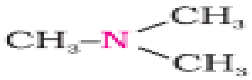
Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among proteins, vitamins, alkaloids and hormones. Synthetic examples include polymers, dyestuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes. In this Unit, you will learn about amines and diazonium salts.

I. AMINES

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.

For example:

$CH_3{-}NH_2$, $C_6H_5{-}NH_2$, $CH_3{-}NH{-}CH_3$,



$CH_3{-}N\begin{matrix}CH_3\\CH_3\end{matrix}$

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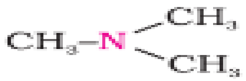
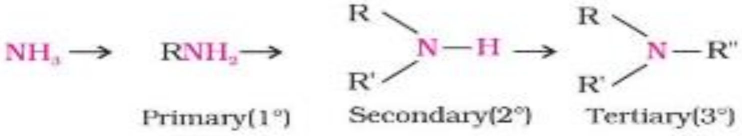


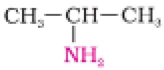
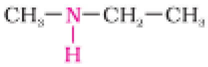
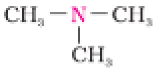
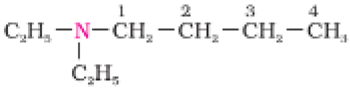
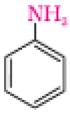
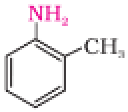
$CH_3{-}N\begin{matrix}CH_3\\CH_3\end{matrix}$

Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule. If one hydrogen atom of ammonia is replaced by R or Ar , we get RNH_2 or $ArNH_2$, a primary amine (1°). If two hydrogen atoms of ammonia or one hydrogen atom of $R\text{-}NH_2$ are replaced by another alkyl/aryl(R') group, what would you get? You get R-NHR', secondary amine. The second alkyl/aryl group may be same or different. Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine. Amines are said to be 'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.



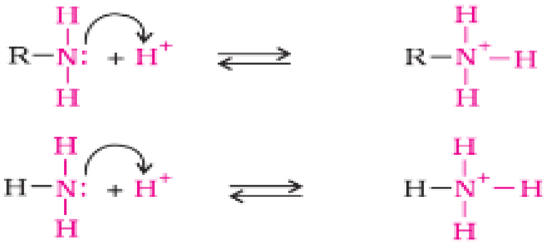
In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word (e.g., methylamine). In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group. In IUPAC system, amines are named as **alkanamines**, derived by replacement of 'e' of alkane by the word amine. For example, CH_3NH_2 is named as methanamine. In case, more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to the carbon atoms bearing $-NH_2$ groups and suitable prefix such as di, tri, etc. is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained. For example, $H_2N\text{–}CH_2\text{–}CH_2\text{–}NH_2$ is named as ethane-1, 2-diamine.

Table 13.1: Nomenclature of Some Alkylamines and Arylamines

Amine	Common name	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	*n*-Propylamine	Propan-1-amine
 $CH_3-\underset{\underset{\displaystyle NH_2}{\vert}}{CH}-CH_3$	Isopropylamine	Propan-2-amine
 $CH_3-\underset{\underset{\displaystyle H}{\vert}}{N}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
 $CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{N}-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
 $C_2H_5-\underset{\underset{\displaystyle C_2H_5}{\vert}}{N}-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3}$	*N,N*-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{CH_2}-\overset{2}{CH}=\overset{3}{CH_2}$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Aminotoluene

(a) Alkanamines versus ammonia

Let us consider the reaction of an alkanamine and ammonia with a proton to compare their basicity.

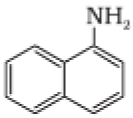


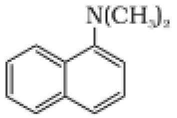
$$R-\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{N}}}: + H^+ \rightleftharpoons R-\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{N^+}}}-H$$

$$H-\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{N}}}: + H^+ \rightleftharpoons H-\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{N^+}}}-H$$

Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia. Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups. This trend is followed in the gaseous phase. The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH_3. The trend is not regular in the aqueous

13.1 Classify the following amines as primary, secondary or tertiary:

(i)


(ii)


(iii) $(C_2H_5)_2CHNH_2$

(iv) $(C_2H_5)_2NH$

13.2 (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.

(ii) Write IUPAC names of all the isomers.

(iii) What type of isomerism is exhibited by different pairs of amines?

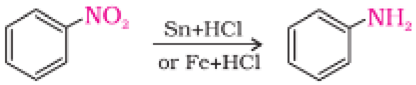
Preparation of Amines

Amines are prepared by the following methods:

1. *Reduction of nitro compounds*

Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.

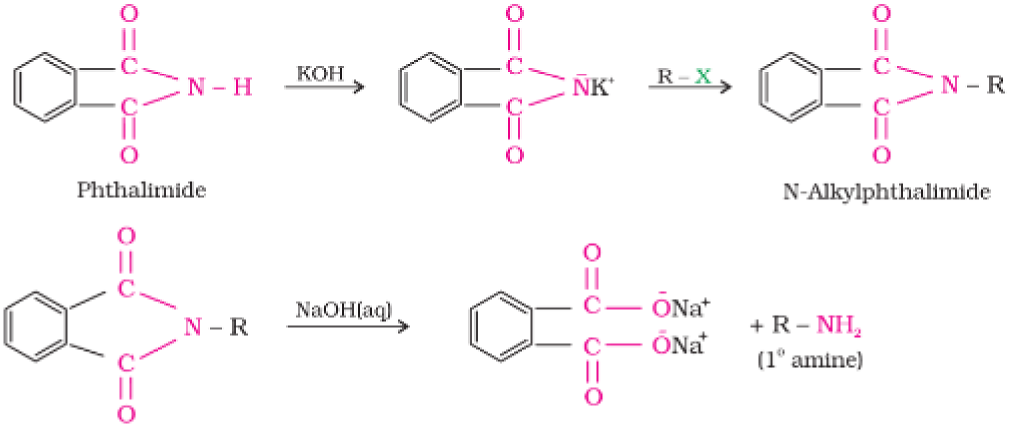
(i)


(ii)


Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

5. *Gabriel phthalimide synthesis*

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



6. *Hoffmann bromamide degradation reaction*

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.

$$R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Example 13.2 Write chemical equations for the following conversions:

(i) $CH_3–CH_2–Cl$ into $CH_3–CH_2–CH_2–NH_2$

(ii) $C_6H_5–CH_2–Cl$ into $C_6H_5–CH_2–CH_2–NH_2$

Solution

(i) $$\underset{\text{Chloroethane}}{CH_3–CH_2–Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\text{Propanenitrile}}{CH_3–CH_2–C\equiv N} \xrightarrow{\text{reduction}} \underset{\text{Propan-1-amine}}{CH_3–CH_2–CH_2–NH_2}$$

(ii) $$\underset{\substack{\text{Chlorophenylmethane}\\\text{(Benzyl chloride)}}}{C_6H_5–CH_2–Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\substack{\text{Phenylethanenitrile}\\\text{(Benzyl cyanide)}}}{C_6H_5–CH_2–C\equiv N} \xrightarrow{H_2/Ni} \underset{\text{2-Phenylethanamine}}{C_6H_5–CH_2–CH_2–NH_2}$$

Example 13.3

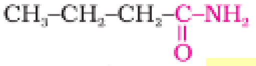
Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

Solution

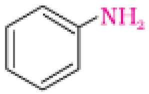
(i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



$$CH_3–CH_2–CH_2–\underset{\underset{\displaystyle O}{||}}{C}–NH_2$$

Butanamide

(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



Aniline or benzenamine

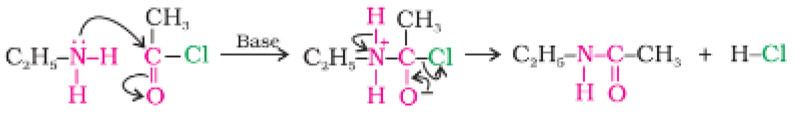
Intext Question

13.3 How will you convert

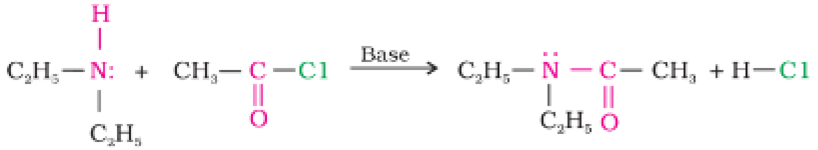
(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline

(iii) $Cl–(CH_2)_4–Cl$ into hexan-1,6-diamine?

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. You can consider this reaction as the replacement of hydrogen atom of $-NH_2$ or $>N-H$ group by the acyl group. The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.

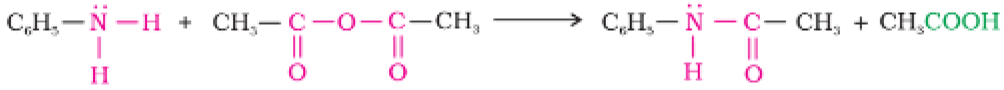


Ethanamine N-Ethylethanamide



$$C_2H_5-\underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{N}}: + CH_3-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{Base} C_2H_5-\underset{\underset{C_2H_5}{|}}{\ddot{N}}-\underset{\underset{O}{\|}}{C}-CH_3 + H-Cl$$

N-Ethylethanamine N,N-Diethylethanamide



$$C_6H_5-\underset{\underset{H}{|}}{\ddot{N}}-H + CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow C_6H_5-\underset{\underset{H}{|}}{\ddot{N}}-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3COOH$$

Benzenamine Ethanoic anhydride N-Phenylethanamide or Acetanilide

Amines also react with benzoyl chloride (C_6H_5COCl). This reaction is known as benzoylation.

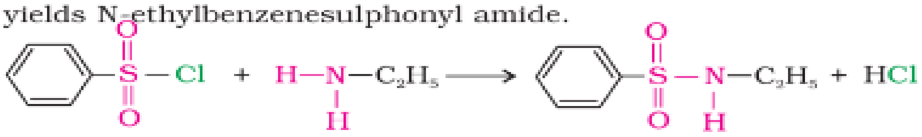
$$CH_3NH_2 + C_6H_5COCl \rightarrow CH_3NHCOC_6H_5 + HCl$$

Methanamine Benzoyl chloride N – Methylbenzamide

6. Reaction with arylsulphonyl chloride

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

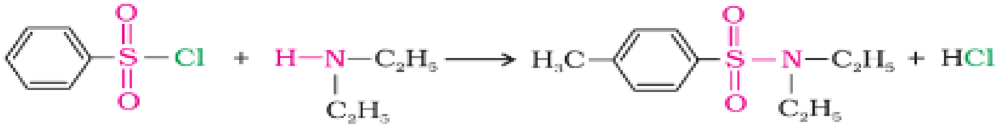
(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.



N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide is formed.



N,N-Diethylbenzenesulphonamide

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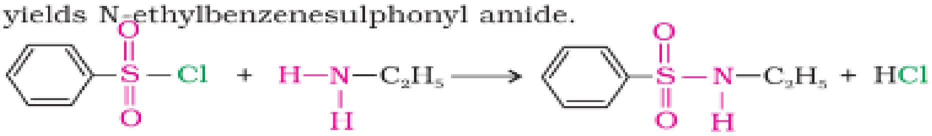

N-Ethylbenzenesulphonamide
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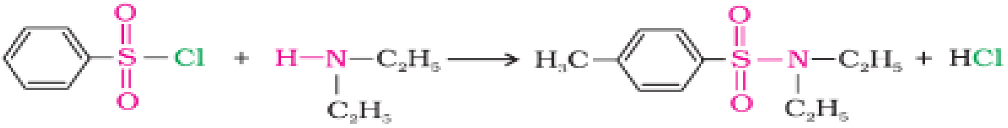
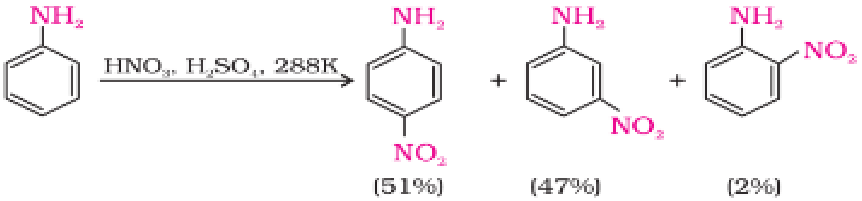
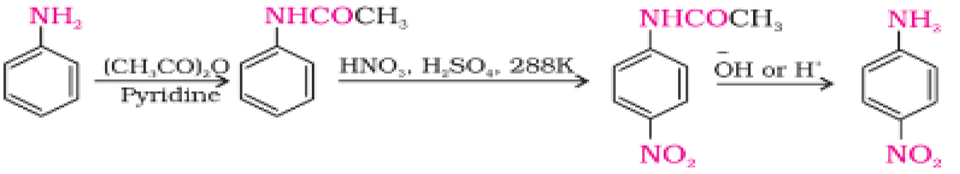


N,N-Diethylbenzenesulphonamide

(b) Nitration: Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.

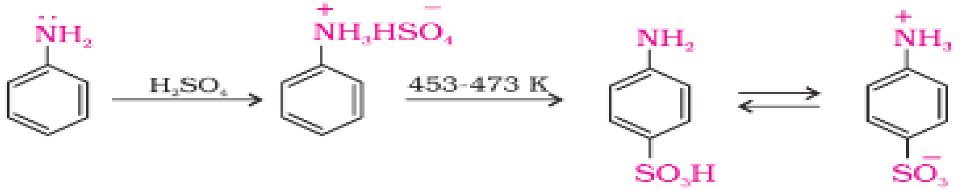


However, by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.



Acetanilide *p*-Nitroacetanilide *p*-Nitroaniline

(c) ***Sulphonation:*** Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.



Anilinium hydrogensulphate

Sulphanilic acid

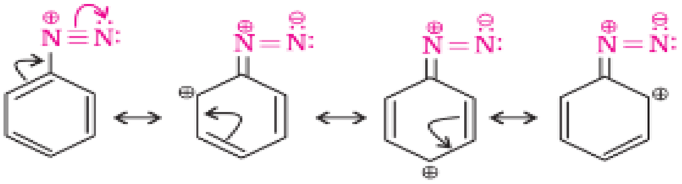
Zwitter ion

Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

II. DIAZONIUM SALTS

The diazonium salts have the general formula $R\overset{+}{N}_2\overset{-}{X}$ where R stands for an aryl group and $\overset{-}{X}$ ion may be Cl^- Br^-, HSO_4^-, BF_4^-, etc. They are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc. The $\overset{+}{N}_2$ group is called diazonium group. For example, $C_6H_5\overset{+}{N}_2\overset{-}{Cl}$ is named as benzenediazonium chloride and $C_6H_5N_2^+HSO_4^-$ is known as benzenediazonium hydrogensulphate.

Primary aliphatic amines form highly unstable alkyldiazonium salts (refer to Section 13.6). Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.



Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as **diazotisation**. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2Cl + NaCl + 2H_2O$$

$$\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{Cl}} + \mathrm{H_3PO_2} + \mathrm{H_2O} \longrightarrow \mathrm{ArH} + \mathrm{N_2} + \mathrm{H_3PO_3} + \mathrm{HCl}$$

$$\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{Cl}} + \mathrm{CH_3CH_2OH} \longrightarrow \mathrm{ArH} + \mathrm{N_2} + \mathrm{CH_3CHO} + \mathrm{HCl}$$

5. *Replacement by hydroxyl group*: If the temperature of the diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolysed to phenol.

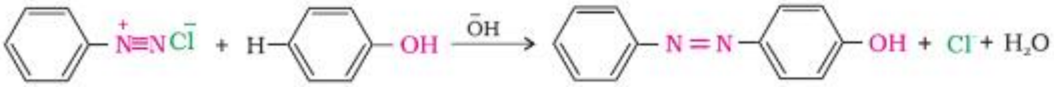
$$\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{Cl}} + \mathrm{H_2O} \longrightarrow \mathrm{ArOH} + \mathrm{N_2} + \mathrm{HCl}$$

6. *Replacement by $-NO_2$ group*: When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-NO_2$ group.

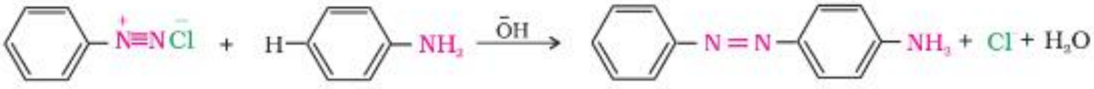
B. Reactions involving retention of diazo group

coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields *p*-aminoazobenzene. This is an example of electrophilic substitution reaction.



p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene (yellow dye)

13.10 Importance of Diazonium Salts in Synthesis of Aromatic Compounds

From the above reactions, it is clear that the diazonium salts are very good intermediates for the introduction of –F, –Cl, –Br, –I, –CN, –OH, $-NO_2$ groups into the aromatic ring.

Aryl fluorides and iodides cannot be prepared by direct halogenation. The cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but cyanobenzene can be easily obtained from diazonium salt.

13.5 How will you convert:

- (i) Ethanoic acid into methanamine
- (ii) Hexanenitrile into 1-aminopentane
- (iii) Methanol to ethanoic acid
- (iv) Ethanamine into methanamine
- (v) Ethanoic acid into propanoic acid
- (vi) Methanamine into ethanamine
- (vii) Nitromethane into dimethylamine
- (viii) Propanoic acid into ethanoic acid?

13.6 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

13.7 Write short notes on the following:

- (i) Carbylamine reaction
- (ii) Diazotisation
- (iii) Hofmann's bromamide reaction
- (iv) Coupling reaction
- (v) Ammonolysis
- (vi) Acetylation
- (vii) Gabriel phthalimide synthesis.

13.8 Accomplish the following conversions:

- (i) Nitrobenzene to benzoic acid
- (ii) Benzene to *m*-bromophenol
- (iii) Benzoic acid to aniline
- (iv) Aniline to 2,4,6-tribromofluorobenzene
- (v) Benzyl chloride to 2-phenylethanamine
- (vi) Chlorobenzene to *p*-chloroaniline
- (vii) Aniline to *p*-bromoaniline
- (viii) Benzamide to toluene
- (ix) Aniline to benzyl alcohol.

13.9 Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

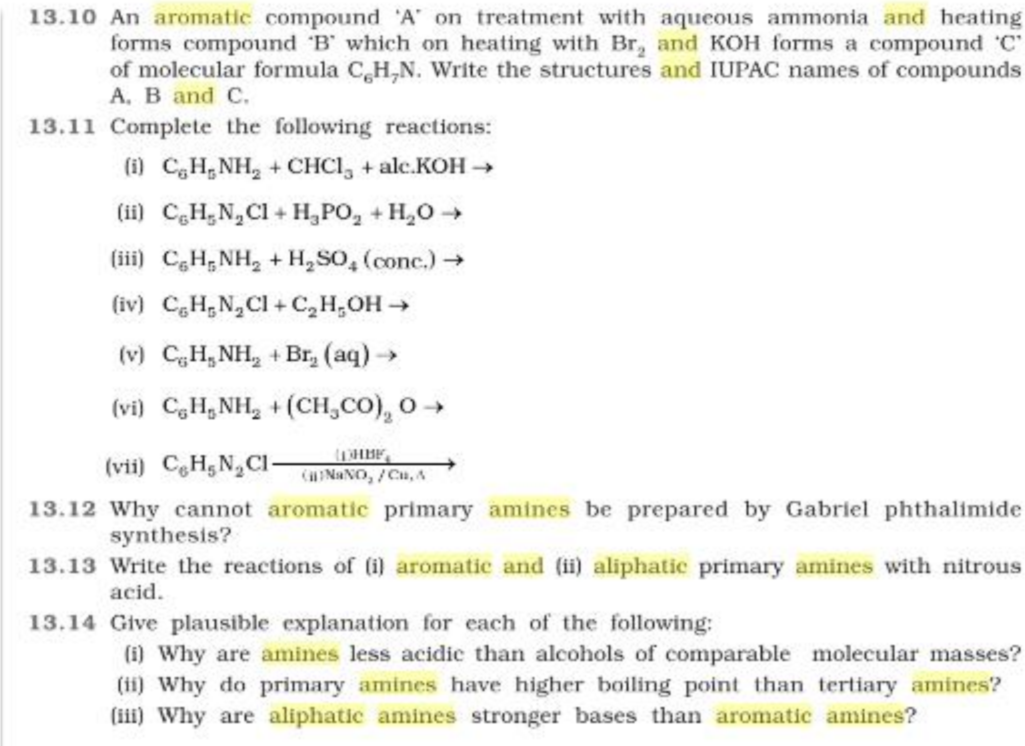
(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O / H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(iv) $C_6H_5NO_2 \xrightarrow{Fe / HCl} A \xrightarrow[273\,K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O / H^+} C$

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2 / HCl} C$

(vi) $C_6H_5NO_2 \xrightarrow{Fe / HCl} A \xrightarrow[273\,K]{HNO_2} B \xrightarrow{C_6H_5OH} C$



13.10 An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

13.11 Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4\,(conc.) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2\,(aq) \rightarrow$

(vi) $C_6H_5NH_2 + (CH_3CO)_2\,O \rightarrow$

(vii) $C_6H_5N_2Cl \xrightarrow[(ii)\,NaNO_2\,/\,Cu,\,\Delta]{(i)\,HBF_4}$

13.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

13.13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

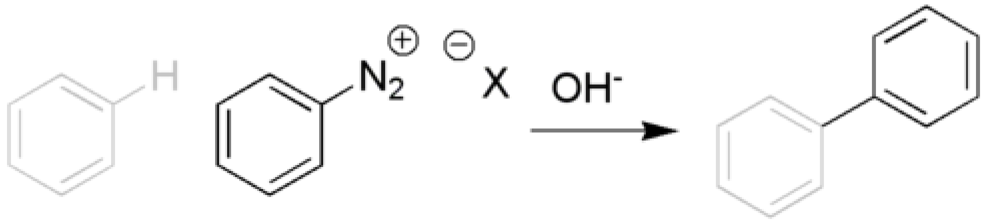
13.14 Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

The **Gomberg–Bachmann reaction**, named for the Russian-American chemist Moses Gomberg and the American chemist Werner Emmanuel Bachmann, is an aryl-aryl coupling reaction via a diazonium salt.[1][2][3]



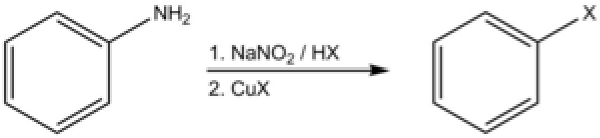
1 **2** **3**

The arene compound **1** (here benzene) is coupled with base with the diazonium salt **2** to the biaryl **3** through an intermediate aryl radical. For example, *p*-bromobiphenyl may be prepared from 4-bromoaniline and benzene:[4]

$$BrC_6H_4NH_2 + C_6H_6 \rightarrow BrC_6H_4{-}C_6H_5$$

The reaction offers a wide scope for both diazonium component and arene component but yields are generally low following the original procedure (less than 40%), given the many side-reactions of diazonium salts. Several improvements have been suggested. One possibility is to employ diazonium tetrafluoroborates in arene solvent together with a phase-transfer catalyst,[5] another is to use 1-aryl-3,3-dialkyltriazenes.[6]

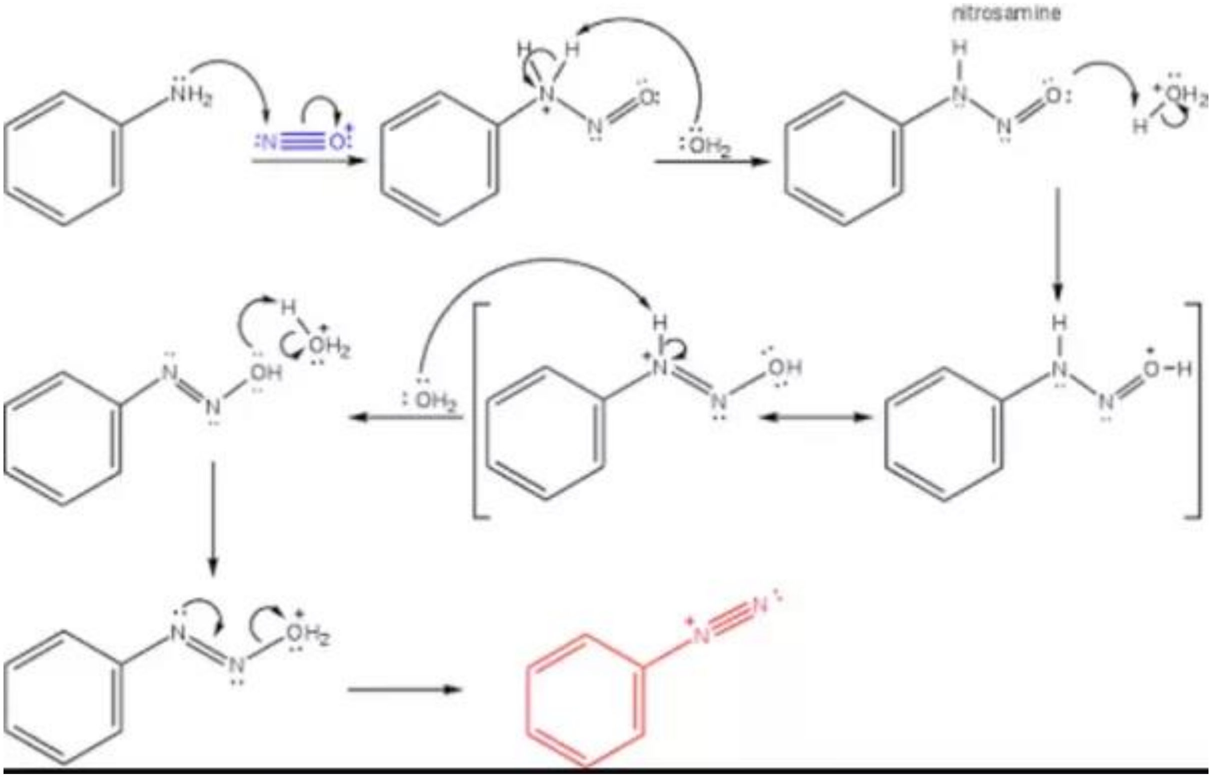
The **Sandmeyer reaction** is a chemical reaction used to synthesize aryl halides from aryl diazonium salts using copper salts as reagents or catalysts.[1][2][3] It is an example of a radical-nucleophilic aromatic substitution. The Sandmeyer reaction provides a method through which one can perform unique transformations on benzene, such as halogenation, cyanation, trifluoromethylation, and hydroxylation.



The reaction was discovered in 1884 by Swiss chemist Traugott Sandmeyer, when he attempted to synthesize phenylacetylene from benzenediazonium chloride and cuprous acetylide. Instead, the main product he isolated was phenyl chloride.[4] In modern times, the Sandmeyer reaction refers to any method for substitution of an aromatic amino group via preparation of its diazonium salt followed by its displacement with a nucleophile in the presence of catalytic copper(I) salts. (Due to the low cost of copper salts, a stoichiometric amount is often employed for better reactivity even when catalysis is possible.) The most commonly employed Sandmeyer reactions are the chlorination, bromination, cyanation, and hydroxylation reactions using CuCl, CuBr, CuCN, and Cu_2O, respectively. More recently, trifluoromethylation of diazonium salts has been developed and is referred to as a 'Sandmeyer-type' reaction. Diazonium salts also react with boronates, iodide, thiols, water, hypophosphorous acid and others,[5] and fluorination can be carried out using tetrafluoroborate anions (Balz–Schiemann reaction). However, since these processes do not require a metal catalyst, they are not usually referred to as Sandmeyer reactions. In numerous variants that have been developed, other transition metal salts, including copper(II), iron(III), and cobalt(III) have also been employed.[6] Due to its wide synthetic applicability, the Sandmeyer reaction, along with other transformations of diazonium compounds, is complementary to electrophilic aromatic substitution.

One common thing in Sandmeyer’s and Gattermann’s reaction is the conversion of aniline into diazonium salt.

Mechanism for formation of benzene diazonium ion:—



Sandmeyer’s reaction:—

In this reaction aniline is treated with mixture of $NaNO_2$ and HCl to form benzene diazonium chloride,which on further reaction with cuprous salts,haloarenes are obtained

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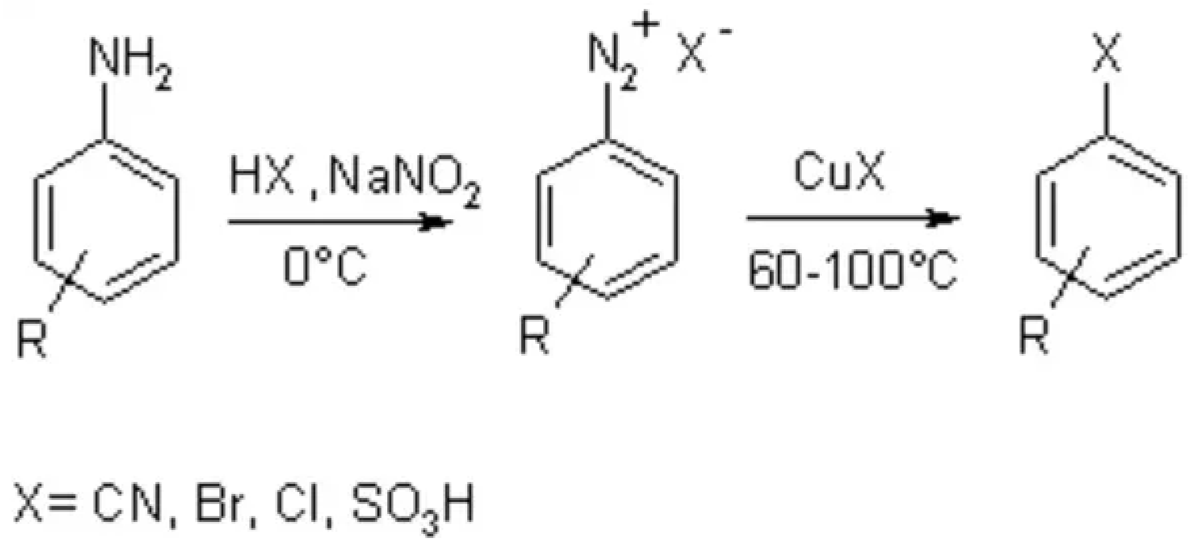
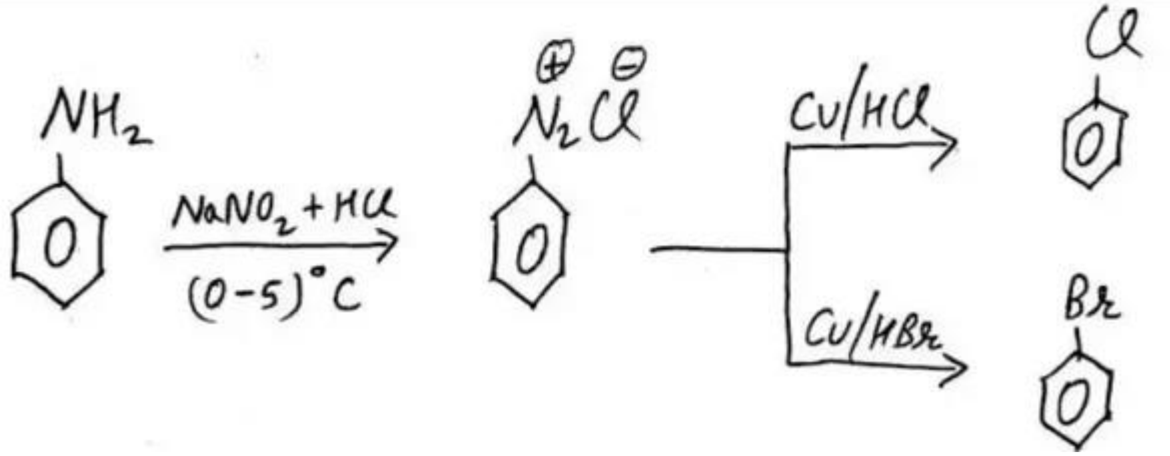
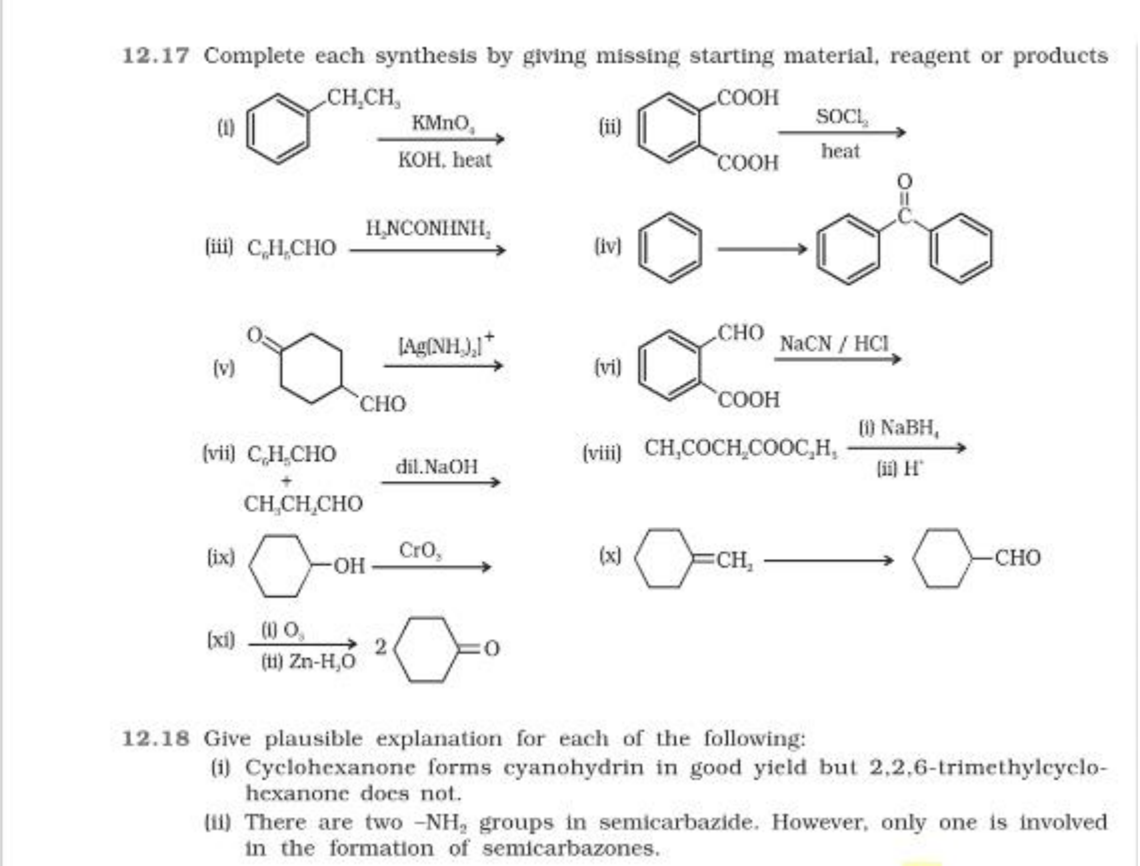


Gattermann’s reaction:—-

In this reaction aniline is converted first into diazonium salt by treating with mixture of $NaNO_2$ and HCl. In very next step diazonium salt is heated with HCl or HBr in presence of copper metal to get haloarenes.



QUESTIONS FOR COC2 UNIT1



12.17 Complete each synthesis by giving missing starting material, reagent or products

(i) $\xrightarrow[\text{KOH, heat}]{KMnO_4}$

(ii) $\xrightarrow[\text{heat}]{SOCl_2}$

(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(iv) $\longrightarrow$

(v) $\xrightarrow{[Ag(NH_3)_2]^+}$

(vi) $\xrightarrow{NaCN\ /\ HCl}$

(vii) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{\text{dil.}NaOH}$

(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4}$

(ix) $\xrightarrow{CrO_3}$

(x) $\longrightarrow$

(xi) $\xrightarrow[\text{(ii) Zn-}H_2O]{\text{(i) } O_3}$ 2

12.18 Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.

(ii) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.