

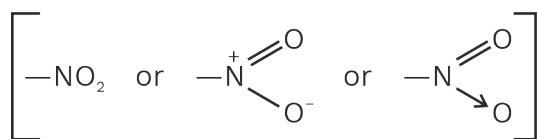
Amines

NITRO COMPOUNDS

- HNO_2 exists in the following two tautomeric forms

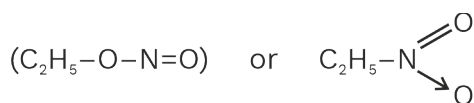


nitrite form



- Alkyl derivatives of the nitrite form are called **alkyl nitrites** while the alkyl derivatives of nitro form are called **nitroalkanes**

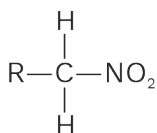
Alkyl Nitrite ($\text{R}-\text{O}-\text{N}=\text{O}$)



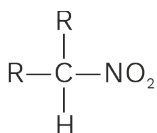
Ethyl nitrite

Nitroalkane

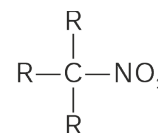
Classification of Nitro Compounds



Primary nitroalkane (1°)

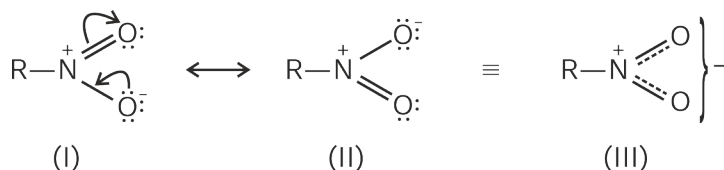


Secondary nitroalkane (2°)



Tertiary nitroalkane (3°)

Structure of Nitro Compounds



The resonance hybrid structure (III) suggests that the two N—O bonds are equal. Bond length of N—O bonds is 121 pm which lies in between N—O single bond length of 136 pm and N=O double bond length of 114 pm.

Concept Ladder



Organic compounds containing nitro as the functional group are called nitro compounds. Nitroalkanes containing α -hydrogen atoms show tautomerism.

Rack your Brain



Will tertiary nitroalkanes show tautomerism?

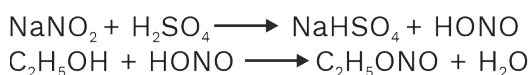


Methods of preparation of Alkyl nitrite

- Alkyl nitrite is prepared by adding concentrated H_2SO_4 to aqueous solution of sodium nitrite and alcohol.



For example,



- Alkyl nitrite is also obtained by the reaction of alkyl iodide and potassium nitrite as follows
- $$\text{RI} + \text{KNO}_2 \longrightarrow \text{RONO} + \text{KI}$$

For example,



- Alkyl nitrite can also be prepared by the action of nitrogen trioxide on alcohol.

For example,

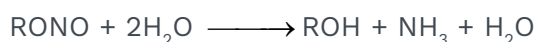


Physical Properties

- At ordinary temperature, ethyl nitrite is a gas which can be liquefied on cooling into a colourless liquid (boiling point 290 K) having a characteristic smell of apples.
- Nitroalkanes are sparingly soluble in water while nitroarenes are insoluble.
- 1° and 2° nitroalkanes dissolve in aq. NaOH to form salts.
- It has an important property of dilating the blood vessels so it reduces hypertension and severe pain of angina pectoris.

Chemical properties

Hydrolysis : Alkyl nitrite can be hydrolysed by water, dilute alkali or dilute acid forming alcohol.



Concept Ladder



Nitro compounds act as versatile building blocks for the synthesis of pharmaceutically relevant substances.

Rack your Brain



What is the hybridisation of nitrogen in nitroalkanes and nitroarenes?

Concept Ladder



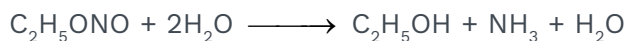
Nitrite ion is an ambident nucleophile since it has two sites (oxygen and nitrogen) through which it can attack an alkyl halide.

Rack your Brain

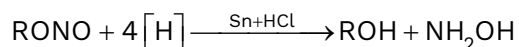
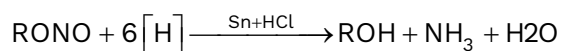


Why nitro compounds are classified as explosive group?

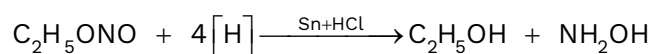
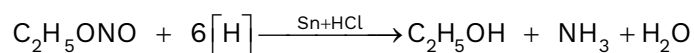
For example



Reduction : On reduction with Sn/HCl, it gives alcohol, ammonia or hydroxyl amine.

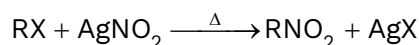


For example,

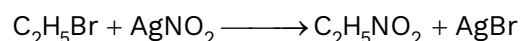


Method of preparation of Nitro Alkanes

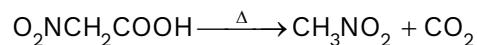
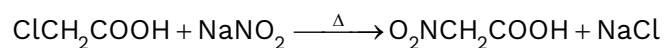
From alkyl halide : When alkyl halides and alcoholic silver nitrate solution react, nitroalkanes are formed as follows:



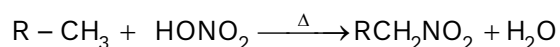
For example,



From α -Halo substituted acids



By nitration of paraffin : As nitration of paraffins (alkanes) is quite difficult in comparison to aromatic hydrocarbons so they can undergo nitration only with fuming HNO_3 in the vapour phase at 423–673K under pressure. Here due to cleavage of C–C bonds a mixture of Nitro alkanes is formed. It occurs by free radical mechanism.



Concept Ladder



When higher alkanes are nitrated, mixtures of nitroalkanes including those formed by the rupture of carbon-carbon bond are also obtained. This method is widely used for the commercial production of nitroalkanes as the mixture of nitroalkanes formed and can be separated by fractional distillation.

Rack your Brain



Why a mixture of nitro and nitrite compound is produced, when alkyl halide is treated with sodium/potassium/silver nitrate?

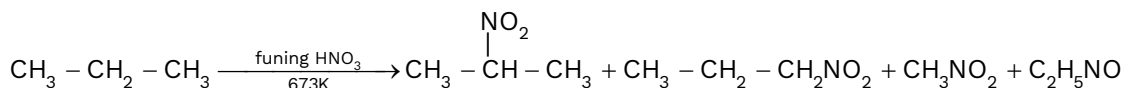
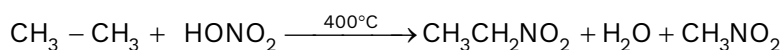
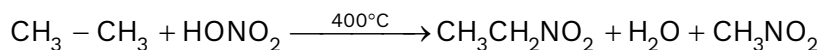
Concept Ladder



Nitroalkanes are also widely used as a propellant in rockets i.e. nitromethane is a liquid propellant and nitrocellulose gel in nitroglycerine are used as solid propellants.



For example,



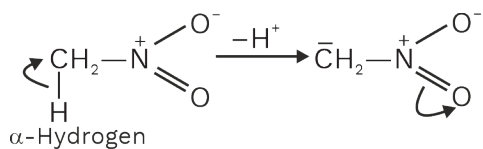
Physical properties

- Nitroalkanes are colourless liquids and have a pleasant smell.
- These are partially soluble in water but readily soluble in organic solvents.
- They have high value of boiling point due to their polar nature.

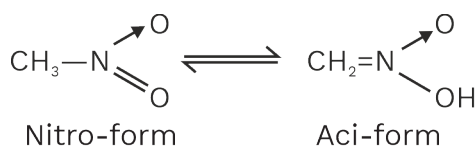
Chemical properties

—NO₂ group is a resonance hybrid of the structures given below. In it, resonance is proved by the fact that both the N—O bonds have the same bond length.

Acidic character : These are slightly acidic due to presence of α-hydrogen atom, so react with strong alkali like aqueous NaOH to form salts.



Due to α-H-atom Tautomerism exists



Rack your Brain



Why the higher nitroalkanes are insoluble in water but readily soluble in organic solvents?

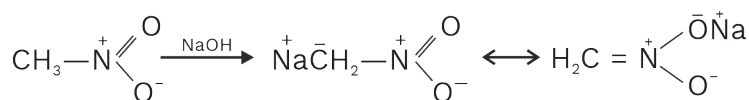
Concept Ladder



The main reason for the acidic character of 1° and 2° nitroalkanes are (i) strong electron withdrawing nature of the nitro group and (ii) the resonance stabilisation of the carbanion of the salt so produced.



In presence of an alkali, mainly aci-form dominates.

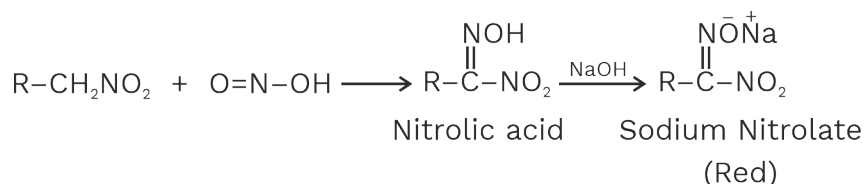


Rack your Brain

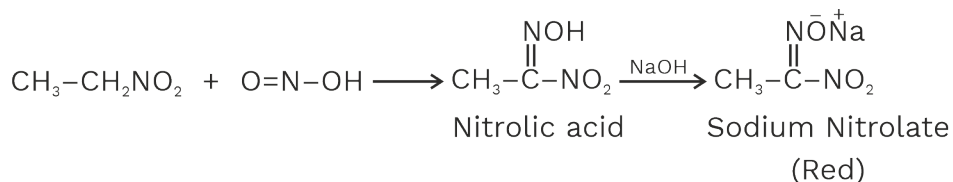


During hydrolysis, how does the aci-form of nitroalkanes acts like - electrophile or nucleophile?

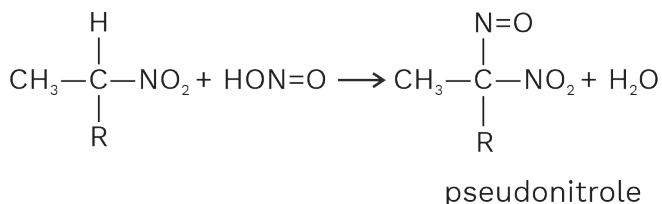
Reaction with nitrous acid : Primary nitroalkanes react with nitrous acid to give nitrolic acid which dissolves in NaOH to give a red solution of sodium nitroate.



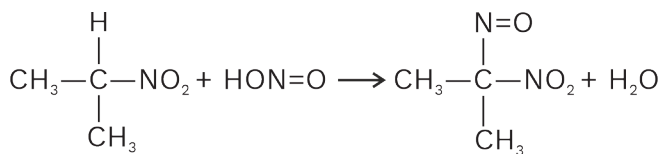
For example,



Secondary nitroalkanes give pseudonitroles with HNO_2 which give blue colour in NaOH solution.



For example



Tertiary nitroalkanes do not give this reaction due to absence of α -hydrogen atom.

This behaviour of HONO with 1° , 2° , 3° to R-NO forms the basis of victor meyer test for alcohols.

Concept Ladder

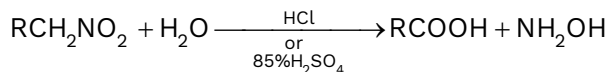


The C—N bond of the primary and secondary nitroalkanes are split by strong mineral acid.

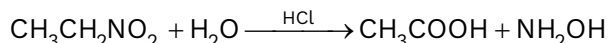
This method of hydrolysis of nitroalkanes has been used for the industrial preparation of Hydroxylamine.



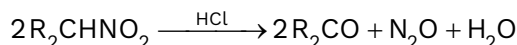
Hydrolysis : Primary nitroalkanes undergo acidic hydrolysis to give acids as follows



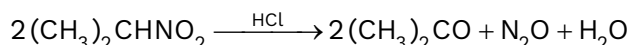
For example,



- Secondary nitroalkanes on hydrolysis give ketones as follows:

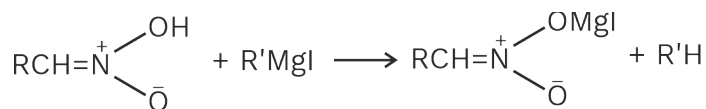


For example

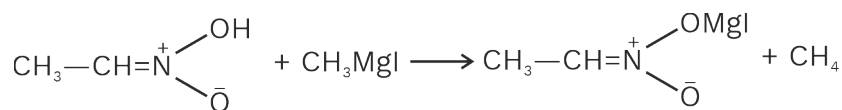


- Tertiary nitroalkanes do not show this reaction

Reaction with grignard reagent : Nitroalkane in Aci-form gives alkanes with Grignard reagent as follows:

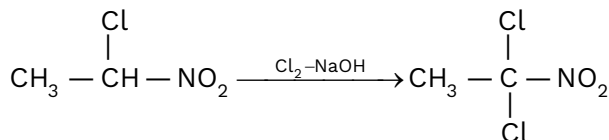
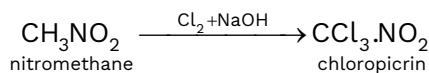
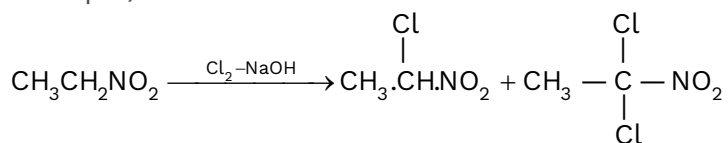


For example,



Halogenation : Nitroalkanes undergo halogenation at α -position.

For example,



Previous Year's Questions



An organic compound ($\text{C}_3\text{H}_9\text{N}$) (A), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with CHCl_3 and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A).

[AIPMT-2012]

- (1) $(\text{CH}_3)_2\text{CH}-\text{NH}_2$
- (2) $\text{CH}_3\text{CH}_2-\text{NH}-\text{CH}_3$
- (3) $(\text{CH}_3)_3\text{N}$
- (4) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$

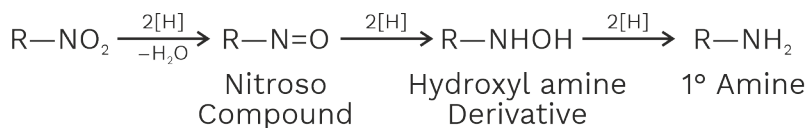
Rack your Brain



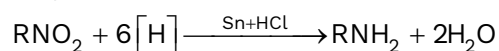
What is chloropicrin and why is it important?



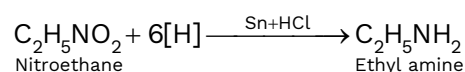
Reduction : Nitroalkanes undergo reduction as follows:



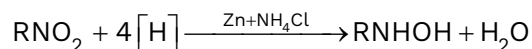
Reduction by Sn+HCl or Zn/HCl or LiAlH₄ gives primary amine as follows:



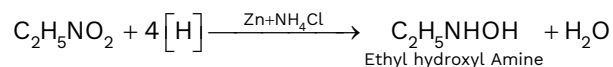
For Example,



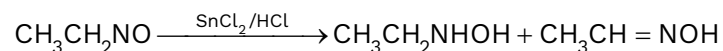
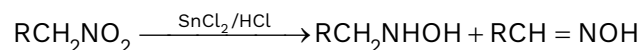
Reduction with zinc dust and NH₄Cl gives hydroxylamines as follows:



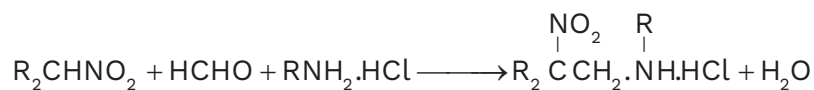
For example



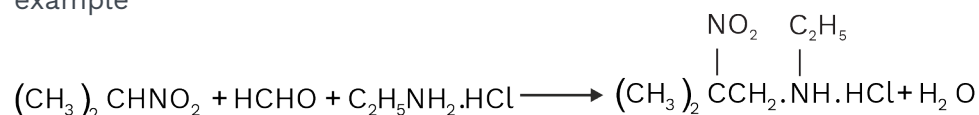
- Reduction with SnCl₂/HCl gives a mixture of oxime and hydroxyl amine as follows:



Mannich reaction : It involves the condensation of nitroalkane, formaldehyde, primary amine and hydrogen chloride as follows:



For example



Rack your Brain



In mannich reaction, the aci form act as - nucleophile or electrophile?

Concept Ladder

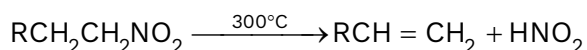


Primary and secondary nitroalkanes undergo mannich reaction with primary and secondary aliphatic amines and formaldehyde, yielding nitroamines in high yield.

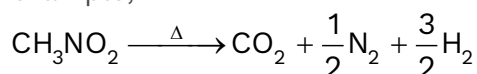


Effect of heat:

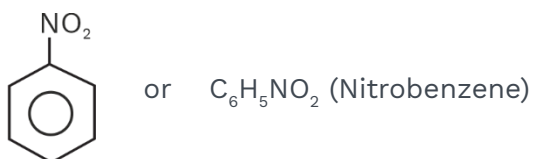
- On moderate heating below 300°C, nitroalkanes form alkenes.



- On heating rapidly, explosion takes place. For example,

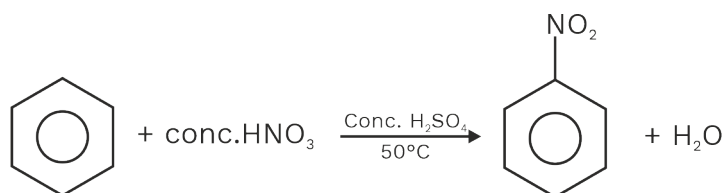


NITROARENES

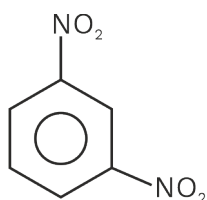


- It is called Oil of Mirbane and has a bitter, almond like odour

Methods of preparation



If temperature is above 100°C, further nitration takes place and the product is meta-dinitrobenzene.



Physical properties

- It is a light brown coloured oily liquid with a boiling point of 210°C.
- It is insoluble in water and volatile in steam.

Concept Ladder



Nitro group can easily be reduced to a variety of products, depending upon the type of reagent and the reaction conditions used. but if the reaction is allowed to completion then the final product of the reaction is primary amines.

Rack your Brain



What is the best reagent for carrying out the reduction of nitroalkane in neutral medium to hydroxylamines?

Concept Ladder



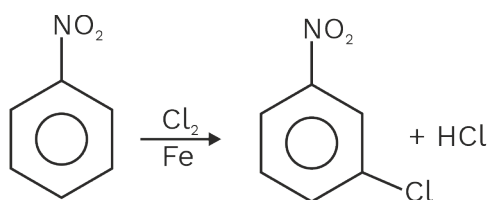
Nitroarenes and chiefly polynitroarenes are unstable and they decompose with explosive violence, when heated.

Chemical properties

Due to benzene ring:

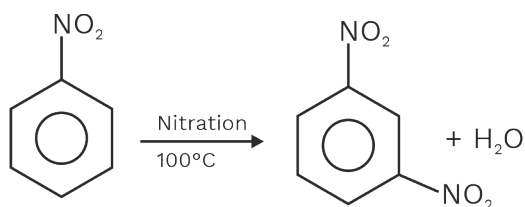
Nitro group deactivates the benzene ring, therefore further substitution takes place only at meta-position and the rate of electrophilic substitution is much slower than that of benzene.

Halogenation:

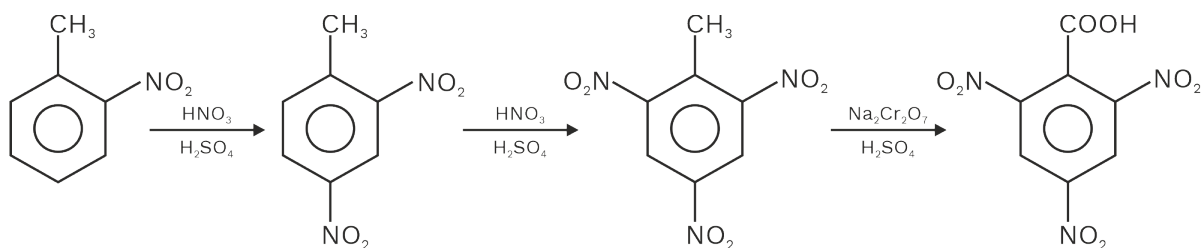


m-chloronitro benzene

Nitration

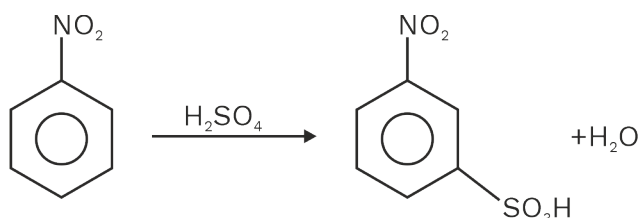


m- dinitrobenzene



2, 4 Dinitro toluene

Sulphonation:



Concept Ladder



If two or more nitro groups are present in the benzene ring, it is possible to reduce one of them without affecting the others. Such reductions are called selective reductions.

Previous Year's Questions



Electrolytic reduction of nitrobenzene in weakly acidic medium gives

[AIPMT]

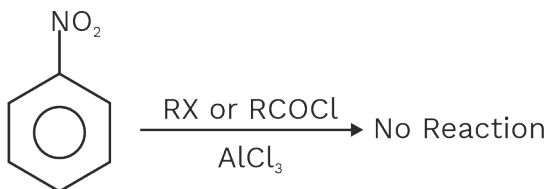
- (1) N-phenylhydroxylamine
- (2) nitrosobenzene
- (3) aniline
- (4) p-hydroxyaniline

Rack your Brain



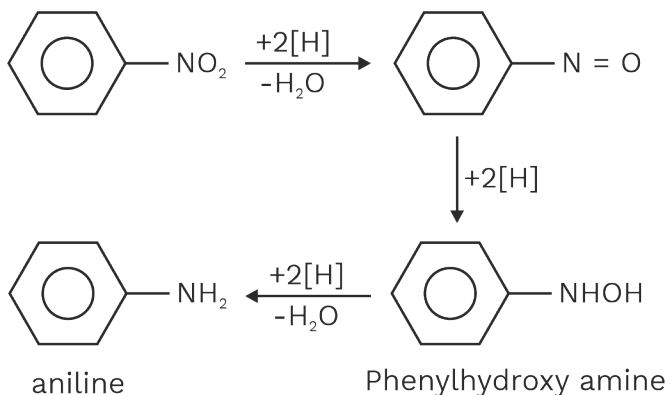
What is TNT?

Friedel crafts reaction

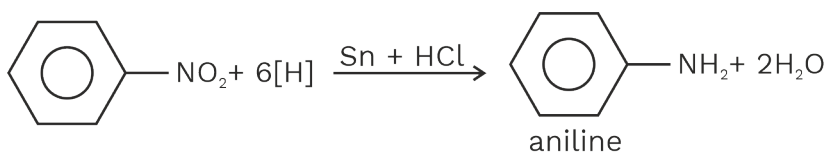


Friedel Crafts reaction does not occur in any of the meta di-recting groups like $-\text{NO}_2$, $-\text{CHO}$, $-\text{COOH}$, $-\text{CX}_3$, $-\text{SO}_3\text{H}$, $-\text{COX}$ etc

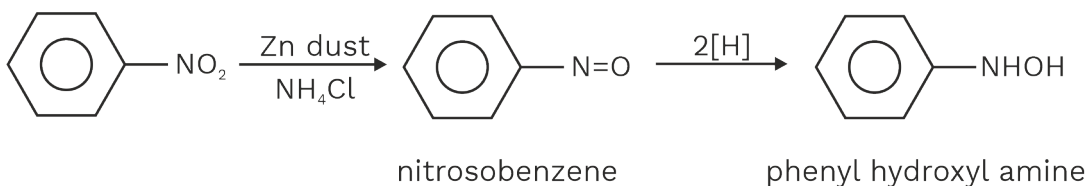
Reduction of nitro benzene



In a strong acidic medium



In a neutral medium



Concept Ladder



Nitro group, due to its electron-withdrawing nature reduces the electron density at the o- and p-positions. Electron density is comparatively more at the m-position, i.e., the nitro group is m-directing.

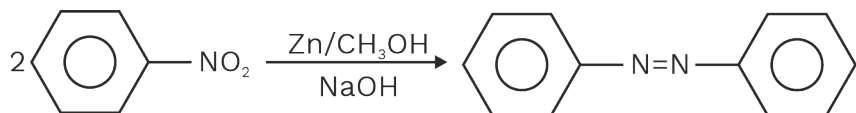
Rack your Brain



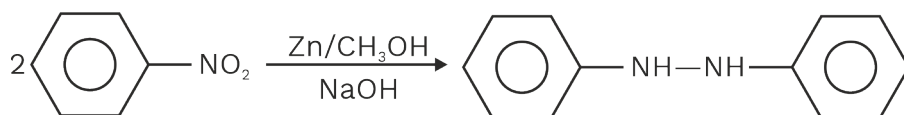
Can nitroarenes go under distillation?



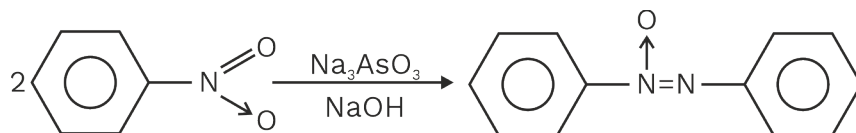
In basic medium



Azobenzene



Hydrazobenzene



Azoxybenzene

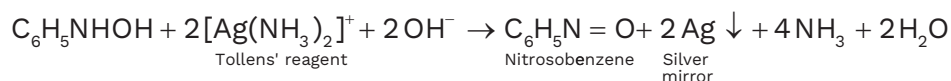
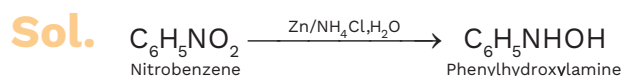
- Nitrosobenzene and Phenylhydroxylamine further react to give following products depending upon reagent used.
- With Zinc dust/NaOH or sodium amalgam, azobenzene and hydrazobenzene are formed.
- With sodium arsenite and NaOH, azoxybenzene is formed.

Concept Ladder



Different product can be obtained from nitrobenzene on reduction but the nature of the product depends upon the reducing agent used.

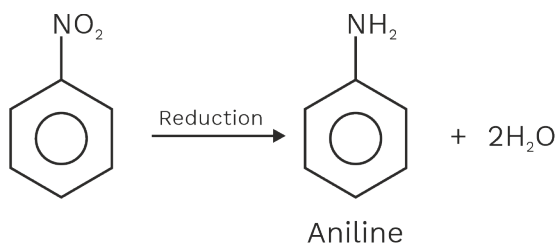
Q1 What is Baker-Mulliken's test?



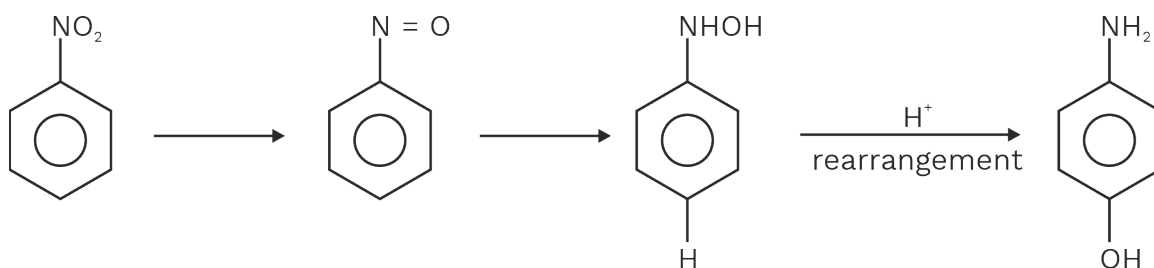


Electrolytic reduction:

In a weak acidic medium

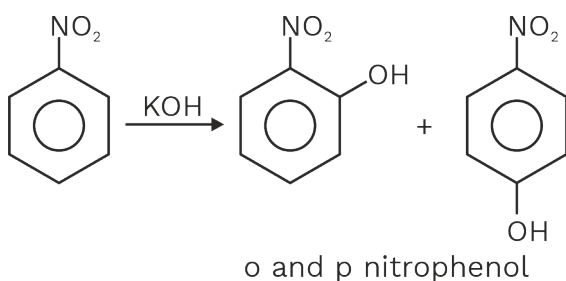


In a strong acidic medium



Reaction with solid KOH :

It is an example of nucleophilic substitution reaction.



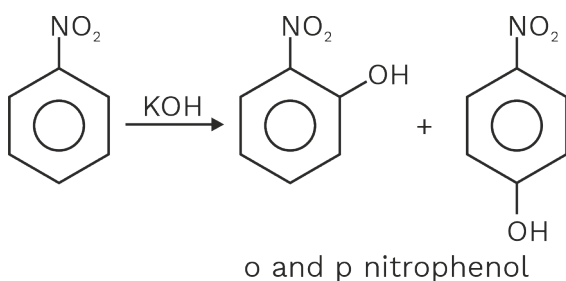
Rack your Brain



Why nitrobenzene is used as a solvent during Friedel-Craft's reaction?

Reaction with solid KOH :

It is an example of nucleophilic substitution reaction.



Previous Year's Questions



Electrolytic reduction of nitrobenzene in strongly acidic medium gives

[AIPMT]

- (1) azobenzene
- (2) aniline
- (3) p-aminophenol
- (4) azoxybenzene

Q2 Toluene is more easily nitrated than benzene. Explain.

Sol. Nitration is an electrophilic substitution reaction and thus occurs more readily at a site where the electron-density is more. Now in toluene, there is electron-donating CH_3 group. In other words, the electron-density in the toluene ring is much more than in the benzene ring. As a result, toluene is nitrated more easily than benzene.

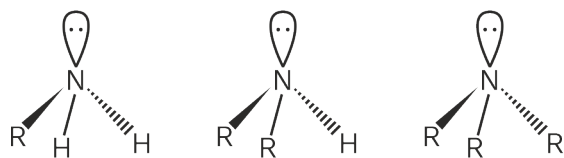
The $-\text{NO}_2$ group is very firmly linked to Benzene- nucleus, moreover partial double bond character develops due to resonance so nitrobenzene becomes inert and does not give displacement reaction.

In case any group like $-\text{X}$ is present at o, p positions to $-\text{NO}_2$ group, it increases the chance of nucleophilic substitution of this group.

Uses

- Nitrobenzene is used in the manufacture of azodyes, aniline and as a perfume material in shoe polish and soaps.
- A mixture of TNT (20%) and NH_4NO_3 (80%) called amatol is used in coal mining.
- A mixture of TNT (15%), NH_4NO_3 (65%), aluminium (17%) and charcoal (3%) is called ammonal and is used for blasting purposes.
- RDX (Research and Development Explosive) is also called cyclonite.
- RDX is prepared by controlled nitration of hexamethylene tetraamine (obtained from formaldehyde) with fuming nitric acid at 293 K.

AMINES



1° Amine

2° Amine

3° Amine

- Amines are the alkyl or aryl derivatives of ammonia.
- Amines have a general formula $\text{C}_n\text{H}_{2n+3}\text{N}$.
- Like NH_3 an amine is also Pyramidal in shape ($3\text{bp} + 1\text{lp}$) with bond angle less than 109.5° . There are three types of amines primary (RNH_2), secondary (R_2NH) and tertiary (R_3N).

Concept Ladder



Nitro group can easily be reduced to a variety of products, depending upon the type of reagent and the reaction conditions used.

Rack your Brain



What are the reagent used for the partial reduction of nitrobenzene?

Previous Year's Questions



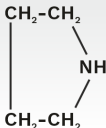
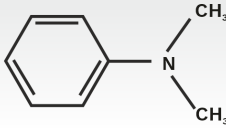
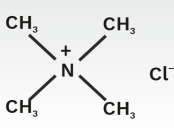
The action of nitrous acid on an aliphatic primary amine gives

[AIPMT]

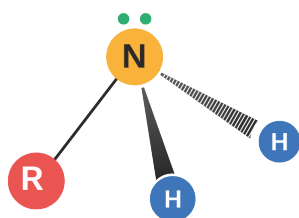
- (1) secondary amine
- (2) nitro alkane
- (3) alcohol
- (4) alkyl nitrite

AMINES

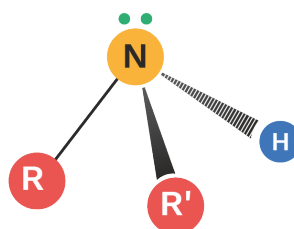
AMINES are the members of a family of nitrogen-containing organic compounds that is derived, either in principle or in practice, from ammonia (NH₃).

Ethylamine	Pyrrolidine	N, N-Dimethylaniline	Tetramethylammonium chloride
CH ₃ CH ₂ NH ₂			
An open-chain aliphatic primary amine.	Acyclic aliphatic secondary amine.	An aromatic tertiary amine	An aliphatic quaternary ammonium salt

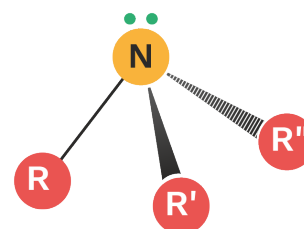
Structure Of Amines



PRIMARY



SECONDARY



TERTIARY

PROPERTIES

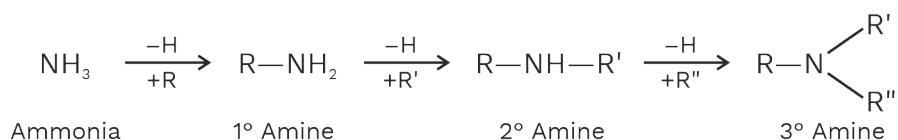
- Water Soluble
- Gaseous at room temperature
- Foul-smelling compounds
- Colourless
- High boiling point
- Burns with a yellow flame

USES OF AMINES

- Corrosion inhibitors in boilers
- Lubricating oils (morpholine)
- Stabilizers for cellulose
- Nitrate explosives (diphenylamine)
- Protectants against damage from gamma radiation (diarylamines)



- All the three types of amine are obtained from ammonia by replacing H-atoms by alkyl or aryl groups.



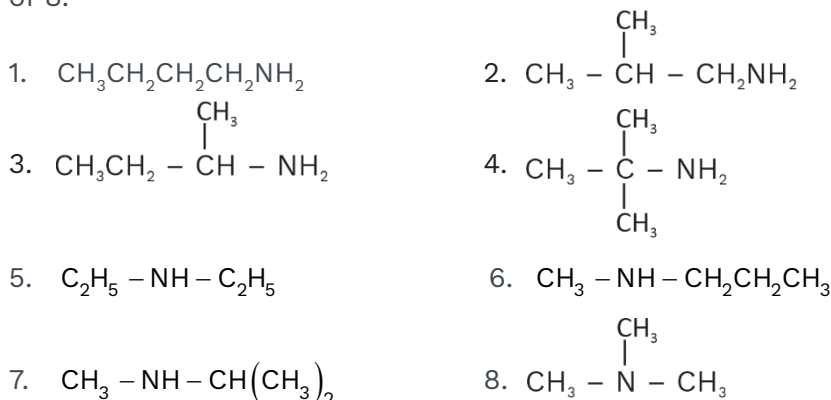
Amine	Common name	IUPAC name
Primary amines		
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	n-Propylamine	1-Propanamine
$(\text{CH}_3)_2\text{CHNH}_2$	Isopropylamine	2-Propanamine
Secondary amines		
CH_3NHCH_3	N-Methylaminomethane	N-Methylmethanamine
$\text{CH}_3\text{CH}_2\text{NHCH}_3$	Ethylmethylamine	N-Methylethanamine
Tertiary amines		
$(\text{CH}_3)_3\text{N}$	N, N-Dimethylaminomethane	N, N-Dimethylmethanamine
$(\text{C}_2\text{H}_5)_2\text{NCH}_3$	N-Ethyl-N-methylaminoethane	N-Ethyl-N-methylethanamine
Aralkylamines		
$\text{C}_6\text{H}_5-\text{CH}_2\text{NH}_2$	Phenylaminomethane	Phenylmethanamine
$\text{C}_6\text{H}_5-\text{CH}_2\text{CH}_2\text{NH}_2$	β -Phenylethylamine	2-Phenylethanamine

- Amines show functional, chain, position and metamerism isomerism.
- Primary, secondary and tertiary amines are functional isomers of each other.

Q3

Calculate the number of primary, secondary and tertiary amines in case of $\text{C}_4\text{H}_{11}\text{N}$?

Sol. $C_4H_{11}N$ has 4-primary, 3-secondary and 1-tertiary amines, that is, a total of 8.



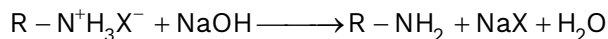
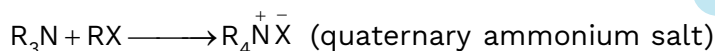
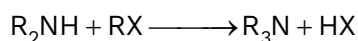
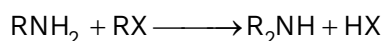
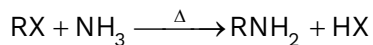
Here (1, 2, 3, 4) w.r.t (5, 6, 7) and (8) are functional isomers.

Here 1 is chain isomer w.r.t to 2 and 4. 1 and 3 are position isomers 5, 6 or 7 are metamers.

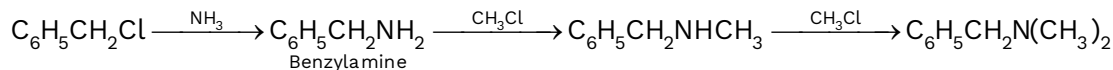
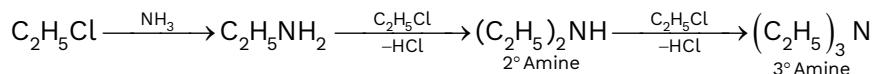
Methods of Preparation for all Types of Amines

By Hoffmann method :

Alkyl halide is treated with alcoholic ammonia as follows:



For Example,



Concept Ladder

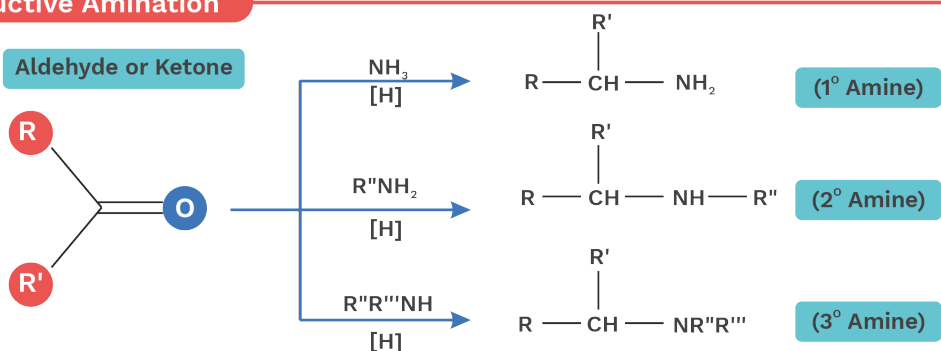


Amines are organic molecules that include a nitrogen atom. Amines show up in our bodies as neurotransmitters, in plants as alkaloids, in our DNA, and in manufacturing processes.

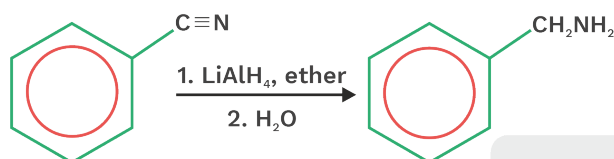


Preparation Of Amines

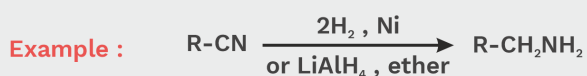
Reductive Amination



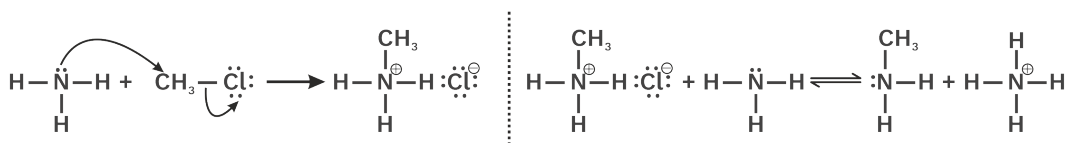
Reduction Of Nitriles



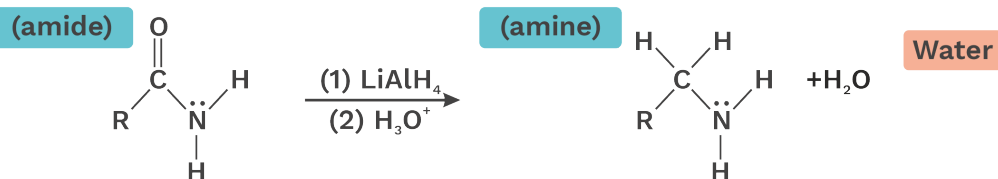
Nitriles can be reduced by strong reducing agents like H_2 with catalyst (example Ni or LiAlH_4) to yield primary amines via nucleophilic addition reaction.



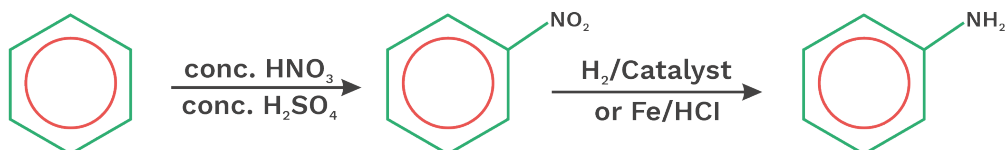
Reduction Of Ammonia With Alkyl Halides



Reduction Of Amides



Reduction Of Nitro Groups



N,N-Dimethyl phenyl methanamine or benzylamine

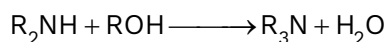
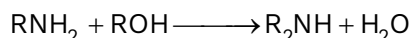
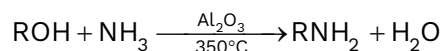
Reactivity order of halides with amines :



When NH_3 is in excess then $R-NH_2$ is the major product and when $R-X$ is in excess, quaternary ammonium salt is the major product. This is called ammonolysis of alkyl halides. It is a nucleophilic substitution reaction.

By ammonolysis of alcohols:

Here, vapours of alcohol and ammonia are passed over heated alumina or thoria at $350^\circ C$ as follows:



Separation of primary, secondary, and tertiary amine and quaternary ammonium salt :

The mixture is first treated with aqueous KOH where the quaternary halide forms quaternary ammonium hydroxide, a solid product. The mixture of primary, secondary and tertiary amines is then distilled, leaving salt residue in the flask. The mixture of primary, secondary, tertiary amines can be separated by any of the following methods: By fractional distillation: The mixture is subjected to fractional distillation by which all the three amines are separated. The method is applicable only when the three amines differ considerably in their boiling points. By Hinsberg method: Here the mixture of amines is treated with Hinsberg reagent (benzene sulphonyl chloride).

- Here only primary and secondary amines react while tertiary does not react with the reagent.
- The mixture is distilled to remove unreacted tertiary amine.

Concept Ladder



Due to electron withdrawing nature of the nitro group it deactivates the ortho and para position of the nitroarene ring towards further electrophilic substitution reaction. This selective deactivation leaves only one reactive site-meta, hence meta substituted products are obtained.

Rack your Brain



Which positions of nitrobenzene are easily attacked by nucleophiles?

Previous Year's Questions



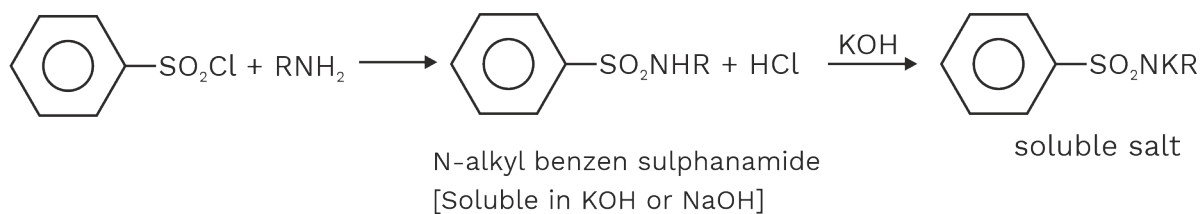
The electrolytic reduction of nitrobenzene in strongly acidic medium produces

[AIPMT]

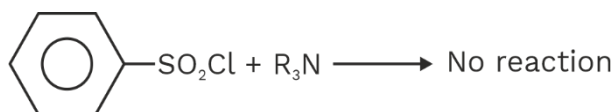
- (1) p-aminophenol
- (2) azoxybenzene
- (3) azobenzene
- (4) aniline



- The remaining mixture is treated with aqueous KOH, in which, the derivative of primary amine becomes soluble and that of secondary amine remains insoluble.



N,N-Dialkyl benzene sulphonamide (insoluble in KOH)



From here the solid residue of 2° amine and soluble salt of 1° are separated by filtration, which on hydrolysis separately gives 2° and 1° amines. The product formed is substituted sulphonamide which are stable solids and it is formed when p-Toluene sulphonyl chloride is preferred over benzene sulphonylchloride. Product can be easily purified by crystallization. By Hoffmann method

- Here, diethyl oxalate is heated with the mixture of amines.
- By primary amines and secondary amines a solid product and an oily product are formed respectively, while it will not react with tertiary amines.
- The mixture is distilled where by unreacted tertiary amines distill out first, followed by the oily product of secondary amine. The derivative of primary amine is left in the flask.

Concept Ladder

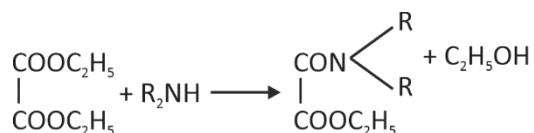
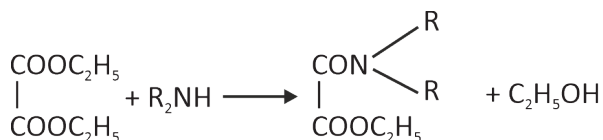


Quaternary ammonium salts have N-stereocentre, therefore it shows enantiomers.

Rack your Brain

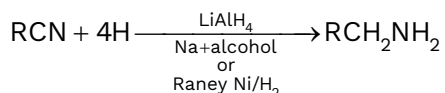


Write the metamer of diethylamine.

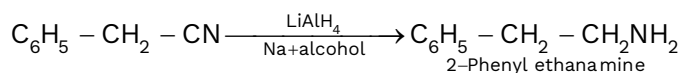
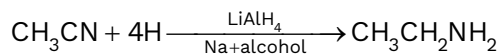


dialkyl oxamic ester
(oily liquid)

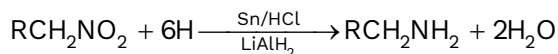
Methods of Preparation of Primary Amines By reduction of cyanides



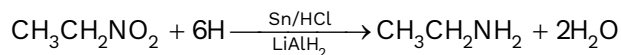
Example,



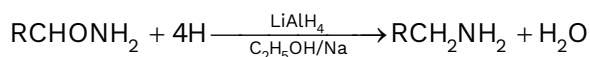
By reduction of nitro alkanes



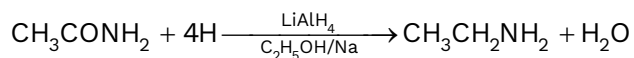
Example,



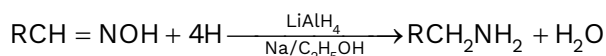
By reduction of amides



Example,



By reduction of oximes



Concept Ladder



The major drawback of Hoffman method is RX limited to methyl and 1° alkyl halides.

Rack your Brain



Which species acts like a nucleophile in this reaction?

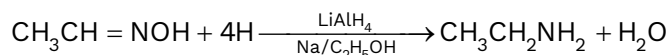
Concept Ladder



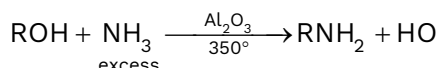
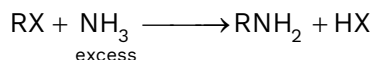
When NH_3 is in excess 1° amine is main product in ammonolysis of alcohol.



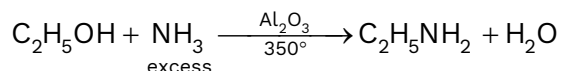
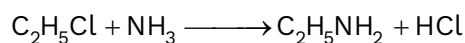
Example,



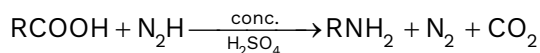
From alkyl halides and alcohols



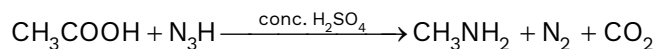
Example,



By Schmidt reaction

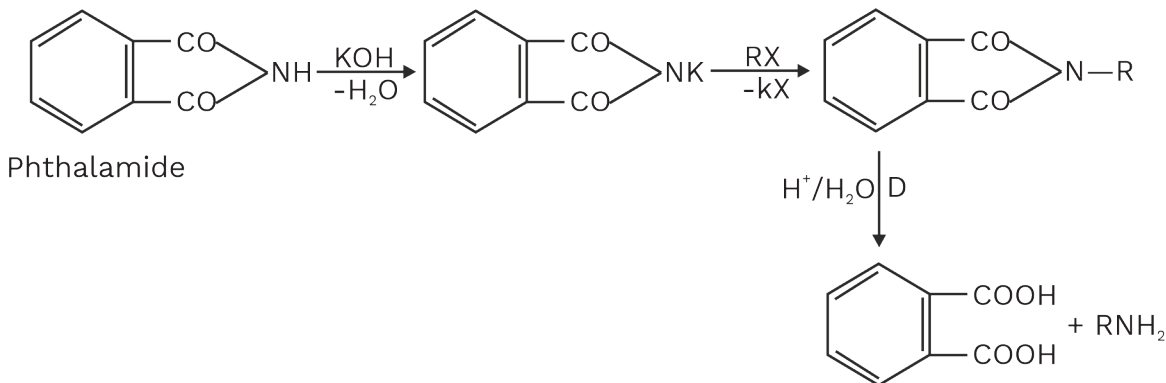


Example,



- In this reaction, acyl azide and alkyl isocyanate are the reaction intermediates and by using Curtius degradation method they give primary amines as the final product.

By Gabriel phthalimide synthesis



R may be $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ etc.

Previous Year's Questions



The number of structural isomers possible from the molecular formula $\text{C}_3\text{H}_9\text{N}$ is

[AIPMT]

- | | |
|-------|-------|
| (1) 4 | (2) 5 |
| (3) 2 | (4) 3 |

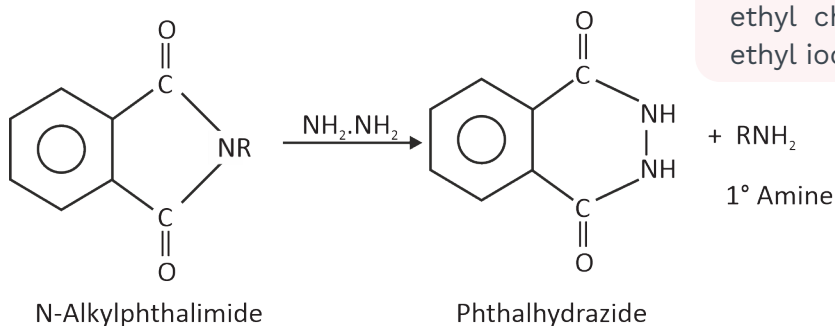
Concept Ladder



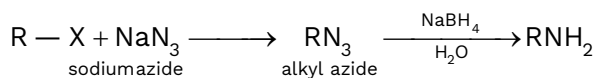
Aromatic 1° amines such as aniline, toluidines etc. cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.



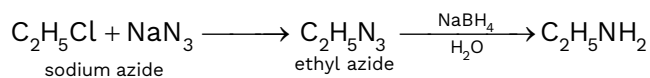
The acidic/basic hydrolysis of N-alkylphthalimides is often slow. Therefore, hydrazinolysis (cleavage by hydrazine) of N-alkylphthalimides is a more convenient and efficient method for obtaining 1° amines using Gabriel synthesis. For example,



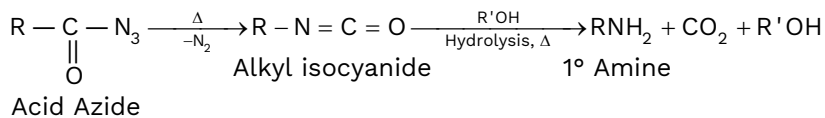
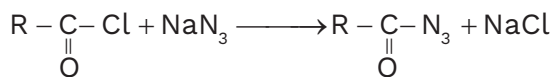
By the reaction of Azide with NaBH₄



For Example,

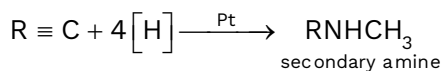


By Curtius Rearrangement

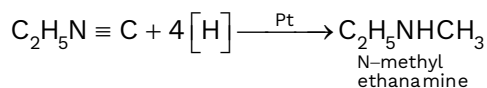


Methods of Preparation for secondary Amines

Platinum catalyzed reduction of Iso cyanides



Example,



Rack your Brain



How can benzylamine be prepared by using benzyl chloride and glycine by using ethyl chloroacetate in place of ethyl iodide?

Concept Ladder



Cyanides on reduction with H₂ and Raney Ni or with LiAlH₄ or with sodium and alcohol (Mendius reaction) give aliphatic or aryl primary amines. While isocyanides on reduction with H₂/Ni or LiAlH₄ give secondary amines.

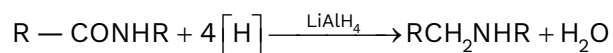
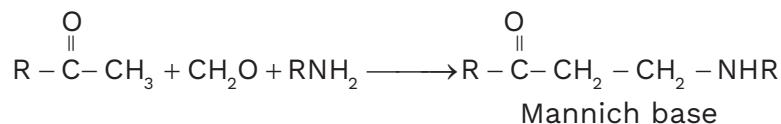
Rack your Brain



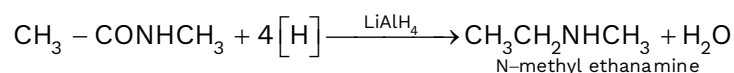
Which method is suitable for the ascent of amines series?



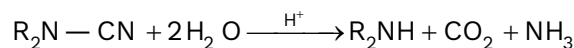
Mannich reaction



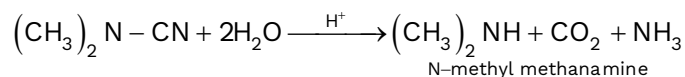
Example,



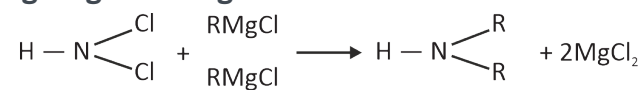
Hydrolysis of Dialkyl cyanamide



Example,

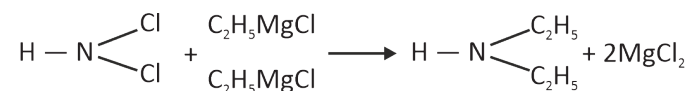


Using Grignard reagent



Dichloroamine

secondary amine

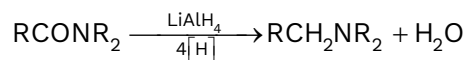


Dichloroamine

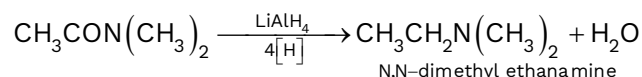
secondary amine

Methods of Preparation for Tertiary Amines

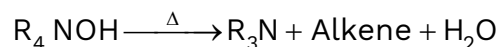
Reduction of N, N-disubstituted amides



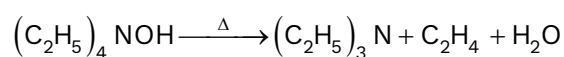
Example,



By decomposition of tetraammonium hydroxides



Example,



Concept Ladder



Amides are reduced to amines, product contains same number of carbon atoms as the original amide.



Previous Year's Questions

Reaction of propanamide with ethanolic sodium hydroxide and bromine will give

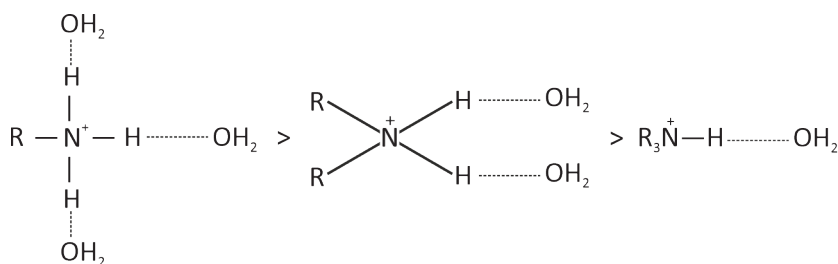
[AIPMT]

- (1) Ethylamine
- (2) Methylamine
- (3) Propylamine
- (4) Aniline



Physical Properties of Amines

- The first 2 members of the amine family, ethyl amine and methyl amine– are gases while the remaining members are either solids or liquids.
- Amines tend to have a unpleasant and distinct odor.
- • Due to presence of hydrogen bonding these are highly soluble in water. Solubility is inversely proportional to Molecular weight therefore, the decreasing order of solubility of amines is given as: $\text{CH}_3\text{NH}_2 > \text{C}_2\text{H}_5\text{NH}_2 > \text{C}_3\text{H}_7\text{NH}_2 > \dots \text{R-NH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$
- These are basic in nature and are inflammable.
- Amines have lower boiling points than alcohols due to presence of weaker hydrogen bonding, e.g.

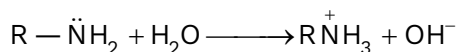
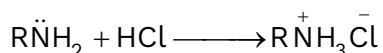


The above is extent of H–bonding in water in decreasing order and stability of ions by solvation

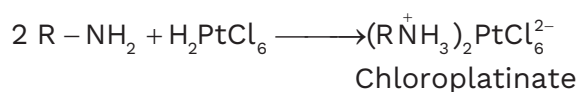
Chemical Properties

Basic nature:

In amines, nitrogen atom has one lone pair of electrons to donate, hence they are basic in nature. So they form salts with acids.



Due to formation of OH⁻ aqueous solution of amines is basic in nature



Concept Ladder



Reduction of nitro compounds can also be carried out with Sn/Fe in HCl or with Na and alcohol.

Previous Year's Questions



Which of the following reactions is appropriate for converting acetamide to methanamine?

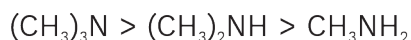
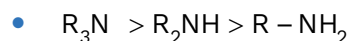
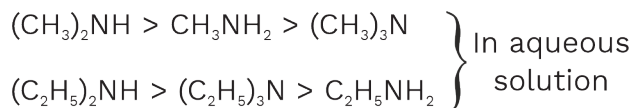
[NEET-2017]

- (1) Hoffmann hypobromamide reaction
- (2) Stephens reaction
- (3) Gabriels phthalimide synthesis
- (4) Carbylamine reaction



Chloroplatinates are used to determine molecular and equivalent masses of amines.

Basic nature orders of amines

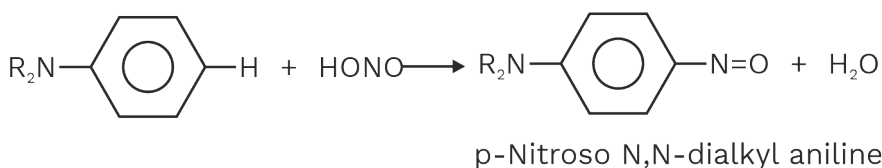
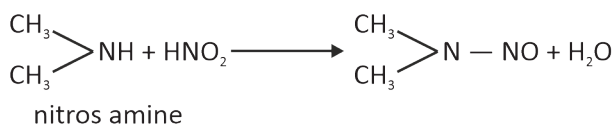


In gas phase or in non-aqueous solvents



Reaction with nitrous acid (HNO_2):

A primary amine on reaction with nitrous acid gives an alcohol, while a secondary amine on reacting with it gives a nitroso amine. Trialkyl ammonium nitrate is formed by tertiary amine.



Reaction with NOCl:

A primary amine on reaction with NOCl gives an alkyl halide whereas a secondary amine on reacting with it gives an oily product; a tertiary amine does not react with NOCl.



Previous Year's Questions



Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine?

[AIPMT]

- (1) NaOH/Br₂
- (2) Sodalime
- (3) Hot conc. H₂SO₄
- (4) PCl₅

Concept Ladder

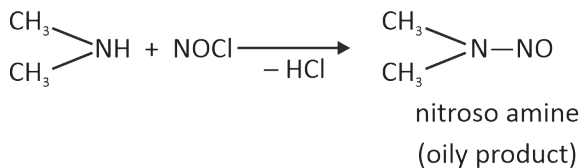


Phthalic acid can again be converted into phthalimide and can be used again and again.

Rack your Brain



Can we form aryl amines by Gabriel synthesis?



This reaction is called Nitrosation

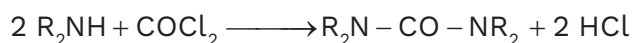
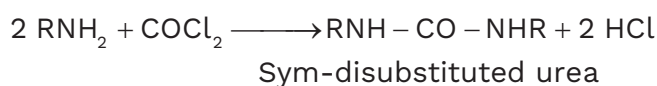
Libermann's nitroso test:

When nitroso amine in the presence of sulphuric acid, is heated with phenol, there is formation of red coloured product takes place, which changes to blue and finally green. This test is used to detect both Aromatic and Aliphatic sec. amines.

- N-Nitrosoamines are cancer producing agents i.e carcinogens.

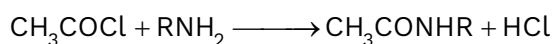
Reaction with COCl_2 :

This reaction is given by primary and secondary amines only.



Acetylation or reaction with CH_3COCl :

The presence of NH_2 group is confirmed by using this reaction.



Carbylamine reaction:

It is a test for primary amines. Here, isocyanide having pungent, bad smelling, is formed. The reaction intermediate is dichloro carbene.

Concept Ladder



Leucart reaction occurs by reductive amination, using an ammonium salt or an amide at high temperatures, usually in the presence of catalysts.

Rack your Brain

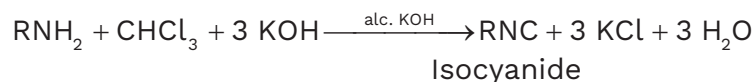
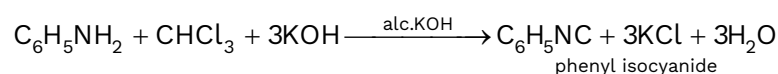
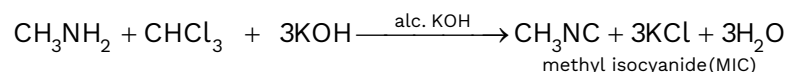


What is leaving group in Curtius reaction?

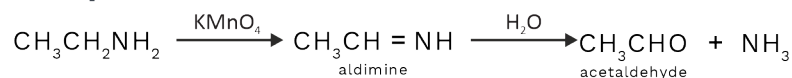
Concept Ladder



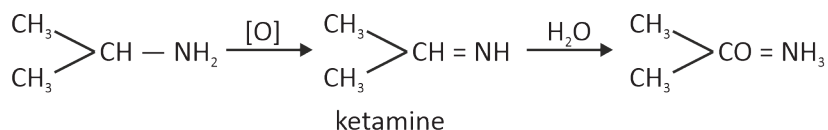
Curtius, Schmidt and Lossen Rearrangement are basically rearrangement reactions in which carbon migrates from carbon to nitrogen with the formation of an isocyanate. i.e., 1, 2 shift, migrating group is an alkyl or aryl group and leaving group.

**Example,****Oxidation:**

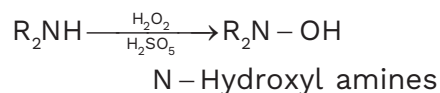
Amines can be distinguished by oxidation process as on oxidation it gives aldimine, which on hydrolysis gives an aldehyde.

For example,

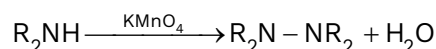
A secondary amine on oxidation gives ketamine which on hydrolysis gives ketone.



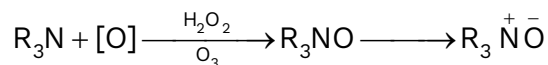
A secondary amine on oxidation by Caro's acid or H_2O_2 gives dialkyl hydroxylamine as follows



Tetraalkyl hydrazine is formed by when secondary amine is oxidised by KMnO_4 as follows



- A tertiary amine on oxidation by Fenton's reagent or Caro's-acid gives tertiary amine oxide.

**Rack your Brain**

What is Hofmann elimination reaction and what are its uses?

Previous Year's Questions

Phenyl isocyanides are prepared by which of the following reaction?

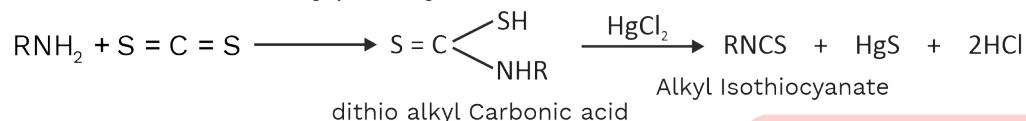
[AIPMT]

- (1) Reimer-Timann reaction
- (2) Carbylamine reaction
- (3) Rosenmund's reaction
- (4) Wurtz reaction



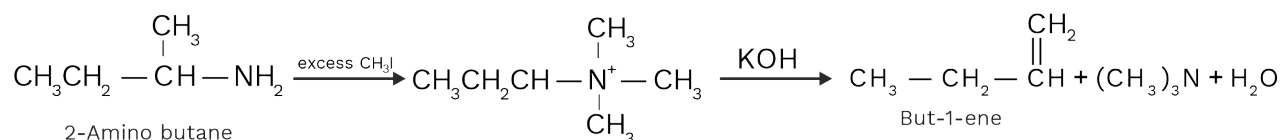
Hoffmann mustard oil reaction:

Primary amine is examined by this reaction. The product alkyl isothiocyanate having mustard oil-like smell is formed by primary amine as follows

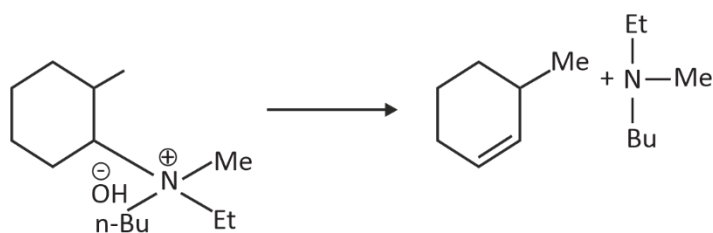


Hoffmann exhaustive methylation and degradation:

By following Hoffman rule, this process involves formation of alkene where less stable alkene will be the major product. For example,



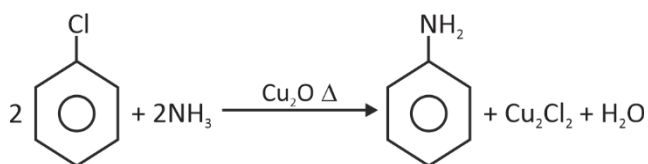
According to Hoffmann rule, the above elimination can be explained as, the carbon containing more hydrogen atoms can eliminate β -hydrogen atom, i.e. there is formation of less stable alkene.



- In commercial preparation, Fe + HCl is used.

Aromatic Amines

From chlorobenzene



From phenol

Rack your Brain



Why N-Nitrosoamines are powerful carcinogens?

Previous Year's Questions



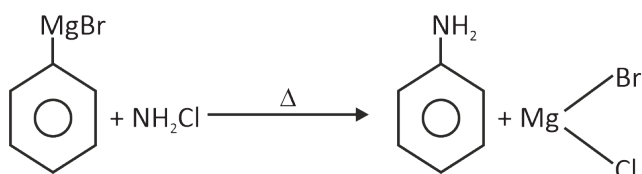
Which of the following statements about primary amines is false?

[AIPMT]

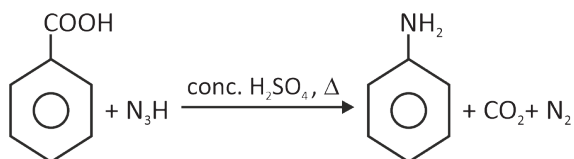
- (1) Alkyl amines are stronger bases than aryl amines
- (2) Alkyl amines react with nitrous acid to produce alcohols
- (3) Aryl amines react with nitrous acid to produce phenols
- (4) Alkyl amines are stronger bases than ammonia



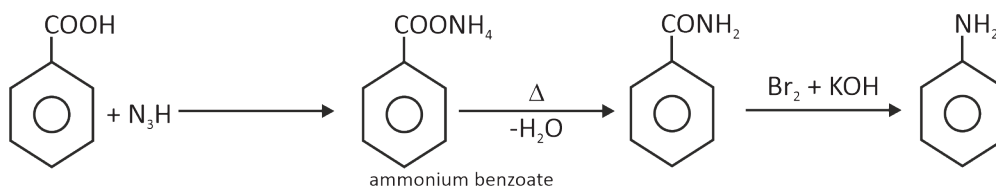
From phenyl magnesium bromide



Schmidt reaction



From benzoic acid



The conversion of benzamide into aniline is referred to as Hoffmann bromamide reaction.

Concept Ladder



The basic strength of an amine is determined by its basicity constant, K_b . Greater the value of K_b , stronger is the base.

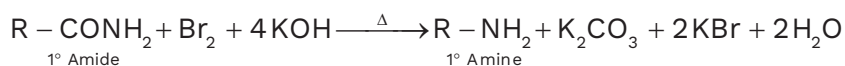
Rack your Brain



Which is more basic 2° amine or ammonia?

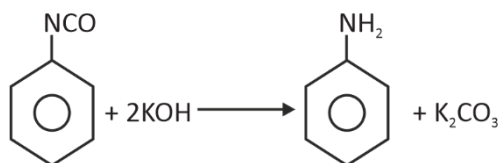
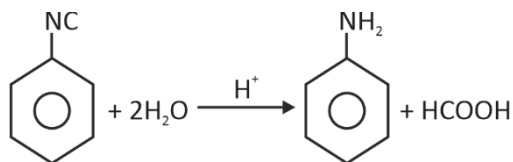
Q4 How can you convert an amide into an amine having one carbon atom less than the starting compound?

Sol. By Hoffmann-bromamide reaction, i.e., by heating a 1° amide with Br_2 and KOH .

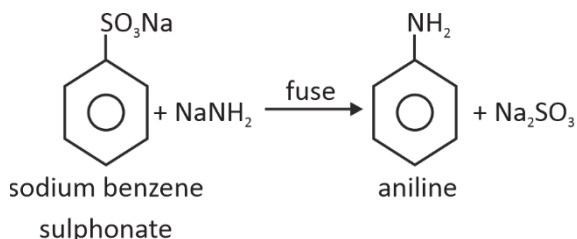




By the hydrolysis of Isocyanide and Isocyanate



From benzene sulphonic acid



Physical Properties

- Pure aniline is colourless oily liquid, but due to the action of light and air it becomes dark brown.
- Its B.P. is 183°C.
- It is volatile in steam and soluble in water.
- It can be purified by steam distillation.

Chemical Properties

Reactions due to benzene ring

Electrophilic substitution:

NH₂ group in aniline is highly ring activating as there is increase in electron density at ortho and para positions because of delocalization of lone pair of electrons present on the nitrogen atom.

Concept Ladder



Nitrous acid (HNO₂ or HONO) reacts with aliphatic in a fashion that provides a useful test for distinguishing, primary, secondary and tertiary amines.

Rack your Brain

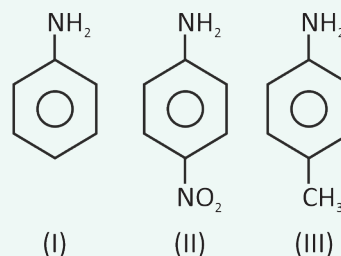


Find out the electrophile generated during the reaction which reacts with amines to give products.

Previous Year's Questions

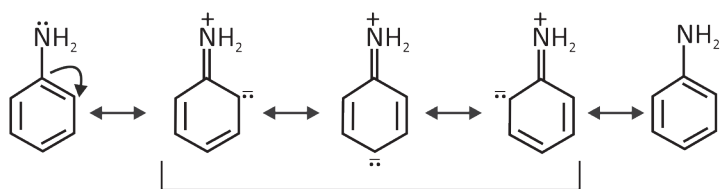


The correct increasing order of basic strength for the following compounds is



[NEET-2017]

- | | |
|------------------|------------------|
| (1) III < I < II | (2) III < II < I |
| (3) II < I < III | (4) II < III < I |

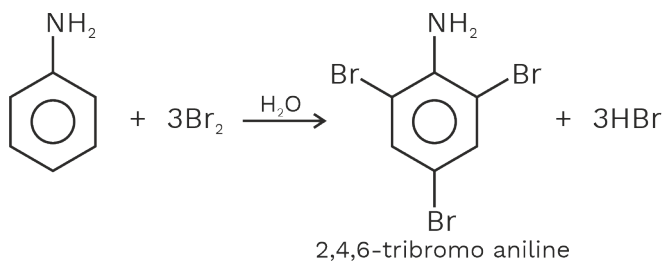


Increase in electron density at o, p positions

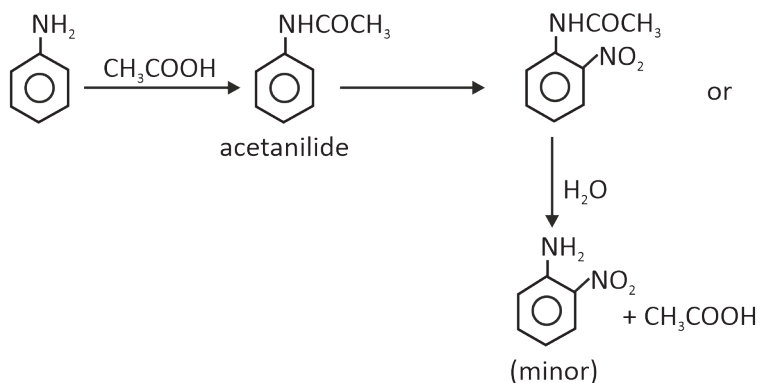
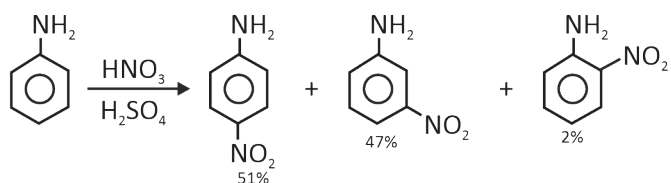
makes attack of E^+ easier.

Decrease in basicity of aniline is also confirmed and it is due to delocalisation of p electrons.

Halogenation



Nitration

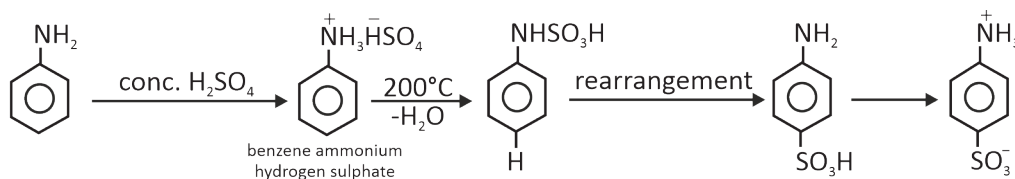
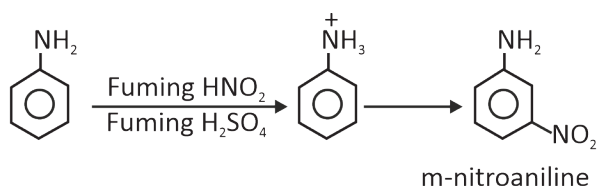


Concept Ladder



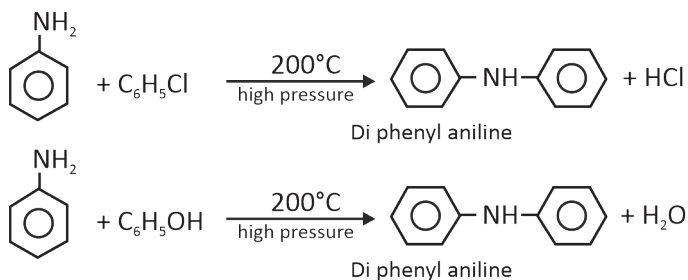
The mechanism of the carbylamine reaction involves the addition of amine to dichlorocarbene which is a reactive intermediate generated by the dehydrohalogenation of chloroform. There are two successive base-mediated steps in the dehydrochlorination of chloroform that result in the formation of an isocyanide.

- Nitric acid is a strong oxidizing agent so it oxidizes NH_2 group also hence direct nitration cannot be carried out. Therefore NH_2 group is protected by acetylation before carrying out nitration.



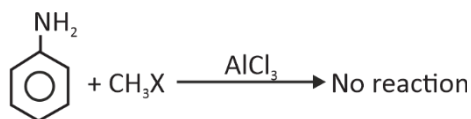
Arylation:

Diphenyl aniline is formed when aniline reacts with chlorobenzene or phenol.



Friedel crafts reaction:

Aniline fails to give Friedel Crafts reaction, as aniline acts as a Lewis base, so AlCl_3 being an electrophile forms salt with it, that is, $\text{C}_6\text{H}_5\text{NH}_3^+\text{AlCl}_4^-$ ($-\text{NH}_3\text{AlCl}_3^-$ is a strong deactivating group)



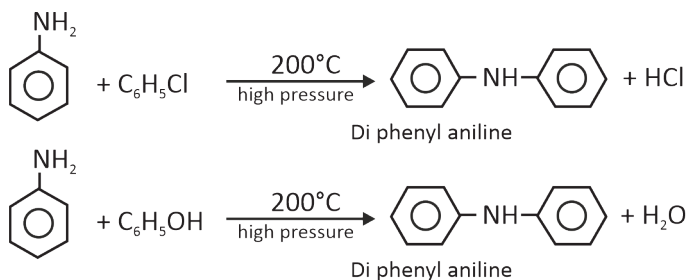
Concept Ladder



Controlled nitration with a mixture of conc. HNO_3 + conc. H_2SO_4 at 293 K gives m-nitroaniline as the major product.

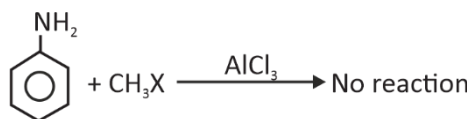
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Previous Year's Questions



Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated to dry. The final product is

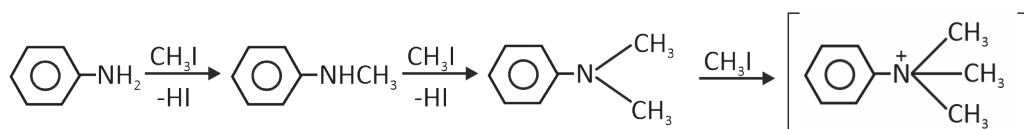
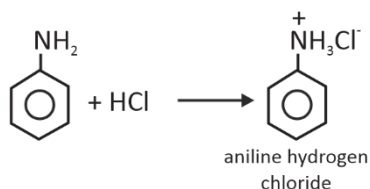
[AIPMT]

- p-bromoaniline
- p-bromofluorobenzene
- 1,3,5-tribromobenzene
- 2,4,6-tribromofluorobenzene



Reaction due to NH₂ group

Salt formation

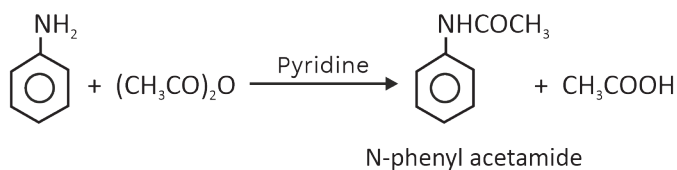
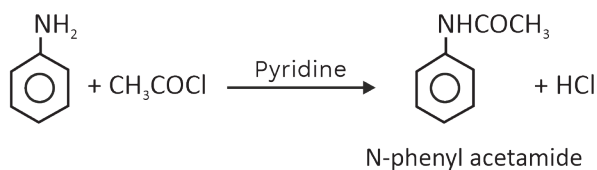


Rack your Brain



How would a tertiary amine react with KMnO₄?

Acylation

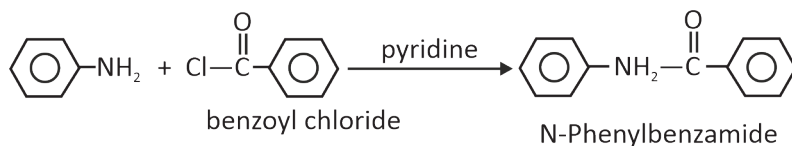


Concept Ladder

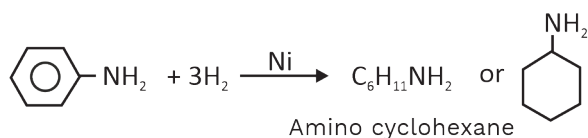


Due to strong activating effect of the amino group, aromatic amines undergo electrophilic substitution reactions readily. To stop the reaction at the monosubstitution stage, the reactivity of the amino group is reduced by protection.

Benylation (Schotten bauman reaction)



Reduction



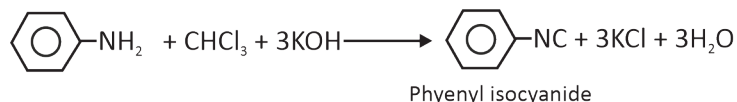
Rack your Brain



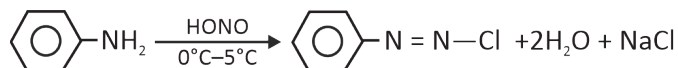
What is black insoluble precipitate formed during the reaction?

**Carbylamine reaction:**

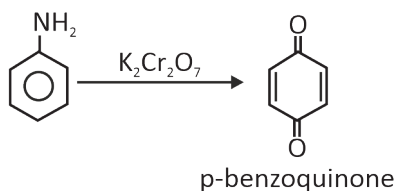
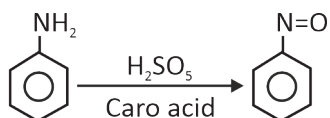
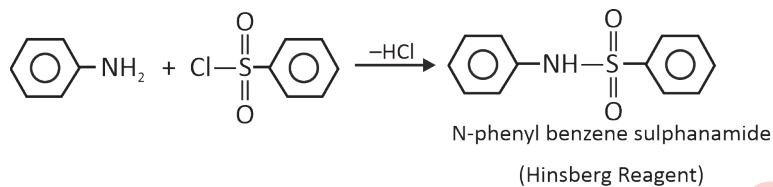
It is a test of chloroform and primary amines. Here dichlorocarbene is the reaction intermediate and pungent, bad smelling isocyanites are formed.

**With HNO_2 :**

When aniline is reacted with a mixture of hydrogen chloride and sodium nitrite in cold, benzene diazonium chloride is formed. This is called diazotization reaction.

**Oxidation :**

Aniline gives different products on oxidation as follows :

**With benzene chlorosulphonic acid****DIAZO COMPOUNDS**

Diazonium compounds or diazonium salts are a group of organic compounds with the general

Rack your Brain

What is the drawback of carbylamines reaction?

Previous Year's Questions

Which of the following is more basic than aniline?

[AIPMT]

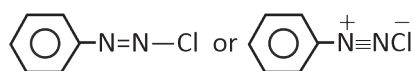
- (1) Benzylamine
- (2) Diphenylamine
- (3) Triphenylamine
- (4) p-Nitroaniline

Rack your Brain

Why less stable alkenes are mirror product in the Hoffman methylation?

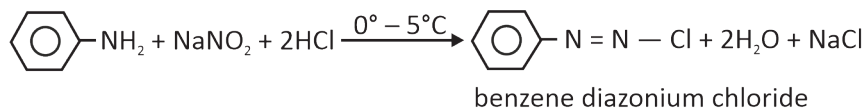
molecular structure $R-N_2^+X^-$, where R may be any alkyl or aryl group and X may be halogens, hydrogen sulphate etc. Aryl diazonium salts have frequently been used as intermediates in organic synthesis.

Benzene Diazonium chloride



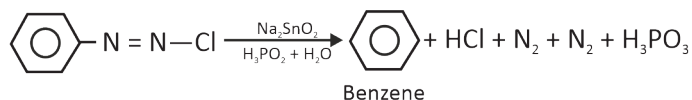
Diazotization

The process of diazotization is used for the production of benzene diazonium chloride, when an aromatic primary amine is treated with HCl and nitrous acid between $0^\circ\text{C} - 5^\circ\text{C}$. The reaction is called as diazo reaction and the process is called as diazotization.

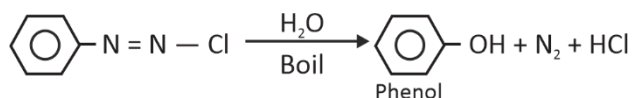


Synthetic applications

- The solution of benzene diazonium chloride can be used for various synthetic applications. For the introduction of $-\text{CN}$, $-\text{X}$, $-\text{OH}$, $-\text{NO}_2$ group in the benzene ring, it acts as a very good intermediate. The preparation of synthesis of those compounds that can not be obtained by direct substitution in benzene can be done by the substitution of diazo group by these groups. A few examples are as follows:
- Synthesis of Benzene**



- Synthesis of Phenol**



Concept Ladder



Being an electron deficient species benzene Diazonium salt shows a coupling reaction with an electron rich species such as phenol and amines.

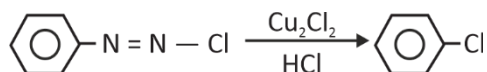
Rack your Brain



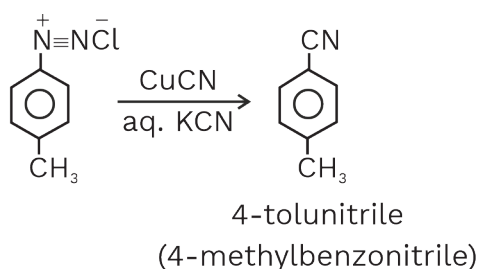
Why aniline is toxic in nature?



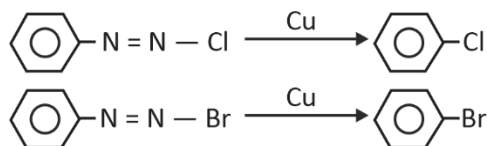
- **Sandmeyer reaction**



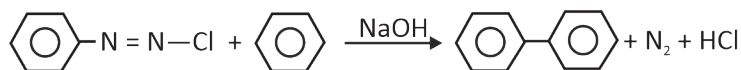
- Cyanobenzene on reduction gives benzyl amine and on hydrolysis, gives benzoic acid as follows



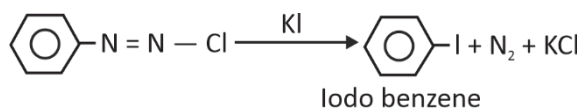
- **Gattermann reaction**



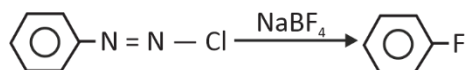
- **Gomberg reaction**



- **Synthesis of Iodo benzene**

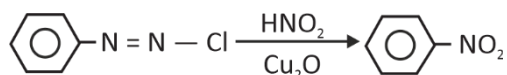


- **Synthesis of C₆H₅F**



It is called Balz-Schiemann Reaction.

- **Synthesis of Nitro benzene**



Previous Year's Questions



Method by which aniline cannot be prepared is

[NEET-2015]

- (1) Hydrolysis phenyl isocyanide with acidic solution
- (2) Degradation of benzamide with bromine in alkaline solution
- (3) Reduction of nitrobenzene with H/Pd in ethanol
- (4) Potassium salt of phthalimide treated with chlorobenzene followed by the hydrolysis aqueous NaOH solution

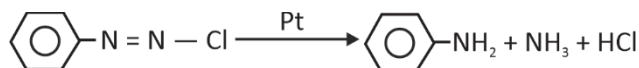
Concept Ladder



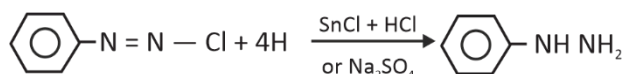
Aniline is a stronger base than diphenylamine which in turn is a much stronger base than triphenyl amine. Thus, $\text{C}_6\text{H}_5\text{NH}_2 > (\text{C}_6\text{H}_5)_2\text{NH} > (\text{C}_6\text{H}_5)_3\text{N}$



- **Synthesis of Aniline**



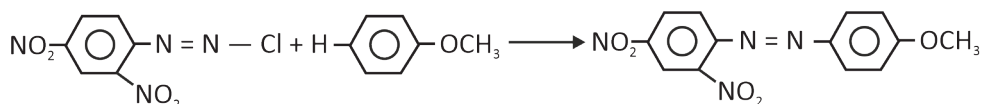
- **Synthesis of phenyl hydrazine**



Coupling Reactions

On condensation with phenol or aniline, benzene diazonium chloride gives dyes as follows:

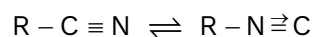
With Anisole



- The presence of aromatic p-amino group can be confirmed by the formation of an orange red dye with alkaline solution of β -naphthol.
- If a compound does not form a dye even when β -naphthol reacts with HNO_2 , the compound may contain NH_2 group in the side chain.

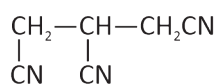
Cyanides and isocyanides

They are two series of isomeric compounds which are derivatives of HCN. These have following Tautomeric structures



Cyanides ($\text{R}-\text{C}\equiv\text{N}$)

These are named as alkane nitriles. For example, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CN}$ butane nitrile



propane-1,2,3-tricarbonitrile

Rack your Brain



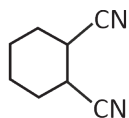
Why the para product is the major product in the nitration of aniline?

Concept Ladder



Basic character of o-, m- and p-nitroanilines relative to aniline is in the following order (effect of electron-withdrawing substituents). Aniline ($K_b = 4.2 \times 10^{-10}$) > m-nitroaniline ($K_b = 2.9 \times 10^{-12}$) > p-nitroaniline ($K_b = 1.0 \times 10^{-13}$) > o-nitroaniline ($K_b = 6 \times 10^{-15}$).

- Carbo- is added before the suffix name of the functional group, when carbon atom of the functional group is not counted, e.g.

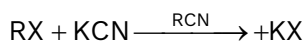


Cyclo hexane
1,2-di carbonitrile

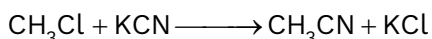
- Cyanides are the functional isomers of isocyanides.



- From alkyl halide: Cyanide is formed when alkyl halides reacts with alcoholic NaCN or KCN.

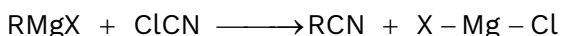


For example,

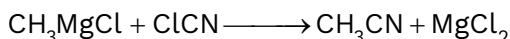


From grignard reagent:

Also cyanides can be formed when grignard reagent reacts with cyanogen chlorides



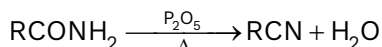
For Example,



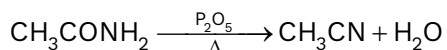
Tertiary alkyl cyanides can be prepared easily by this method.

By the dehydration of amides:

Dehydrating agents are P_2O_5 , $POCl_3$, $SOCl_2$ etc.



For example



Previous Year's Questions



Nitration of aniline in strong acidic medium also gives m-nitroaniline because

[NEET-2018]

- In spite of substituents nitro group always goes to only m-position
- In electrophilic substitution reactions amino group is meta directive
- In absence of substituents nitro group always goes to only m-position
- In acidic (strong) medium aniline is present as anilinium ion

Rack your Brain



Why isocyanides are not hydrolysed by bases?

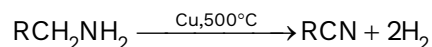
Concept Ladder



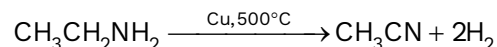
Alkyl cyanides act as both nucleophile and electrophile. cyanide provides a synthetic root for stepping up in a particular series.



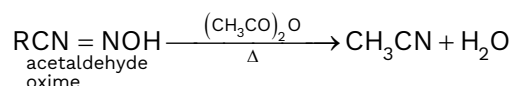
By the dehydrogenation of primary amines



For example,



From oximes



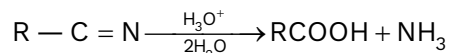
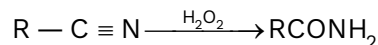
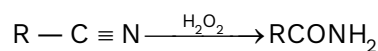
Physical Properties

- These have bitter almond like smell, are neutral polar liquids and poisonous in nature. They have higher B.P and more dipole moment than that of isocyanides.
- They are soluble in organic solvent as well as in water but solubility decreases with the increase of molar mass.

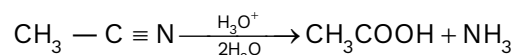
Chemical Properties

Hydrolysis:

Cyanides can be hydrolyzed easily by both bases and acids. An amide is formed on partial hydrolysis with H_2O_2 , whereas on complete hydrolysis, an acid is formed.

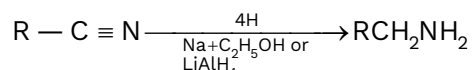


For example,



Reduction:

Cyanides after get reduced by $LiAlH_4$ or Na/C_2H_5OH , give primary amines.



Rack your Brain



What is the disadvantage of the method dehydration of amides?



Concept Ladder



If this reaction is carried out at ordinary temperature then phenol is obtained.

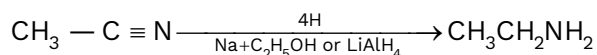
Rack your Brain



Why nitrous acid used in reaction is freshly prepared?

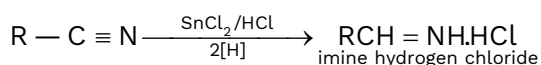
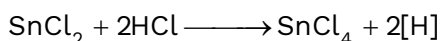


Example,

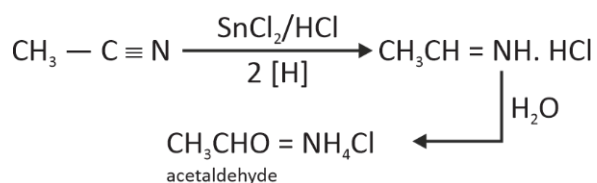


Stephen's reduction:

Aldehyde are formed when cyanides are reduced by SnCl_2/HCl followed by hydrolysis process.

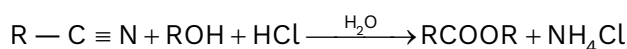


Example,

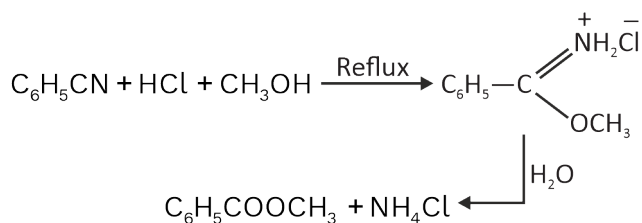
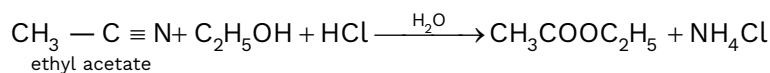


Alcoholysis:

Esters are formed when cyanides reacts with alcohol and dry HCl, followed by hydrolysis,



Example,



Rack your Brain



Why stephen's reduction is known as partial reduction?

Concept Ladder



Aniline is used in the manufacture of Schiff base (anti-oxidant in rubber industry) and some sulphadruugs.

Aniline in sulphuric acid with $\text{K}_2\text{Cr}_2\text{O}_7$ first gives a red coloured product which ultimately changes its colour to deep blue.

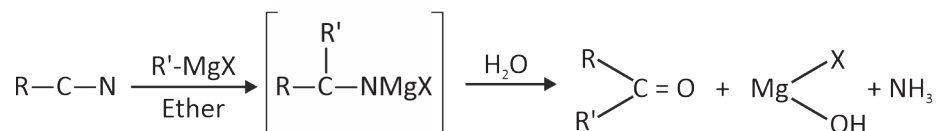
Rack your Brain



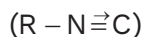
What is the reactive species in the diazotization?



With Grignard reagent



Isocyanides



- These are named as alkyl carbylamines or alkyl isonitrile.

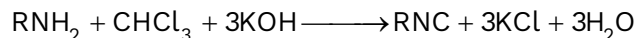
For ex. CH_3NC methyl carbylamine or methyl isonitrile.

$\text{C}_2\text{H}_5\text{NC}$ ethyl carbylamine or ethyl isonitrile.

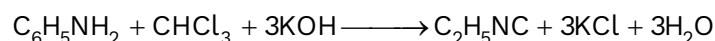
Preparation of RNC

Carbylamine Reaction :

Here, isocyanides are formed when primary amines react with chloroform and alcoholic KOH as follows

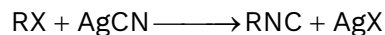


Example,

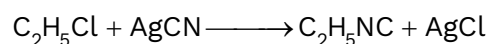


From alkyl halides

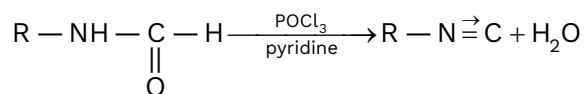
Alkyl isocyanide is formed as major product when an alkyl halide reacts with alcoholic solution of silver cyanide.



Example,



By the dehydration of N-substituted formamides



Concept Ladder



Diazonium salts of alkanes, alkenes and alkynes are not at all stable at room temperature while benzene Diazonium salts are stable to some extent due to delocalization of the positive charge in the benzene ring.

Concept Ladder



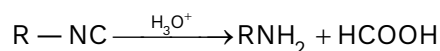
Replacement of diazonium group by hydrogen, thereby effecting the overall removal of amino group is known as deamination.

**Physical Properties**

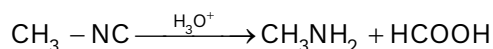
- They are soluble in organic solvents but soluble in water.
- These have highly poisonous nature and colourless liquids with a pleasant smell.
- Their B.P. are lower than the corresponding cyanides.

Chemical Properties**Hydrolysis :**

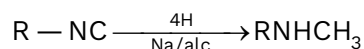
Isocyanides undergo acidic hydrolysis to give primary amine as follows:



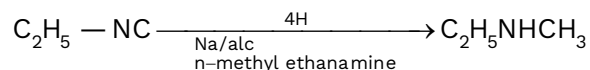
Example,

**Reduction :**

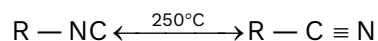
Isocyanides on reduction with $LiAlH_4$ or $Na/$ alcohol give secondary amine as follows



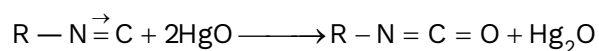
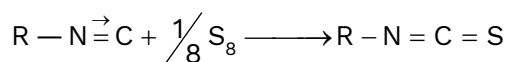
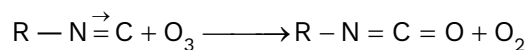
Example,

**Heating effect or isomerization**

Isocyanides isomerizes into cyanides on heating for a long time.

**Addition reactions**

Isocyanides undergo addition reaction with O_3 , sulphur, HgO as follows:

**Concept Ladder**

The reaction involves treatment of diazonium salt solution with a solution of copper (I) cyanide in aqueous potassium cyanide.

Rack your Brain

In the synthesis of phenol, the diazo group has been replaced by which group or atom?

Concept Ladder

Gatterman reaction is a modification of Sandmeyer's reaction and instead of cuprous salts, finely divided copper or copper bronze is used for the decomposition of diazonium salt solution.



- Q5** The correct IUPAC name for $\text{CH}_2=\text{CHCH}_2\text{NHCH}_3$ is
(a) Allylmethylamine (b) 2-amino-4-pentene
(c) 4-aminopent-1-ene (d) N-methylprop-2-en-1-amine

Sol. N-methylprop-2-en-1-amine

- Q6** Benzylamine may be alkylated as shown in the following equation :
 $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + \text{R-X} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{NHR}$
Which of the following alkyl halides is best suited for this reaction through $\text{S}_{\text{N}}1$ mechanism?
(a) CH_3Br (b) $\text{C}_6\text{H}_5\text{Br}$ (c) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (d) $\text{C}_2\text{H}_5\text{Br}$

Sol. $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$

- Q7** The best reagent for converting, 2-phenylpropanamide into 1- phenylethanamine is _____.
(a) excess H_2/Pt (b) NaOH/Br_2
(c) $\text{NaBH}_4/\text{methanol}$ (d) $\text{LiAlH}_4/\text{ether}$

Sol. NaOH/Br_2

- Q8** Hoffmann Bromamide Degradation reaction is shown by _____.
(a) ArNH_2 (b) ArCONH_2 (c) ArNO_2 (d) ArCH_2NH_2

Sol. ArCONH_2

- Q9** Acid anhydrides on reaction with primary amines give _____.
(a) amide (b) imide (c) secondary amine (d) imine

Sol. Amide



Q10 Under which of the following reaction conditions, aniline gives p-nitro derivative as the major product?

- (a) Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3
- (b) Acetic anhydride/pyridine followed by conc. H_2SO_4 + conc. HNO_3
- (c) dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3
- (d) Reaction with conc. HNO_3 + conc. H_2SO_4

Sol. Option (a) and (b) are the correct answer.

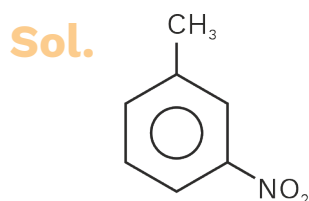
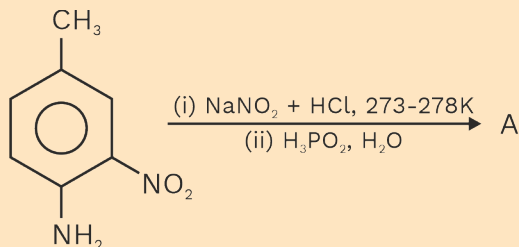
Q11 What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

Sol. Nitrating mixture is used for the nitration of organic compounds and it is the mixture of 1:1 solution of HNO_3 and H_2SO_4 . It provides electrophile in the nitration process of benzene.

Q12 Why is NH_2 group of aniline acetylated before carrying out nitration?

Sol. To control the nitration reaction and to avoid oxidation products and nitro derivatives products formation, the NH_2 group of aniline is acetylated before carrying out nitration. Here, the major product is p-nitroaniline.

Q13 Give the structure of 'A' in the following reaction.



3-Methylnitrobenzene is the product formed due to this chemical reaction.



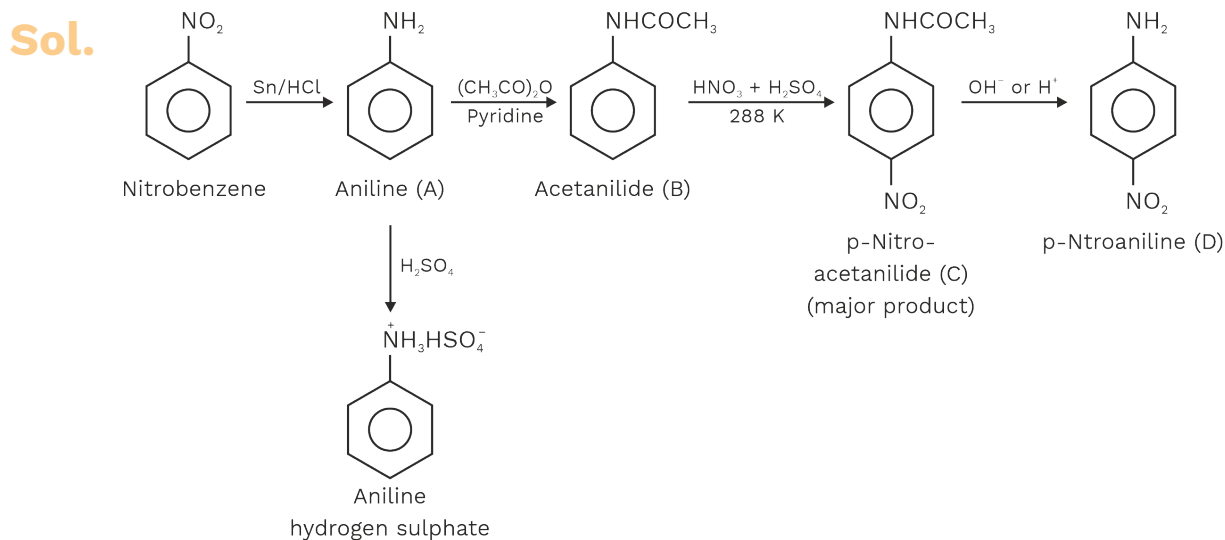
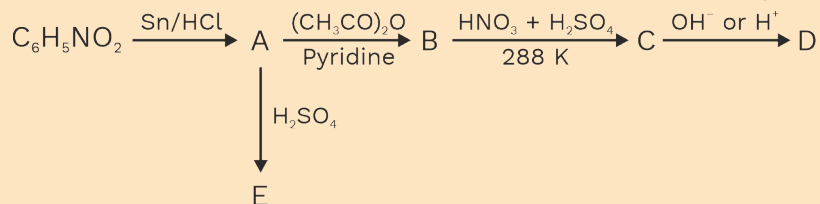
Q13 Why is benzene diazonium chloride not stored and is used immediately after its preparation?

Sol. Benzene diazonium chloride can not be stored because of its unstability. It is highly soluble in water at high temperature and is itself very stable at low temperature.

Q14 Why does the acetylation of $-\text{NH}_2$ group of aniline reduce its activating effect?

Sol. It is because the lone pair of electrons on the N atom of acetanilide interacts with O atom due to resonance.

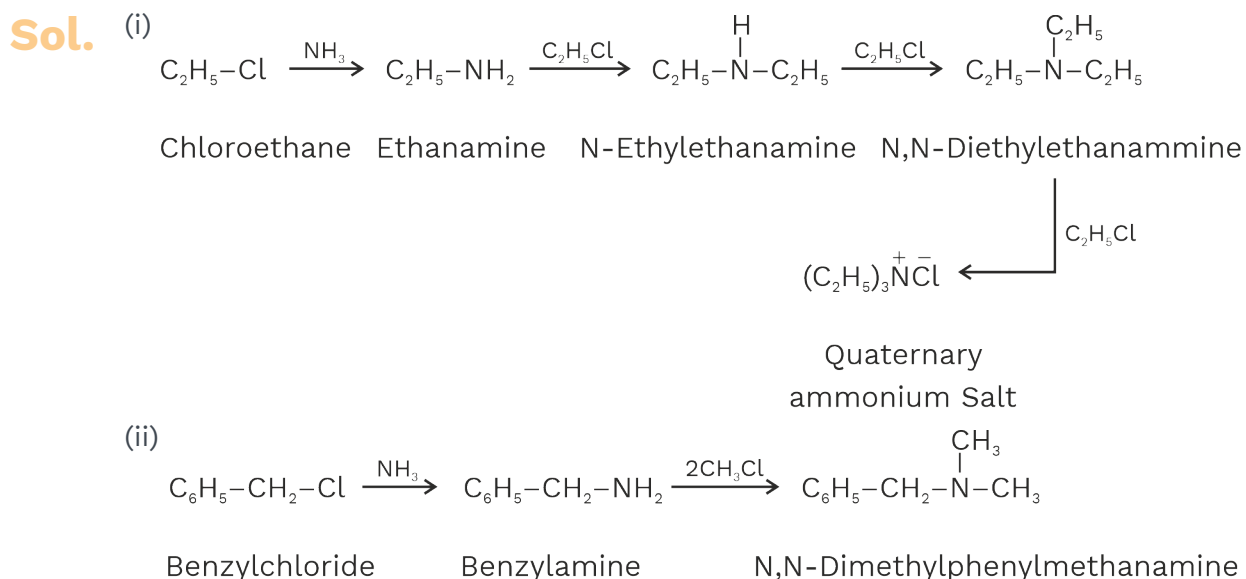
Q16 Write the structures of A, B, C, D and E in the following reaction :





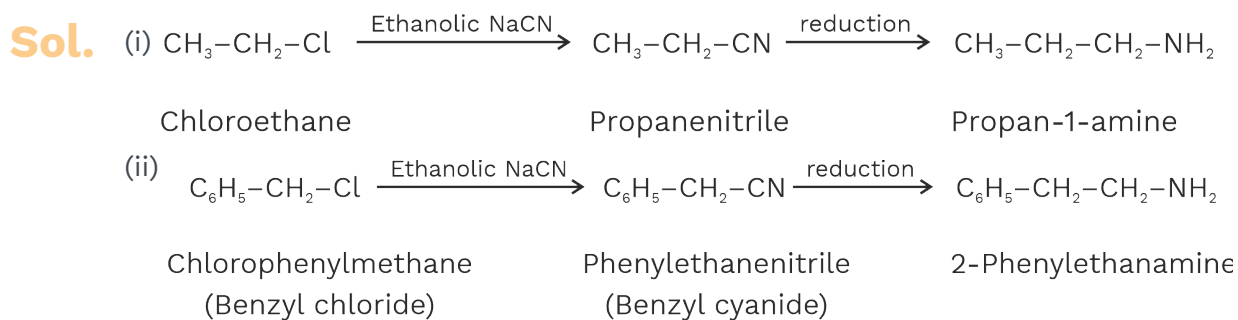
Q17 Write chemical equations for the following reactions:

- (i) Reaction of ethanolic NH_3 with $\text{C}_2\text{H}_5\text{Cl}$.
 (ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl .



Q18 Write chemical equations for the following conversions:

- (i) $\text{CH}_3\text{-CH}_2\text{-Cl}$ into $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$
 (ii) $\text{C}_6\text{H}_5\text{-CH}_2\text{-Cl}$ into $\text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_2\text{-NH}_2$



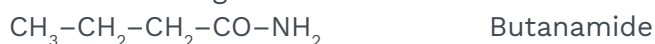


Q19 Write structures and IUPAC names of

- the amide which gives propanamine by Hoffmann bromamide reaction.
- the amine produced by the Hoffmann degradation of benzamide.

Sol.

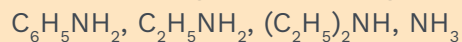
- Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



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



Q20 Arrange the following in decreasing order of their basic strength:



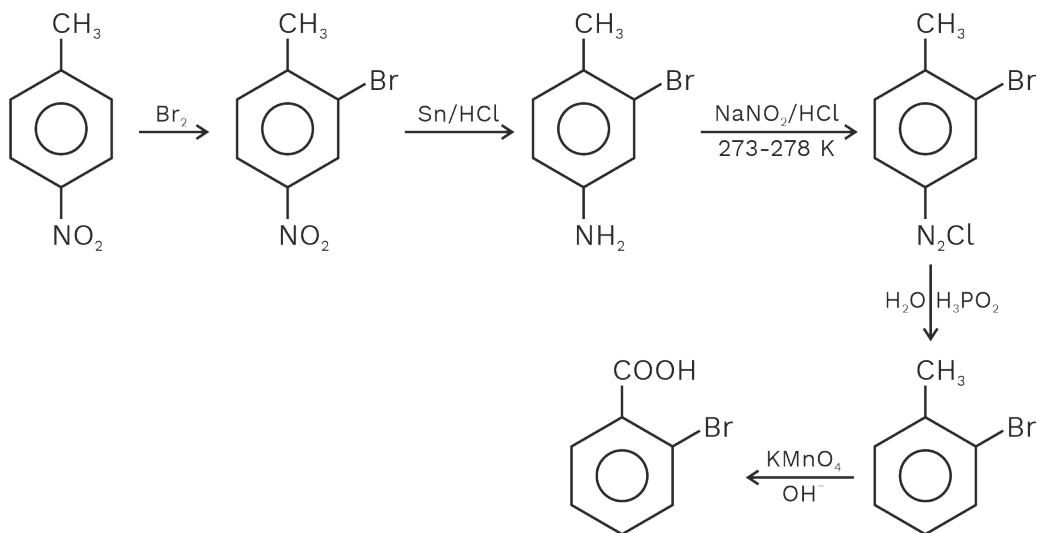
Sol.

The decreasing order of basic strength of the above amines and ammonia follows the following order:



Q21 How will you convert 4-nitrotoluene to 2-bromobenzoic acid ?

Sol.

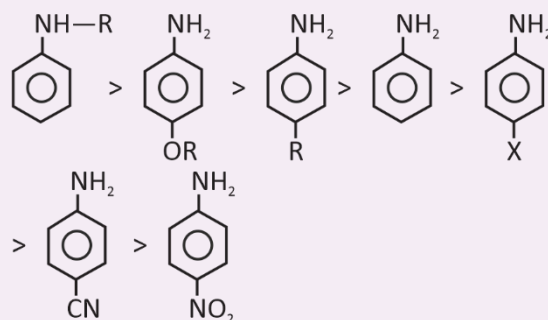




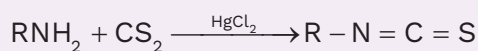
Summary



- Methyl isocyanate (MIC) $\text{CH}_3\text{N}=\text{C}=\text{O}$ was responsible for Bhopal gas tragedy in December 1984.
- CN^- and NO_2^- are ambident nucleophiles.
- Amatol is $\text{NH}_4\text{NO}_3 + \text{TNT}$ (trinitro toluene) and is used as blasting material.
- Sweet spirit of nitre is 4% alcoholic solution of ethyl nitrite and is used as diuretic.
- Benzaldehyde and nitrobenzene both case smell of bitter almond.
- Order of basicity among amines
 - (i) in aqueous solution : $2^\circ > 1^\circ > 3^\circ$
 - (ii) in gas state (or non-aqueous solution) : $3^\circ > 2^\circ > 1^\circ$.
- o-substituted amines are weaker base than aniline irrespective of nature of substituent (due to ortho effect)
- Among p-substituted anilines the order of basic strength is as follows :



- Mixture of 1° , 2° and 3° amines is separated by Hinsberg reagent and Hoffmann method.
- Aniline on nitration gives m-nitroaniline through $-\text{NH}_2$ group is ortho, paradirecting.
- In diazotization of arylamines with $\text{NaNO}_2 - \text{HCl}$ excess of HCl is used to suppress concentration of free aniline available for chlorination.
- Carbylamine test is given by 1° aromatic and 1° aliphatic amines both.
- Gabriel phthalimide synthesis is done to prepare 1° aliphatic amines only.
- Libermann's nitroso test is given by 2° amines only.
- Hoffmann mustard oil reaction :



or

