideal" $sp^3$ bond angle of $109.5^{\circ}$ in this geometry, which is represented by $sp^3$ hybridization of nitrogen. Because the bulky methyl groups expand the angle slightly, trimethylamine shows less compression.



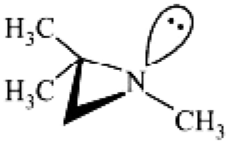
The mirror counterpart of a tetrahedral amine with three distinct substituents (including a lone pair) is non-superimposable. However, because the enantiomers interconvert rapidly, we cannot usually resolve such an amine into two enantiomers. The lone pair transfers from one face of the molecule to the other during this conversion, which is called nitrogen inversion.



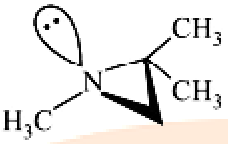
Inversion of configuration is not conceivable in quarterary ammonium salts with asymmetric nitrogen atoms because there is no lone pair to undergo nitrogen inversion.



Amines that are unable to achieve the $sp^2$ -hybrid transition state for nitrogen inversion exhibit chirality as well. If the nitrogen atom is enclosed in a tiny ring, for example, it is unable to achieve the $120^\circ$ bond angles that allow inversion to occur.



(R)-1,2,2-Trimethylaziridine



(S)-1,2,2-Trimethylaziridine

**Physical Properties**

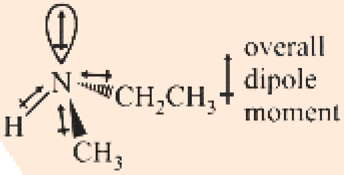
**1. State**

Lower aliphatic amines are gaseous compounds with a fishy odour. Primary amines with three or more carbon atoms are liquid, while those with more than three carbon atoms are solid.

Aniline and other aryl amines are generally colourless, but due to air oxidation, they become coloured over storage.

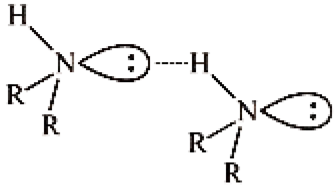
**2. Dipole Moment**

Because the significant dipole moment of the lone pair of electrons contributes to the dipole moments of the $C-H$ and $H-N$ bonds, amines are highly polar.

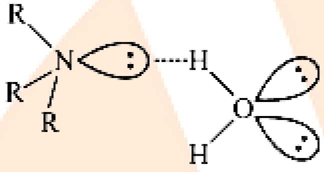


**3. Solubility**

$N-H$ bonds in primary and secondary amines allow them to create hydrogen bonds. Pure tertiary amines cannot form hydrogen bonds because they lack $N-H$ bonds. They can accept hydrogen bonds from molecules that have $O-H$ or $N-H$ bonds, though.



1° or 2° Amine:
Hydrogen Bond Donor and Acceptor



3° Amine:
Hydrogen Bond Acceptor only

As a result of their ability to establish hydrogen bonds with water, lower aliphatic amines are soluble in water. However, when the molar mass of amines increases, solubility decreases due to the increased size of the hydrophobic alkyl component. Higher amines are essentially water insoluble.

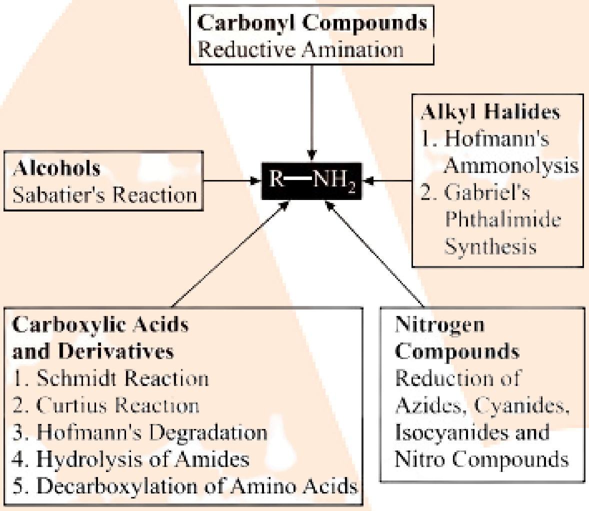
## 4. Boiling Point

The $N-H$ bond is less polar than the $O-H$ bond because nitrogen is less electronegative than oxygen. As a result, amines and alcohols with similar molecular weights form weaker hydrogen bonds. The boiling temperatures of primary and secondary amines are lower than those of alcohols, but higher than those of ethers with equal molecular weights. Tertiary amines have lower boiling temperatures than primary and secondary amines with equal molecular weights because they lack hydrogen bonds.

| **Compound** | **BP** $(^{\circ}C)$ | **Type** | **Molecular weight** |
|---|---|---|---|
| $(CH_3)_3N$ | 3 | Tertiary Amine | 59 |
| $CH_3-O-CH_2-CH_3$ | 8 | Ether | 60 |

| | | | |
|---|---|---|---|
| $CH_3-NH-CH_2-CH_3$ | 37 | Secondary Amine | 59 |
| $CH_3CH_2CH_2-NH_2$ | 48 | Primary Amine | 59 |
| $CH_3CH_2CH_2-OH$ | 97 | Alcohol | 60 |

## Preparation of Amines



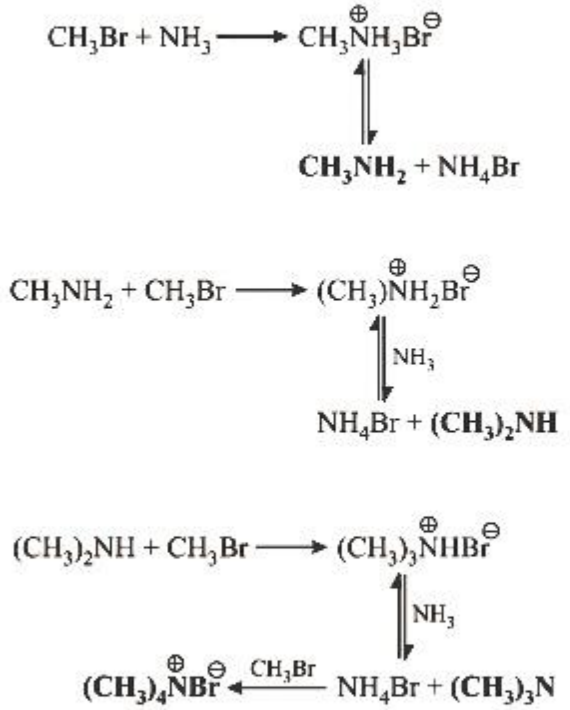
## Alkyl Halides

### Hoffmann's Ammonolysis Method

It's a case of ammonolysis. In a sealed tube, an alkyl halide and an ethanolic ammonia solution are heated to $100^\circ C$.

(a) A combination of goods is produced by the method.
(b) Tertiary alkyl halide isn't recommended because it produces an alkene.
(c) The reaction is initiated by a bimolecular substitution $(S_{N^2})$ .

### Example 1:



## Gabriel’s Phthalimide Synthesis

After treating phthalamide with **KOH, alkyl phthalamide is produced by heating potassium phthamide with alkyl halide. The hydrolysis that follows generates only primary amine. To improve the yield of primary amine, alkyl phthalamide is also treated with hydrazine.**

**Example 2:**

Grignard Reagent

The primary amine is obtained using the Grignard reagent or a trialkyl borane after chloramine treatment.

$RMgX + ClNH_2 \rightarrow R - NH_2 + MgXCl$

Alcohols

Sabatier Reaction

Under pressure, alcohols and ammonia are heated in the presence of a catalyst, such as copper chromite or alumina. It is possible to obtain a blend of items.

**Example 3:**

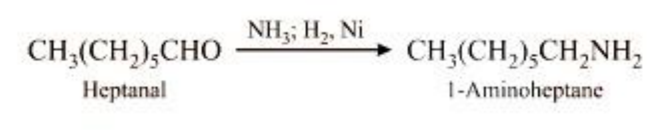
Carbonyl Compounds

Reductive Amination

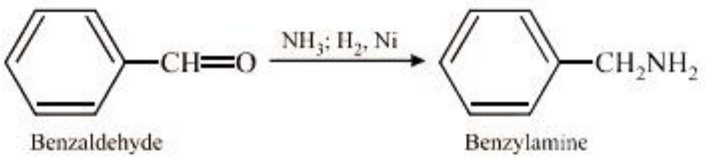
In the presence of ammonia, a number of aldehydes and ketones are reduced to amines.

The reduction process can be catalysed (hydrogen 20-150 atm over Raney nickel $40-150^{\circ}C$ or by use of sodium cyanohydridoborate, $NaBH_3CN$ ).

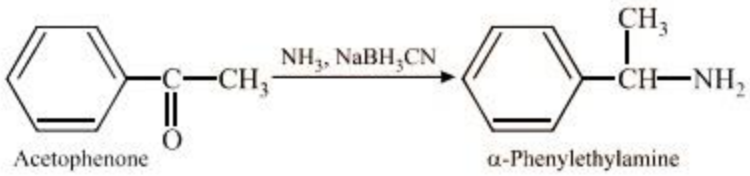
**Example 4:**



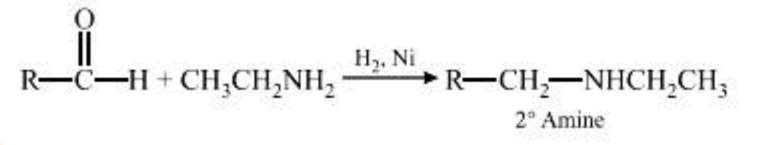
**Example 5:**



**Example 6:**



**Example 7:**



$$R-\overset{\overset{O}{\|}}{C}-H + CH_3CH_2NH_2 \xrightarrow{H_2,\ Ni} \underset{2^\circ\ Amine}{R-CH_2-NHCH_2CH_3}$$

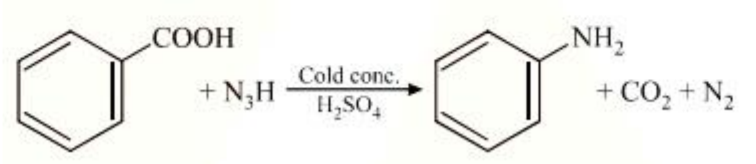
### Carboxylic Acids and Derivatives

### Schmidt Reaction

Primary amine is produced by treating a mixture of carboxylic acid and hydrazoic acid with cold concentrated sulphuric acid.

$$RCOOH + N_3H \xrightarrow[H_2SO_4]{Cold\ conc.} RNH_2 + CO_2 + N_2$$

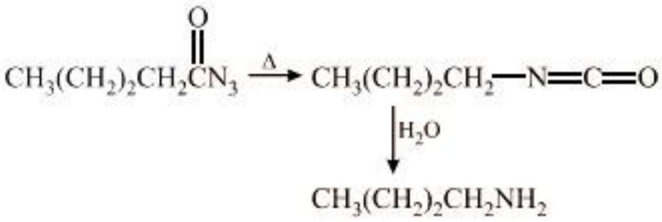
**Example 8:**



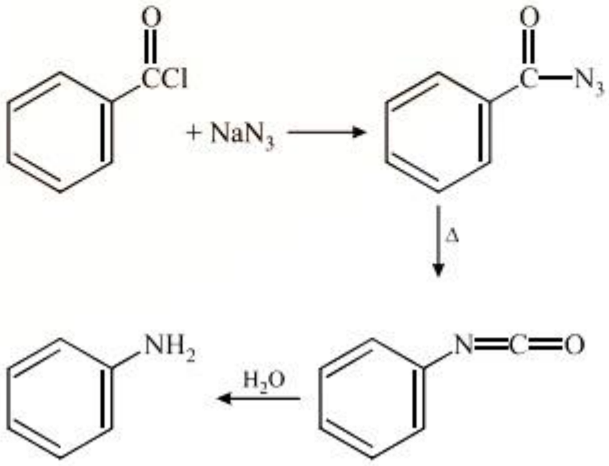
### Curtius Reaction

The acyl azide is pyrolyzed to create isocyanates in this process. As a result of the following hydrolysis, amine is produced.

**Example 9:**



**Example 10:**

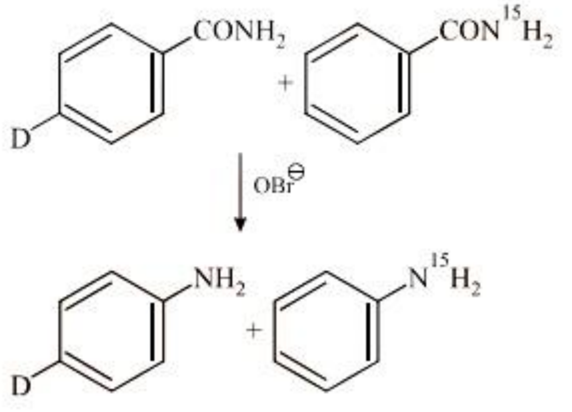


## Hofmann's Degradation of Amides

Bromine and a strong aqueous KOH or NaOH solution are used to warm the amide.

(a) The product is a primary amine with one less carbon than amide.
(b) The intermediate is alkyl isocyanate, and the rearrangement is intramolecular.

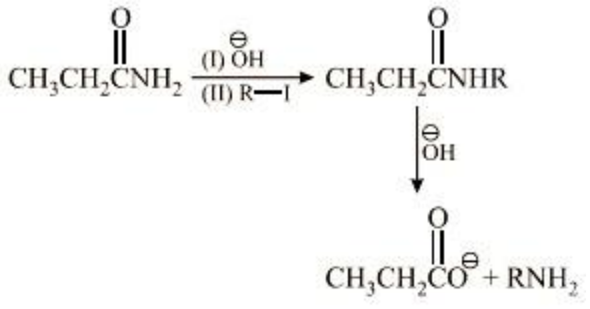
**Example 11:**



## Hydrolysis of Amides and Isocyanides

Primary amine is given on the hydrolysis of N-substituted amide and isocyanide.

### Example 12:



### Example 13:

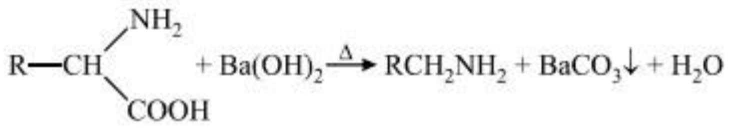
$$R-NC\xrightarrow[\Delta]{KOH,\,H_2O}R-NH_2+HCOOK$$

Hydrolysis of Isocyantes also yields amines.

$$R-N=C=O\xrightarrow[\Delta]{H_3O^+}R-NH_2$$

## Decarboxylation of Amino Acids

When amino acids are heated with barium hydroxide, primary amine is produced. If there is no $\beta$ -hydrogen in the alkyl group, quaternary ammonium hydroxide decomposes into alcohol on heating, but if there is $\beta$ -hydrogen, Hofmann elimination occurs.



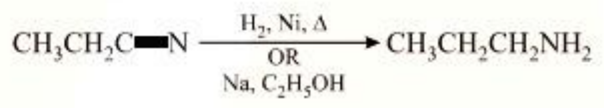
$$R-CH(NH_2)(COOH) + Ba(OH)_2 \xrightarrow{\Delta} RCH_2NH_2 + BaCO_3\downarrow + H_2O$$

## Nitrogen Compounds

### Reduction of Cyanides, Isocyanides, Oximes, Imines

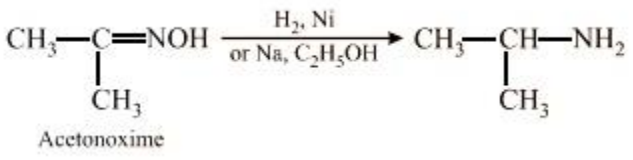
Nitrile $(-CN)$ , oxime $(=NOH)$ , imine $(=NH)$ , enamine etc, on catalytic reduction with $H_2$ , nickel gives corresponding amine.

**Example 14:**



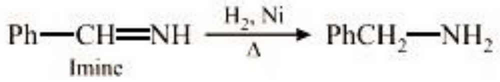
$$CH_3CH_2C\equiv N \xrightarrow[\text{Na, } C_2H_5OH]{H_2\text{, Ni, }\Delta \text{ OR}} CH_3CH_2CH_2NH_2$$

**Example 15:**



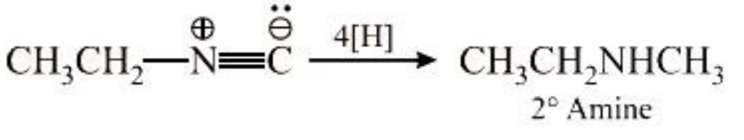
$$\underset{\text{Acetonoxime}}{CH_3-C(CH_3)=NOH} \xrightarrow[\text{or Na, } C_2H_5OH]{H_2\text{, Ni}} CH_3-CH(CH_3)-NH_2$$

**Example 16:**



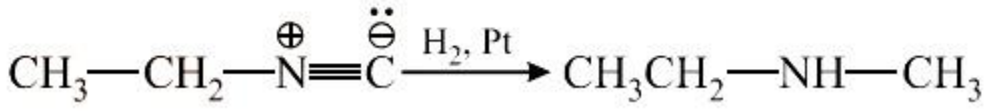
$$\underset{\text{Imine}}{Ph{-}CH{=}NH} \xrightarrow[\Delta]{H_2,\ Ni} PhCH_2{-}NH_2$$

**Example 17:**



$$CH_3CH_2{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{\ddot{C}} \xrightarrow{4[H]} \underset{2^\circ\ \text{Amine}}{CH_3CH_2NHCH_3}$$

**Example 18:**



$$CH_3{-}CH_2{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{\ddot{C}} \xrightarrow{H_2,\ Pt} CH_3CH_2{-}NH{-}CH_3$$

## Reduction of Nitro Compounds

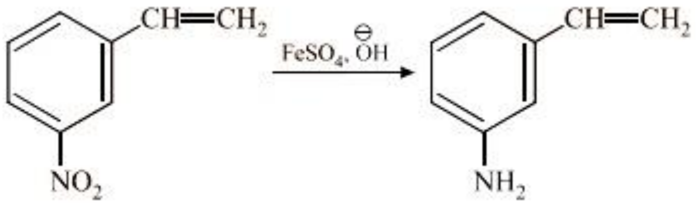
NItroalkanes are commonly converted to amines using tin and hydrochloric acid or lithium aluminium hydride. For such a reduction, $H_2$ and a catalyst are also used.

**Example 19:**

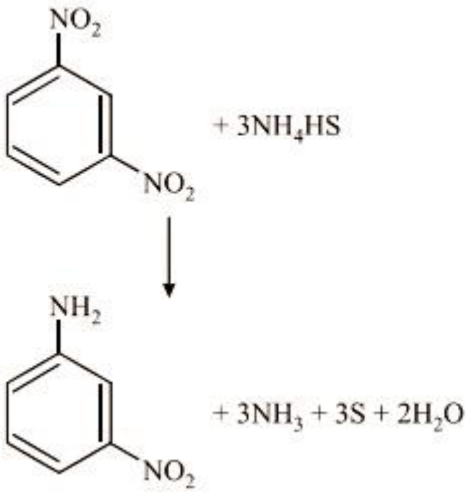
$$CH_3CH_2NO_2 + 6[H] \xrightarrow{Sn,\ HCl} CH_3CH_2NH_2$$

$$CH_3CH_2NO_2 + 3H_2 \xrightarrow{Pt} CH_3CH_2NH_2$$

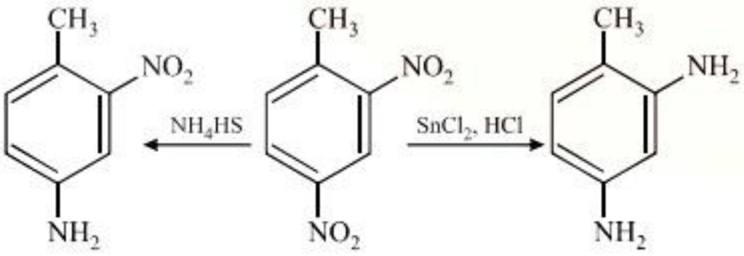
**Example 20:**



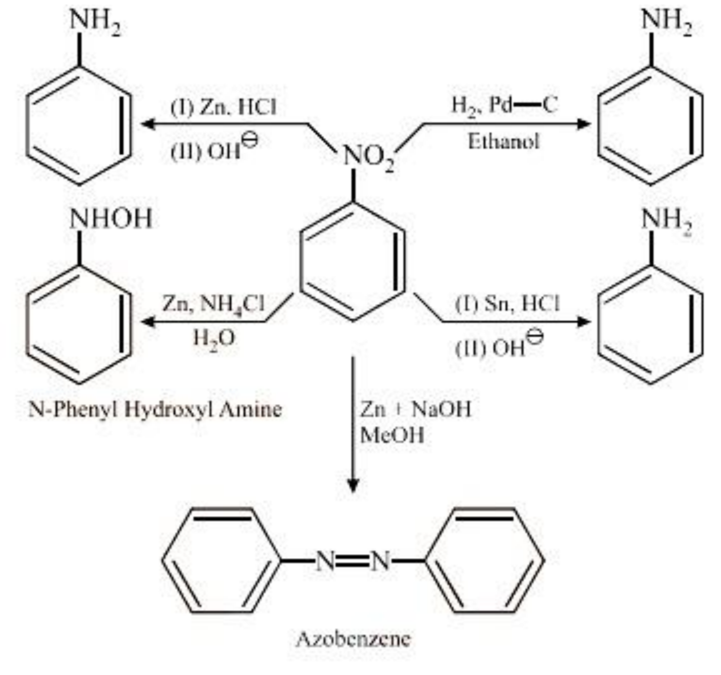
## Example 21:



## Example 22:



## Example 23:



**Reactions of Amines**

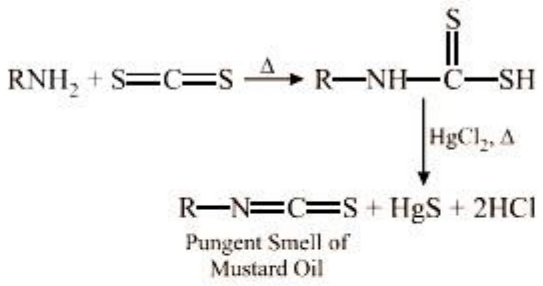
**Sulphonylation – Hinsberg Test**

Treatment with benzene sulphonyl chloride (Hinsberg reagent) or p-toluene sulphonyl chloride.

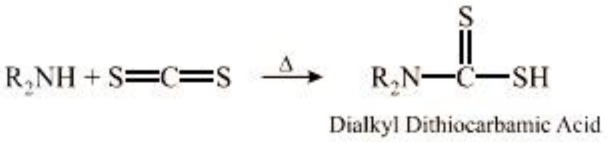
(a) The reaction is used to separate the amine mixture.

(b) $1^\circ$ and $2^\circ$ amine, due to the presence of active hydrogen react and give corresponding sulphonamide while $3^\circ$ amine does not react.

(c) $1^\circ$ amine product N-alkyl benzene sulphonamide is soluble in KOH forming a water-soluble salt.



$$RNH_2 + S{=}C{=}S \xrightarrow{\Delta} R{-}NH{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SH \xrightarrow{HgCl_2,\ \Delta} R{-}N{=}C{=}S + HgS + 2HCl$$

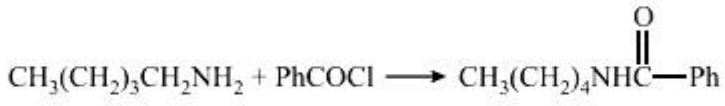


$$R_2NH + S{=}C{=}S \xrightarrow{\Delta} R_2N{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SH$$

## Acylation

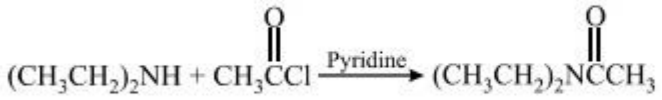
N-substituted amide is formed when primary and secondary amines react with acid halide or anhydride. The reaction is used to protect the ring in aniline.

### Example 27:



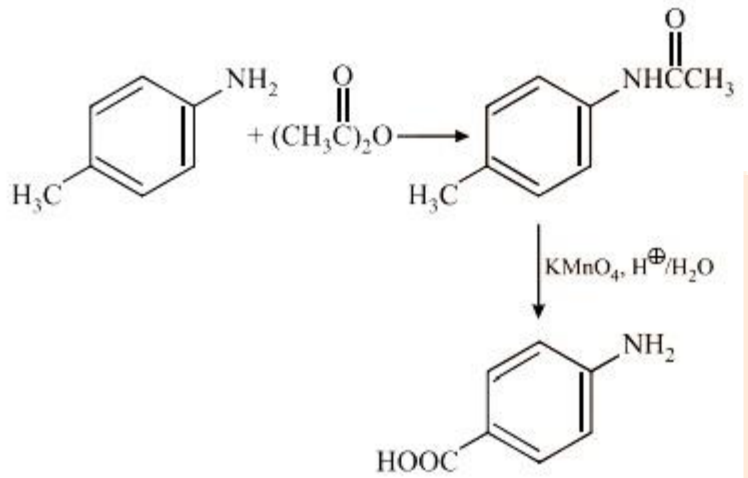
$$CH_3(CH_2)_3CH_2NH_2 + PhCOCl \longrightarrow CH_3(CH_2)_4NH\overset{\overset{\displaystyle O}{\|}}{C}{-}Ph$$

### Example 28:

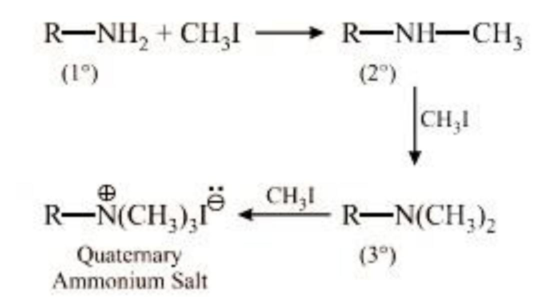


$$(CH_3CH_2)_2NH + CH_3\overset{\overset{\displaystyle O}{\|}}{C}Cl \xrightarrow{\text{Pyridine}} (CH_3CH_2)_2N\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

### Example 29:

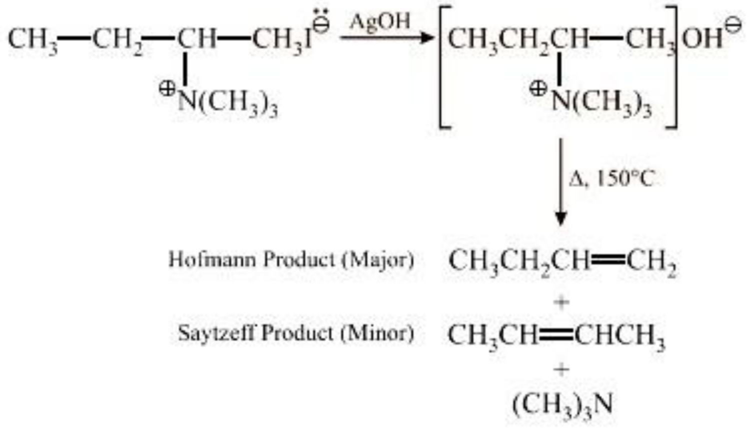


## Hofmann’s Exhaustive Methylation and Elimination

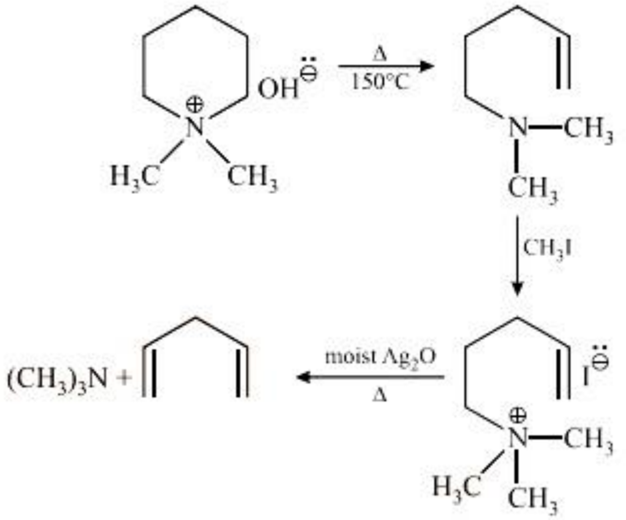


With damp $Ag_2O$ , quaternary ammonium iodides are transformed to hydroxides. Heat causes the hydroxide to be eliminated, resulting in tertiary amines and alkenes. The fact that the least substituted alkene is the primary product is a significant component of this elimination. Hofmann's Elimination is the name given to this process.

**Example 30:**



## Example 31:



## Metal Ions

Amines form coordination compounds with metal ions.

## Example 32:

$$AgCl \longrightarrow [Ag(CH_3NH_2)_2]^{\oplus}Cl^{\ominus}$$

Soluble Complex

$$Cu^{2\oplus} \longrightarrow [Cu(CH_3NH_2)_2]^{2\oplus}$$

Deep Blue Complex

## Preparation of Aromatic Amines

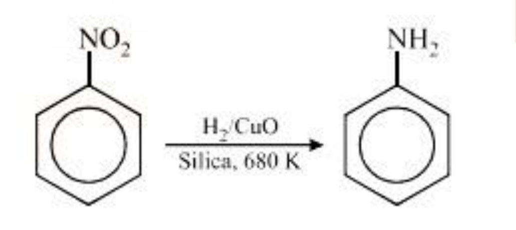
Besides the methods in the preparation of aliphatic amines, following methods can also be used.

### Reduction of Nitro Compounds

### Vapour – Phase Reduction

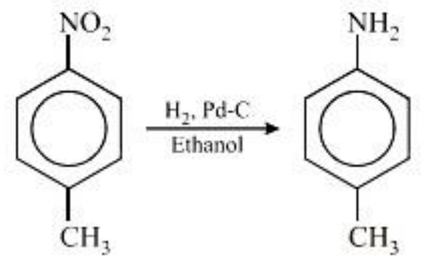
The reducing agents used were: CuO on $SiO_2$ or $V-Pt$ Catalyst.

**Example 33:**

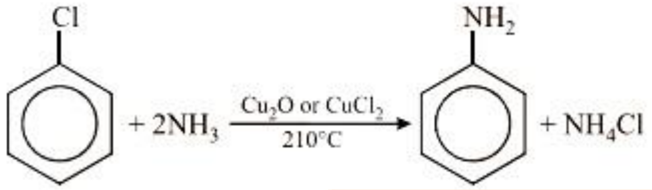


### Catalytic Hydrogenation

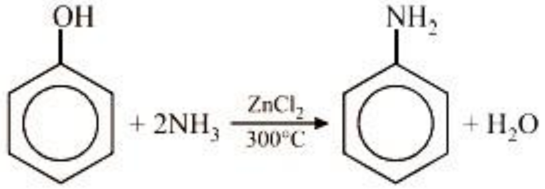
The reducing agents used were $H_2, Pd-C/Et-OH$



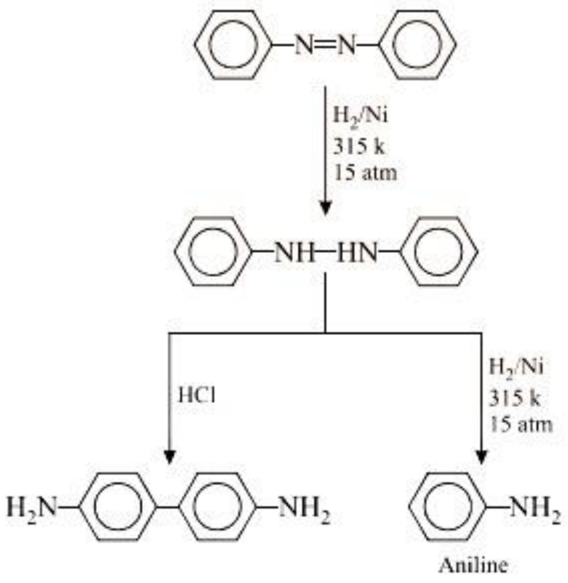
### Ammonolysis of Aryl Halides



## Phenol and Ammonia

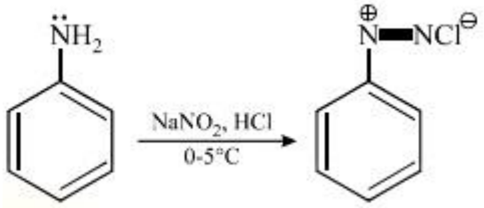


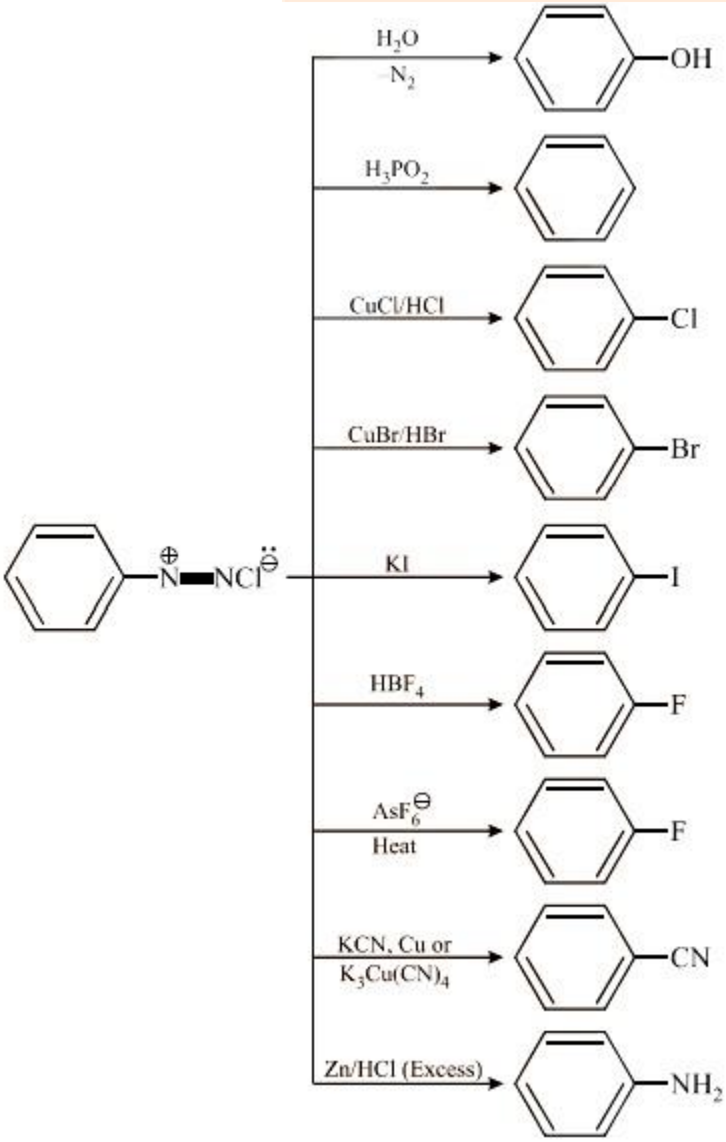
## Reduction of Azo Compounds

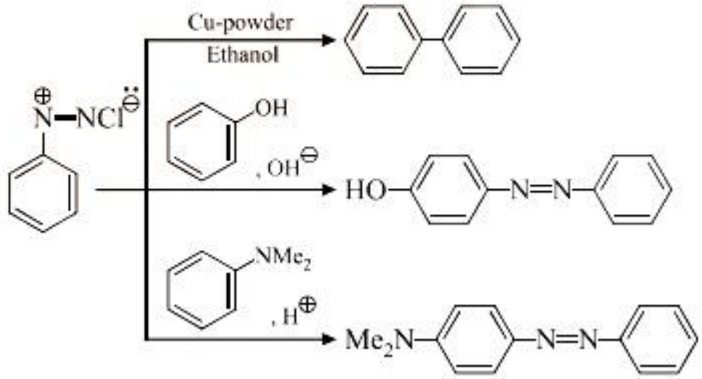


## Reactions of Aromatic Amines

## Diazonium Salt and Reactions


$\ddot{N}H_2$
NaNO$_2$, HCl
0-5°C
$\overset{\oplus}{N}$≡NCl$^{\ominus}$

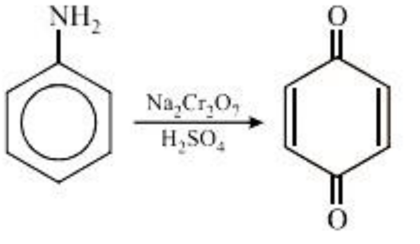

$\overset{\oplus}{N}$≡NCl$^{\ominus}$
$H_2O$
$-N_2$
OH
$H_3PO_2$
CuCl/HCl
Cl
CuBr/HBr
Br
KI
I
$HBF_4$
F
$AsF_6^{\ominus}$
Heat
F
KCN, Cu or
$K_3Cu(CN)_4$
CN
Zn/HCl (Excess)
$NH_2$



## Oxidation

Depending on the conditions, aromatic amines are easily oxidised to a variety of compounds. Aniline is converted to p-benzoquinone through controlled oxidation with $Na_2Cr_2O_7$ and $H_2SO_4$ . In fact, p-benzoquinone is generated when a substance is exposed to air.

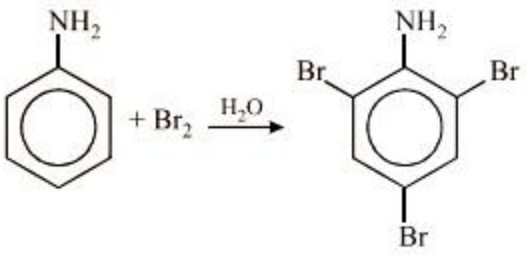
If oxidation is not controlled, aniline black, a black dye, is produced.



(Brown Colour)

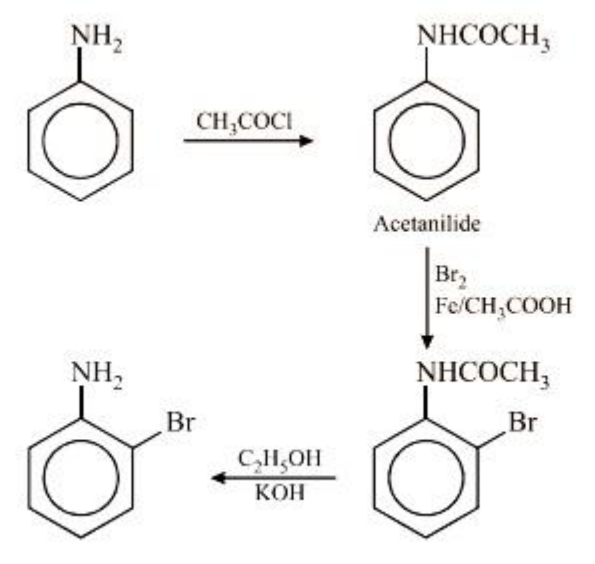
## Halogenation

The amine group $(NH_2)$ is a powerful activator and ortho/para director. On typical bromination in $H_2O$ , it generated 2,4, 6-tribromo aniline.



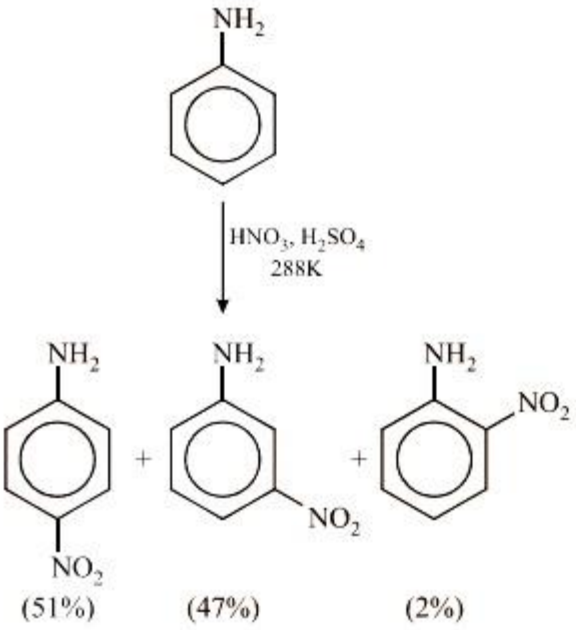
The $-NHCOCH_3$ group is a mild ortho and para director, and it can be used to make ortho and para derivatives by reducing the activating power of amino groups by acetylation of aniline.

### Example 34:

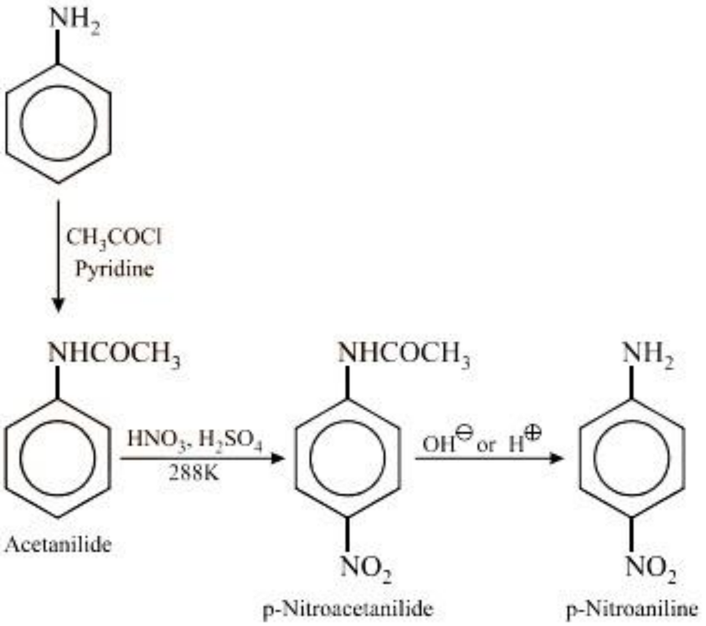


### Nitration

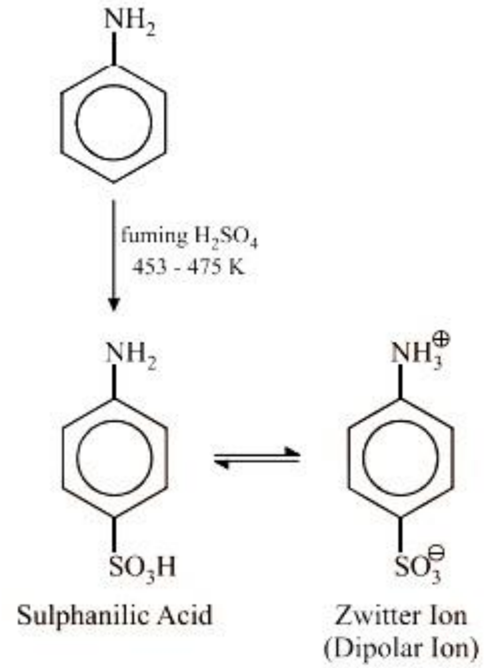
Because the nitrating mixture is oxidising and $NH_2$ is a strong activating group, typical nitration of aniline is not done. Furthermore, at 288 K, aniline is protonated to generate the meta-directing anilinium ion. As a result, in addition to ortho and para derivatives, a considerable number of meta derivatives are generated.



The nitration reaction can be regulated and the p-nitro derivative obtained as the primary product by shielding the $-NH_2$ group with an acetylation reaction with acetic anhydride.



## Sulphonation



**Note:** Normally, the $-NH_2$ group linked to benzene is incapable of forming the zwitter ion, but $-SO_3H$ is extremely acidic. As a result, sulphanilic acid produces the zwitter ion. When the $-NH_2$ group is linked to benzoic acid in any location, for example, no zwitter ion is generated.

## Analysis of Amines

Amines are distinguished primarily by their basicity. An amine is nearly often a water-insoluble chemical that dissolves in cold dilute hydrochloric acid or a water-soluble compound whose aqueous solution colours litmus blue. The Hinsberg test is the best way to determine whether an amine is primary, secondary, or tertiary. In the presence of aqueous potassium hydroxide, the amine is shaken with benzenesulfonyl chloride. Substituted sulfonamides are formed by primary and secondary amines, but not by tertiary amines. A primary amine's monosubstituted sulfonamide has an acidic hydrogen linked to nitrogen. This amide is converted to a soluble salt by reacting with potassium hydroxide. Because there is no acidic hydrogen in the disubstituted sulfonamide from a secondary amine, it is insoluble in the alkaline reaction mixture. The way an amine reacts to nitrous acid can help determine its classification. Primary aromatic amines, in particular, have a distinct behaviour:

treatment with nitrous acid transforms them to diazonium salts, which generate brightly coloured azo compounds when treated with beta-naphthol.