CHAPTER 13

Organic Compounds Containing Nitrogen

Introduction, Methods of Preparation and Physical Properties

• Amines: Amines can be considered as the amino derivatives of hydrocarbons or alkyl derivatives of ammonia. Amines are obtained by replacing one, two or three hydrogen atoms by alkyl and/or aryl groups.

For example, $CH_3NH_2, C_2H_5NH_2, C_6H_5NH_2$ etc.

• Classification of amines:



• Structure of amines:



Pyramidal shape of trimethylamine

Nitrogen orbitals in amines are sp^3 hybridised and the geometry of amines is pyramidal. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C - N - E is less than 109.5°.

Amines	Common Names	IUPAC name		
$CH_3 - CH_2 - NH_2$	Ethylamine	Ethanamine		
$CH_3 - CH_2 - CH_2 - NH_2$	n-Propylamine	Propan-1-amine		
$\begin{array}{c} CH_3-CH-CH_3\\ \\ NH_2 \end{array}$	Isopropylamine	Propane-2-amine		
$\begin{array}{c} CH_3-N-CH_2-CH_3\\ \\ H\\ H\end{array}$	Ethylmethylamine	N-Methylethanamine		
$\begin{array}{c} CH_3-N-CH_3\\ \\ CH_3\end{array}$	Trimethylamine	N,N-Dimethylmethaneamane		
NH ₂	Aniline	Aniline or benzenamine		
NH ₂ Br	<i>p</i> -Bromoanaline	4-Bromobenzylamine Or 4-Bromoaniline		

• Nomenclature of some alkylamines and arylamines:

• Preparation of Amines:

> By reduction of nitro compounds:

$$R - NO_2 + 3H_2 \xrightarrow{Ni} R - NH_2 + 2H_2O$$

 $1^0 a mine$

> By ammonolysis of alkyl halides:

$$\begin{array}{ccc} R-X+NH_{3}\rightarrow RNH_{2} & \xrightarrow{RX} & R_{2}NH & \xrightarrow{RX} & R_{3}N & \xrightarrow{RX} & R_{4} \stackrel{+}{N} \stackrel{-}{X} \\ & \left(1^{o}\right) & \left(2^{o}\right) & \left(3^{o}\right) & Quaternary \\ & ammonium \ salt \end{array}$$

The free amine can be obtained from the ammonium salt by treatment with a strong base:

$$R - \overset{+}{N}H_3 \stackrel{-}{X} + NaOH \rightarrow R - NH_2 + H_2O + \overset{+}{Na}\stackrel{-}{X}$$

> By reduction of nitriles:

$$2H_2 + R - C \equiv N \xrightarrow{N_i} R - CH_2 - NH_2$$
$$R - C \equiv N + 4[H] \xrightarrow{Na(Hg)/C_2H_5OH} R - CH_2 - NH_2$$

1^o amine

> Gabriel phthalmide synthesis:



> By reduction of amides:

$$R - \stackrel{\|}{C} - NH_2 \xrightarrow{(i)LiAlH_4} R - CH_2 - NH_2$$

> By Hoffmann Bromamide degradation reaction:

$$\overset{\parallel}{R-C-NH_2} + Br_2 + 4NaOH \longrightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O_3 + 2NBr + 2H_2O_3 +$$

- Physical properties:
 - > Lower members are combustible gases, members from C_3 to C_1 are volatile liquids and C_{12} onwards are gaseous. Lower aromatic amines are liquids.
 - > Pure amines are colourless, although they develop colour on keeping in air for a long time.
 - > With increase in molecular weight, the boiling point also increases. The order of boiling points of isomeric amines is, Primary > Secondary > Tertiary.
 - > Lower members of amine are readily soluble in water. They decrease in water and increase in organic solvents with an increase in molecular weight.

Chemical Reaction of Amines and Diazonium Salts

- Chemical properties:
 - > Reactions due to alkyl group:

$$R - \stackrel{\bullet \bullet}{N} H_2 + HX \rightleftharpoons R - \stackrel{+}{N} H_3 \overline{X}(Salt)$$



Aniline

Anilinium chloride

Amines, being basic in nature, react with acids to form salts. When these amine salts are treated with a base such as *NaOH*, they regenerate the parent amine.

 $R\overset{+}{N}H_3 \overline{X} + \overline{O}H \longrightarrow R\overset{\bullet \bullet}{N}H_2 + H_2O + \overline{X}$ Amine base parent Salts amine Amine salts are soluble in water but insoluble in organic compounds like ether. This reaction helps in separating the amines from the non basic organic compounds insoluble in water.

The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. The order of basic strength in case of methyl Substituted amines and ethyl substituted amines in aqueous solution is as follows:

$$\left(C_{2}H_{5}\right)_{2}NH>\left(C_{2}H_{5}\right)_{3}N>C_{2}H_{5}NH_{2}>NH_{3}$$

$$(CH_3)_2 NH > CH_3 NH_2 > (CH_3)_3 N > NH_3$$

The $-NH_2$ group is attached directly to the benzene ring in aryl amines, which results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.

In case of substituted aniline, it is observed that electron releasing groups increase basic strength whereas electron withdrawing groups decrease it.

Alkylation:

$$\begin{array}{c} CH_{3}-CH_{2}-NH_{2} \xrightarrow{+CH_{3}-CH_{2}-Br} \\ -HBr \end{array} \\ (CH_{3}-CH_{2})_{3} N \xrightarrow{+CH_{3}-CH_{2}-Br} \\ -HBr \end{array} \\ (CH_{3}-CH_{2})_{3} N \xrightarrow{+CH_{3}-CH_{2}-Br} \\ -HBr \end{array} \\ (CH_{3}-CH_{2})_{4} \overset{+}{N} \overset{-}{Br} \\ Tetraethyl \\ ammonium bromide \end{array}$$

Acylation:

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophillic substitution reaction. This reaction is known acylation.

$C_{6}H_{5} - N - H$	$+ CH_{3} - C - O - C - CH_{3} - C$	\longrightarrow C ₆ H ₅ – \ddot{N} – C – CH ₃ + CH ₃ COOH
Н	0 O	Н О
Benzenamine	Ethanoic anhydride	N-Phenylethanamide
		or Acetanilide

Benzoylation:

$$\begin{array}{rcl} CH_3NH_2 &+& C_6H_5COCl \longrightarrow CH_3NHCOC_6H_5 &+& HCl \\ Methyl \ amine & Benzoyl & N-Methylbenzamide \\ Chloride & \end{array}$$

Carbylamine reaction: Secondary and tertiary amines do not give this reaction. This reaction is used as a test for primary amines.

Reaction with nitrous acid:

$$R - NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} \left[R - N_2 \stackrel{+}{Cl} \stackrel{-}{Cl} \right] \xrightarrow{H_2O} ROH + N_2 + HCl$$

1° amine

 $R_2NH + HNO_2 \longrightarrow R_2N - N = O + H_2O$ 2^o amine N-Nitrosamine

 $R_3N + HNO_2 \longrightarrow$ No Reaction

 3^o amine

 $\begin{array}{c} C_{6}H_{5}-NH_{2} & \xrightarrow{NaNO_{2}+2HCl} \\ \hline 273-278k \end{array} \rightarrow C_{6}H_{5}-N_{2}^{+} \stackrel{-}{Cl}+NaCl+2H_{2}O \\ \text{Aromatic} \\ \text{amine} \\ \text{chloride} \end{array}$

Secondary and tertiary amines react with nitrous acid in a different manner.

Reaction with arylsulphonyl chloride:



N, N-Diethylbenzenesulphonamide

Tertiary amines do not react with benzenesulphonyl chloride and therefore, benzenesulphonyl chloride is used to differentiate between primary, secondary and tertiary amines.

Bromination:

Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoanaline.



Nitration:

2, 4, 6- Tribromoaniline

Direct nitration of aniline yields nitro derivatives.









Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride.

Ammonolysis:

Alkyl halide reacts with ammonia to form primary amine. The reaction of ammonia with alkyl halide is known as ammonolysis.

$$C_{2}H_{5}I \xrightarrow{NH_{3}/343K} C_{2}H_{5}NH_{2} \xrightarrow{C_{2}H_{5}I} (C_{2}H_{5})_{2}NH$$
$$(C_{2}H_{5})_{2}NH \xrightarrow{C_{2}H_{5}I} (C_{2}H_{5})_{3}N \xrightarrow{C_{2}H_{5}I} [(C_{2}H_{5})_{4}\overset{+}{N}]I$$

Gabriel Phthalimide Synthesis: In Gabriel phthalimide synthesis, phthalimide reacts with alcoholic KOH to get potassium phthalimide which reacts with alkyl halide to form N-alkyl phthalimide which on basic hydrolysis gives primary amine and phthalic acid.



Phthalimide

N-Alkyphthalimide

Friedel-Crafts reaction: Aniline does not undergo Friedel-Crafts reaction as it forms a salt with AlCl₃ which is a Lewis acid.

- **Diazonium salts:**
 - > General formula: $RN_2 X$, where R stands for an aryl group and \overline{X} ion may be for halides
 - > Stability of diazonium salts: Primary aliphatic amines are highly unstable alkyldiazonium salts. Arenediazonium salts, made up of primary aromatic amines are more stable than alkyl diazonium salts due to the dispersal of the positive charge over the benzene ring.



> Preparation of diazonium salts:

$$\underbrace{NH_2}_{+ \text{ NaNO}_2 + 2\text{HCl}} + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{0^\circ - 5^\circ\text{C}} \underbrace{O}_{+ \text{ NaCl} + 2\text{H}_2\text{O}}^{N_2^+\text{Cl}^-}$$

Benzene diazonium

Chemical properties:
 Reactions involving displacement of nitrogen:
 Replacement by halide or cyanide ion-

$$\operatorname{ArN}_{2}^{+}\overline{X} \xrightarrow[CuCl/HCl]{CuBr/HBr} \operatorname{ArCl} + N_{2}$$

$$\operatorname{ArN}_{2}\overline{X} \xrightarrow[CuCn/KCN]{CuCN/KCN} \operatorname{ArCN} + N_{2}$$

Sandmeyer reaction

$$\operatorname{ArN}_{2}^{+}\overline{X} \xrightarrow{\operatorname{Cu/HCl}} \operatorname{ArCl} + \operatorname{N}_{2} + \operatorname{CuX}_{\operatorname{Cu/HBr}} \xrightarrow{\operatorname{ArCl}} \operatorname{ArCl} + \operatorname{N}_{2} + \operatorname{CuX}_{\operatorname{Cu/HBr}}$$

Gatterman's reaction

Replacement by iodide ion-

Replacement by fluoride ion-

$$Ar \stackrel{+}{N_2} \stackrel{-}{Cl} + HBF_4 \longrightarrow Ar \stackrel{+}{N_2} \stackrel{-}{BF_4}$$
$$Ar \stackrel{+}{N_2} \stackrel{-}{BF_4} \stackrel{-}{\longrightarrow} Ar - F + BF_3 + N_2$$

Replacement by H-

$$\begin{array}{l} Ar\, \stackrel{-}{N_2} \stackrel{-}{Cl} + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl \\ Ar\, \stackrel{+}{N_2} \stackrel{-}{Cl} + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl \end{array}$$

Replacement by hydroxyl group-

$$Ar \stackrel{+}{N_2} \stackrel{-}{Cl} + H_2 O \xrightarrow{\Delta} ArOH + N_2 + HCl$$

$$Phenol$$

Replacement by $-NO_2$ group-



Reactions involving retention of diazo group:

Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds with the general formula, Ar - N = NAr is known as coupling reaction.

$$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\$$

p-Hydroxyazobenzene (orange dye)

$$\underbrace{ \overset{+}{\bigvee}}_{N} = \underbrace{\mathrm{N}}_{\mathrm{Cl}} + \mathrm{H} - \underbrace{ \overset{-}{\bigvee}}_{N} + \mathrm{N}_{2} - \underbrace{\mathrm{O}}_{\mathrm{H}} + \underbrace{\mathrm{N}}_{2} - \mathrm{N}_{2} + \mathrm{N}_{2} + \mathrm{Cl}^{-} + \mathrm{H}_{2} \mathrm{O}$$

p-Aminoazobenzene (yellow dye)

- > Importance of Diazonium salts: They are very good intermediates for the introduction of -F, -Cl, Br, -I, -CN, -OH, $-NO_2$ groups into aromatic ring. Cyanobenzene can be prepared from diazonium salts.
- Synthesis of organic compounds from diazonium salts:

$$\begin{array}{c} C_{6}H_{5}\stackrel{+}{N_{2}}\bar{Cl} \xrightarrow{CH_{3}CH_{2}OH} C_{6}H_{6} \\ C_{6}H_{5}\stackrel{+}{N_{2}}\bar{Cl} \xrightarrow{H_{2}O} C_{6}H_{5}OH \\ C_{6}H_{5}\stackrel{+}{N_{2}}\bar{Cl} \xrightarrow{HBF_{4}} C_{6}H_{5}F \\ C_{6}H_{5}\stackrel{+}{N_{2}}\bar{Cl} \xrightarrow{C_{6}H_{6}/NaOH} C_{6}H_{5}C_{6}H_{5} \\ C_{6}H_{5}\stackrel{+}{N_{2}}\bar{Cl} \xrightarrow{C_{6}H_{5}NH_{2}/acid} \longrightarrow \swarrow N = N \xrightarrow{\swarrow} NH_{2} \end{array}$$

• Identification of primary, secondary and tertiary amines:

Test	Primary amine	Secondary amine	Tertiary amine	
Reaction with nitrous acid.	Gives alcohol with efferve scence of $N_2{\rm gas}.$	Gives only nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold soluble in water and on heating gives nitrosoamine.	
Recation with benzene sulphonyl chloride (Hiesenberg's reagent).	cation with benzene lphonyl chlorideGives N-alkyl benzene- sulphonamide which is soluble in alkali.		No reaction.	
Carbylamine test: Reaction with chloroform and alcoholic KOH.	Forms carbylamines or isocyanide (RNC) with characteristic unpleasant odour.	No reaction.	No reaction.	
Hoffman's Mustard oil reaction: Recation with CS_2 and $HgCl_2$.	Forms N-substituted isotiocyanate with characteristic unpleasant smell of mustard oil.	No reaction.	No reaction.	

EXERCISE

1.	C ₃ H ₉ N represents				
	(a) Primary amine	<i>(b)</i>	Secondary amine		
	(c) Tertiary amine	(d)	All of these		
2.	Triaminobenzene is a				
	(a) 2° amine	<i>(b)</i>	3° amine		
	(c) 1° amine	(d)	Quarternary salt		
3.	Which of the following i	s no	ot a nitro-derivative.		
	(a) $C_6H_5NO_2$	<i>(b)</i>	CH ₃ CH ₂ ONO		
	,0		5 <u>2</u>		
	(c) CH. CH – N	(<i>d</i>)	C.H.(OH)NO.		
		(4)	0614(011)1(02		
4.	Number of isomeric pr	ima	ry amines obtained		
	from $C_4H_{11}N$ are		0		
	(<i>a</i>) 3	<i>(b)</i>	4		
	(c) 5	<i>(d)</i>	6		
5.	The molecular formula	of b	enzonitrile is		
	(a) C_6H_5CN	<i>(b)</i>	C_6H_5NC		
	(c) C_6H_5CNO	(d)	C_6H_5NCO		
6.	6. Amides may be converted into amines b				
	named after				
	(a) Parkin	(<i>b</i>)	Claisen		
	(c) Hoffmann	(d)	Kolbe		
7.	$CH_3C \equiv N + 4[H] - \frac{Na+6}{Rec}$	C ₂ H ₅ ductio	$\xrightarrow{OH} CH_3CH_2NH_2$		
	The compound 'X' is				
	(a) CH_3CONH_2	(<i>b</i>)	$\rm CH_3 CH_2 NH_2$		
	(c) C_2H_6	(d)	$\mathrm{CH}_3\mathrm{NHCH}_3$		
8.	Reduction of nitroalkan	les y	rields		
	(a) Acid	(<i>b</i>)	Alcohol		
	(c) Amine	(d)	Diozo compounds		
9.	When methyl iodide is the product obtained is	hea	ited with ammonia,		
	(a) Methylamine				
	(b) Dimethylamine				
	(c) Trimethylamine				
	(d) A mixture of the ab	ove	three amines		
10.	Identify 'B' in the reacti	on			
	Acetamide $\xrightarrow{P_2O_5} A$	4H	$\xrightarrow{\mathrm{I}} \mathrm{B}$		
	(a) CH_3NH_2				
	(b) $CH_3CH_2NH_2$				
	(c) CH ₃ CN				
	(d) CH_3COONH_4				

11.	 When aniline reacts with NaNO₂ and dil. HCl at 0° - 5° C, the product formed is (a) Nitroaniline (b) Benzene diazonium chloride (c) Benzene 					
	(d) Trinitroanilina					
10	$(u) \text{IIIIIIII I O all line } \\ (U) \text{IIIIII I O all line } \\ (u) \text{IIIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIIII I O all line } \\ (u) \text{IIIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIII I O all line } \\ (u) \text{IIIII I O all line } \\ (u) \text{IIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIII I O all line } \\ (u) \text{IIIIIII I O all line } \\ (u) $					
12.	$CH_3DI + KCN (alc) \longrightarrow A \xrightarrow{Na+C_2H_5OH} I$					
	What is Y in the series?					
	(a) $\operatorname{CH}_3\operatorname{CN}$ (b) $\operatorname{C}_2\operatorname{H}_5\operatorname{CN}$					
	(c) $C_2H_5NH_2$ (d) CH_3NH_2					
13.	Which of the following compound is expected to be most basic					
	(a) Aniline (b) Methylamine					
	(c) Hydroxylamine (d) Ethylamine					
14.	Aniline when treated with HNO_2 and HCl at $0^{\circ}\mathrm{C}$					
	gives.					
	(a) Phenol (b) Nitrobenzene					
	(c) A diazo compound (d) None of these					
15.	Ethyl amine undergoes oxidation in the presence of KMnO ₄ to form					
	(a) An acid (b) An alcohol					
	(c) An aldehyde (d) A nitrogen oxide					
16.	Reaction of primary amines with aldehyde yields					
	(a) Amides (b) Aldimines					
	(c) Nitriles (d) Nitro compounds					
17.	Nitrobenzene on nitration gives					
	(a) o-dinitrobenzene					
	(b) p-dinitrobenzene					
	(c) m-dinitrobenzene					
	(d) o-and p-nitrobenzene					
18.	When primary amines are treated with HCl. the Product obtained is					
	(a) An Alcohol (b) A cyanide					
	(c) An amide (d) Ammonium salt					
19.	Which of the following do not react with HNO ₂					
	(a) Primary nitroalkanes					
	(b) Secondary nitroalkanes					
	(c) Tertiary nitroalkanes					
	(<i>d</i>) All of these					
20.	The product of mustard oil reaction is					
	(a) Alkyl isothiocyanate					
	(b) Dithio carbonamide					
	(c) Dithio ethylacetate					
	(d) Thioether					
	()					

- **21.** The maximum number of $-NO_2$ groups that can be introduced by nitration in benzene is usually
 - (a) 4 (*b*) 2
 - (c) 3 (d) 6
- 22. Primary nitro compounds when reacts with HNO₂ forms crystalline solids which on treatment with NaOH gives
 - (a) Red solution (b) Blue solution
 - (c) White precipitate (d) Yellow colouration

23. When methyl cyanide is hydrolysed in presence of alkali, the product is

	(a) Acetamide	(b) Methane
	(c) $CO_2 + H_2O$	(d) Acetic acid
24.	Methyl amine reacts v	with HNO_2 giving
	(a) $CH_3O - N = O$	(b) CH_3 –O– CH_3
	(c) CH ₃ OH	(d) (a) and (b) both

Answer Keys

1.(d)	2. (<i>c</i>)	3. (<i>b</i>)	4. (<i>b</i>)	5. (<i>a</i>)	6. (<i>c</i>)	7. (<i>b</i>)	8. (<i>c</i>)	9. (<i>d</i>)	10. (<i>b</i>)
11. (b)	12. (<i>c</i>)	13. (<i>d</i>)	14. (<i>c</i>)	15. (<i>c</i>)	16. (<i>b</i>)	17. (<i>c</i>)	18. (<i>d</i>)	19. (c)	20. (<i>a</i>)
21. (<i>c</i>)	22. (<i>a</i>)	23. (d)	24. (d)						

Solutions

1. C_3H_9N can form all the 3 amines. CH₃CH₂CH₂-NH₂, 1° amine CH₃-CH₂-NH-CH₃,

 2° amine

$$\begin{array}{c} \operatorname{CH}_3 - \operatorname{N} - \operatorname{CH}_3 \\ I \\ \operatorname{CH}_3 \\ 3^\circ \text{ amine} \end{array}$$

2.
$$\operatorname{NH}_2$$
 $\bigvee_{\operatorname{NH}_2}$ NH_2 NH_2

- 1° amine
- 3. $CH_3CH_2-O-N = O$ is a nitrite derivative, hence it is not a nitro derivative.
- 4. Four 1° amines are possible $\mathrm{CH_3CH_2CH_2CH_2NH_2,\ (CH_3)_2\ CHCH_2NH_2,}$ CH₃CH(NH₂) CH₂CH₃, (CH₃)₃ CNH₂
- 5. The molecular formula of benzonitrile of phenyl cyanide is C₆H₅CN.
- 6. Hofmann's bromamide reaction

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CO}-\mathrm{NH}_{2}+\mathrm{Br}_{2}+4\mathrm{KOH} \overset{\mathrm{H}_{2}\mathrm{O}}{\longrightarrow} \\ \mathrm{Acetamide} \\ \mathrm{CN}_{3}\mathrm{NH}_{2}+\mathrm{K}_{2}\mathrm{CO}_{3}+2\mathrm{KBr}+2\mathrm{H}_{2}\mathrm{O} \\ \mathrm{Methyl\ amine} \end{array}$$

7.
$$CH_3C \equiv N + 4[H] \xrightarrow{Na+C_2H_5OH} CH_3CH_2NH_2$$

8. $CH_3 - CH_2 - NO_2 + 6[H] \xrightarrow{Sn/HCl}$
Nitro ethane
 $CH_3 - CH_2 - NH_2 + 2H_2O$

Ethyl amine

9.
$$CH_3 \xrightarrow{NH_3} CH_3NH_2 \xrightarrow{CH_3I}$$

Methyl amine
 $(CH_3)_2NH \xrightarrow{CH_3I} (CH_3)_3N$
Dimethyl amine

10. $CH_3CONH_2 \xrightarrow{P_2O_5} CH_3CN \xrightarrow{4H} CH_3CH_2NH_2$

11.
$$\underbrace{\bigcirc}_{\text{Aniline}}^{\text{NH}_2} \xrightarrow[0^\circ - 5^\circ \text{C}]{N_2\text{Cl}} \xrightarrow[V_2\text{Cl}]{N_2\text{Cl}} + 2\text{H}_2\text{O}$$

Benzene diazonium Chloride

12.
$$CH_3Br \xrightarrow{alc.KCN} CH_3CN \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$$

[x] reduction $CH_3CH_2NH_2$

13. Due to +ve I.E. of alkyl group, N-atom of amines acquires partial -ve charge thus electron pair is easily donated.



 $-\mathrm{NO}_2$ group is meta directed group.

18.
$$CH_3 - CH_2 - NH_2 + HCl \rightarrow CH_3CH_2 - NH_3^+Cl^-$$

Ethyl ammonium chloride

Amines are basic in nature they reacts with acid to form salt.

- 19. Tertiary nitroalkanes do not react with HNO_2 because in tertiary nitroalkanes α H atom is absent.
- 20. Mustard oil reaction

$$\begin{array}{ll} \mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{NH}_2 + \mathrm{CS}_2 \xrightarrow{\mathrm{HgCl}_2} & \mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{N} = \mathrm{C} = \mathrm{S} + \mathrm{H}_2 \mathrm{S} \\ & \text{Ethyl amine} & & \text{Ethyl isothiocyanate} \end{array}$$

1, 3, 5-trinitrobenzene

3-nitro group can be introduced.

23. $CH_3 - C \equiv N + 2H_2O \rightarrow CH_3COOH + NH_3$ Methyl cyanide Acetic acid

24.
$$CH_3NH_2 + 2HNO_2 \rightarrow CH_3 - O - N = O + N_2 + 2H_2O$$

 $2CH_3NH_2 + 2HNO_2 \rightarrow CH_3 - O - CH_3 + 2N_2 + 3H_2O$