25. AMINES AND AROMATIC COMPOUNDS CONTAINING NITROGEN

1. INTRODUCTION

- (a) Alkyl derivatives of NH₃ are called Amines.
- (b) If a hydrogen atom of NH₃ is replaced by an alkyl group, then it is called a primary amine and possesses -NH₂ (amino) group.
- (c) If two hydrogen atoms of NH₃ are replaced then it is called a secondary amine and it posseses NH (Imino) group.
- (d) If all hydrogen atoms of NH₃ are replaced then it is called a tertiary amine and has a nitrile N group.
- (e) N is in sp³ hybridisation and has tetrahedral geometry.
- (f) The bond angle increases from ammonia to 3° amines. $NH_3(107^{\circ}) < RNH_2 < R_2NH < R_3N$

2. STRUCTURE AND BONDING



Figure 25.1: Hybridisation in primary and tertiary amine

- (a) Trigonal pyramidal geometry
- (b) High negative potential on N



Figure 25.2: Bond Structure of primary and tertiary amine

(c) Amine N can be a stereogenic centre.



Figure 25.3: Amines as a Pair of enantiomer

(d) Enantiomers rapidly interconvert.



Figure 25.4: Interconversion of Enantiomers

(e) Enantiomers of quaternary ammonium salts:



Figure 25.5: Isomerism shown by quaternary ammonium salt

3. PREPARATION OF AMINES

3.1 Nucleophilic Substitution

(a) Hofmann's Ammonolysis Reactions:

Direct Nucleophilic Substitution

$$R = X + NH_{3} \xrightarrow{S_{N}^{2}} R \xrightarrow{H} N^{+} - H \xrightarrow{NH_{3}} R - NH_{2} + NH_{4}$$

Drawback:

- (i) RX limited to methyl and 1° alkyl halides.
- (ii) Complicated by polyalkylation.
- (iii) Useful for preparing 1° amines and quaternary ammonium salts.



(b) Gabriel Phthalamide Synthesis:



3.2 Reduction of Nitrogen Containing Functional Groups

(a) From Nitro Componds

$$R - NO_2 \xrightarrow{\text{reduce}} R - NH_2$$

Reducing Agents:

(i)	H ₂ /Pd-C	
(ii)	(1) Fe, HCl	(2) OH⁻
(iii)	(1) Zn, or Sn, or SnCl ₂ + HCl	(2) OH⁻

(b) From Nitriles

$$CH_{3}CH_{2}CH_{2} - C \equiv N \xrightarrow{1 \sqcup AIH_{4}} CH_{3}CH_{2}CH_{2} - CH_{2}NH_{2}$$

Nitriles from alkyl halides:

$$CH_3CH_2CH_2 - Br \xrightarrow{NaCN} CH_3CH_2CH_2 - C \equiv N$$

(c) From Amides



3.3 Reductive Amination



Methamphetamine

3.4 Rearrangement Reactions

(a) Hofmann's Bromamide Reaction: $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = X_2, \text{ base, } H_2O$ $I = I = I = X_2, \text{ base, } H_2O$ I = I = I = I = I I = I = I = I I = I = I = I I = I = I = I I = I = I = I I = I = I = I I = I = I = I I = I = I = I I = I = I = I I = I = I = I I = I I = I = I

$$X = CI, Br$$

Mechanism:



(b) Curtius Rearrangement: O \parallel R C N_3 $\xrightarrow{\Delta}$ R-N=C=O $\xrightarrow{H_2O}$ $R-NH_2$

Mechanism:

Step 1 Preparation of azides:



Step 2 Decomposition:

$$R \xrightarrow{O}_{N=N=N} \xrightarrow{A}_{N_2} R = N = C = O$$

Reaction with water to the unstable carbamic acid derivative which will undergo spontaneous decarboxylation:



Isocyanates are versatile starting materials:



(c) Leuckart Thiophenol Reaction:



The Leuckart Thiophenol Reaction allows the preparation of thiophenols and corresponding thioethers from anilines or their corresponding diazonium salts. The first step of the reaction of an aryl diazonium salt with a potassium alkyl xanthate to give an aryl xanthate, which affords an aryl mercaptan upon the basic hydrolysis or an aryl thioether upon warming.

(d) Ritter Reaction:



The acid-induced nucleophilic addition of a nitrile to a carbonium ion, followed by the hydrolysis to the corresponding amide.

Mechanism of the Ritter Reaction: Any substrate capable of generating a stable carbonium ion is a suitable starting material; primary alcohols do not react under these conditions, with the exception of benzylic alcohols.



The carbonium ion adds to the nitrile nitrogen to give a nitrilium ion intermediate, which undergoes hydrolysis to the corresponding amide upon the aqueous work-up.



(e) Lossen's Rearrangement:



Mechanism:



(f) Claisen Schmidt rearrangement:

RCOOH $\xrightarrow{HN_3}_{H_2SO_4}$ R \xrightarrow{O}_{II}_{I} N₃ $\xrightarrow{(i) \Delta}_{(ii) H_2O}$ RNH₂ + CO₂

Illustration 1: Prepare n-butylamine by Gabriel synthesis.

(JEE MAIN)

Sol: This method is mainly used in preparation of Primary amine by use of alkyl halide and Potassium phthalimide. After the attack of alkyl halide, Potassium phthalimide no longer behaves as a nucleophile. Product is cleaved by reaction with base or hydrazine, which leads to a stable cyclic product. The by-product of this reaction is an acid.



Sol: Reaction between aldehyde and piperidine proceed via formation of carbinolamine which gets converted to Iminium ion intermediate. On reduction with Raney Ni, tertiary amine is formed.



Illustration 3: Complete the following reactions:



(JEE ADVANCED)

(JEE ADVANCED)

Illustration 4: Complete the following:



Sol: It is an example of region selective reaction. One of the nitro group preferentially gets reduced by NH_4SH $(NH_4)_2S$ or NH_4SH reduces only one nitro group. (B) is



4. PHYSICAL PROPERTIES OF AMINES

- (a) Unlike most other organic compounds, amines are far more soluble in water, this is because all amines form a stronger H–bond with water.
- (b) Like ammonia, amines are polar compounds and apart from 3° amines, they can form intermolecular H– bonds that's why they have higher b.p.s'.
- (c) The boiling points of amines are lesser than of alcohols and acids of comparable mol. weight because H– bonding in amines is less pronounced in 1° and 2° than that in alcohols and carboxylic acids. This is because nitrogen is less electronegative than oxygen.
- (d) Boiling point of 1°, 2° and 3° amines follow the order.

 $1^{\circ} > 2^{\circ} > 3^{\circ}$ amine

(e) Solubility in water follow the order.

 $1^{\circ} > 2^{\circ} > 3^{\circ}$ amine

This is all due to H–Bonding.

Basicity of Amines: Due to basic nature, they react with acids to form salts.

$$R \rightarrow H_2 + H \rightarrow X \implies R \rightarrow H_3 X^{\Theta}$$
 (Salt)

 $Ph \longrightarrow H_2 + HCl \implies R \longrightarrow H_3Cl^{\Theta}$ (Anilinium chloride)

Amine salts on treatment with bases such as NaOH regenerate the parent amine.

$$RNH_3X^- + OH \longrightarrow RNH_2 + H_2O + X$$

Relative Basicity of Amines: Compare basicities by using conjugate acid pK_a values.

(a) An Amine and Ammonia

$$\begin{split} H-NH_3^{\ +} & pK_a=9.3 \quad NH_3 \ (weaker \ base) \\ CH_3CH_2-NH_3^{\ +} & pK_a=10.8 \quad CH_3CH_2NH_2 \ \left(strong \ base\right) \end{split}$$

- (i) Alkyl amines are stronger bases than NH₃
- (ii) Electron-donating alkyl group increase the electron density on N.

(b) An Alkylamine and an Arylamine

Aniline is a weaker base that ethylamine. Why?



CH₃CH₂NH₂ localized lone pair

(i) Electron donors increase basicity.

(ii) Electron withdrawers decrease basicity.



Figure 25.6: Order of Relative basicity of Amine

Order of Relative basicity of Amine

(c) An Alkylamine and an Amide



Lone pair on N is resonance delocalized.

- (i) Amides are less basic than alkyl amines.
- (ii) Preferred site of protonation is on oxygen.



(d) Heterocyclic Aromatic Amines



(i) Pyridine – stronger base – lone pair localized

(ii) Pyrrole – weaker base – lone pair delocalized

(e) Effect of Hybridization



 $pK_a = 5.3$ pyridine $pK_a = 11.1$ piperidine

(i) Pyridine – weaker base – lone pair in sp² orbital

(ii) Piperidine – stronger base – lone pair in sp³ orbital

Illustration 5: Give the decreasing order of boiling points for the following:

(JEE MAIN)

I. Et₂NH

II. Me NH₂ III. Et-N Me

Sol: Extent of hydrogen bonding decreases in the order $(1^{\circ} > 2^{\circ} > 3^{\circ})$ amine) thus boiling point also decreases in the order $(1^{\circ} > 2^{\circ} > 3^{\circ})$ amine)

 $(II) > (I) > (III) (1^{\circ} > 2^{\circ} > 3^{\circ} amine)$

Illustration 6: Arrange the following	g in the decreasing order of their basi	c strength: (JEE MAIN)

a.	i. PhNH ₂	ii. EtNH ₂	iii. Et ₂ NH	iv. NH ₃	
b.	i. EtNH ₂	ii. PhNH ₂	iii. NH₃	iv. PhCH ₂ NH ₂	v. Et ₂ N

Sol: Extent of hydrogen bonding decreases in the order $(1^{\circ} > 2^{\circ} > 3^{\circ} \text{ amine})$ thus boiling point also decreases in the order $(1^{\circ} > 2^{\circ} > 3^{\circ} \text{ amine})$

- a. Aliphatic 2° amine > Aliphatic 1° amine > NH₃: Aromatic amine (iii) > (iv) > (i)
- b. (v) > (i) > (iv) > (iii) > (ii)

Illustration 7: Complete the following acid-base reaction and name the products. (JEE ADVANCED)

(i) $Me^{NH_2} + HCI \longrightarrow$ (ii) $Et_3N + HCI \longrightarrow$

Sol: (i) $(i) \xrightarrow{\bigoplus} NH_3Cl^{\Theta}$ (Propanammonium chloride)

(ii) $Et_3N^+Cl^-$ (Triethylammonium chloride)

MASTERJEE CONCEPTS

Preparation of amines:

 reduction of nitro compounds to amines by metals(Fe, Sn, Zn) in dil HCl or SnCl₂ or by hydrogen in presence of Ni, Pt, Pd.

Misconception: $LiAlH_4$ doesn't reduce the nitro compounds to amines. Instead it reduces it to R-N=N-R.

Amines can also be prepared by the Hoffmann ammonolysis reaction which is a S_N2 reaction. NH₃ reacts with the alkyl halide to give primary halides which in turn react with more alkyl halides to give 2° and 3 amines and then gives 4° ammonium salts.

Exception: Hoffmann ammonolysis reaction cannot be used to prepare aromatic amines.

• Amines can also be produced by the reduction of nitriles with LiAlH₄ or catalytic hydrogenation. But note that only primary amines can be produced.

Misconception: Besides NaBH₄ does not give primary amines.

- Amines can also be prepared by the reduction of amides, oximes and azides by LiAlH₄. But again only primary amines can be produced by this method.
- Primary amines can also be produced by Gabriel phthalamide synthesis. In this pthalic anhydride is converted to phthalamide which is then treated with an alkyl halide to give N-alkyl pthalamide. Finally it is treated with hydrazine to give a primary amine.

Exception: primary aromatic amines cannot be prepared by Gabriel phthalamide synthesis because aromatic halide doesn't give a substitution reaction with phthalamide.

- Primary amines can be prepared by Hoffmann bromamide reaction where the amide is treated with Br₂ in the presence of an alkali to give a primary amine. The intermediate species is nitrene which undergoes intra rearrangement to give RNH₂.
- Some other methods to prepare primary amines are Lossen rearrangement, Curtius rearrangement, Claisen-Schmidt rearrangement. All have one thing in common, i.e., they proceed through the nitrene mechanism.
- Amines can also be produced by the reductive amination of carbonyl compounds. Carbonyl compounds give imines which on reduction with H₂ in presence of Ni gives an amine. Aldehydes give primary amines and ketones give secondary amines.

5. VARIOUS TESTS FOR AMINES

(a) Hofmann Mustard Oil Reaction (Test for 1° Amines)

 $\begin{array}{c} S \\ || \\ RNH_2 + S = C = S \xrightarrow{\text{Warm}} RNH - C - SH \xrightarrow{\text{HgCl}_2} 2HCI + HgS + R - N = C = S \\ 1^{\circ} \text{ amine} \xrightarrow{\text{Dithioalkyl}} carbamic acid} \xrightarrow{\text{HgCl}_2} 2HCI + HgS + R - N = C = S \\ Alkyl \\ isothiocyanate \end{array}$

Alkyl isothiocyanates gives a smell like that a mustard oil and this is used as a test for 1° amines.

(b) Carbylamine Reaction (Test for 1° Amine): It consists of heating a mixture of 1° aliphatic or aromatic amines and chloroform with alcoholic KOH solution. The reaction proceeds via carbene mechanism.

$$R - NH_2 + CHCI_3 + 3KOH (Alcoholic) \xrightarrow{\Delta} R - N^+ \equiv C^- + 3KCI + 3H_2O$$

Mechanism:

 $R - NH_2 + : CCI_2 \longrightarrow RN^+ \equiv C^- + 2HCI_2$

Isocyanides have a very offensive smell. So, this reaction is use to distinguish 1° amines.

- (c) Hinsberg's Test (for distinguishing 1°, 2° and 3° amines): Three classes of amines are distinguished by Hinsberg reagent test. The Hinsberg reagent is a benzene sulphonyl chloride ($C_6H_5SO_2CI$).
- (d) Reaction of Hinsberg Reagent with Primary Amines: A primary amine forms a precipitate of N-alkyl benzene sulphonamide with Hinsberg reagent. This precipitate is soluble in alkali.

 RNH_2 (primary amine) + $C_6H_5SO_2CI$ (Hinsberg reagent) $\longrightarrow R - NH - SO_2 - C_6H_5 \longrightarrow R - N^-Na^+ - SO_2C_6H_5$ (soluble)

(e) Reaction of Hinsberg Reagent with a Secondary Amine: Secondary amine reacts with the Hinsberg reagent to form a precipitate N,N-dialkyl benzene sulphonamide. But this precipitate is insoluble in alkalis.

 $R_2NH (secondary amine) + C_6H_5SO_2CI (Hinsberg reagent) \longrightarrow R_2NSO_2C_6H_5 \xrightarrow[(Precipitate)]{NaOH} Insoluble (no reaction)$

(f) Reaction of Hinsberg Reagent with a Tertiary Amine: Tertiary amines do not react with Hinsberg reagent.

 R_3N (Tertiary amine) + $C_6H_5SO_2CI$ (Hinsberg reagent) \longrightarrow No reaction

(g) Reaction with Nitrous acid (For Distinguishing 1°, 2° and 3° amines): 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 Bronsted acid of moderate strength ($pK_a = 3.3$). Because it is insoluble, it is prepared immediately before use in the following manner.

 $NaNO_2 + H_2SO_4 \xrightarrow{H_2O, 0^\circ} H \longrightarrow \ddot{N} = \ddot{O} + NaHSO_4$

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

$$R^{2} - N: + HX \implies R^{2} - N - H X^{\Theta} [X = HSO_{4} \text{ or } NO_{2}]$$

$$R^{3} \qquad R^{3} \qquad R^{3}$$

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

Mechanism of reaction of Nitrous acid with primary amine



6. CHEMICAL REACTIONS OF AMINES

6.1 Reaction with Carbonyl Compounds

(a) Imine Formation



Imines are formed when any primary amine reacts with an aldehyde or ketone under appropriate conditions. Imine formation requires an acid catalyst, otherwise the reaction is very slow. The acid is needed for the elimination of water.

(b) Enamine Formation:



Under the appropriate conditions, secondary amines react with carbonyl compounds to form enamines. Like imine formation, the formation of an enamine also requires an acid catalyst for the removal of water.

6.2 Elimination

(a) Hofmann Elimination: When a primary amine bearing one of more beta hydrogens is treated with methyl iodide, followed by aqueous silver oxide, followed by heat, the primary amine is converted to an alkene. This reaction is known as Hofmann elimination, not to be confused with Hofmann rearrangement.

E.g.
$$CH_3CH_2NH_2 \xrightarrow{1.3 \text{ eq. CH}_3I} CH_2 = CH_2$$

The net reaction is 1,2-elimination, hence the name Hofmann Elimination.

$$H_{2}C \rightarrow CH_{2} \rightarrow H_{2}$$

Hofmann elimination occurs in three stages.

$$CH_{3}CH_{2}NH_{2} \xrightarrow{3 CH_{3}I} CH_{3}CH_{2}N(CH_{3})_{3}I^{-}$$

$$\int Stage 2 aq. Ag_{2}O$$

$$CH_{2} = CH_{2} \xrightarrow{\Delta} CH_{3}CH_{2}N(CH_{3})_{3} OH$$

Mechanism:

Stage 1:



Stage 2:





Stage 3 is a 1,2-elimination via E1CB mechanism. Hofmann elimination is regioselective. Since the 1,2-elimination in Stage 3 occurs via E1CB mechanism. Hofmann rule is used to predict the major product.



(b) Cope's Elimination: Tertiary amine oxides undergo the elimination of a dialkylhydroxylamine when they are heated. This reaction is called the Cope elimination:



The Cope elimination is a syn elimination and proceeds through a cyclic transition state:



Tertiary amine oxides are easily prepared by treating amines with hydrogen peroxide.

The Cope elimination is useful synthetically. Consider the following synthesis of methylenecyclohexane:



6.3 Reaction with Acid Halides and Anhydrides



6.4 Electrophilic Substitution Reaction for Aniline

Electrophilic substitution: Due to +M effect of $-NH_2$ generate electron density at ortho and para position hence, aniline active toward electrophilic substitution

(a) **Bromination:** Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



If we have to prepare a monosubstituted aniline derivative. This can be done by protecting the $-NH_2$ group by acetylation with an acetic anhydride, then carrying out the desired substitution followed by the hydrolysis of the substituted amide to the substituted amine.



The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:



Hence, the lone pair of electrons on nitrogen is less available for donation to the benzene ring by resonance. Therefore, activating the effect of –NHCOCH₃ group is less than that of amino group.

(b) Nitration: Direct nitration of aniline is not possible because in the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing.



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.





MASTERJEE CONCEPTS

Chemical reaction of amines:

- Tips and tricks: Only primary amines react with carbonyl compounds to give imines while secondary
 amines react with carbonyl compounds to give enamines.
- **Tips and tricks:** In Hoffman elimination, the alkene which is substituted least is the major product while in Cope's elimination the alkene which is most substituted is the major product..
- Tips and tricks: In the Hoffmann elimination, there is anti-elimination while in Cope's elimination, there
 occurs syn elimination.
- In electrophilic substitution of bromine on aniline, if the medium is CS₂ then only 1 Br is substituted while in aqueous solution, the substitution of bromine occurs 3 times.
- If bromination is to be done once in aqueous solution then acetylation of bromine is carried out due to which the ring becomes less activated.
- In nitration, the major products are para and metanitroaniline while the ortho product is very less. This is because of the acid base reaction between aniline and nitrous acid due to which some of aniline becomes meta directing.

Vaibhav Krishnan (JEE 2009 AIR 22)

Illustration 8: Complete the following reactions:

(JEE MAIN)



Sol: Attack of nitrous acid forms a primary carbocation which gets rearranged to more stable secondary carbocation. Attack of nucleophile (OH⁻) result in formation of secondary alcohol which on treatment with acid forms alkene.





Thus, the acidity of β –H is more important than the stability of the alkene that is formed.

Illustration 10: Give the products of the following by the application of Hofmann's exhaustive methylation and elimination: (JEE ADVANCED)



Sol: This process involves thermal decomposition of quaternary ammonium hydroxide compounds to yield an olefin and water is known as Hofmann's exhaustive methylation reaction. This method has been employed in identifying site of unsaturation present in the given compound.



7. DIAZONIUM SALTS

7.1 Introduction

The diazonium salts have the general formula RN_2X where R stands for an aryl group and X ion may be Cl, Br, HSO₄, BF₃ etc.

Resonance of benzene diazonium ion is



7.2 Preparation

PhNH + NaNO₂ + HCI $\xrightarrow{273-278 \text{ K}}$ $\left[Ph-N=N\right]CI \xrightarrow{\ominus} NaCI+2H_2O$

7.3 Chemical Reactions Involving Displacement of Nitrogen

$$ArN_{2}-X \rightarrow Ar - \overset{\oplus}{N_{2}} \xrightarrow{Slow} Ar \xrightarrow{\oplus} Ar \xrightarrow{HOH} ArOH + H^{\oplus}$$

$$\xrightarrow{+} \chi^{\bigoplus} Ar - CN$$

$$\xrightarrow{+} ArX$$

- (a) **Replacement by –OH group:** $ArN_2CI + HOH \xrightarrow{Boiling} ArOH + N_2 + HCI$
- **(b) Replacement by H:** ON reduction with sodium stannite (Na₂SnO₂) (alkaline SnCl₂) or hypophosphorous acid (H₃PO₂) or on warming with C₂H₅OH, ArN₂Cl gives benzene.

 $ArN_{2}Cl+H_{3}PO_{2}+H_{2}O \rightarrow ArH+N_{2}+2CuCl_{2}$

 $ArN_2CI + Na_2SnO_2 + H_2O \rightarrow ArH + N_2 + Na_2SnO_3 + HCI$

(c) Sandmeyer reaction (replacement by halogen):

 $ArN_2CI+Cu_2CI_2+HCI \rightarrow ArCI+N_2+2CuCI_2$ $ArN_3Br+Cu_3Br_2+HBr \rightarrow ArBr+N_2+2CuBr_2$

(d) Gattermann reaction:

 $ArN_{2}CI \xrightarrow{\text{Finely divided Cu/HCI}} ArCI + N_{2}$ $ArN_{2}Br \xrightarrow{\text{Finely divided Cu/HBr}} ArBr + N_{2}$

- (e) lodo compounds: $ArN_2CI+KI(Aq.) \xrightarrow{Boiling} Ar-I + N_2+KCI$
- (f) Balz-Schiemann reaction:

Ar-NH₂
$$\xrightarrow{(Fluoroboric acid)}_{273-298K}$$
 Ar-NH₂ $\xrightarrow{\oplus}_{1273-298K}$ Ar-NH₂ $\xrightarrow{\oplus}_{1273-298K}$ Ar-NH₂ $\xrightarrow{\oplus}_{1273-298K}$ ArF+BF₃+N₂

(g) Cyano compounds:

 $ArN_{2}CI+KCN \xrightarrow{CuCN} ArCN+N_{2}+KCI$ $ArN_{2}CI+KCN \xrightarrow{K_{3}[Cu(CN)_{4}]} ArCN+N_{2}+KCI$

(h) Nitro compounds:

 $ArN_{2}CI+HONO \xrightarrow{Cu_{2}O} ArNO_{2}+N_{2}+HCI$ $ArN_{2}CI+CuNO_{2} \xrightarrow{\Delta} ArNO_{2}+N_{2}+CuCI$ $ArN_{2}BF_{4}+NaNO_{2} \xrightarrow{\Delta} Ar-NO_{2}+NaBF_{4}+N_{2}$

(i) Gomberg reaction (replacement by an aryl group)

$$ArN_{2}CI+PhH+NaOH \longrightarrow Ar-Ar+N_{2}+NaCI+H_{2}O$$
Benzene Diphenyl
$$Br \longrightarrow N_{2}CI + C_{6}H_{6}+NaOH \longrightarrow Br \longrightarrow N_{2}+N_{2}+NaCI+H_{2}O$$

$$PhN_{2}^{+}CI + (NO_{2}+NaOH \longrightarrow O) \longrightarrow NO_{2}+N_{2}+NaCI+H_{2}O$$

Whatever is the nature of the substituent in the second component, o-and p-substitutions occur and the reaction takes place by the free radical mechanism.

$$Ph\overset{\bigoplus}{N_2}Cl^{\ominus} \xrightarrow{\Theta} Ph-N=OH \rightarrow Ph^{\bullet}+N_2+^{\bullet}OH$$
$$Ph^{\bullet}+PhNO_2+^{\bullet}OH \rightarrow O \rightarrow NO_2+H_2O$$

- (j) Meerwein Reaction:
 - (i) PhN₂Cl+CH₂=CH-CN(Acrylonitrile)

(ii)
$$Ph^{+}+CH_{2}=CHCN \rightarrow PhCH_{2}CHCN$$

 $Cu^{2+} \downarrow CI$
 $PhCH_{2}CHCN + Cu^{\oplus} CI^{\oplus} \rightarrow PhCH_{2}CH-CN$

(iii) Addition to α , β -unsaturated acid is accompanied by decarboxylation.

(iv) Mechanism:

PhCH=CH-COOH

$$\xrightarrow{\oplus \text{Arcl}}$$

 $\xrightarrow{-CO_2}$
 $\xrightarrow{\text{and}}$ Ph-CH-CH-COOH
 $\xrightarrow{-HCI}$
 $\xrightarrow{-HCI}$
CI Ar
Ph-CH=CH-Ar

Reduction:

$$Ar-N=N-CI \xrightarrow{Zn+HCI} [Ar-NH.NH_2] \xrightarrow{Zn+HCI} Ar-NH_2 + NH_3$$





(d) With excess of diazonium salts, the bisazo (o- and p-) and the trisazo compounds may be produced. Ph-N=N-Cl+PhOH ______



The introduction of a second azo group is facilitated by the presence of an alkyl group in the *para*-position to the hydroxyl group or by two (–OH) groups in the *m*-position.

(e) Dye test (test for 1° aromatic amine):



Coupling with α -or 1-naphthol takes places at the position shown by an arrow.



(Coupling position)

(f) In case, a compound contains both (–OH) and (–NH₂) groups, the coupling takes place at o-position of the amino group in the acid solution.

In the alkaline solution, coupling takes place at *o*-position to the (–OH) group.



(g) In cases where a (–COOH) or (–SO₃H) group is present at p-position to (–OH) or to (–NH₂). it is an example of ipso substitution, special case of electrophilic aromatic substitution where the leaving group is not hydrogen.



(JEE MAIN)

MASTERJEE CONCEPTS

- Diazonium salts of alkanes, alkenes and alkynes are not at all stable at room temperature while benzene Diazonium salts are stable to some extent due to delocalization of the positive charge in the benzene ring.
- Whenever you see a nucleophile with benzene Diazonium salt, substitute it in place of N₂, as it is a very good leaving group.
- Benzene Diazonium salt gives an orange red dye with β-naphthol due to extended conjugation and is hence a test for it.
- Being an electron deficient species benzene Diazonium salt shows a coupling reaction with an electron rich species such as phenol and amines.

Nikhil Khandelwal (JEE 2009 AIR 94)

Illustration 11: Give the decreasing order of the reactivity of the diazonium ion coupling with the phenol.

(I) $p-NO_2-C_6H_4N_2$ (II) $p-CI-C_6H_4N_2$ (III) $C_6C_5N_2$ (IV) $p-Me-C_6H_4N_2$ (V) $p-MeO-C_6H_4N_2$

Sol: The more Electron withdrawing group in diazonium ion, the faster the coupling is.

The more EWG in diazonium ion, the faster the coupling is.

(V) \Rightarrow [p-MeO–, –I, and + R, net ED power of Me–O is greater than ED power of (Me–) group

Illustration 12: Starting from benzene or toluene or aniline and with the aid of the diazonium salt synthesise the following: p-Nitrobenzene (JEE MAIN)

Sol: We are going to prepare p-Nitrobenzene from Aniline. Since, $-NH_2$ is o- and p- directing, introduce one $(-NO_2)$ group directly by nitration after protecting $(-NH_2)$ group (direct nitration of aniline would yield mixture and tarry products).

Nitration is done using the nitrating mixture (conc.HNO₃+conc.H₂SO₄).Next step is deprotection which is done by using an aqueous base. Now we can introduce the





Illustration 13: Explain why 2,4-dinitrobenzene diazonium ion couples with anisole but PhN_2^{\oplus} does not. Write the coupling reaction. (JEE ADVANCED)

O₂N

NO₂

Sol: The ring is not sufficiently activated by –OMe group for it does not react with most PhN_2^{\oplus} However, \overline{e} -withdrawing (–NO₂) groups make this diazonium ion less stable and thus more reactive than PhN_2^{\oplus} .

The ring is not sufficiently activated by –OMe group for it does not react with most PhN_2^{\oplus} . However, \overline{e} -withdrawing (–NO₂) groups make this diazonium ion less stable and thus more reactive than PhN_2^{\oplus} .

Illustration 14: Convert the following:

Aniline -+ H₂N--SO₂NH₂ Sulphanilamide



OMe

OMe

Anisole

NO₂



POINTS TO REMEMBER

