

Class 12th Chemistry Chapter 13 Amines Notes and Important Question.

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Introduction

- Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s).
- In nature, they occur among proteins, vitamins, alkaloids and hormones.
- Amines have lot of importance in our day to day life.
- For example:-
 - Polymers, dyestuffs and drugs contain amines.
 - Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure.
 - Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry.
 - Benadryl, a well-known antihistaminic drug also contains tertiary amino group.
 - Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes.



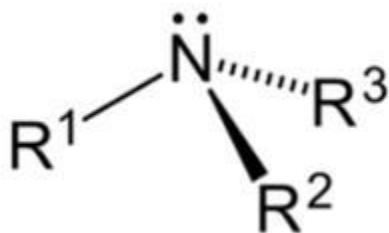
Hormones

Alkaloids



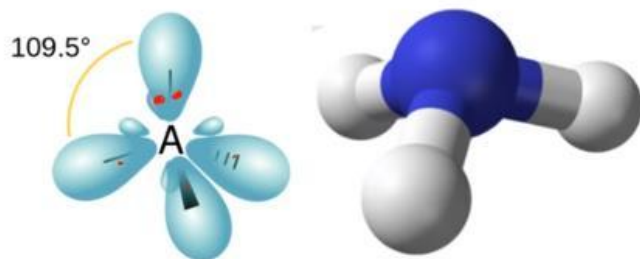
Structure of Amines

- Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.
- Nitrogen atom of amines is trivalent and carries an unshared pair of electrons.



- Nitrogen orbitals of amines are sp^3 hybridized and the geometry of amines is pyramidal.
- Each of the three sp^3 hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines.
- The fourth orbital of nitrogen in all amines contains an unshared pair of electrons.
- Due to the presence of unshared pair of electrons, the angle C–N–E, (where E can be either C or H). is less than 109.5° .

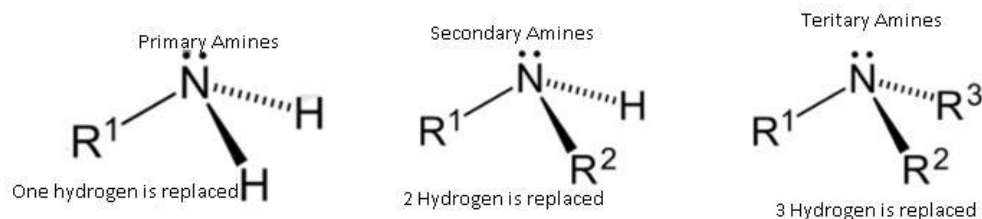
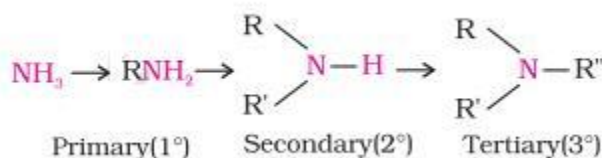
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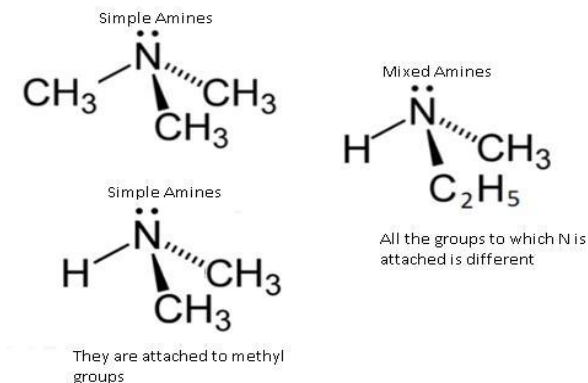
- In case of trimethylamine the bond angle is 108° .

Classification of Amines as Primary, Secondary & Tertiary

- Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule.
- If one hydrogen atom of ammonia is replaced by R or Ar, we get RNH_2 or ArNH_2 , a primary amine (1°).
- If two hydrogen atoms of ammonia or one hydrogen atom of RNH_2 are replaced by another alkyl/aryl (R') group then it is called as secondary amine.
- The second alkyl/aryl group may be same or different.
- Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine.



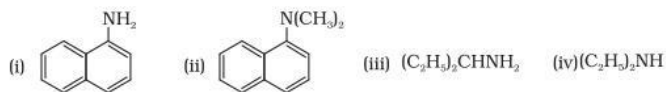
- Amines are said to be 'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.



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Problem:-

Classify the following amines as primary, secondary or tertiary:



Answer:-

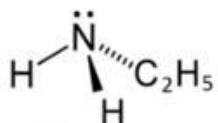
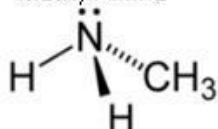
- It is a primary amine because only 1 hydrogen is replaced if we compare this structure with ammonia.
- It is a tertiary amine as all the 3 hydrogen is replaced.
- It is a primary amine as only 1 hydrogen is replaced.
- It is a secondary amine as 2 hydrogens are

Nomenclature of Amines by IUPAC System

Common Names of Amines

- An aliphatic amine is named by prefixing alkyl group to amine, i.e. alkylamine as 1 word.
- We are considering primary amines.

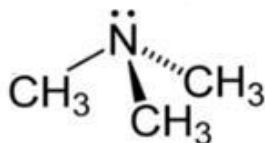
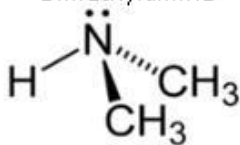
Methylamine



Ethylamine as ethyl amine is attached to this amine

- In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is added to the before the name of alkyl group.

Dimethylamine

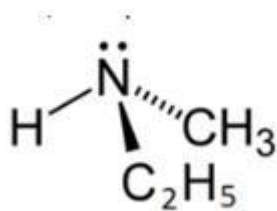


Trimethylamine

- In case of mixed amine, alkyl group are written in alphabetical order.

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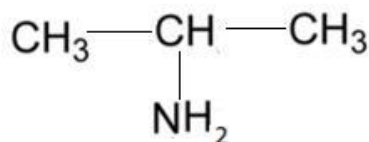
Ethyl Methyl Amine



IUPAC System

- In IUPAC system, amines are named as alkanamines, derived by replacement by 'e' of alkane by the word amine.
- For Example: - Methanamine (CH₃NH₂), Ethan amine (C₂H₅NH₂).
- For naming higher member hydrocarbon, longest chain containing amino group is selected. C atom to which amino group is attached is given to lower number.

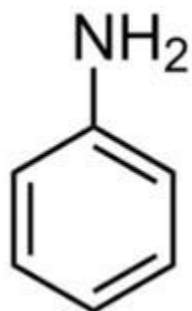
Propan 2 Amine



- In case, more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to carbon atoms bearing -NH₂ groups and suitable prefix such as di, tri etc. is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained.
- For Example:- (Ethane 1,2 diamine) H₂N-CH₂-CH₂-NH₂
- Each alkyl group bonded to the N atom is named as N-alkyl group.

Aryl Amines

- In aryl amines, -NH₂ group is directly attached to the benzene ring.
- C₆H₅NH₂ is the simplest example of aryl amine. It is also known as aniline.



- Naming aryl amines according to IUPAC system, suffix 'e' of arene is replaced by 'amine'.
- For Example: - C₆H₅-NH₂ is named as benzenamine.

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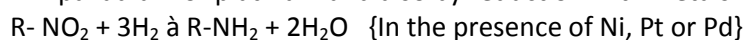
Preparation of Amines

- Amines are prepared by the following methods:

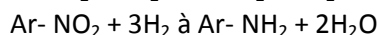
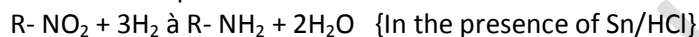
1. Reduction of nitro compounds
2. Ammonolysis of alkyl halides
3. Reduction of nitriles
4. Reduction of amides
5. Gabriel phthalimide synthesis
6. Hoffmann bromamide degradation reaction

1. Reduction of nitro compounds

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

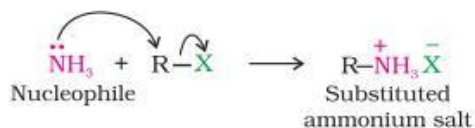


- Nitro alkanes can also be similarly reduced to the corresponding alkanamines.
- Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction.
- Thus, only a small amount of hydrochloric acid is required to initiate the reaction.
- Nitro compounds can also be reduced with active metals such as Fe, Sn, Zn etc. with conc. HCl

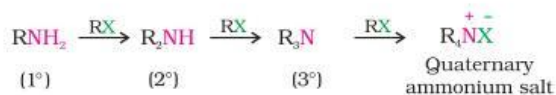


2. Ammonolysis of alkyl halides

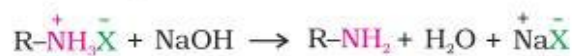
- The carbon - halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile.



- Therefore, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group.
- This process of cleavage of the C-X bond by ammonia molecule is known as ammonolysis.



- The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.
- The free amine can be obtained from the ammonium salt by treatment with a strong base:



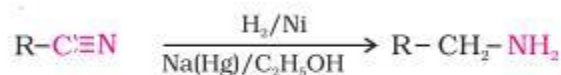
- Disadvantages:-
- When ammonia is taken in excess primary amine is formed as main Product
- When alkyl halide is used in excess quaternary ammonium salt is formed as main product

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- Note: - This method is not suitable for preparation of aryl amines because aryl amines are relatively less reactive than alkyl halides towards nucleophilic substitution reactions.

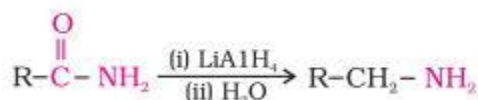
3. Reduction of nitriles

- Nitriles on reduction with lithium aluminium hydride (LiAlH_4) or catalytic hydrogenation produce primary amines.
- This reaction is used for ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.



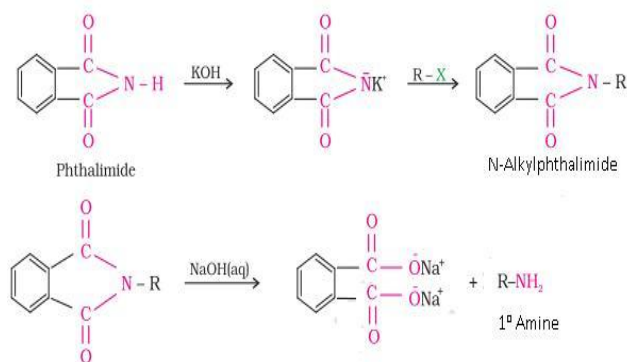
4. Reduction of amides

- The amides on reduction with lithium aluminium hydride yield amines.



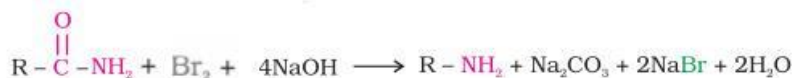
5. Gabriel phthalimide synthesis

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



6. Hoffmann bromamide degradation reaction

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



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Physical & Chemical Properties of Amines

General:-

- The lower aliphatic amines are gases with fishy odour.
- Primary amines with three or more carbon atoms are liquid and still higher ones are solid.
- Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.

1. Solubility:-

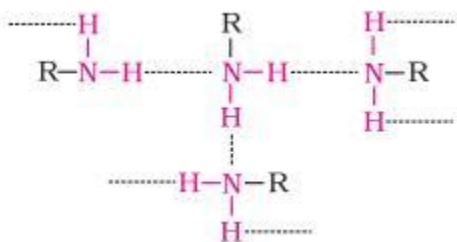
1. Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules.
2. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water.
3. Amines are soluble in organic solvents like alcohol, ether and benzene.

2. Boiling Points:-

- Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule.
- This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it.
- Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

- Intermolecular hydrogen bonding in primary amines is as:-



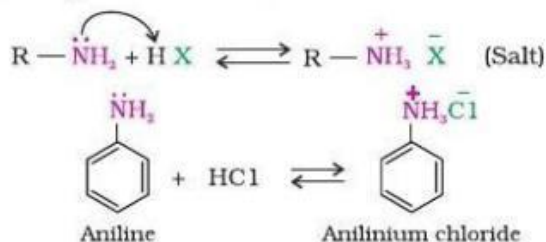
Chemical Properties of Amines

- Amines behave as nucleophiles due to the presence of unshared electron pair.
- Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive.
- Primary, secondary and tertiary amines differ in reactions because of number of hydrogen attached to nitrogen.

Following are the chemical properties of Amines:-

1. Basicity of Amines

1. They are basic in nature and form salts when react with acids.



1. Amine salts on treatment with a base like NaOH, regenerate the parent amine.

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1. Amine salts are soluble in water but insoluble in organic solvents like ether.
2. They form ammonium salts when react with mineral acids.
3. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base.

Why Amines are basic in nature in terms of K_b and pK_b values?

- Larger the value of K_b or smaller the value of pK_b , stronger is the base. The pK_b values of few amines are given in.



$$K = \frac{[\text{R}-\text{NH}_3^+][\bar{\text{OH}}]}{[\text{R}-\text{NH}_2][\text{H}_2\text{O}]}$$

$$\text{or } K[\text{H}_2\text{O}] = \frac{[\text{R}-\text{NH}_3^+][\bar{\text{OH}}]}{[\text{R}-\text{NH}_2]}$$

$$\text{or } K_b = \frac{[\text{R}-\text{NH}_3^+][\bar{\text{OH}}]}{[\text{R}-\text{NH}_2]}$$

$$pK_b = -\log K_b$$

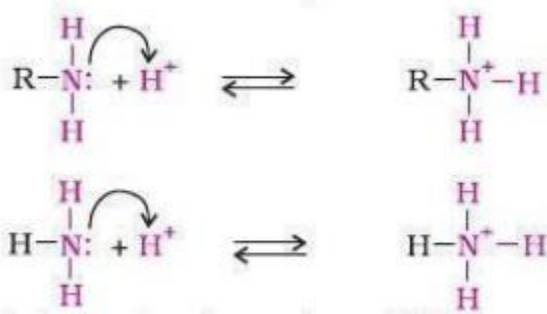
- pK_b value of ammonia is 4.75. Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom.
- Their pK_b values lie in the range of 3 to 4.22. On the other hand, aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group.

Structure-basicity relationship of amines

- Basicity of amines to their structure.

1. Alkanamines versus ammonia

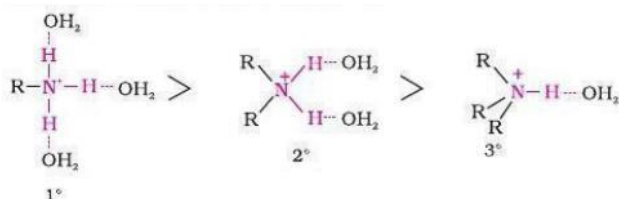
1. Reaction of alkanamines and ammonia in order to compare their basicity.



1. Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus making them available for the unshared electron pair for the proton of the acid.
2. The substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group.
3. Hence, alkylamines are stronger bases than ammonia. Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups.

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4. The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH_3 .
5. But this not same in aqueous state, in that the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules.
6. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion.
7. The order of stability of ions are as follows:

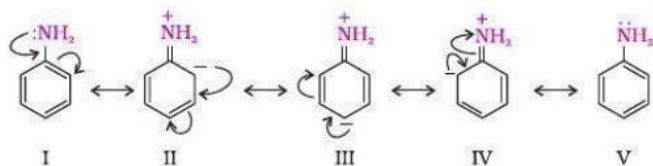


Decreasing order of extent of H-bonding in water and order of stability of ions by solvation.

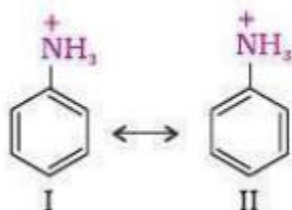
1. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order.
 2. When the alkyl group is small, like $-\text{CH}_3$ group, there is no steric hindrance to H-bonding.
 3. In case the alkyl group is bigger than CH_3 group, there will be steric hindrance to H-bonding.
 4. Therefore, the change of nature of the alkyl group, e.g., from $-\text{CH}_3$ to $-\text{C}_2\text{H}_5$ results in change of the order of basic strength.
 5. Thus, there is a subtle interplay of the inductive effect, solvation effect and steric hindrance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state.
 6. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:
- $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
 - $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$

1. Arylamines versus ammonia

1. pK_b value of aniline is quite high because in aniline or other arylamines, the $-\text{NH}_2$ group is attached directly to the benzene ring.
2. As a result the unshared electron pair on nitrogen atom will be less available for protonation as it is in conjugation with the benzene ring.
3. Aniline is resonance hybrid of 5 resonance structures.



1. On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures (kekule).



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1. Aniline is more stable than anilinium ion as it has greater number of resonating structure.
2. Therefore, the proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia.
3. In case of substituted aniline, it is observed that electron releasing groups like $-\text{OCH}_3$, $-\text{CH}_3$ increase basic strength whereas electron withdrawing groups like $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{X}$ decrease it.

Alkylation

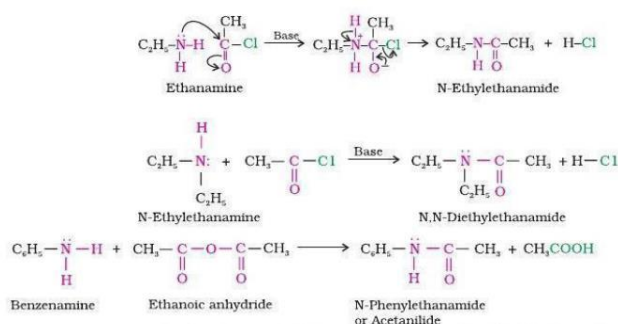
Amines undergo alkylation on reaction with alkyl halides.

Acylation

The reaction of aliphatic and aromatic primary and secondary amines with acid chlorides, anhydrides and esters by nucleophilic substitution reaction is known as Acylation.

In this reaction there will be replacement of hydrogen atom of $-\text{NH}_2$ or $>\text{N}-\text{H}$ group by the acyl group.

The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.



Amines also react with benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$). This reaction is known as benzoylation.

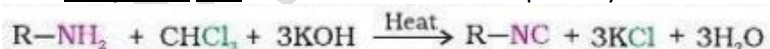


They form salts when they react with carboxylic acids at room temperature.

Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.

Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamines reaction or isocyanide test and is used as a test for primary amines.



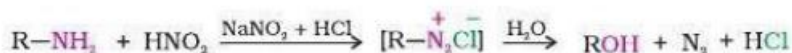
Reaction with nitrous acid

Different types of amines react differently with nitrous acid which is prepared in situ from a mineral acid and sodium nitrite.

(i) Primary Amines:-

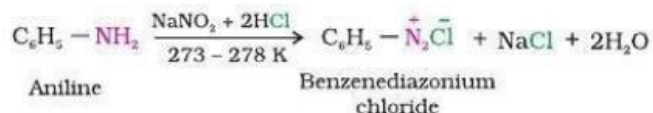
1. Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols.
2. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

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(ii) Secondary Amines:-

1. Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds.

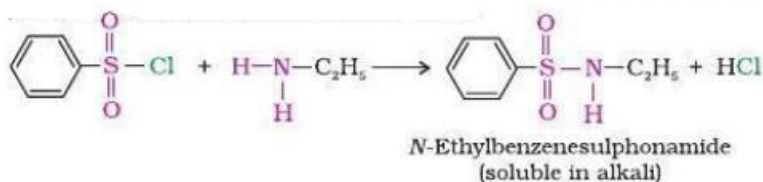


- Secondary and tertiary amines react with nitrous acid in a different manner.

Reaction with aryl sulphonyl chloride

Reaction with Benzene sulphonyl Chloride: - Benzene sulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzene sulphonyl amide.

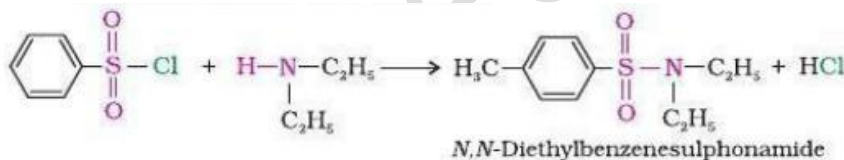


The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group.

Hence, it is soluble in alkali.

Reaction of secondary Amine benzenesulphonyl chloride: - In this reaction, N, N-diethylbenzenesulphonamide is formed.

Since N, N-diethyl benzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom; it is not acidic and hence insoluble in alkali.



Tertiary amines do not react with benzenesulphonyl chloride.

Note:-

- Amine reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.
- These days benzenesulphonyl chloride is replaced by p-toluenesulphonyl chloride.

Electrophilic Substitution

Bromination :-

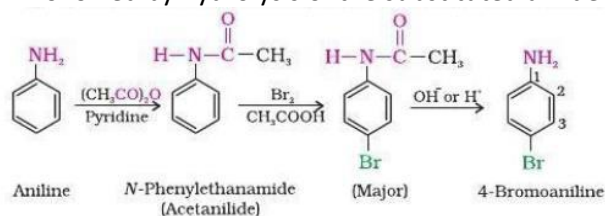
Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.

Because of high reactivity of aromatic amines problems occur during electrophilic substitution because it occurs at ortho- and para-positions.

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- In order to prepare monosubstituted aniline derivative activating effect of –NH₂ group be controlled done by protecting the –NH₂ group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.



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



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

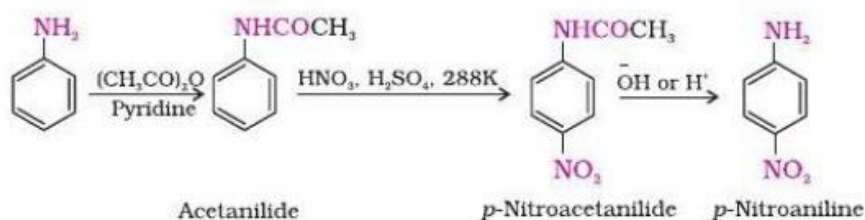
Nitration:-

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



- In order to protect –NH₂ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the p-nitro derivative can be obtained as the major product.

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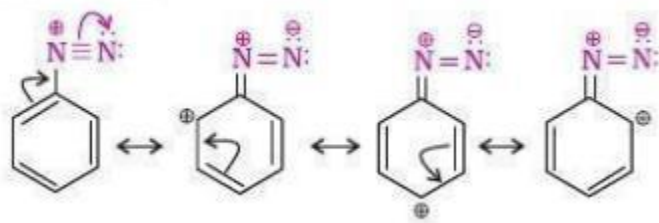


Sulphonation:-

- Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.
- Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst.
- Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

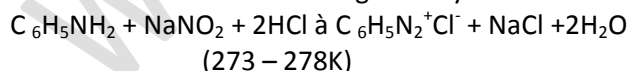
Diazonium Salts

- General formula of diazonium salts is RN_2^+X^- where R = aryl group and X^- ion can be Cl^- , Br^- , HSO_4^- and BF_4^- .
- Diazonium salts are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc.
- The N_2^+ group is called diazonium salt.
 - For example, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ is named as benzenediazonium chloride and $\text{C}_6\text{H}_5\text{N}_2^+\text{HSO}_4^-$ is known as benzenediazonium hydrogensulphate.
- Primary aliphatic amines form highly unstable alkyl diazonium salts. Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.



Preparation of Diazonium Salts

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



Properties of Diazonium Salts

Physical Properties:-

- Benzenediazonium chloride is a colourless crystalline solid.
- It is readily soluble in water and is stable in cold but reacts with water when warmed.

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- It decomposes easily in the dry state. Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

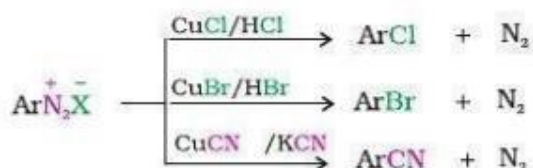
Chemical Properties:-

There are 2 reactions into with diazonium salts can be divided:-

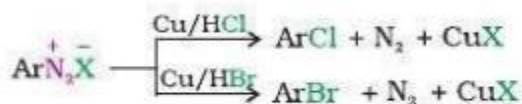
- Reactions involving displacement of nitrogen
- Reactions involving retention of diazo group.

Reactions involving displacement of nitrogen

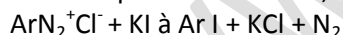
- Diazonium group being a very good leaving group is substituted by other groups such as Cl^- , Br^- , I^- , CN^- and OH^- which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.
- Replacement by halide or cyanide ion:
- The Cl^- , Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion.
- This reaction is called Sandmeyer reaction.



- Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as Gatterman reaction.

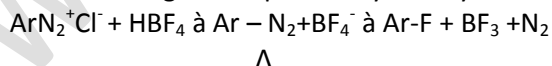


- The yield in Sandmeyer reaction is found to be better than Gatterman reaction.
- Replacement by iodide ion:
- Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.



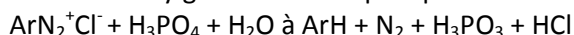
Replacement by fluoride ion:

- When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.



Replacement by H:

- Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and they get oxidised to phosphorous acid and ethanal, respectively.

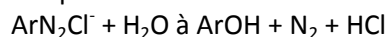


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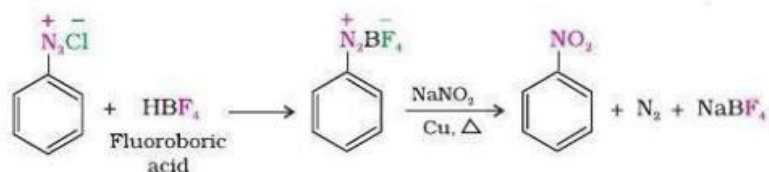
Replacement by hydroxyl group:

- If the temperature of the diazonium salt solution is allowed to raise upto 283 K, the salt gets hydrolysed to phenol.



Replacement by $-\text{NO}_2$ group:

- When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-\text{NO}_2$ group



(B)

Reactions involving retention of diazo group coupling reactions:-

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