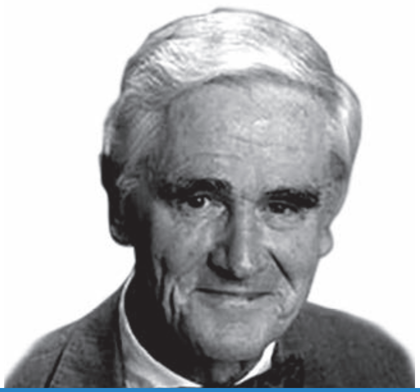
UNIT 13

ORGANIC NITROGEN COMPOUNDS



Donald James Cram

Donald James Cram was an American chemist who shared the 1987 Nobel Prize in Chemistry with Jean-Marie Lehn and Charles J. Pedersen "for their development and use of molecules with structure-specific interactions of high selectivity." They were the founders of the field of host–guest chemistry Cram expanded upon Charles Pedersen's ground-breaking synthesis of crown ethers, two-dimensional organic compounds that are able to recognize and selectively combine with the ions of certain metal elements. He also did work in stereochemistry and Cram's rule of asymmetric induction is named after him.

U3U7L5

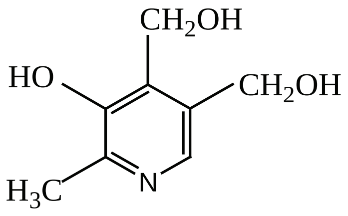
Learning Objectives

After studying this unit the student will be able to

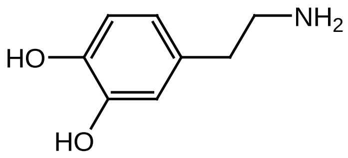
- understand isomerism in organic nitro compounds
- describe the preparation and properties of nitro compounds
- classify amines as primary, secondary and tertiary
- describe the methods of preparation of amines
- explain the properties of amines
- distinguish between primary, secondary and tertiary amines
- describe the method of preparation of diazonium salts
- explain the preparation and properties of cyanides

INTRODUCTION

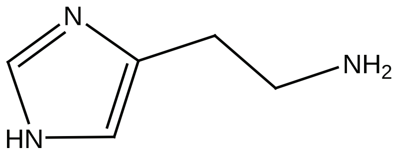
Organic compounds containing nitrogen are essential to life. For example; amines, the organic derivatives of ammonia play an important role in bioregulation, neurotransmission,etc., Pyridoxine, Vitamin B_6 is an organic nitrogen compound which is needed to maintain the health of nerves, skin and red blood cells. Plants synthesise alkaloids, and biologically active amines to protect them from being eaten away by insects and other animals. Diazonium salts finds important applications in synthetic organic chemistry. Nitrogen compounds are the important constituents of explosives, drugs, dyes, fuels, polymers, synthetic rubbers, etc.,



Vitamin B_6



dopamine
neurotransmitter



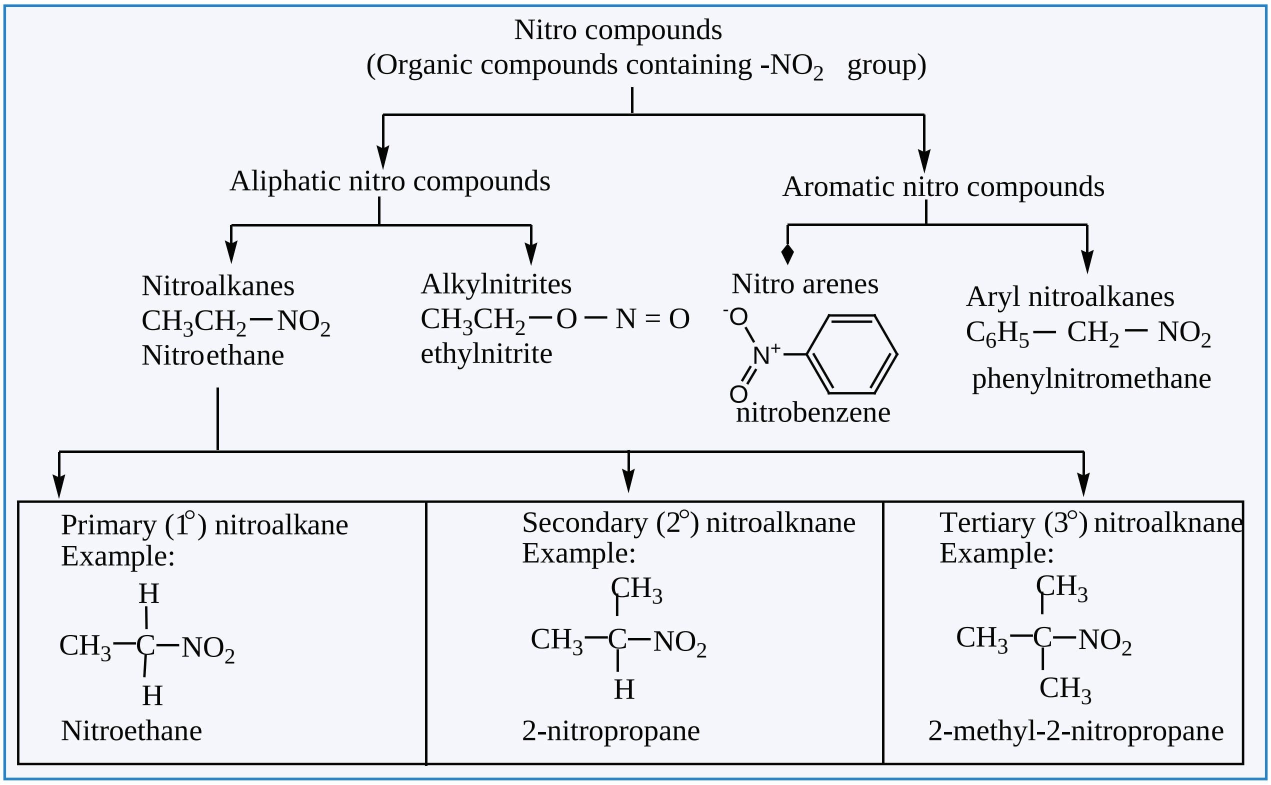
Histamine
dilates blood vessels

In this unit, we will learn the preparation, properties and uses of nitrocompounds and amines.

13.1 NITRO COMPOUNDS

Nitro compounds are considered as the derivaties of hydrocarbons. If one of the hydrogen atom of hydrocarbon is replaced by the $-NO_2$ group, the resultant organic compound is called a nitrocompound.

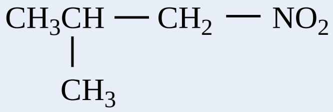
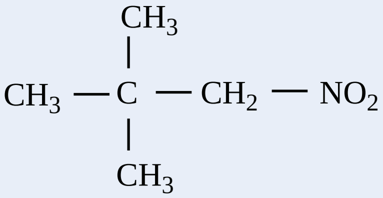
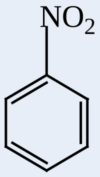
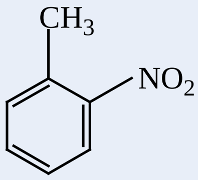
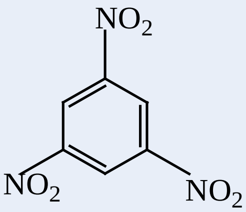
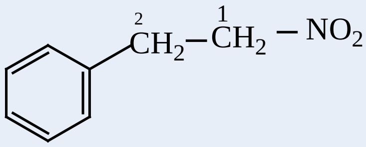
13.1.1 Classification of nitrocompounds



Nitroalkanes are represented by the formula, $R\text{-}NO_2$ where R is an alkyl group $(C_nH_{2n+1}\text{-})$. Nitroalkanes are further classified into primary, secondary, tertiary nitroalkanes on the basis of type of carbon atom to which the nitro $(\text{-}NO_2)$ group is attached.

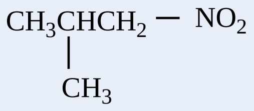
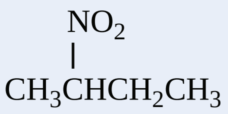
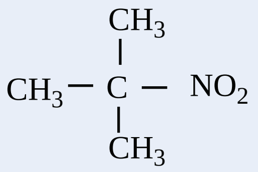
13.1.2 Nomenclature of nitroalkanes

In the IUPAC nomenclature, the nitroalkanes are named by adding prefix nitro before the name of alkane, the position of the nitro group is indicated by number.

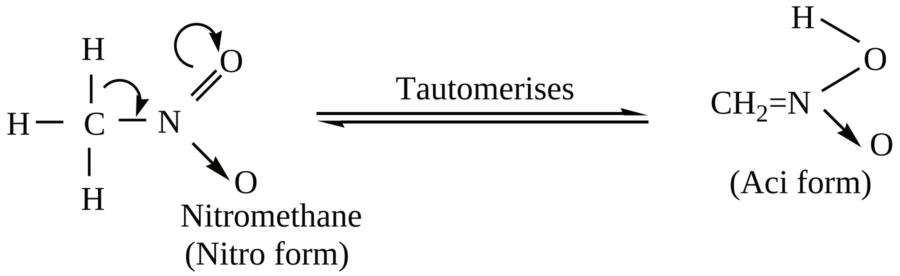
Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	**Root used**	**Primary suffix**	**Secondary Suffix**
 $CH_3\underset{\underset{CH_3}{\vert}}{CH}-CH_2-NO_2$ 2- Methyl – 1- nitropropane	2- Methyl – 1- nitro	prop	ane	–
 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2-NO_2$ 2,2 – dimethyl – 1- nitro propane	2,2 – dimethyl – 1- nitro	prop	ane	–
 Nitrobenzene	nitro	benzene	–	–
 2-nitro -1-methyl benzene	2-nitro-1-methyl	benzene	–	–
 1,3,5 – trinitrobenzene	1,3,5 – trinitro	benzene	–	–
 2 – phenyl – 1- nitroethane	2 – phenyl – 1- nitro	eth	ane	

13.1.3 ISOMERISM

Nitroalkanes exhibit chain and position isomerism among their own class and functional isomerism with alkyl nitrites and special type tautomerism can also exist in nitro alkanes having an α-H atom. For example, nitro compounds having the molecular formula $C_4H_9NO_2$ exhibit the following isomerisms.

Isomerism	Structural formula of isomers
Chain isomerism: They differ in the length of carbon chain.	$CH_3CH_2CH_2CH_2-NO_2$ 1 - nitrobutane and $CH_3CH(CH_3)CH_2-NO_2$ 2 - methyl - 1-nitropropane
Position isomerism: They differ in the position of nitro group.	$CH_3CH_2CH_2CH_2-NO_2$, 1 - nitrobutane $CH_3CH(NO_2)CH_2CH_3$ 2 - nitrobutane and $CH_3-C(CH_3)_2-NO_2$ 2 - methyl - 2-nitropropane
Functional isomerism: Nitroalkanes exhibit functional isomerism with alkylnitrites	$CH_3CH_2CH_2CH_2-NO_2$ 1 - nitrobutane and $CH_3CH_2CH_2CH_2-O-N=O$ butyl nitrite

Tautomerism: Primary and secondary nitroalkanes, having α-H , also show an equilibrium mixture of two tautomers namely nitro – and aci – form

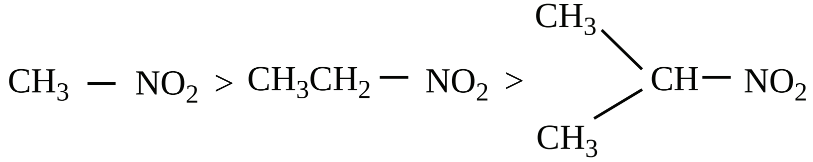


Tertiary nitro alkanes donot exhibit tautomerism due to absence of α-H atom.

S.No.	Nitro form	Aci – form
1.	Less acidic	More acidic
2.	Dissolves in NaOH slowly	Dissolves in NaOH instantly
3.	Decolourises $FeCl_3$ solution	With $FeCl_3$ gives reddish brown colour
4.	Electrical conductivity is low	Electrical conductivity is high

13.1.4 Acidic nature of nitro alkanes

The α-H atom of 1° & 2° nitroalkanes show acidic character because of the electron with drawing effect of NO_2 group. These are more acidic than aldehydes, ketones, ester and cyanides. Nitroalkanes dissolve in NaOH solution to form a salt. Aci – nitro derivatives are more acidic than nitro form. When the number of alkyl group attached to α carbon increases, acidity decreases. due to +I effect of alkyl groups.



$$CH_3-NO_2 > CH_3CH_2-NO_2 > (CH_3)_2CH-NO_2$$

Evaluate yourself

Write all possible isomers for the following compounds.

i) C_2H_5-NO_2 ii) C_3H_7-NO_2

13.1.5 Preparation of nitroalkanes

1) From alkyl halides: (Laboratory method)

a) Alkyl bromides (or) iodides on heating with ethanolic solution of potassium nitrite gives nitroethane.

$$\underset{\text{Ethyl bromide}}{CH_3CH_2\text{-}Br} + KNO_2 \xrightarrow[SN^2]{\text{ethanol}/\Delta} \underset{\text{Nitroethane}}{CH_3CH_2\text{-}NO_2} + KBr$$

The reaction follows SN2 mechanism.

This method is not suitable for preparing nitrobenzene because the bromine directly attached to the benzene ring cannot be cleaved easily.

2) Vapour phase nitration of alkanes: (Industrial method)

Gaseous mixture of methane and nitric acid passed through a red hot metal tube to give nitromethane.

$$\underset{\text{Methane}}{CH_{4(g)}} + HNO_{3\,(g)} \xrightarrow[\text{Red hot Si tube}]{675\text{ K}} \underset{\text{nitro methane}}{CH_3\text{-}NO_2} + H_2O$$

Except methane, other alkanes (upto n – hexane) give a mixture of nitroalkanes due to C-C cleavage. The individual nitro alkanes can be separated by fractional distillation.

$$\underset{\text{Ethane}}{CH_3\text{-}CH_3} + HNO_3 \xrightarrow{675\text{ K}} \underset{\text{Nitroethane(73\%)}}{CH_3CH_2\text{-}NO_2} + \underset{\text{Nitromethane (27\%)}}{CH_3NO_2}$$

3) From α- halocarboxylic acid

α- choloroacetic acid when boiled with aqueous solution of sodium nitrite gives nitromethane.

$$\underset{\alpha\text{ - chloro acetic acid}}{Cl\text{ - }CH_2\text{-}COOH} + NaNO_2 \xrightarrow[SN^2]{H_2O/\text{Heat}} \underset{\text{Nitromethane}}{CH_3\text{-}NO_2} + CO_2 + NaCl$$

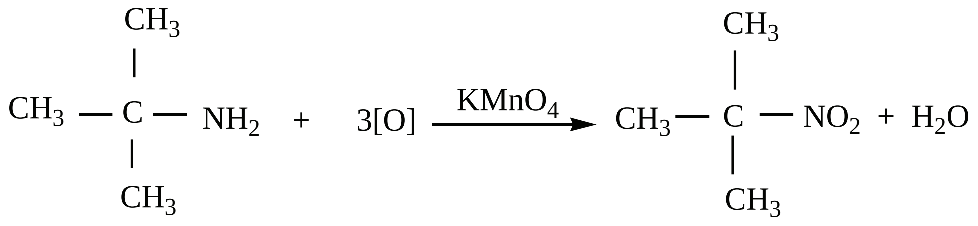
Evaluate yourself

4) Find out the product of the following reactions.

i) $CH_3CH(Cl)COOH \xrightarrow[\text{ii) } H_2O/\Delta]{\text{i) } NaNO_2} ?[X]$ ii) $CH_3CH_2\text{-}Br + NaNO_2 \xrightarrow{\text{alcohol }/\Delta} [Y]$

4) Oxidation of tert – alkyl amines

tert – butyl amine is oxidised with aqueous $KMnO_4$ to give tert – nitro alkanes.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-NH_2 + 3[O] \xrightarrow{KMnO_4} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-NO_2 + H_2O$$

tert-butylamine 2 - methyl - 2 - nitro propane

5) Oxidation of Oximes

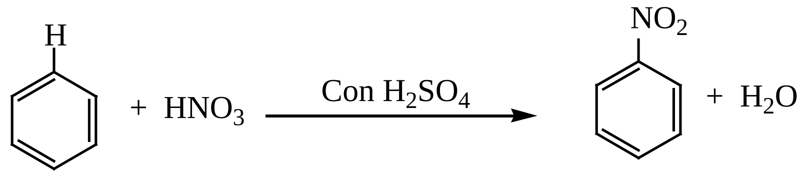
Oxidation of acetaldoxime and acetoneoxime with trifluoroperoxy acetic acid gives nitroethane (1^0) and 2 – nitropropane (2^0) respectively.

$$\underset{\text{Acetaldoxime}}{CH_3\text{-}CH{=}N\text{-}OH} \xrightarrow[{[O]}]{CF_3COOOH} \underset{\text{Nitroethane}}{CH_3CH_2\text{-}NO_2}$$

13.1.6 Preparation of Nitroarenes

1) By Direct nitration

When benzene is heated at 330K with a nitrating mixture ($Con.HNO_3 + Con.H_2SO_4$), electrophilic substitution takes place to form nitro benzene. (Oil of mirbane)

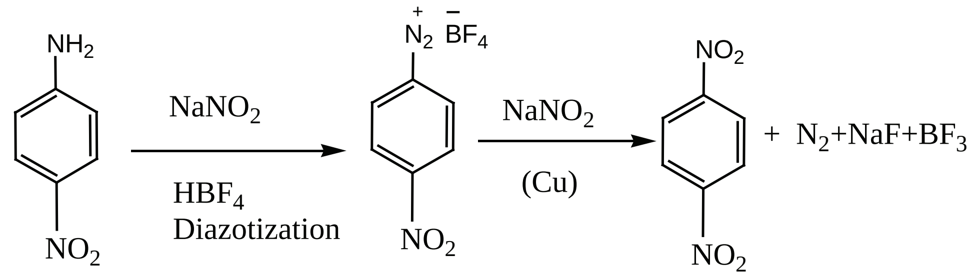


On direct nitration of nitrobenzene m- dinitrobenzene is obtained

2) Indirect method

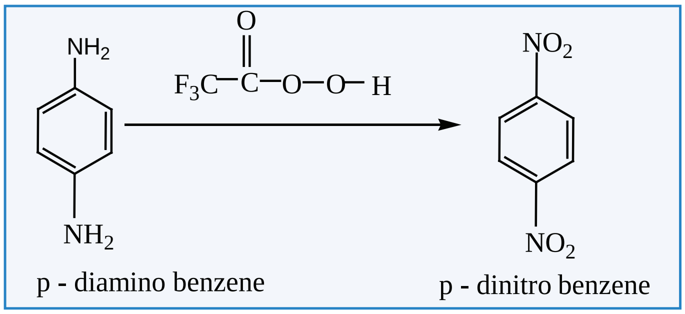
Nitration of nitro benzene gives m-dinitrobenzene. The following method is adopted for the preparation of p-dinitrobenzene.

For example



p - nitroaniline p - nitrodiazo fluoroborate p - dinitro benzene

Amino group can be directly converted into nitro group, using caro's acid (H_2SO_5) (or) persulphuric acid ($H_2S_2O_8$) (or) peroxytrifluro acetic acid ($F_3C.CO_3H$) as oxidising agent.



p - diamino benzene

p - dinitro benzene

13.1.7 Physical properties of nitro alkane

The lower nitroalkanes are colourless pleasant smelling liquids, sparingly soluble in water, but readily soluble in organic solvents like benzene, acetone etc… They have high boiling points because of their highly polar nature. Alkylnitrites have lower boiling points than nitro alkanes.

13.1.8 Chemical properties of nitroalkanes

Nitroalkanes undergo the following common reactions.

i. Reduction ii. Hydrolysis iii. Halogenations

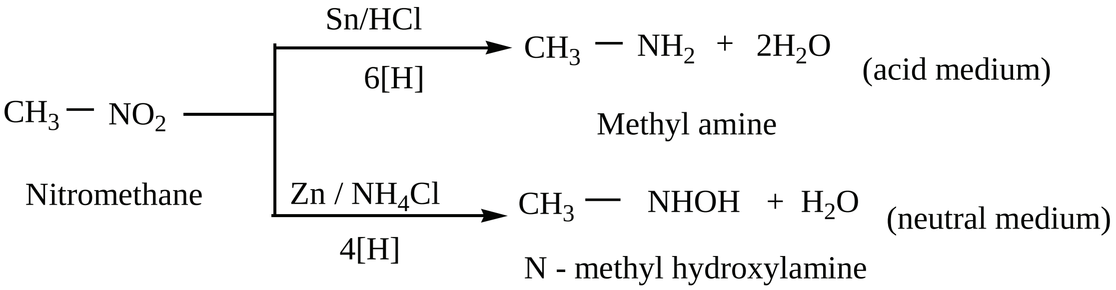
i. Reduction of nitroalkanes

Reduction of nitroalkanes has important synthetic applications. The various reduction stages of nitro group are given below.

$$CH_3-NO_2 \xrightarrow[-H_2O]{+2[H]} CH_3-N=O \xrightarrow{+2[H]} CH_3-NHOH \xrightarrow[-H_2O]{+2[H]} CH_3-NH_2$$

nitromethane nitroso methane N - methyl hydroxylamine methylamine

The final product depends upon the nature of reducing agent as well as the pH of the medium.



$$CH_3-NO_2 \xrightarrow[6[H]]{Sn/HCl} CH_3-NH_2 + 2H_2O \quad \text{(acid medium)}$$

Nitromethane → Methyl amine

$$CH_3-NO_2 \xrightarrow[4[H]]{Zn / NH_4Cl} CH_3-NHOH + H_2O \quad \text{(neutral medium)}$$

N - methyl hydroxylamine

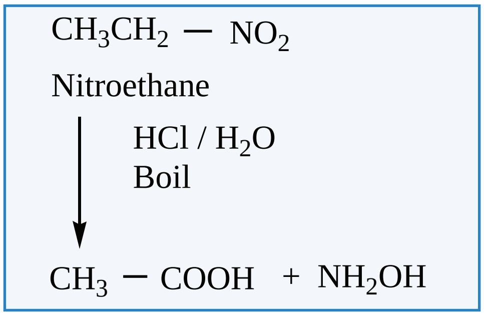
Reduction of alkyl nitrites

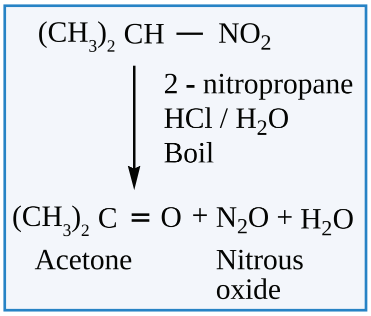
Ethylnitrite on reduction with Sn / HCl gives ethanol

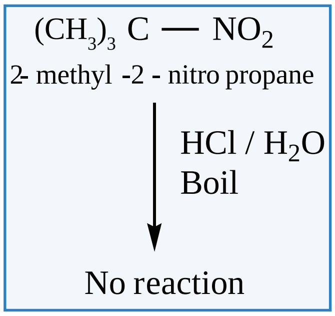
$$CH_3CH_2-O-N=O + 6[H] \xrightarrow{Sn / HCl} CH_3CH_2-OH + NH_3 + H_2O$$

ii. Hydrolysis of nitroalkanes

Hydrolysis can be effected using conc. HCl or conc. H_2SO_4. Primary nitroalkanes on hydrolysis gives carboxylic acid, and the secondary nitroalkanes give ketones. The tertiary nitroalkanes have no reaction.







On the other hand, the acid or base hydrolysis of ethyl nitrite gives ethanol.

$$\underset{\text{Ethylnitrite}}{CH_3CH_2-O-N=O} + HOH \xrightarrow[\text{(or) } H^+]{OH^-} \underset{\text{Ethanol}}{CH_3CH_2-OH} + HNO_2$$

iii. Halogenation of nitroalkanes

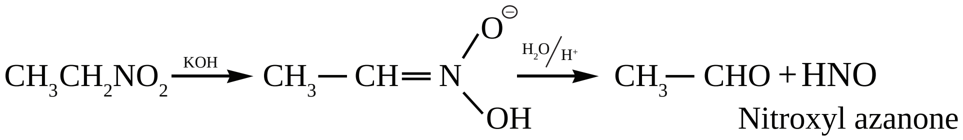
Primary and secondary nitroalkanes on treatement with Cl_2 or Br_2 in the presence of NaOH give halonitroalkanes. The α - H atom of nitroalkanes are successively replaced by halogen atoms.

$$CH_3-NO_2 + 3Cl_2 \xrightarrow{NaOH} \underset{\text{Chloropicrin (trichloronitromethane)}}{CCl_3-NO_2} + 3HCl$$

Toxicity

Nitroethane is suspected to cause genetic damage and be harmful to the nervous system.

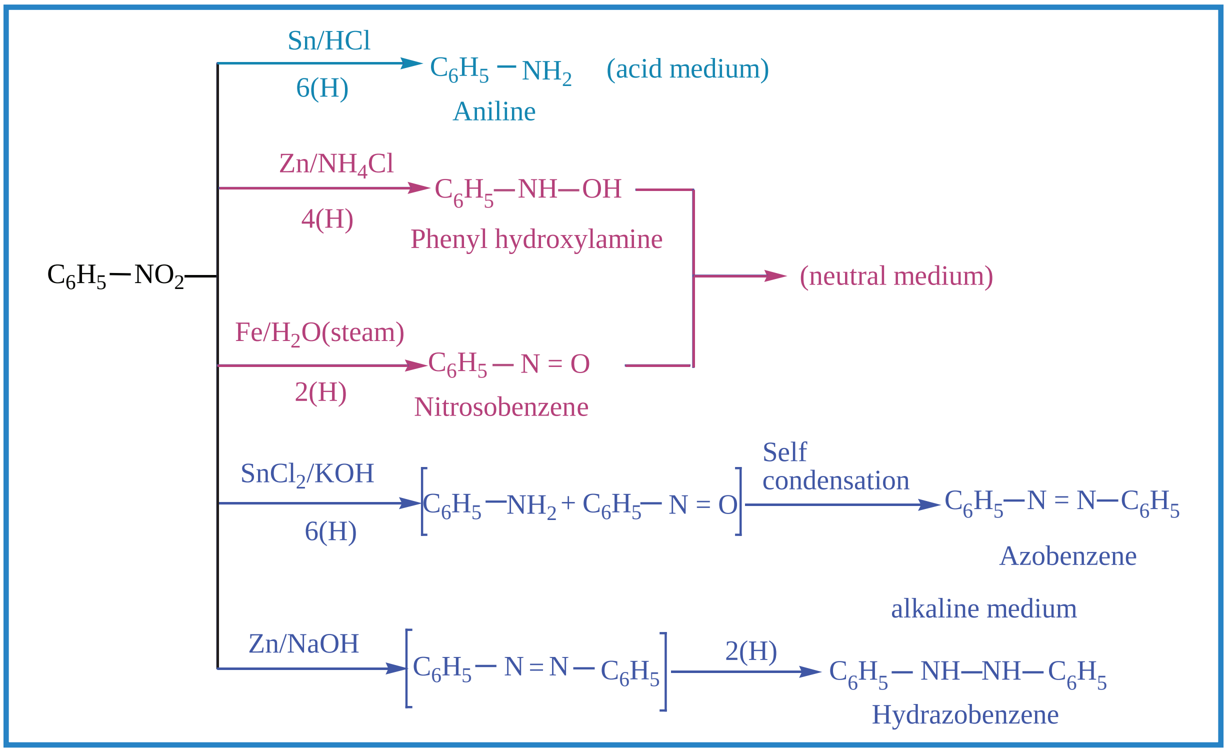
iv. Nef carbonyl synthesis :



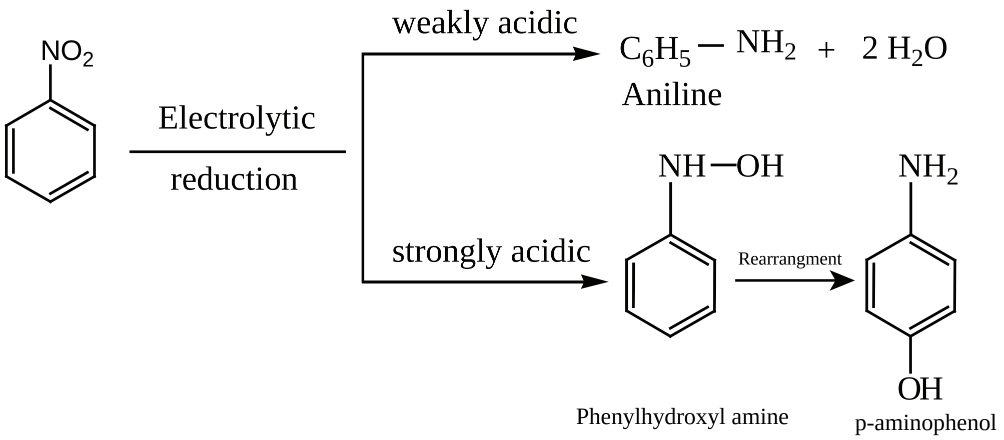
$$CH_3CH_2NO_2 \xrightarrow{KOH} CH_3-CH=N\begin{smallmatrix}O^{\ominus}\\ OH\end{smallmatrix} \xrightarrow{H_2O/H^+} CH_3-CHO + HNO$$

Nitroxyl azanone

Chemical Properties of nitrobenzene



Electrolytic reduction:

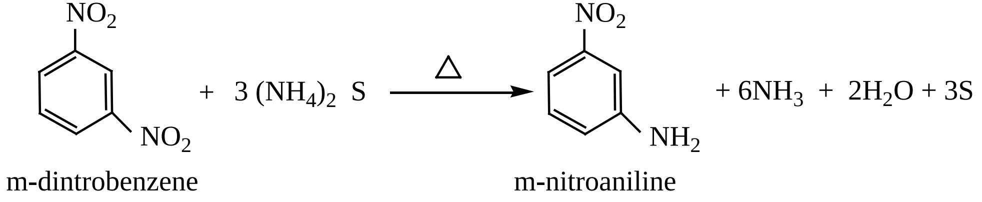


Reduction of catalytic and metal hydrides

Nitrobenzene reduction with Ni (or) Pt, (or) $LiAlH_4$ to give aniline

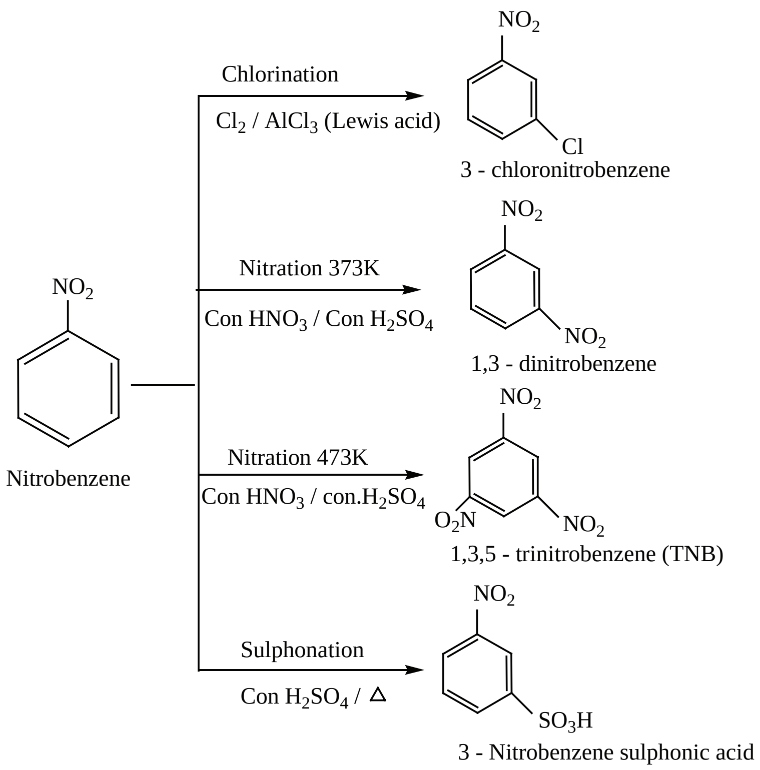
$$C_6H_5 - NO_2 + 6\,[H] \xrightarrow[\text{(or) LiAH}_4]{\text{Ni (or) Pt / H}_2} C_6H_5 - NH_2 + 2\,H_2O$$

Selective reduction of polynitro compounds



Electrophilic substitution reaction

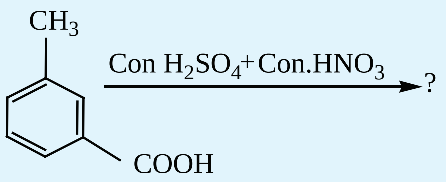
The electrophilic substitution reactions of nitrobenzene are usually very slow and vigorous reaction condition have to be employed (- NO_2 group is stongly deactivating and m – directing).



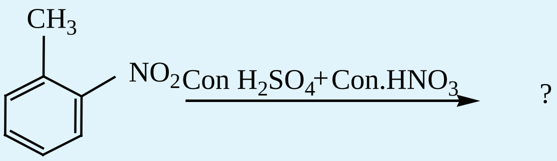
Nitrobenzene does not undergo Friedel – Crafts reactions due to the strong deactivating nature of -NO_2 group.

Evaluate yourself Predict the major product that would be obtained on nitration of the following compounds

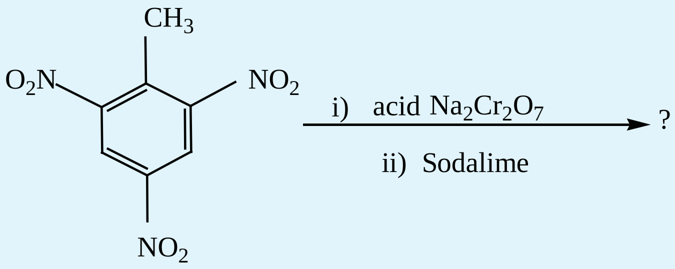
i)



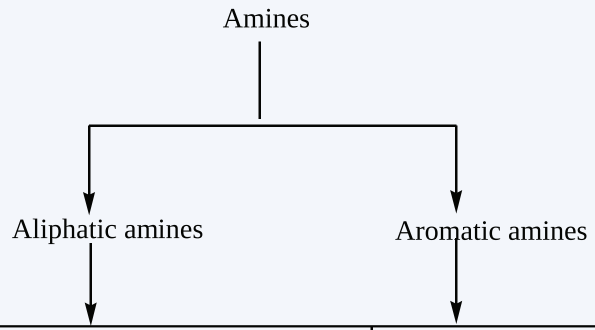
ii)



iii)



13.2 Amines - clasification



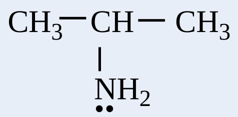
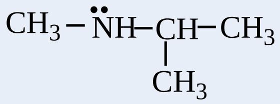
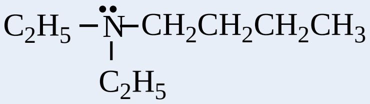
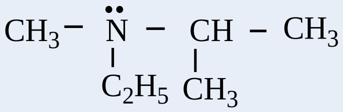
		Aliphatic amines	Aromatic amines
Primary		$CH_3-CH_2-NH_2$ ethanamine	$C_6H_5-NH_2$ benzenamine(aniline)
Secondary	simple	$CH_3-NH-CH_3$ N-methylmethanamine	$C_6H_5-NH-C_6H_5$ N-phenylbenzenamine
	mixed	$CH_3-NH-CH_2-CH_3$ N-methylethanamine	$C_6H_5-NH-CH_3$ N-phenylmethanamine
Tertiary	simple	$CH_3-\overset{CH_3}{\overset{\mid}{N}}-CH_3$ N,N-dimethylmethanamine	$C_6H_5-\overset{C_6H_5}{\overset{\mid}{N}}-C_6H_5$ N,N-diphenylbenzenamine
	mixed	$CH_3-\underset{\underset{H_3C-CH-CH_3}{\mid}}{N}-CH_2-CH_3$ (N-ethyl-N-methyl) propan–2–amine	$C_6H_5-\overset{CH_3}{\overset{\mid}{N}}-CH_2-CH_3$ N-methyl-N-phenylethanamine

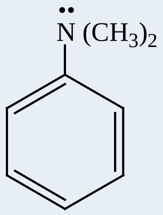
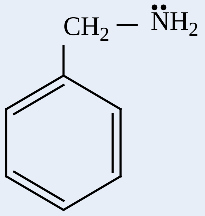
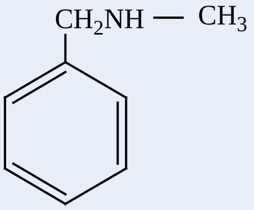
13.2.1 Nomenclature

a) Common system:

In common system, an aliphatic amine is named by prefixing alkyl group to amine. The prefixes di-,tri-, and tetra-, are used to describe two, three(or) four same substituent's.

b) IUPAC System:

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	**Root used**	**Primary suffix**	**Secondary Suffix**
Isopropylamine  $CH_3-CH(\ddot{N}H_2)-CH_3$ Propan – 2- amine	–	prop	an$\cancel{e}$	2- amine
Allylamine $^3CH_2 = {}^2CH-{}^1CH_2-\ddot{N}H_2$ Prop-2-en-1-amine	–	prop	2-en	-1-amine
Hexamethylene diamine $H_2\ddot{N}-(CH_2)_6-\ddot{N}H_2$ Hexane – 1, 6 – diamine	–	Hex	ane	– 1, 6 – diamine
Methyl isopropyl amine  $CH_3-\ddot{N}H-CH(CH_3)-CH_3$ N – methyl propan – 2- amine	N – methyl	prop	an$\cancel{e}$	– 2- amine
Diethyl butylamine  $C_2H_5-\ddot{N}(C_2H_5)-CH_2CH_2CH_2CH_3$ N, N – Diethyl butan-1-amine	N, N – Diethyl	but	an$\cancel{e}$	-1-amine
Ethyl methyl isopropylamine  $CH_3-\ddot{N}(C_2H_5)-CH(CH_3)-CH_3$ N – ethyl – N- methyl propan – 2 – amine	N – ethyl – N- methyl	prop	an$\cancel{e}$	-2-amine

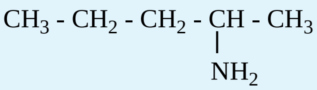
N,N – Dimethyl aniline  N,N – Dimethylbenzenamine	N,N – Dimethyl	benzen~~e~~	–	amine
Benzylamine  Phenyl methanamine	Phenyl	meth	an~~e~~	amine
N – methyl benzylamine  N – methyl phenyl methanamine	N – methyl phenyl	meth	an~~e~~	amine

Evaluate yourself

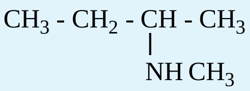
Draw the structure of the following compounds

- i. Neopentylamine
- ii. Tert – butylamine
- iii. α - amino propionaldehyde
- iv. Tribenzylamine
- v. N – ethyl – N – methylhexan – 3- amine

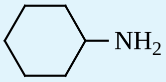
8) Give the correct IUPAC names for the following amines

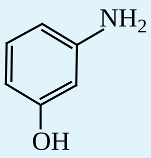
i) 

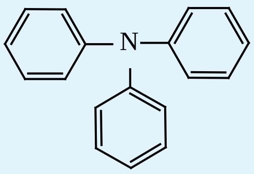
$CH_3 - CH_2 - CH_2 - \underset{NH_2}{\underset{|}{CH}} - CH_3$

ii) 

$CH_3 - CH_2 - \underset{NH\,CH_3}{\underset{|}{CH}} - CH_3$

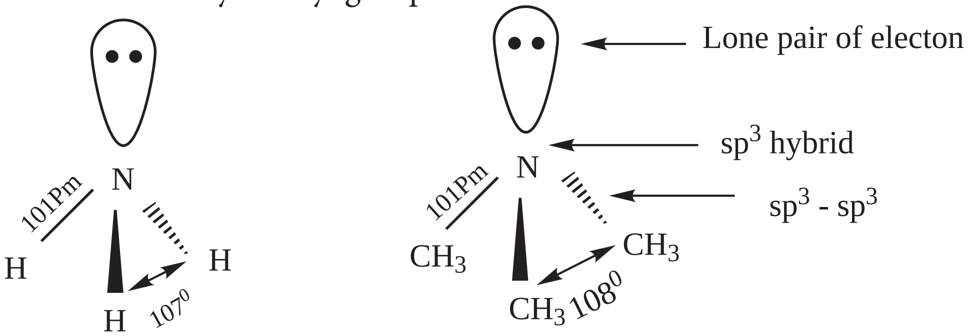
iii) 

iv) 

v) 

13.2.2 Structure of amines

Like, ammonia, nitrogen atom of amines is trivalent and carries a lone pair of electron and sp^3 hybridised, out of the four sp^3 hybridised orbitals of nitrogen, three sp^3 orbitals overlap with orbitals of hydrogen (or) alkyl groups of carbon, the fourth sp^3 orbital contains a lone pair of electron. Hence, amines posses pyramidal geometry. Due to presence of lone pair of electron $C-N-H$ (or) $C-N-C$ bond angle is less than the normal tetrahedral bond angle 109.5^0. For example, the $C-N-C$ bond angle of trimethylamine is 108^0 which is lower than tetrahedral angle and higher than the $H-N-H$ bond angle of 107°. This increase is due to the repulsion between the bulky methyl groups.



13.2.3 General methods of preparation Amines

Aliphatic and aromatic amines are prepared by the following methods.

1) From nitro compounds

Reduction of Nitro compounds using H_2 / Ni (or) Sn / HCl or Pd/H_2 gives primary amines.

$$CH_3CH_2-NO_2 \xrightarrow[\text{Fe / HCl, 6 [H]}]{3H_2\text{ / Ni (or)}} CH_3CH_2-NH_2 + 2H_2O$$

Nitroethane ethanamine

$$C_6H_5-NO_2 \xrightarrow[\text{(or) Sn / HCl}]{3H_2\text{ / Pt, 680 K}} C_6H_5-NH_2 + 2H_2O$$

Nitrobenzene Aniline

2) From nitriles

a) Reduction of alkyl or aryl cyanides with H_2/Ni (or) $LiAlH_4$ (or) Na / C_2H_5OH gives primary amines. The reduction reaction in which Na / C_2H_5OH is used as a reducing agent is called mendius reaction

$$CH_3-CN \xrightarrow[\text{4 [H]}]{Na(Hg)\text{ / }C_2H_5OH} CH_3CH_2-NH_2$$

ethanenitrile ethanamine

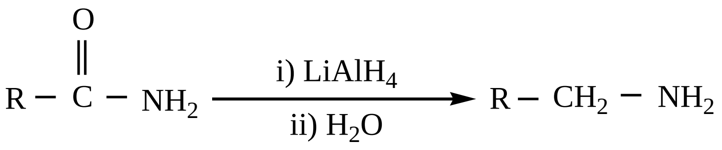
b) Reduction of isocyanides with sodium amalgam / C_2H_5OH gives secondary amines

$$CH_3-NC \xrightarrow[\text{4 [H]}]{Na(Hg)\text{ / }C_2H_5OH} CH_3-NH-CH_3$$

Methyl isocyanide N-methylmethanamine

3) From amides

a) Reduction of amides with $LiAlH_4$ gives amines

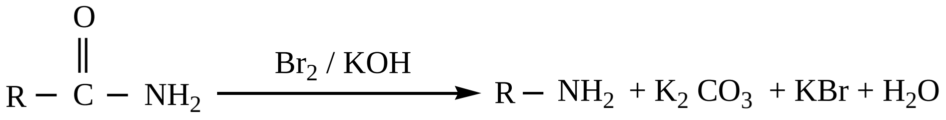


$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[ii)\ H_2O]{i)\ LiAlH_4} R-CH_2-NH_2$$

b) Hoffmann's degradation reaction

When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

Example:



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2\,/\,KOH} R-NH_2 + K_2CO_3 + KBr + H_2O$$

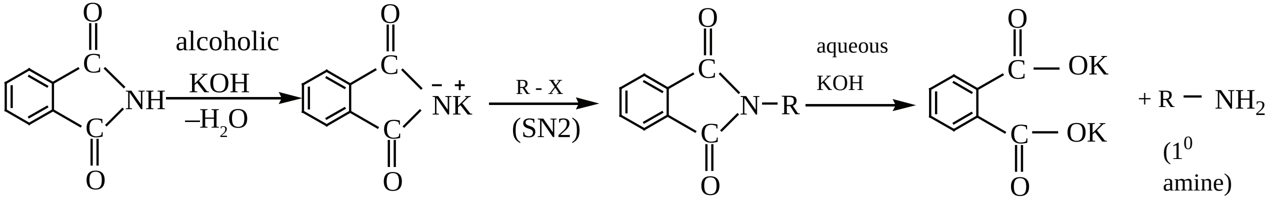
amide
R = Alkyl (or) Aryl

Primary amine

4) From alkyl halides

a) Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of Aliphatic primary amines. Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline cannot be prepared by this method because the arylhalides do not undergo nucleophilic substitution with the anion formed by phthalimide



Phthalimide

Potassium phthalimide

N - alkyl phthalimide

Potassium pthalati

b) Hoffmann's ammonolysis

When Alkyl halides (or) benzylhalides are heated with alcoholic ammonia in a sealed tube, mixtures of 1^0, 2^0 and 3^0 amines and quaternary ammonium salts are obtained.

$$CH_3-Br \xrightarrow[\Delta]{\ddot{N}H_3} \underset{1^0\text{ - amine}}{CH_3-\ddot{N}H_2} \xrightarrow{CH_3\text{ - }Br} \underset{2^0\text{ - amine}}{(CH_3)_2\ddot{N}H} \xrightarrow{CH_3\,Br} \underset{3^0\text{- amine}}{(CH_3)_3\ddot{N}} \xrightarrow{CH_3\,Br} \underset{\text{Quarternary ammonium bromide}}{(CH_3)_4\overset{+}{N}\,Br^-}$$

This is a nucleophilic substitution , the halide ion of alkyl halide is substituted by the $-NH_2$ group. The product primary amine so formed can also has a tendency to act as a nucleophile and hence if excess alkyl halide is taken, further nucleophilic substitution takes place leading to the formation of quarternary ammonium salt. However, if the process is carried out with excess ammonia, primary amine is obtained as the major product.

The order of reactivity of alkylhalides with amines.

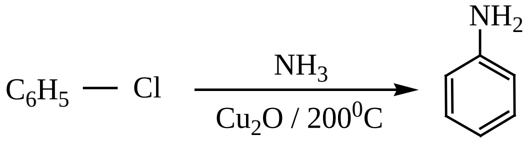
$$RI > RBr > RCl$$

c) **Alkyl halide can also be converted to primary amine by treating it with sodium azide** (NaN_3) **followed by the reduction using lithium aluminium hydride.**

$$\underset{\text{Methylbromide}}{CH_3-Br} \xrightarrow{NaN_3} \underset{\text{Methyl azide}}{CH_3-N_3} \xrightarrow{LiAlH_4} \underset{\text{Methylamine}}{CH_3-NH_2} + N_2$$

d) **Preparation of aniline from chlorobenzene**

When chlorobenzene is heated with alcoholic ammonia, aniline is obtained.



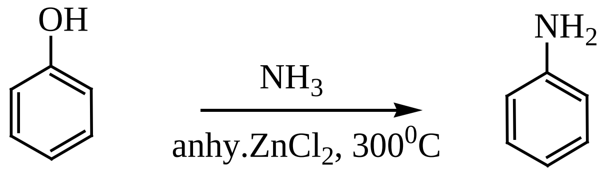
aniline

5) Ammonolysis of hydroxyl compounds

a) when vapour of an alcohol and ammonia are passed over alumina, W_2O_5 (or) silica at 400⁰C, all types of amines are formed. This method is called **Sabatier – Mailhe** method.

$$C_2H_5OH \xrightarrow[Al_2O_3,\ -H_2O]{\ddot{N}H_3} C_2H_5-\ddot{N}H_2 \xrightarrow[-H_2O]{C_2H_5OH} (C_2H_5)_2\ddot{N}H \xrightarrow[-H_2O]{C_2H_5OH} (C_2H_5)_3\ddot{N}$$

b) Phenol reacts with ammonia at 300⁰C in the presence of anhydrous $ZnCl_2$ to give aniline



Phenol aniline

13.2.4 Properties of amines

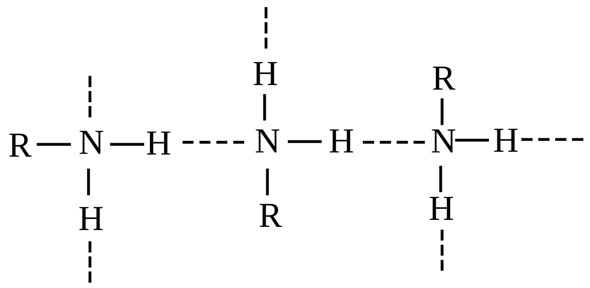
1. Physical state and smell

The lower aliphatic amines (C_1-C_2) are colourless gases and have ammonia like smell and those with four or more carbons are volatile liquids with fish like smell.

Aniline and other arylamines are usually colourless but when exposed to air they become coloured due to oxidation.

2. Boiling point

Due to the polar nature of primary and secondary amines, can form intermolecular hydrogen bonds using their lone pair of electorn on nitrogen atom. There is no such H-bonding in tertiary amines.



The boiling point of various amines follows the order,

$$CH_3-\ddot{N}H_2 > (CH_3)_2\ddot{N}H > (CH_3)_3\ddot{N}$$

$$1^\circ > 2^\circ > 3^\circ$$

Amines have lower boiling point than alcohols because nitrogen has lower electronegative value than oxygen and hence the N-H bond is less polar than -OH bond.

Table Boiling points of amines, alcohols and alkanes of comparable molecular weight.

S.NO.	Compound	Molecular mass	Boiling point (K)
1.	$CH_3(CH_2)_2NH_2$	59	321
2.	C_2H_5-NH-CH_3	59	308
3.	$(CH_3)_3N$	59	277
4.	$CH_3CH(OH)CH_3$	60	355
5.	$CH_3CH_2CH_2CH_3$	58	272.5

3) Solubility

Lower aliphatic amines are soluble in water, because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molecular mass of amines due to increase in size of the hydrophobic alkyl group. Amines are insoluble in water but readily soluble in organic solvents like benzene, ether etc.

13.2.5 Chemical properties

The lone pair of electrons on nitrogen atom in amines makes them basic as well as nucleophilic. They react with acids to form salts and also react with electrophiles.

They form salts with mineral acids

Example:

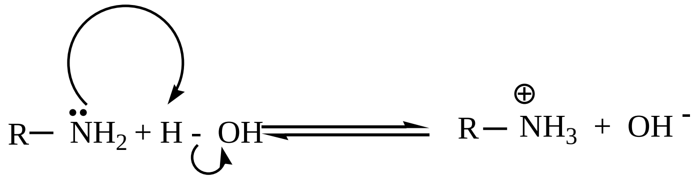
$$C_6H_5-\ddot{N}H_2 + HCl \rightleftharpoons C_6H_5-\overset{+}{N}H_3Cl^-$$

Aniline

Anilinium chloride

Expression for basic strength of amines

In the aqueous solutions, the following equilibrium exists and it lies far to the left, hence amines are weak bases compared to NaOH.



basicity constant $$K_b = \frac{\left[R-\overset{+}{N}H_3\right]\left[OH^-\right]}{\left[R-NH_2\right]}$$

The basicity constant K_b gives a measure of the extent to which the amine accepts the hydrogen ion (H^+) from water,

we know that,

Larger the value of K_b or smaller the value of pK_b, stronger is the base.

Table : pK_b values of Amines in Aqueous solution. (pK_b for NH_3 is 4.74)

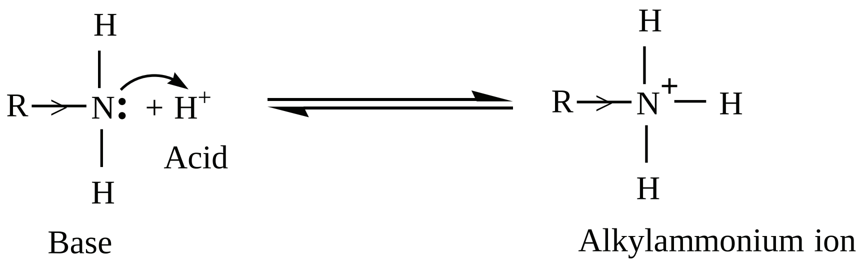
Amines	pKb	Amines	pKb	Amines	pKb
$CH_3-\ddot{N}H_2$	3.38	$C_2H_5\ddot{N}H_2$	3.29	$C_6H_5CH_2-\ddot{N}H_2$	4.70
$(CH_3)_2\ddot{N}H$	3.28	$(C_2H_5)_2\ddot{N}H$	3.00	$C_6H_5-\ddot{N}HCH_3$	9.30
$(CH_3)_3\ddot{N}$	4.22	$(C_2H_5)_3\ddot{N}$	3.25	$C_6H_5\ddot{N}(CH_3)_2$	8.92

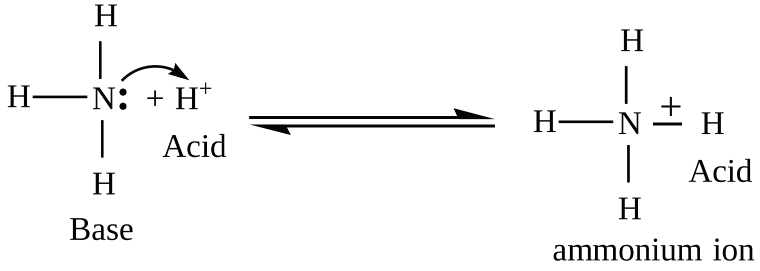
Influence of structure on basic character of amines

The factors which increase the availability of electron pair on nitrogen for sharing with an acid will increase the basic character of an amine. When a +I group like an alkyl group is attached to the nitrogen increase the electron density on nitrogen which makes the electron pair readily available for protonation.

a) Hence alkyl amines are stronger bases than ammonia.

Consider the reaction of an alkyl amine $(R-\ddot{N}H_2)$ with a proton





The electron – releasing alkyl group R pushes electron towards nitrogen in the amine ($R-\ddot{N}H_2$) and provide unshared electron pair more available for sharing with proton.

Therefore, the expected order of basicity of aliphatic amines (in gas phase) is

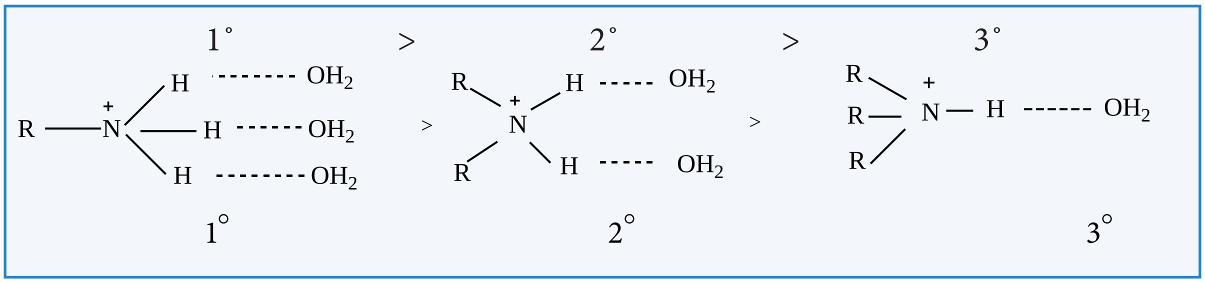
$$\underset{(3^0)}{R_3\ddot{N}} > \underset{(2^0)}{R_2\ddot{N}H} > \underset{(1^0)}{R\text{-}\ddot{N}H_2}$$

The above order is not regular in their aqueous solution as evident by their pKb values given in the table.

To compare the basicity of amines, the inductive effect, solvation effect, steric hindrance, etc., should be taken into consideration.

Solvation effect

In the aqueous solution, the substituted ammonium cations get stabilized not only by electron releasing (+I) effect of the alkyl group but also by solvation with water molecules. The greater the size of the ion, lesser will be the solvation. The order of stability of the protonated amines is greater the size of the ion, lesser is the solvation and lesser is the stability. In case of secondary and tertiary amines, due to steric hindrance, the alkyl groups decrease the number of water molecules that can approach the protonated amine. Therefore the order of basicity is,



Based on these effects we can conclude that the order of basic strength in case of alkyl substituted amines in aqueous solution is

$$(CH_3)_2\ddot{N}H > CH_3-\ddot{N}H_2 > (CH_3)_3\ddot{N} > \ddot{N}H_3$$

$$(C_2H_5)_2\ddot{N}H > (C_2H_5)_3\ddot{N} > C_2H_5\ddot{N}H_2 > \ddot{N}H_3$$

The resultant of +I effect, steric effect and hydration effect cause the 2^0 amine, more basic.

Basic strength of aniline

In aniline, the NH_2 group is directly attached to the benzene ring. The lone pair of electron on nitrogen atom in aniline gets delocalised over the benzene ring and hence it is less available for protonation makes the, aromatic amines (aniline) less basic than NH_3.

In case of substituted aniline, electron releasing groups like $-CH_3$,$-OCH_3$,$-NH_2$ increase the basic strength and electron withdrawing group like $-NO_2$,$-X$,$-COOH$ decrease the basic strength.

Table pK_b's of substituted anilines (pK_b value of aniline is 9.376)

Substituent	pK_b	Substituent	pK_b	Substituent	pK_b
o - CH_3	9.60	m - CH_3	9.31	p - CH_3	8.92
o - NH_2	9.52	m - NH_2	9.00	P - NH_2	7.83
o - OCH_3	9.52	m - OCH_3	9.70	p - OCH_3	8.70
o - NO_2	14.30	m - NO_2	11.52	p - NO_2	13.00
o - Cl	11.25	m - Cl	10.52	p - Cl	10.00

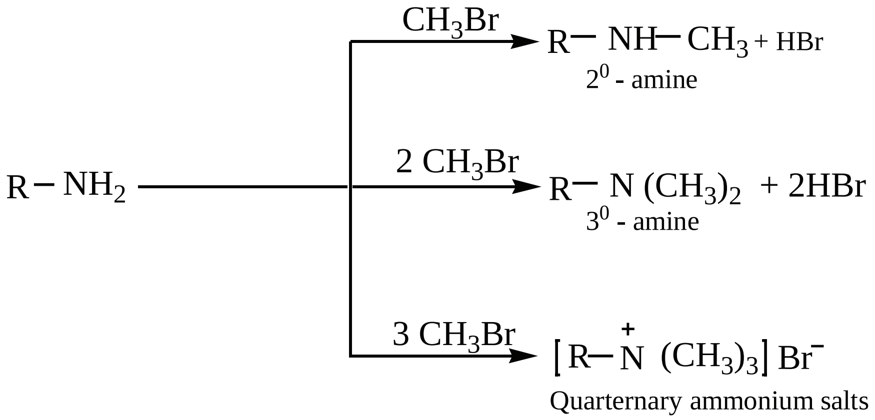
The relative basicity of amines follows the below mentioned order

Alkyl amines > Aralkyl amines > Ammonia > N – Aralkyl amines > Aryl amines

13.2.6 Chemical properties of amines

1) Alkylation

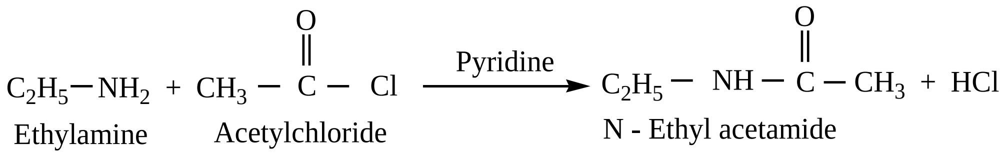
Amines reacts with alkyl halides to give successively 2^0 and 3^0 amines and quaternary ammonium salts.



2) Acylation

Aliphatic / aromatic primary and secondary amines react with acetyl chloride (or) acetic anhydride in presence of pyridine to form N – alkyl acetamide.

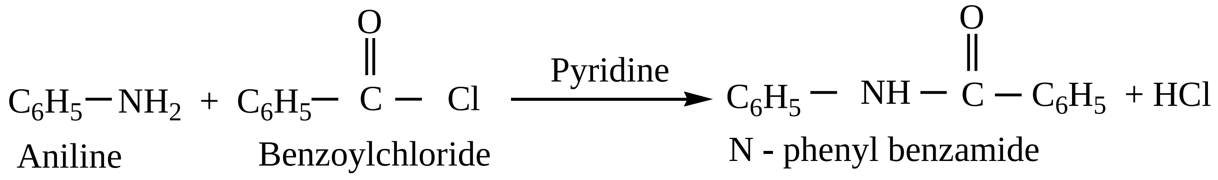
Example



$$\underset{\text{Ethylamine}}{C_2H_5-NH_2} + \underset{\text{Acetylchloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} \xrightarrow{\text{Pyridine}} \underset{\text{N - Ethyl acetamide}}{C_2H_5-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + HCl$$

3) Schotten – Baumann reaction

Aniline reacts with benzoylchloride (C_6H_5COCl) in the presence of NaOH to give N – phenyl benzamide. This reaction is known as Schotten – Baumann reaction. The acylation and benzoylation are nucleophilic substitutions.



$$\underset{\text{Aniline}}{C_6H_5-NH_2} + \underset{\text{Benzoylchloride}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} \xrightarrow{\text{Pyridine}} \underset{\text{N - phenyl benzamide}}{C_6H_5-NH-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5} + HCl$$

4) Reaction with nitrous acid

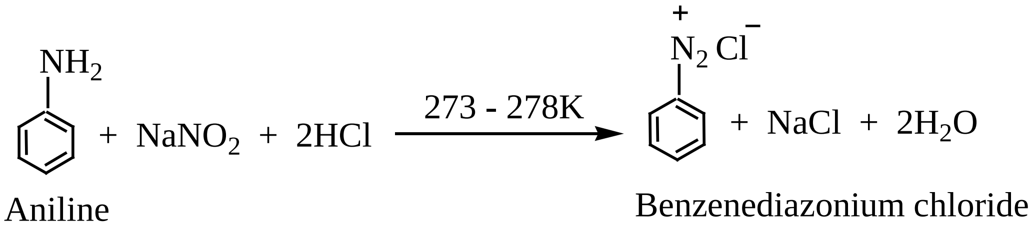
Three classes of amines react differently with nitrous acid which is prepared in situ from a mixture of $NaNO_2$ and HCl .

a) primary amines

i) Ethylamine reacts with nitrous acid to give ethyl diazonium chloride, which is unstable and it is converted to ethanol by liberating N_2.

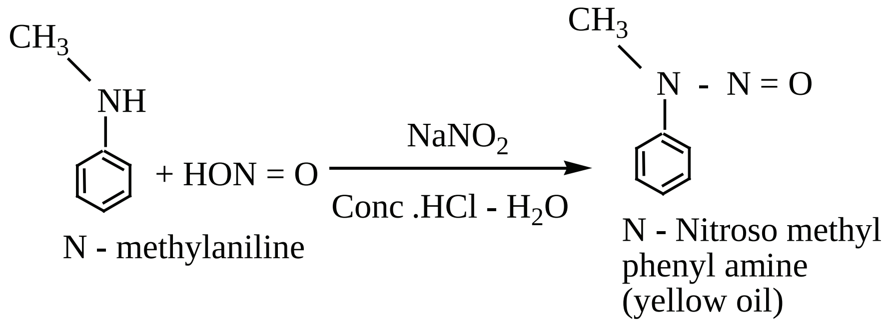
$$\underset{\text{Ethylamine}}{C_2H_5-NH_2} + HNO_2 \xrightarrow[\text{Conc. HCl}]{NaNO_2} \underset{\text{Unstable}}{[C_2H_5\overset{+}{N_2}\overset{-}{Cl}]} \xrightarrow{H_2O} \underset{\text{Ethanol}}{C_2H_5OH} + N_2$$

ii) Aniline reacts with nitrous acid at low temperature (273 – 278 K) to give benzene diazonium chloride which is stable for a short time and slowly decomposes even at low temperatures. This reaction is known as diazotization.



b) secondary amines

Alkyl and aryl secondary amines react with nitrous acid to give N – nitroso amine as yellow oily liquid which is insoluble in water.



This reaction is known as Libermann's nitroso test,

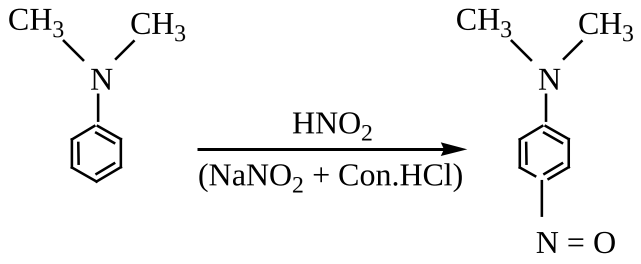
c) Teritiary amine

i) Aliphatic tertiary amine reacts with nitrous acid to form trialkyl ammonium nitrite salt, which is soluble in water.

$$(CH_3)_3N + HNO_2 \longrightarrow [(CH_3)_3\overset{+}{N}H]\,NO_2^-$$

trimethylamine — trimethyl ammonium nitrite

ii) Aromatic tertiary amine reacts with nitrous acid at 273K to give p – nitroso compound.



N, N - dimethyl aniline

p - Nitroso N,N - dimethyl aniline

5) Carbylamine reaction

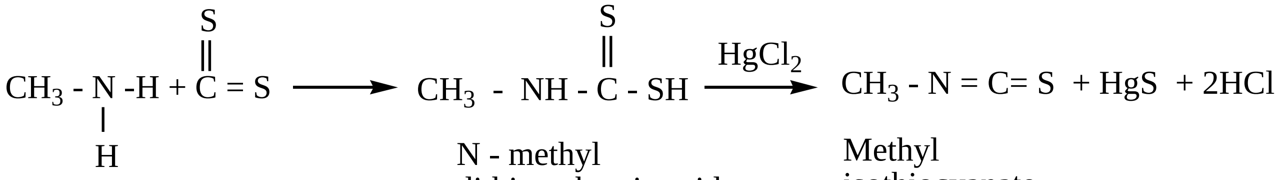
Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell. This reaction is known as carbylamine test. This test used to identify the primary amines.

$$C_2H_5 - NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5 - NC + 3KCl + 3H_2O$$

Ethylamine — Chloroform — Ethylisocyanide

6) Mustard oil reaction

i) When primary amines are treated with carbon disulphide (CS_2), N - alkyldithio carbomic acid is formed which on subsequent treatment with $HgCl_2$, give an alkyl isothiocyanate.



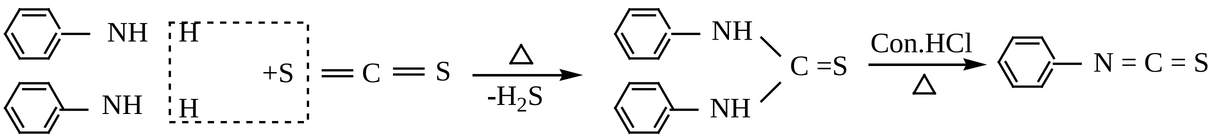
$$CH_3 - \underset{\underset{\displaystyle H}{|}}{N} - H + \overset{\overset{\displaystyle S}{\|}}{C} = S \longrightarrow CH_3 - NH - \overset{\overset{\displaystyle S}{\|}}{C} - SH \xrightarrow{HgCl_2} CH_3 - N = C = S + HgS + 2HCl$$

Methylamine

N - methyl dithiocarbamic acid

Methyl isothiocyanate (Mustard oil smell)

ii) When aniline is treated with carbon disulphide, or heated together, S- diphenylthio urea is formed, which on boiling with strong HCl, phenyl isothiocyanate (phenyl mustard oil), is formed.



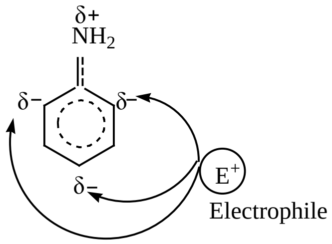
Aniline

S - diphenyl thiourea

Phenyl isothiocyanate

These reactions are known as Hofmann – Mustard oil reaction. This test is used to identify the primary amines.

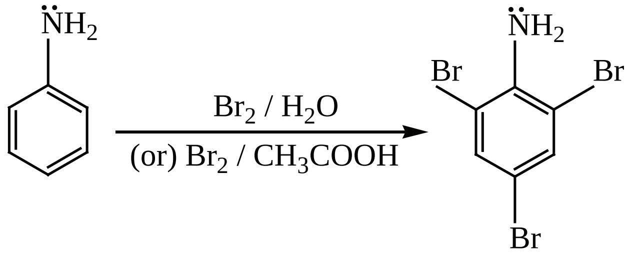
7. Electrophilic substitution reactions in Aniline



The $-\ddot{N}H_2$ group is a strong activating group. In aniline the NH_2 is directly attached to the benzene ring, the lone pair of electrons on the nitrogen is in conjugation with benzene ring which increases the electron density at ortho and para position, thereby facilitating the electrophilic attack at ortho and para positions.

i) Bromination

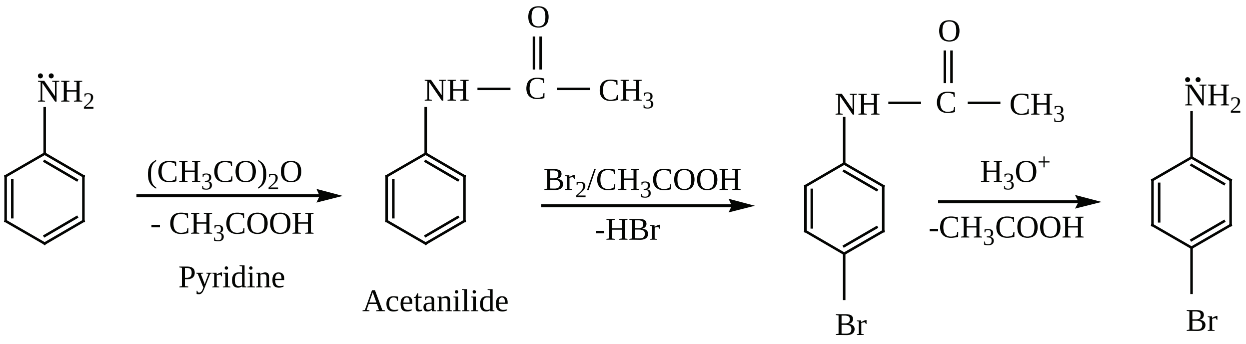
Aniline reacts with Br_2 / H_2O to give 2,4,6 – tribromo aniline a white precipitate.



Aniline

2,4,6, tribromo aniline
(white precipitate)

To get mono bromo compounds, - NH_2 is first acylated to reduce its activity.

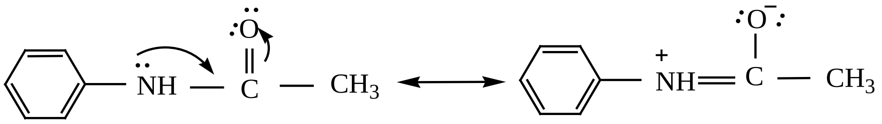


Acetanilide

p - bromo acetanilide

p-bromo aniline
(Major product)

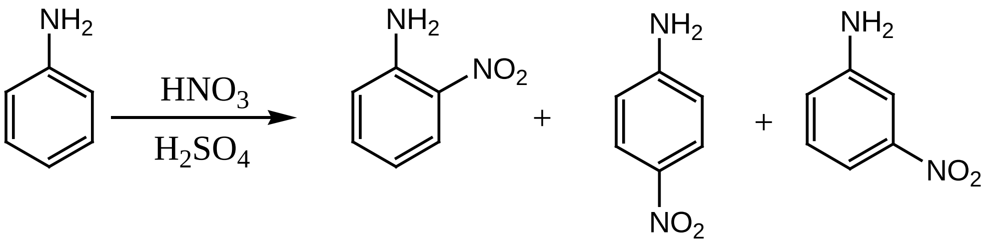
When aniline is acylated, the lone pair of electron on nitrogen is delocalised by the neighbouring carbonyl group by resonance. Hence it is not easily available for conjugation with benzene ring.



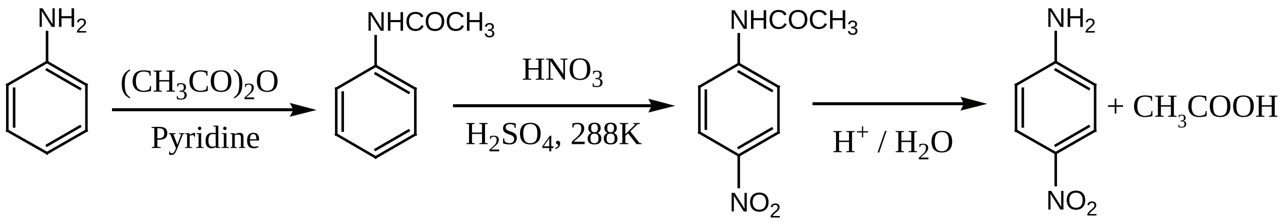
The acetylamino group is thus less activating than the amino group in electrophilic substitution reaction.

ii) Nitration

Direct nitration of aniline gives o and p – nitro aniline along with dark coloured 'tars' due to oxidation. Moreover in a strong acid medium aniline is protonated to form anilinium ion which is m – directing and hence m – nitro aniline is also formed.



To get para product, the - NH_2 group is protected by acetylation with acetic anhydride. Then, the nitrated product is hydrolysed to form the product.



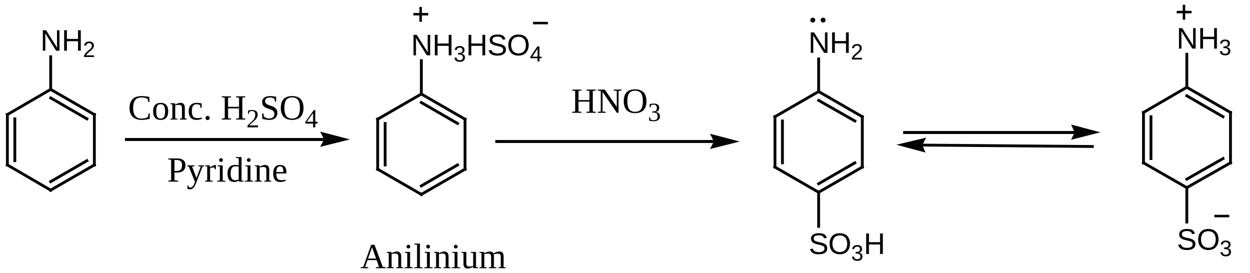
Acetanilide

P-nitroacetanilide

p-nitro aniline

iii) Sulphonation

Aniline reacts with Conc. H_2SO_4 to form anilinium hydrogen sulphate which on heating with H_2SO_4 at 453 – 473K gives p- aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.



Anilinium hydrogensulphate

Sulphanilic acid

Zwitter ion

iv) Aniline

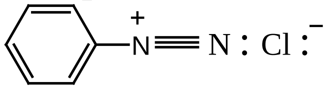
It does not under go Friedel – Crafts reaction (alkylation and acetylation) we know aniline is basic in nature and it donates its lone pair to the lewis acid $AlCl_3$ to form an adduct which inhibits further the electrophilic substitution reaction.

13.3 DIAZONIUM SALTS

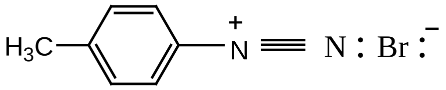
13.3.1 Introduction

We have just learnt that aromatic amines on treatment with $(NaNO_2+HCl)$ gives diazonium salts. They are stable only for a short time and hence are used immediately after preparation.

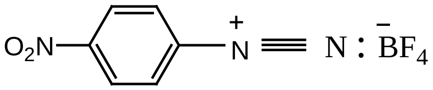
Example



Benzenediazonium
Chloride



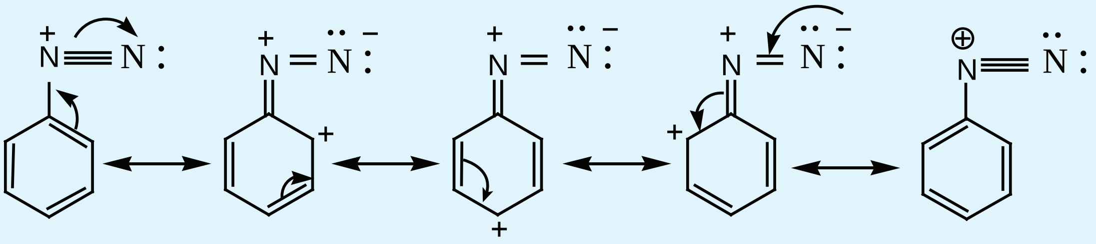
p - Toluenediazonium
Bromide



p- Nitrobenzenediazonium
tetra fluoroborate

13.3.2 Resonance structure

The stability of arene diazonium salt is due to the dispersal of the positive charge over the benzene ring.



Resonating structures of benzenediazonium salt

13.3.3 Method of preparation of Diazonium salts

We have already learnt that benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid (Which is produced by the reaction of $NaNO_2$ and HCl) at 273 – 278K

13.3.4 Physical properties

- Benzene diazonium chloride is a colourless, crystalline solid.
- These are readily soluble in water and stable in cold water. However it reacts with warm water.
- Their aqueous solutions are neutral to litmus and conduct electricity due to the presence to ions.
- Benzenediazonium tetrafluoro borate is soluble in water and stable at room temperature.

13.3.5 Chemical reactions

Benzene diazoniumchloride gives two types of chemical reactions

A. Replacement reactions involving loss of nitrogen

In these reactions diazonium group is replaced by nucleophiles such as X^-,CN^-,H^-,OH^- etc.,

B. Reactions involving retention of diazogroup.

Coupling reaction.

A. Replacement reactions involving loss of nitrogen

1. Replacement by hydrogen

Benzene diazonium chloride on reduction with mild reducing agents like hypophosphrous acid (phosphinic acid) or ethanol in the presence of cuprous ion gives benzene. This reaction proceeds through a free-radical chain mechanism.

$$C_6H_5\text{-}\overset{+}{N}_2\,Cl^- + H_3PO_2 + H_2O \xrightarrow{CuCl} C_6H_6 + H_3PO_3 + HCl + N_2\uparrow$$

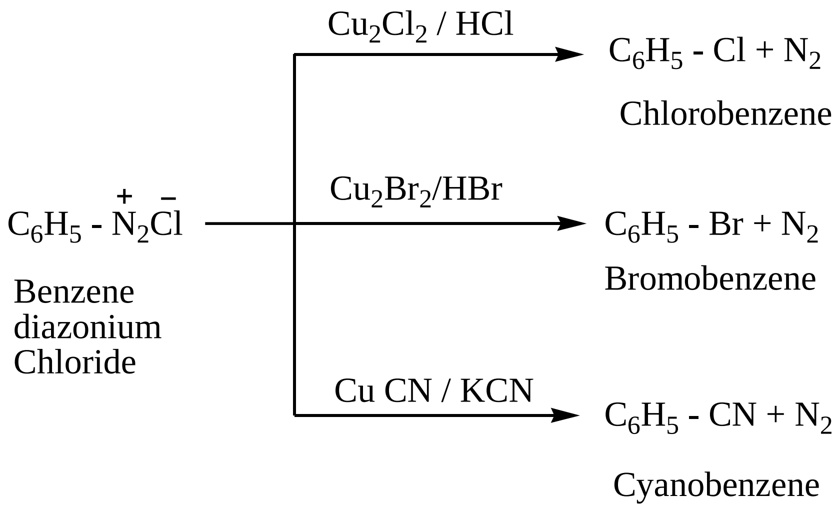
$$C_6H_5\text{-}\overset{+}{N}_2\,Cl^- + CH_3CH_2OH \rightarrow C_6H_6 + N_2 + CH_3CHO + HCl$$

2. Replacement by Chlorine, Bromine, Cyanide group

a) Sandmeyer reaction

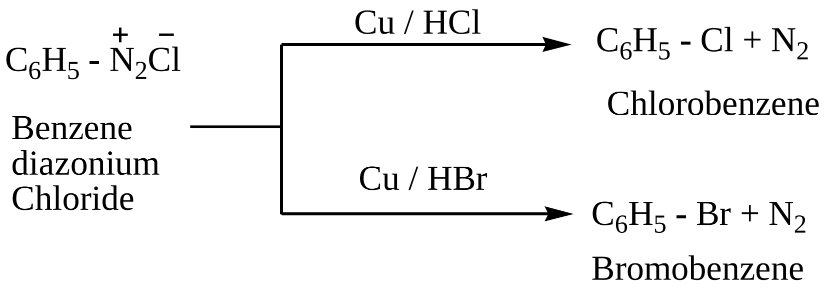
On mixing freshly prepared solution of benzene diazonium chloride with cuprous halides (chlorides and bromides), aryl halides are obtained. This reaction is called Sandmeyer reaction.

When diazonium salts are treated with cuprous cyanide, cyanobenzene is obtained.



b) Gattermann reaction

Conversion of benzene diazonium chloride into chloro / bromo arenes can also be effected using hydrochloric / hydrobromic acid and copper powder. This reaction is called Gattermann reaction.



The yield in Sandmeyer reaction is found to be better than the Gattermann reaction.

3. Replacement by iodine

Aqueous solution of benzene diazonium chloride is warmed with KI to form iodobenzene

$$C_6H_5-\overset{+}{N_2}\,Cl^- + KI \rightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + KCl + N_2$$

4. Replacement of fluorine (Baltz – schiemann reaction)

When benzene diazonium chloride is treated with fluoroboric acid, benezene diazonium tetra fluoroborate is precipitated which on heating decomposes to give fluorobenzene.

$$C_6H_5-\overset{+}{N_2}\overset{-}{Cl} + \underset{\substack{\text{Fluoroboric}\\\text{acid}}}{HBF_4} \longrightarrow \underset{\substack{\text{Benzenediazonium}\\\text{fluoroborate}}}{C_6H_5-\overset{+}{N_2}\overset{-}{BF_4}} \xrightarrow{\triangle} \underset{\text{Fluorobenzene}}{C_6H_5-F} + BF_3 + N_2$$

5. Replacement by hydroxyl group

Benzene diazonium chloride solution is added slowly to a large volume of boiling water to get phenol.

$$C_6H_5-N_2Cl + H_2O \xrightarrow[283K]{\triangle} \underset{\text{Phenol}}{C_6H_5-OH} + N_2 + HCl$$

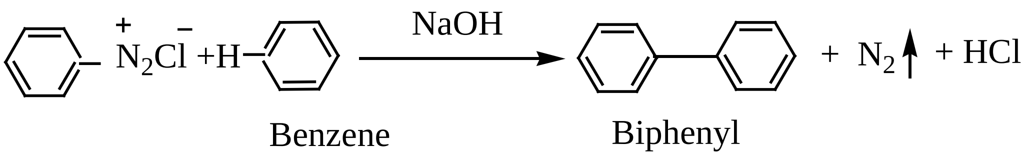
6. Replacement by nitrogroup

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

$$C_6H_5-\overset{+}{N_2}\overset{-}{Cl} + \underset{\substack{\text{Fluoroboric}\\\text{acid}}}{HBF_4} \longrightarrow C_6H_5-\overset{+}{N_2}\overset{-}{BF_4} \xrightarrow[Cu,\ \triangle]{NaNO_2} \underset{\text{Nitrobenzene}}{C_6H_5-NO_2} + N_2 + NaBF_4$$

7. Replacement by aryl group (Gomberg reaction)

Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction in known as the Gomberg reaction.



8. Replacement by carboxylic acid group

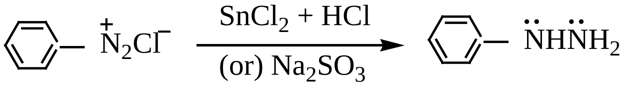
When diazonium fluoroborate is heated with acetic acid, benzoic acid is obtained. This reaction is used to convert the of aliphatic carboxylic acid into aromatic carboxylic acid.

$$\underset{\substack{\text{Benzene diazonium}\\\text{fluoroborate}}}{C_6H_5-N_2BF_4} + CH_3-COOH \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5-COOH} + BF_3 + CH_3F + N_2$$

B. Reactions involving retention of diazo group

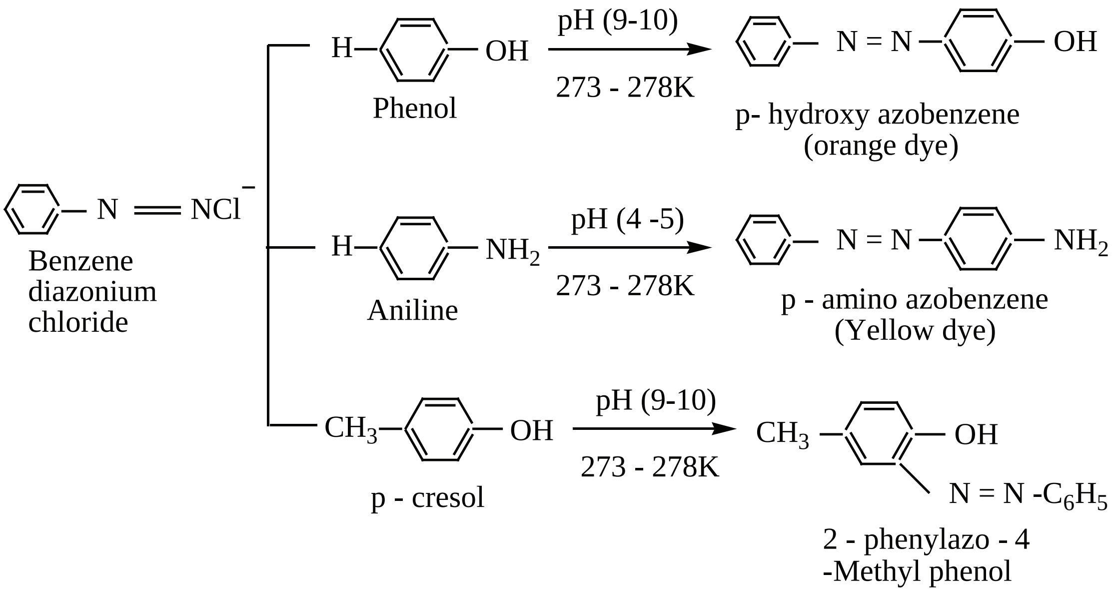
9. Reduction to hydrazines

Certain reducing agents like $SnCl_2$ / HCl; Zn dust / CH_3COOH, sodium hydrosulphite, sodium sulphite etc. reduce benzene diazonium chloride to phenyl hydrazine.



10. Coupling reactions

Benzene diazonium chloride reacts with electron rich aromatic compounds like phenol, aniline to form brightly coloured azo compounds. Coupling generally occurs at the para position. If para position is occupied then coupling occurs at the ortho position. Coupling tendency is enhanced if an electron donating group is present at the para – position to $-\overset{+}{N}_2Cl^-$ group. This is an electrophilic substitution.



Aryl fluorides and iodides cannot be prepared by direct halogenation and the cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorbenzene. For introducing such a halide group, cyano group -OH, NO_2 etc.. benzenediazonium chloride is a very good intermediate Diazo compounds obtained from the coupling reactions of diazonium salts are coloured and are used as dyes.

13.4 CYANIDES AND ISOCYANIDES

13.4.1 Introduction

These are the derivatives of hydrocyanic acid (HCN), and is known to exist in two tautomeric forms

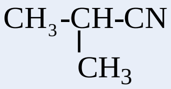
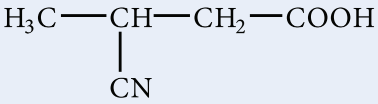
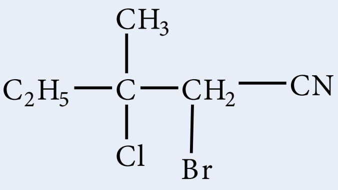
$$H - C \equiv N \rightleftharpoons H - N \equiv C$$

Hydrogencyanide   Hydrogen isocyanide

Two types of alkyl derivatives can be obtained. Those derived by replacement of H – atom of hydrogen cyanide by the alkyl groups are known as alkyl cyanides ($R\text{-}C \equiv N$). and those obtained by the replacement of H – atom of hydrogen isocyanide are known as alkyl isocyanides ($R\text{-}N \overset{\rightarrow}{\equiv} C$)

In IUPAC system, alkyl cyanides are named as "alkanenitriles" whereas aryl cyanides as " arenecarbonitrile".

Table : Nomenclature of cyanides

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	**Root used**	**Primary suffix**	**Secondary Suffix**
acetonitrile $CH_3\text{-}CN$ Ethane nitrile	–	Eth	ane	nitrile
Propiononitrile $CH_3CH_2\text{-}CN$ Propanenitrile	–	Prop	ane	nitrile
Butyronitrile $CH_3CH_2CH_2\text{-}CN$ butanenitrile	–	But	ane	nitrile
Isobutronitrile  $CH_3\text{-}\underset{\mid}{CH}\text{-}CN$, CH_3 on CH 2-methylpropanenitrile	2-methyl–	prop	ane	nitrile
Benzonitrile $C_6H_5\text{-}CN$ Benzene Carbonitrile	–	Benzene	Carbo	nitrile
 $H_3C\text{—}\underset{CN}{\underset{\mid}{CH}}\text{—}CH_2\text{—}COOH$ 3-Cyanobutanoicacid	3-Cyano	but	$an\cancel{e}$	oicacid
 $C_2H_5\text{—}\overset{CH_3}{\overset{\mid}{\underset{Cl}{\underset{\mid}{C}}}}\text{—}\underset{Br}{\underset{\mid}{CH_2}}\text{—}CN$ 2-Bromo-3-chloro-3- methyl pentanenitrile.	2-Bromo-3- chloro-3- methyl	pent	ane	nitrile

13.4.2 Methods of preparation of cyanides

1) From alkyl halides

When alkyl halides are treated in the solution $NaCN$ (or) KCN, alkyl cyanides are obtained. In this reaction a new carbon – carbon bond is formed.

Example

$$KCN + \underset{\text{Ethyl bromide}}{CH_3CH_2-Br} \longrightarrow \underset{\text{Propanenitrile}}{CH_3CH_2-CN} + KBr$$

Aryl cyanide cannot be prepared in this method because of their less reactivity towards nucleophilic substitution. Aryl cyanides are prepared using Sandmeyers reactions.

2. By dehydration of primary amides and aldoximes with P_2O_5

$$\underset{\text{Acetamide}}{CH_3-CONH_2} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Ethanenitrile}}{CH_3-CN} \qquad \underset{\text{Acetaldoximes}}{CH_3-CH{=}NOH} \xrightarrow[-H_2O]{P_2O_5} CH_3-CN$$

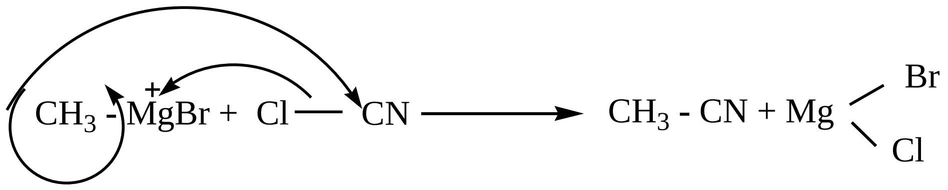
3. By dehydration of ammonium carboxylates with P_2O_5

$$\underset{\text{Ammonium acetate}}{CH_3-COONH_4} \xrightarrow[\Delta]{P_2O_5} \underset{\text{Ethanenitrile}}{CH_3-CN} + 2H_2O$$

This method suitable for large scale preparation of alkyl cyanides.

4. From Grignard reagent

Methyl magnesium bromide on treatment with cyanogen chloride $(Cl-CN)$ forms ethanenitrile.



methyl magnesium bromide　　　　ethanenitrile

13.4.3 Properties Of Cyanides

Physical Properties

The lower members (up to C_{14}) are colourless liquids with a strong characteristic sweet smell. The higher members are crystalline solids, They are moderately soluble in water but freely souble in organic solvents. They are poisonous.

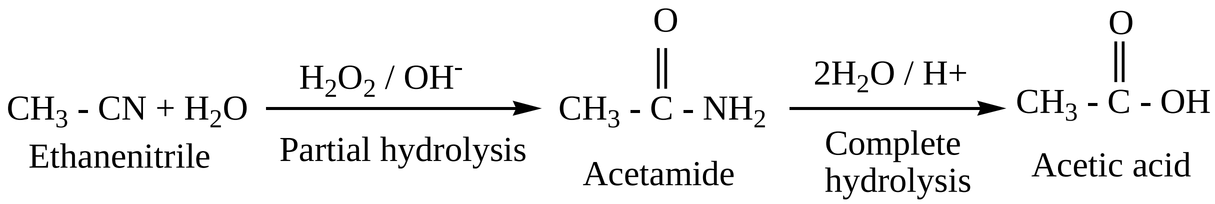
They have higher boiling points than analogous acetylenes due to their high dipole moments.

13.4.4 Chemical properties

1. Hydrolysis

On boiling with alkali (or) a dilute mineral acid, the cyanides are hydrolysed to give carboxylic acids.

For example



$$\underset{\text{Ethanenitrile}}{CH_3-CN+H_2O}\xrightarrow[\text{Partial hydrolysis}]{H_2O_2\,/\,OH^-}\underset{\text{Acetamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2}\xrightarrow[\text{Complete hydrolysis}]{2H_2O\,/\,H+}\underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

2. Reduction

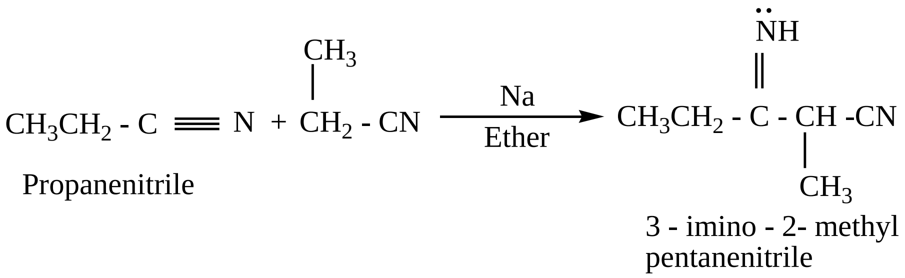
On reduction with $LiAlH_4$ (or) $Ni\,/\,H_2$, alkyl cyanides yields primary amines.

$$\underset{\text{Ethanenitrile}}{CH_3-CN+2H_2}\xrightarrow{Ni}\underset{\text{Ethanamine}}{CH_3-CH_2-NH_2}$$

3. Condensation reaction

a) Thorpe nitrile condensation

Self condensation of two molecules of alkyl nitrile (containing α–H atom) in the presence of sodium to form iminonitrile.

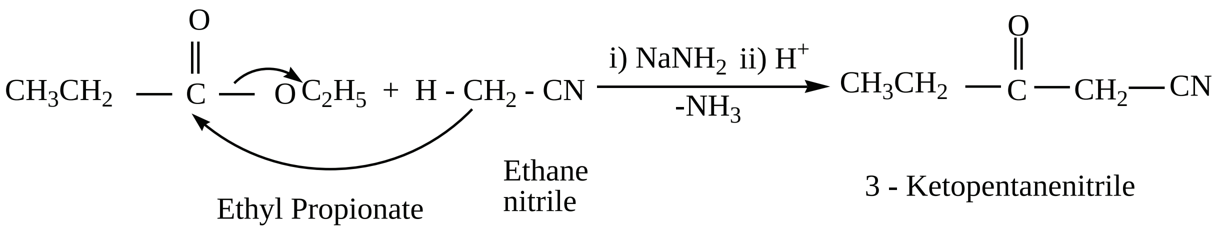


$$\underset{\text{Propanenitrile}}{CH_3CH_2-C\equiv N+\overset{\overset{\displaystyle CH_3}{|}}{CH_2}-CN}\xrightarrow[\text{Ether}]{Na}CH_3CH_2-\overset{\overset{\displaystyle \ddot{N}H}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CN$$

3 - imino - 2- methyl pentanenitrile

b) The nitriles containing α- **hydrogen** also undergo condensation with esters in the presence of sodamide in ether to form ketonitriles. This reaction is known as " Levine and Hauser" acetylation

This reaction involves replacement of ethoxy (OC_2H_5) group by methylnitrile $(-CH_2CN)$ group and is called as cyanomethylation reaction.



$$\underset{\text{Ethyl Propionate}}{CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5}+\underset{\text{Ethane nitrile}}{H-CH_2-CN}\xrightarrow[-NH_3]{\text{i) }NaNH_2\text{ ii) }H^+}\underset{\text{3 - Ketopentanenitrile}}{CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CN}$$

13.4.5 Alkyl Isocyanides (Carbylamines)

Nomenclature of isocyanides

They are commonly named as Alkyl isocyanides. The IUPAC system names them as alkylcarbylamines

Table : Nomenclature of alkylisocyanides

Structural formula	Common name	IUPAC name
$CH_3 - NC$	Methyl isocyanide	Methylcarbylamine
$CH_3CH_2 - NC$	Ethylisocyanide	Ethylcarbylamine
$CH_3CH_2CH_2 - NC$	Propyl isocyanide	Propylcarbylamine
$C_6H_5 - NC$	Phenyl isocynaide	Phenylcarbylamine

13.4.6 Methods of preparation of isocyanides

1. From primary amines (carbylamines reaction)

Both aromatic as well as aliphatic amines on treatment with $CHCl_3$ in the presence of KOH give carbylamines

$$\underset{\text{Methylamine}}{CH_3-NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\text{Methyl isocyanide}}{CH_3-N\equiv C} + 3KCl + 3H_2O$$

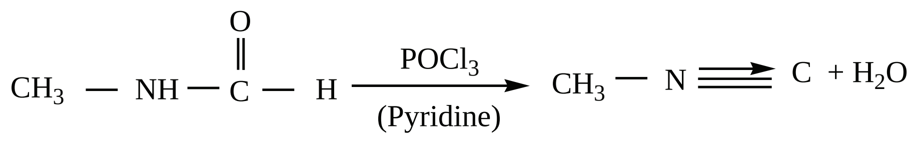
$$\underset{\text{Aniline}}{C_6H_5-NH_2} + CH.Cl_3 + 3KOH \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5-N\equiv C} + 3KCl + 3H_2O$$

2. From alkyl halides

Ethyl bromide on heating with ethanolic solution of AgCN give ethyl isocyanide as major product and ethyl cyanide as minor product.

$$\underset{\text{Ethyl bromide}}{CH_3CH_2 - Br} + AgCN \xrightarrow[\text{heat}]{C_2H_5OH} \underset{\text{Ethyl isocyanide}}{CH_3CH_2 - NC} + AgBr$$

3. From N – alkyl formamide. By reaction with $POCl_3$ in pyridine.



$$CH_3 - NH - \overset{\overset{\displaystyle O}{\|}}{C} - H \xrightarrow[\text{(Pyridine)}]{POCl_3} CH_3 - N \equiv C + H_2O$$

13.4.7 Properties of isocyanides

Physical properties

- They are colourless, highly unpleasant smelling volatile liquids and are much more poisonous than the cyanides.
- They are only slightly soluble in water but are soluble in organic solvents.
- They are relatively less polar than alkyl cyanides. Thus, their melting point and boiling point are lower than cyanides.

13.4.8 Chemical properties

1) **Hydrolysis**: Alkyl isocyanides are not hydrolysed by alkalies. However they are hydrolysed with dilute mineral acids to give primary amines and formic acids.

$$\underset{\text{Methyl isocyanide}}{CH_3-NC} + 2H_2O \xrightarrow{\text{acid}} \underset{\text{Methylamine}}{CH_3-NH_2} + \underset{\text{Formicacid}}{HCOOH}$$

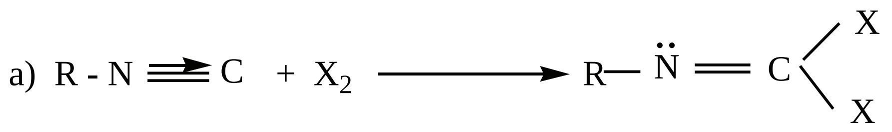
2. **Reduction:** When reduced catalytically (or) by nascent hydrogen, they give secondary amines.

$$\underset{\text{Methyl isocyanide}}{CH_3-NC} + 4\,[H] \xrightarrow[\text{(or) Ni / }H_2]{\text{Na / }C_2H_5OH} \underset{\text{Dimethylamine}}{CH_3-NH-CH_3}$$

3. **Isomerisation:** When Alkyl isocyanides and heated at 250⁰C, they change into the more stable, isomeric cyanides

$$\underset{\text{Methyl isocyanide}}{CH_3-N\equiv C} \xrightarrow[250^0C]{\text{Heat}} \underset{\text{Methylcyanide}}{CH_3-C\equiv N:}$$

4. **Addition reaction**. Alkyl isocyanides add on halogen, sulphur, and oxygen to form the corresponding addition compounds.



$$\text{a)}\ R-N\equiv C + X_2 \longrightarrow R-\ddot{N}=CX_2$$

$$\text{b)}\ R-N\equiv C + S \longrightarrow \underset{\text{Alkyl isothiocyanate}}{R-\ddot{N}=C=S}$$

$$\text{c)}\ R-N\equiv C + O \xrightarrow[\text{(or) }O_3]{2HgO} \underset{\text{Alkyl isocyanate}}{R-\ddot{N}=C=O} + Hg_2O$$

13.4.9 Uses of organic nitrogen compounds

nitroalkanes

1. Nitromethane is used as a fuel for cars
2. Chloropicrin (CCl_3NO_2) is used as an insecticide
3. Nitroethane is used as a fuel additive and precursor to explosive and they are good solvents for polymers, cellulose ester, synthetic rubber and dyes etc.,
4. 4% solution of ethylnitrite in alcohol is known as sweet spirit of nitre and is used as diuretic.

nitrobenzene

1 Nitrobenzene is used to produce lubricating oils in motors and machinery.

2 It is used in the manufacture of dyes, drugs, pesticides, synthetic rubber, aniline and explosives like TNT, TNB.

cyanides and isocyanides

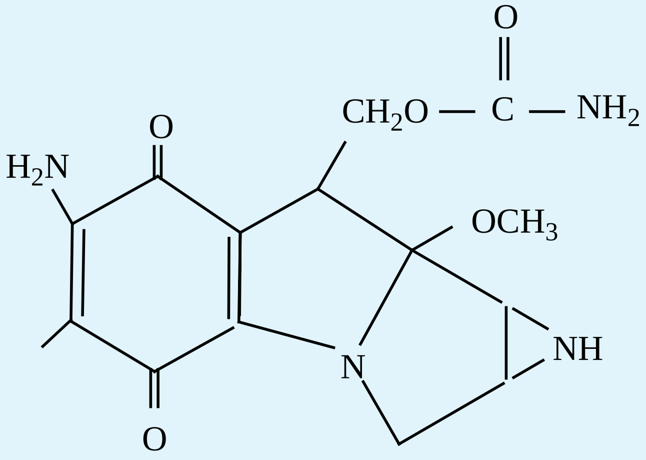
1. Alkyl cyanides are important intermediates in the organic synthesis of larger number of compounds like acids, amides, esters, amines etc.

2 Nitriles are used in textile industry in the manufacture of nitrile rubber and also as a solvent particularly in perfume industry.

DO YOU KNOW?

Cancer Drug

Mitomycin C, and anticancer agent used to treat stomach and colon cancer, contains an aziridine ring. The aziridine functional group participates in the drug's degradation by DNA, resulting in the death of cancerous cells.



Mitomycin

EVALUATION

Choose the correct answer:

1. Which of the following reagent can be used to convert nitrobenzene to aniline

   a) Sn / HCl b) ZnHg / NaOH c) Zn/NH_4Cl d) All of these

2. The method by which aniline cannot be prepared is

   a) degradation of benzamide with Br_2 / NaOH

   b) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

   c) reduction of Nitrobenzene with $LiAlH_4$

   d) reduction of nitrobenzene by Sn / HCl.

3. Which one of the following will not undergo Hofmann bromamide reaction

   a) $CH_3CONHCH_3$ b) $CH_3CH_2CONH_2$

   c) CH_3CONH_2 d) $C_6H_5CONH_2$

4. Assertion : Acetamide on reaction with KOH and bromine gives acetic acid

   Reason : Bromine catalyses hydrolysis of acetamide.

   a) if both assertion and reason are true and reason is the correct explanation of assertion.

   b) if both assertion and reason are true but reason is not the correct explanation of assertion.

   c) assertion is true but reason is false

   d) both assertion and reason are false.

T7H3A9

5. $CH_3CH_2Br \xrightarrow[\Delta]{\text{aq NaOH}} A \xrightarrow[\Delta]{KMnO_4/H^+} B \xrightarrow[\Delta]{NH_3} C \xrightarrow{Br_2/NaOH} D$ 'D' is

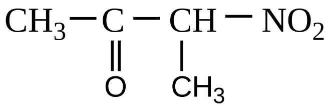
   a) bromomethane b) α - bromo sodium acetate

   c) methanamine d) acetamide

6. Which one of the following nitro compounds does not react with nitrous acid

   a) CH_3-CH_2-CH_2-NO_2 b) $(CH_3)_2CH$ - CH_2NO_2

   c) $(CH_3)_3C\ NO_2$ d)



$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-NO_2$$

7. Aniline + benzoylchloride $\xrightarrow{NaOH}$ C_6H_5 - NH - COC_6H_5 this reaction is known as

   a) Friedel – crafts reaction b) HVZ reaction

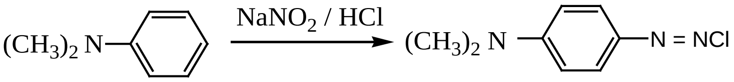
   c) Schotten – Baumann reaction d) none of these

8. The product formed by the reaction an aldehyde with a primary amine (NEET)

a) carboxylic acid
b) aromatic acid
c) schiff's base
d) ketone

9. Which of the following reaction is not correct.

a) $CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH + N_2$

b) 

c) $CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$
d) none of these

10. When aniline reacts with acetic anhydride the product formed is
a) o – aminoacetophenone
b) m-aminoacetophenone
c) p – aminoacetophenone
d) acetanilide

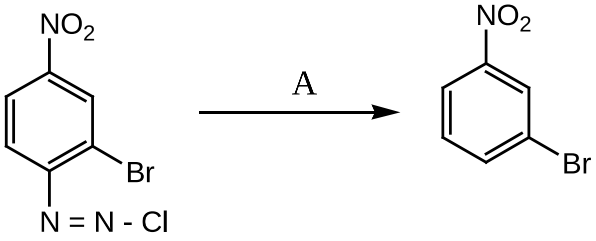
11. The order of basic strength for methyl substituted amines in aqueous solution is

a) $N(CH_3)_3 > N(CH_3)_2H > N(CH_3)H_2 > NH_3$

b) $N(CH_3)H_2 > N(CH_3)_2H > N(CH_3)_3 > NH_3$

c) $NH_3 > N(CH_3)H_2 > N(CH_3)_2H > N(CH_3)_3$

d) $N(CH_3)_2H > N(CH_3)H_2 > N(CH_3)_3 > NH_3$

12. 

'A' is (NEET)

a) H_3PO_2 and H_2O
b) H^+/H_2O
c) $HgSO_4 / H_2SO_4$
d) Cu_2Cl_2

13. $C_6H_5NO_2 \xrightarrow{Fe / Hcl} A \xrightarrow[273K]{NaNO_2\ /\ HCl} B \xrightarrow[283K]{H_2O} C$ 'C' is
a) C_6H_5- OH
b) C_6H_5 - CH_2OH
c) C_6H_5 - CHO
d) $C_6H_5NH_2$

14. Nitrobenzene on reaction with Con HNO_3 / H_2SO_4 at 80-100°C forms which one of the following products?

a) 1,4 – dinitrobenzene
b) 2,4,6 – tirnitrobenzene
c) 1,2 – dinitrobenzene
d) 1,3 – dinitrobenzene

15. $C_5H_{13}N$ reacts with HNO_2 to give an optically active compound – The compound is
a) pentan – 1- amine
b) pentan – 2- amine
c) N,N – dimethylpropan -2-amine
d) diethyl methyl amine

16. Secondary nitro alkanes react with nitrous acid to form

a) red solution b) blue solution c) green solution d) yellow solution

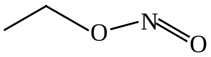
17. Which of the following amines does not undergo acetylation?

a) t – butylamine b) ethylamine c) diethylamine d) triethylamine

18. Which one of the following is most basic?

a) 2,4 – dichloroaniline b) 2,4 – dimethyl aniline

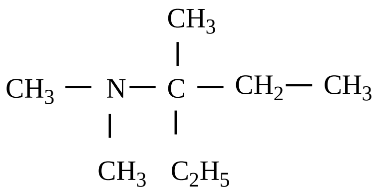
c) 2,4 – dinitroaniline d) 2,4 – dibromoaniline

19. When  is reduced with Sn / HCl the pair of compounds formed are

a) Ethanol, hydroxylamine hydrochloride b) Ethanol, ammonium hydroxide

c) Ethanol, . NH_2OH . d) $C_3H_5NH_2$, H_2O

20. IUPAC name for the amine



$$CH_3-\underset{\underset{CH_3}{|}}{N}-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-CH_2-CH_3$$

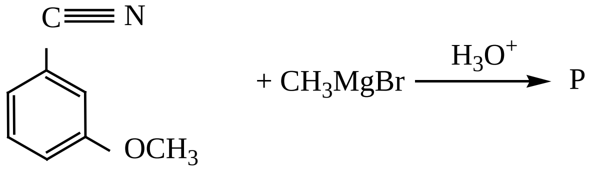
is

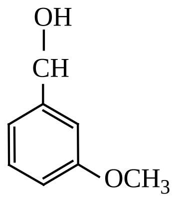
a) 3 – Bimethylamino – 3 – methyl pentane

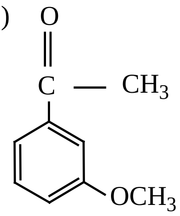
b) 3 (N,N – Triethyl) – 3- amino pentane

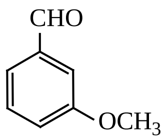
c) 3 – N,N – trimethyl pentanamine

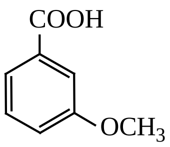
d) N,N – dimethyl – 3- methyl - pentan - 3 amine

21.  Product ‘P’ in the above reaction is

a) 

b) 

c) 

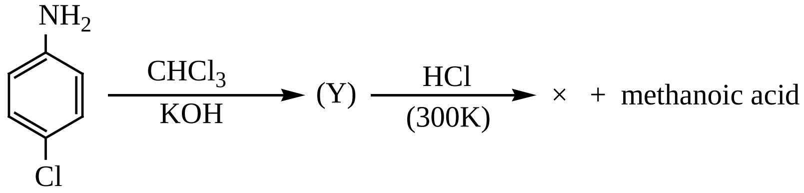
d) 

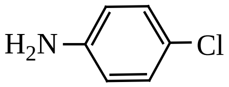
22. Ammonium salt of benzoic acid is heated strongly with P_2O_5 and the product so formed is reduced and then treated with $NaNO_2$ / HCl at low temperature. The final compound formed is

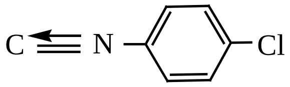
a) Benzene diazonium chloride b) Benzyl alcohol

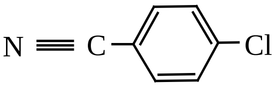
c) Phenol d) Nitrosobenzene

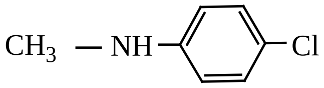
23. Identify X in the sequence given below.



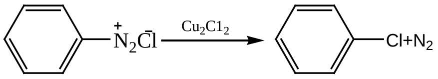
a) 

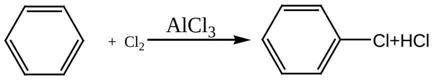
b) 

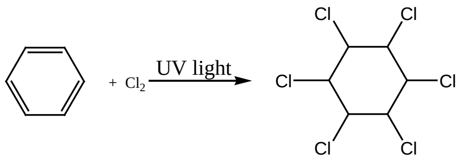
c) 

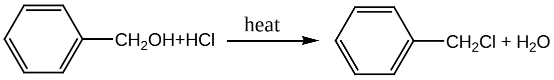
d) 

24. Among the following, the reaction that proceeds through an electrophilic substitution, is :

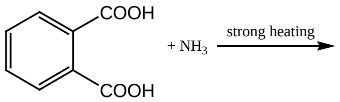
a) 

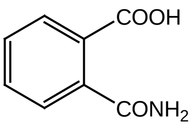
b) 

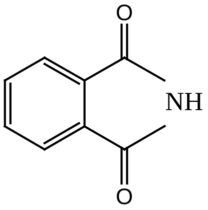
c) 

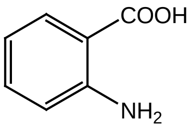
d) 

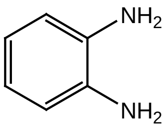
25. The major product of the following reaction



a) 

b) 

c) 

d) 

Short answer Questions

1. Write down the possible isomers of the $C_4H_9NO_2$ give their IUPAC names
2. There are two isomers with the formula CH_3NO_2. How will you distinguish between them?
3. What happens when
   - i. 2 – Nitropropane boiled with HCl
   - ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.
   - iii. Oxidation of tert – butylamine with $KMnO_4$
   - iv. Oxidation of acetoneoxime with trifluoroperoxy acetic acid.
4. How will you convert nitrobenzene into
   - i. 1,3,5 - trinitrobenzene
   - ii. o and p- nitrophenol
   - iii. m – nitro aniline
   - iv. azoxybenzene
   - v. hydrozobenzene
   - vi. N – phenylhydroxylamine
   - vii. aniline
5. Identify compounds A,B and C in the following sequence of reactions.

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

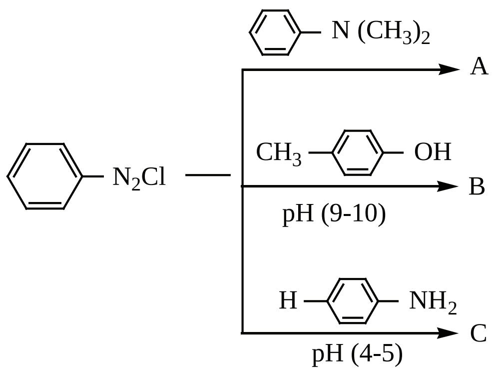
ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O / H^+} B \xrightarrow{NH_3} C$

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

iv) $CH_3NH_2 \xrightarrow{CH_3\ Br} A \xrightarrow{CH_3COCl} B \xrightarrow{B_2H_6} C$

v) $C_6H_5NH_2 \xrightarrow[\text{pyridine}]{(CH_3CO)_2O} A \xrightarrow[H_2SO_4, 288K]{HNO_3} B \xrightarrow{H_2O / H^+} C$

vi)



vii) $CH_3CH_2NC \xrightarrow{HgO} A \xrightarrow{H_2O} B \xrightarrow[ii)H_2O]{i)NaNO_2 / HCl} C$

6. Write short notes on the following
   - i. Hofmann's bromide reaction
   - ii. Ammonolysis
   - iii. Gabriel phthalimide synthesis
   - iv. Schotten – Baumann reaction
   - v. Carbylamine reaction
   - vi. Mustard oil reaction
   - vii. Coupling reaction
   - viii. Diazotisation
   - ix. Gomberg reaction
7. How will you distinguish between primary secondary and tertiary alphatic amines.
8. Account for the following
   - i. Aniline does not undergo Friedel – Crafts reaction
   - ii. Diazonium salts of aromatic amines are more stable than those of aliphatic amines
   - iii. pK_b of aniline is more than that of methylamine
   - iv. Gabriel phthalimide synthesis is preferred for synthesising primary amines.
   - v. Ethylamine is soluble in water whereas aniline is not
   - vi. Amines are more basic than amides
   - vii. Although amino group is o – and p – directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m – nitroaniline.
9. Arrange the following
   - i. In increasing order of solubility in water, $C_6H_5NH_2, (C_2H_5)_2NH, C_2H_5NH_2$
   - ii. In increasing order of basic strength
   - a) aniline, p- toludine and p – nitroaniline
   - b) $C_6H_5NH_2, C_6H_5NHCH_3, C_6H_5NH_2, p\text{-}Cl\text{-}C_6H_4\text{-}NH_2$
   - iii. In decreasing order of basic strength in gas phase

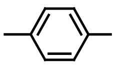
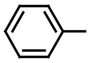
     $(C_2H_5)NH_2, (C_2H_5)NH, \left(C_2H_5\right)_3 N$ and NH_3
   - iv. In increasing order of boiling point

     $C_6H_5OH, (CH_3)_2NH, C_2H_5NH_2$
   - v. In decreasing order of the pK_b values

     $C_2H_5NH_2$, $C_6H_5NHCH_3, (C_2H_5)_2NH$ and CH_3NH_2
   - vi. Increasing order of basic strength

     $C_6H_5NH_2, C_6H_5N(CH_3)_2, (C_2H_5)_2$ NH and CH_3 NH_2

vii. In decreasing order of basic strength

$CH_3CH_2NH_2$, O_2N––NH_2,  NH_2 , CH_3 - NH_2

10. How will you prepare propan – 1- amine from

    i) butane nitrile ii) propanamide ii) 1- nitropropane

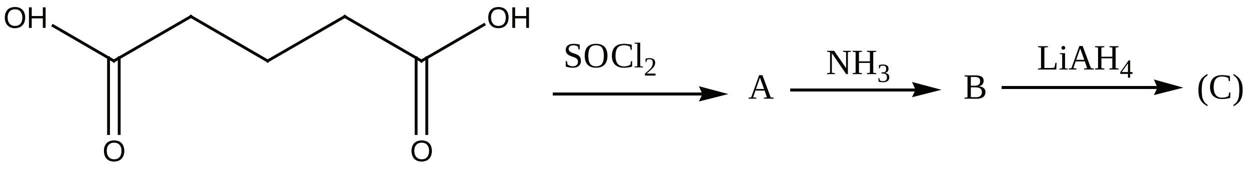
11. Identify A,B,and C

    $CH_3\text{-}NO_2 \xrightarrow{\text{Li AlH}_4} A \xrightarrow{2CH_3CH_2Br} B \xrightarrow{H_2SO_4} C$

12. How will you convert diethylamine into

    i) N, N – diethylacetamide ii) N – nitrosodiethylamine

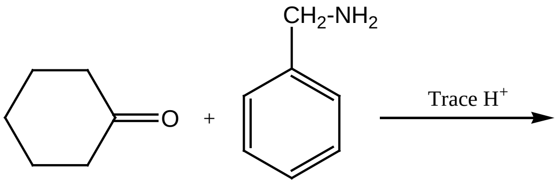
13. Identify A,B and C



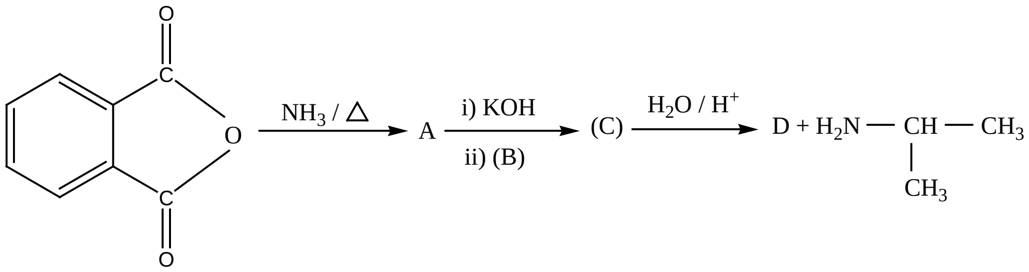
14. Identify A,B,C and D

    aniline+benzaldehyde → A

15. Complete the following reaction

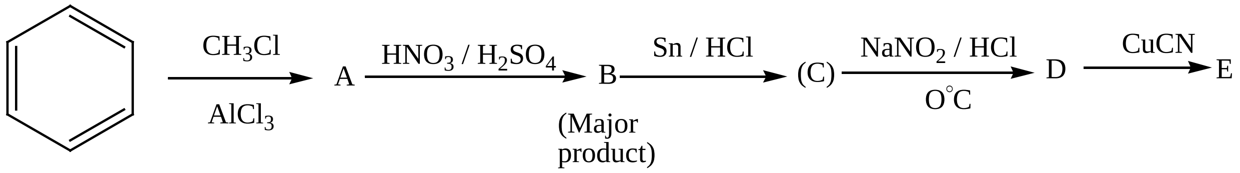


16. Predict A,B,C and D for the following reaction



17. A dibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of CO_2. (B) on heating with liquid ammonia followed by treating with Br_2/KOH gives (c) which on treating with $NaNO_2$ and HCl at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74. Identify A to D.

18. Identify A to E in the following sequence of reactions.



NITRO COMPOUNDS

Chemical properties of Nitro alkane (RNO_2)

Reduction

$$R-NO_2 \xrightarrow[\text{acid}]{Sn/HCl} RNH_2$$

$$R-NO_2 \xrightarrow[\text{Neutral}]{Zn/NH_4Cl} RNHOH$$

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

Hydrolysis

$$RCH_2NO_2 \xrightarrow[\Delta]{HCl/H_2O} RCOOH$$

$$R_2CHNO_2 \xrightarrow{HCl/H_2O} \underset{\text{Ketone}}{R_2CO} + N_2O + H_2O$$

Halogenation

$$CH_3NO_2 \xrightarrow[NaOH]{Cl_2} \underset{\text{Chloropicrin}}{CCl_3NO_2} + 3\,HCl$$

Methods of preparation of
R - NO_2 and RONO

From alkyl halides

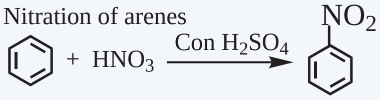
$$R-X \xrightarrow{2\,AgNO_2} \underset{\substack{\text{Nitroalkane}\\ \text{(Major)}}}{RNO_2} + \underset{\substack{\text{Alkylnitrite}\\ \text{(Minor)}}}{RONO} + 2AgI$$

$$R-X \xrightarrow{KNO_2} \underset{\text{(Minor)}}{RNO_2} + \underset{\text{(Major)}}{R-O-N=O}$$

Nitration of alkane

$$CH_3-CH_3 \xrightarrow{HNO_3} CH_3CH_2NO_2 + CH_3NO_2$$

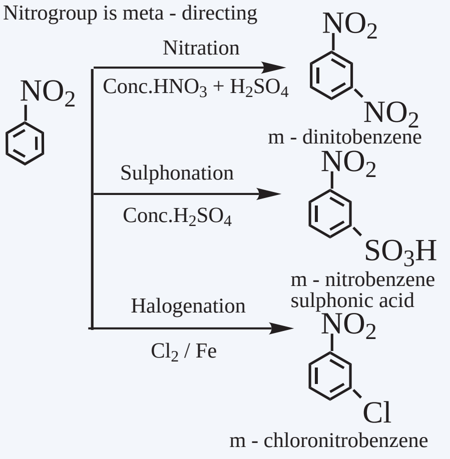
Nitration of arenes



$\underbrace{HNO_3 + H_2SO_4}_{NO_2^{+}}$ nitratingmixture

electrophile

Electrophilic Substituion Reaction
Nitrogroup is meta - directing



Nitrobenzene (oil of mirabane) reduction