

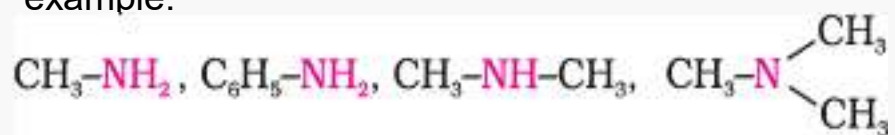
UNIT II	A. Phenols* B. Aromatic Amines* C. Aromatic Acids*	10 Hours
Aromatic Amines* - Basicity of amines, effect of substituents on basicity, and synthetic uses of aryl diazonium salts		

Note: Need to study, general methods of preparation and reactions of compounds superscripted with asterisk (*).

Aromatic Amines

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl group(s) (alkylamines) and /or aryl group(s) (aromatic amines). In nature, they occur among proteins, vitamins, alkaloids (e.g. like opium alkaloids morphine, codeine, nicotine alkaloid of tobacco, etc.) and hormones. Synthetic examples include polymers, dyestuffs and drugs. 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 and starting material in the preparation of many substituted benzene compounds (both in laboratory and in industry).

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. For example:

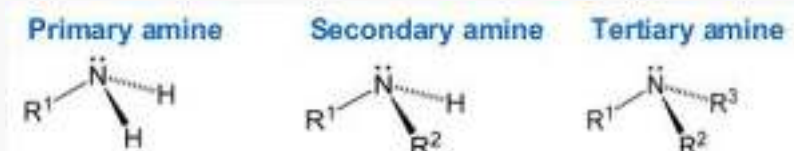


Functional
group:



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Classification of Amines:



- Primary (1°) amine: one alkyl or aryl (C₆H₅NH₂) group attached to the nitrogen atom.
- Secondary (2°) amine: two alkyl or aryl group attached to the nitrogen atom.
- Tertiary (3°) amine: three alkyl or aryl group attached to the nitrogen atom.
- Quaternary (4°) amine: an ion in which nitrogen is bonded to four alkyl or aryl groups and bears a positive charge.

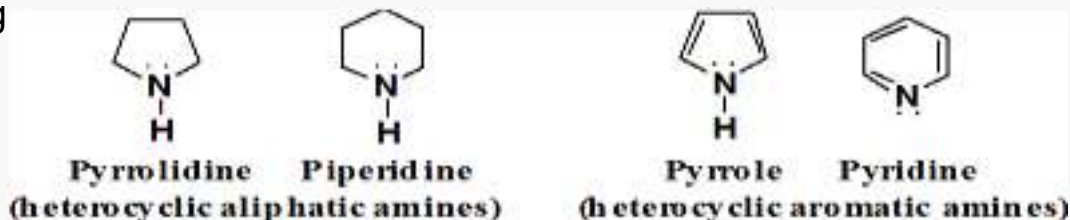


Amines are further divided into aliphatic, aromatic, and heterocyclic amines:

Aliphatic amine: An amine in which nitrogen is bonded only to alkyl groups. **Aromatic amine:** An amine in which nitrogen is bonded to one or more aryl groups.



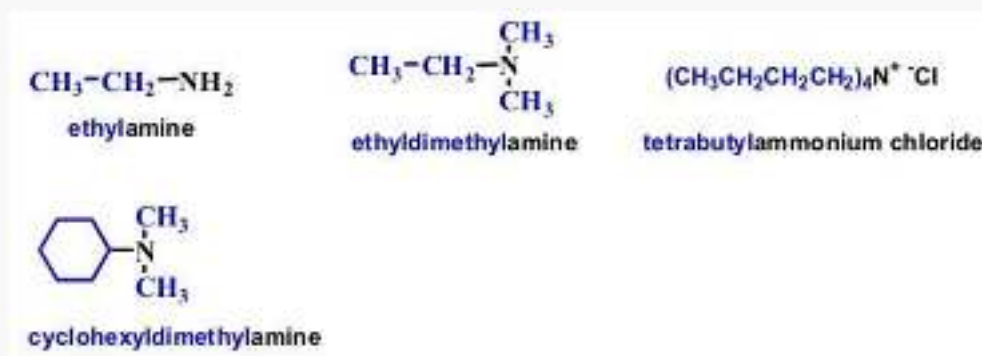
Heterocyclic amine: An amine in which nitrogen is one of the atoms of a ring



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Nomenclature:

Common names: - formed from the names of the alkyl groups bonded to nitrogen, followed by the suffix –amine. - the prefixes di-, tri-, and tetra- are used to describe two, three or four identical substituents.

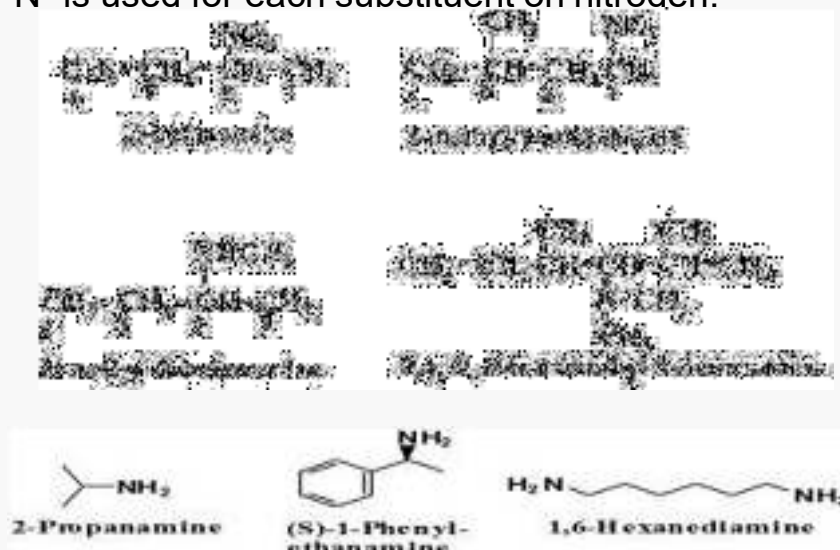


IUPAC names

Aliphatic amines: replace the suffix -e of the parent alkane by –

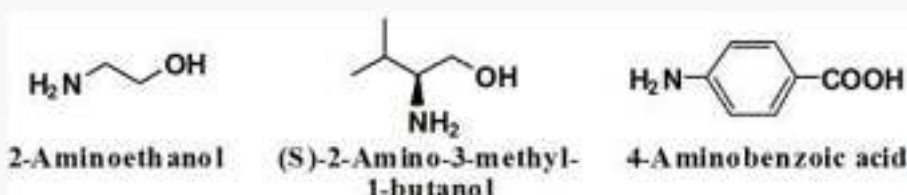
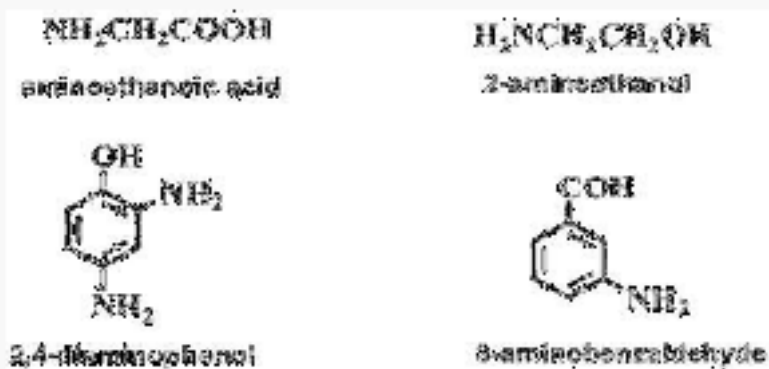
amine. OR similar to that alcohols

- the longest continuous chain of carbon atoms determine the root name.
- the –e in alkane name is changed to –amine, and a number shows the position of the amino group along the chain.
- other substituents on the carbon chain are given numbers, and the prefix N- is used for each substituent on nitrogen.



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- The prefix 'amino' is used to indicate the presence of an $-NH_2$ group in a molecule containing than one functional group OR
- Among the various functional groups, $-NH_2$ is one of the lowest in order of precedence. For example,

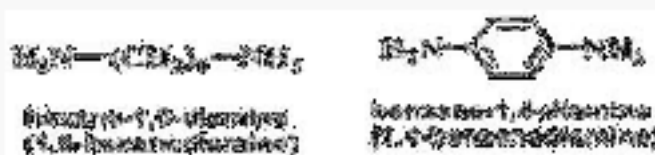


Aromatic amines:

- Aromatic amines have an amine group ($-NH_2$) attached directly to the aromatic ring.
- Aromatic amines known as arylamines. Examples,



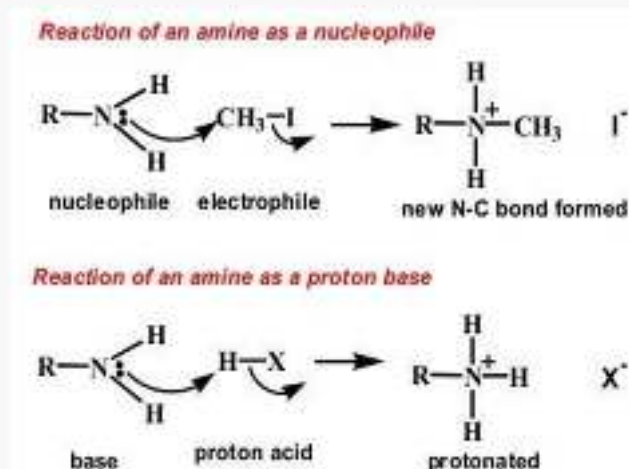
Compounds with two $-NH_2$ groups are named by adding the suffix 'diamine' to the name of the corresponding alkane or aromatic compounds.



THE BASICITY OF AMINES

Amines can act as:

- a nucleophile (a Lewis base) because its lone pair none bonding electrons can form a bond with an electrophile.
- a Brønsted-Lowry base because it can accept a proton from a proton acid.



General Reaction: $:B + H^+ \rightarrow {}^+BH$ (conjugate acid)

- The basicity of the amines depends on the ability of the lone pair none bonding electrons at nitrogen atom to form bond with an acid.
- The more easier the lone pair electrons formed bond with the acid, will make the amines a stronger base.
- The equilibrium constant for this reaction is called base-dissociation constant, symbolized by K_b .
- $K_b = [BH^+] / [:B] [H^+]$ (Strong base have higher values of K_b)
- $pK_b = -\log K_b$ (Stronger base have smaller values of pK_b)

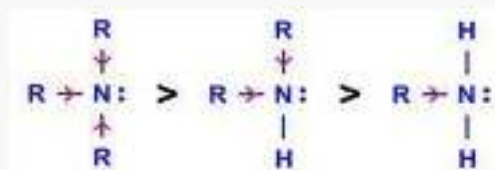
	:NH₃	(1°) R-NH₂	(2°) R-NH-R	(3°) R₃-N
pK_b	4.74	3.36	3.27	4.19
pK_a	9.26	10.64	10.73	9.81

Note: Strong bases have weak conjugate acids, and weak bases have strong conjugate acids.

Factors That Affect the Basicity of the Amines

Amines are basic because they possess a pair of unshared electrons, which they can share with other atoms. These unshared electrons create an electron density around the nitrogen atom.

- The greater the electron density, the more basic the molecule.
- Groups that donate or supply electrons (by means of positive inductive effect) will increase the basicity of amines like alkyl groups (-CH₃, etc.) while groups that decrease the electron density like -NO₂ etc., (by means of negative inductive effect) around the nitrogen decrease the basicity of the molecule.
- Due to this property of the alkyl group (electron-donating group such as CH₃- and CH₃CH₂-) attached to the nitrogen of the amine, the electron density around the nitrogen atom increases and its electron releasing ability increases too.
- Due to the greater and easier release of electrons in the alkyl amine, the molecule becomes more basic than ammonia.
- the order of basicity: 3>2>1>NH₃



- Whereas in ammonia, no such releasing group attached. So, obviously the basicity of ammonia is much less than that of an alkyl amine.

In comparison, the basicity of the aliphatic amines i.e. tertiary amines to be the greatest, followed by secondary amine and then primary amine. BUT THIS IS NOT SO. The order of basicity is NH₃ < primary amine ~ tertiary amine < secondary amine respectively because of due to

Steric hindrance:

- The size of an alkyl group is more than that of a hydrogen atom.
- So, an alkyl group would hinder the attack of a hydrogen atom, thus decreasing the basicity of the molecule.
- The more the number of alkyl groups attached, lesser will be its basicity.

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- So, the decreasing order of basicity will be: Primary amine > secondary amine > tertiary amine.

Hydrogen bonding or Solvation effects:

- Amines are fairly strong base and their aqueous solutions are basic.
- The differences in the basicity order in the gas phase and aqueous solutions are the result of solvation effects (hydrogen bonding).
- An amine can abstract a proton from water, giving an ammonium ion and a hydroxide ion.



$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

In water, the ammonium salts of primary and secondary amines undergo solvation effects (due to hydrogen bonding) to a much greater degree than ammonium salts of tertiary amines. These solvation effects increase the electron density on the amine nitrogen to a greater degree than the inductive effect of alkyl groups.

When amines are dissolved in water, they form protonated amines. Also, the number of possibilities of hydrogen bonding formation increases. More the number of hydrogen bonding, more is the hydration that is released in the process of the formation of hydrogen bonds.

The more the hydration energy of the molecule, more is the stability of the amine. Experiments have indicated, in terms of hydration energy, that the tertiary amines are the least stable followed by the secondary amines followed by the primary amines.

This can be explained on the basis of the following reactions.



OH^-

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So, the number of hydrogen bonds possible when primary amines are dissolved in water is the greatest, implying that they are most stable species of amine, the least being the tertiary amines.

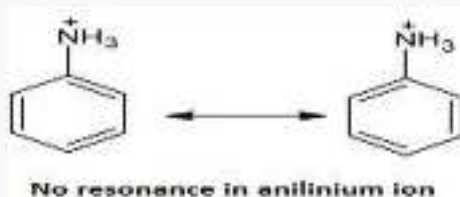
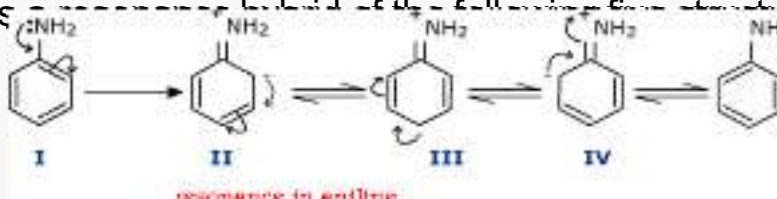
Conclusion: The combined effect of the pushing effect of the alkyl group (+I effect), steric hindrance and the solvation of amines causes the basicity order to be: (basicity of tertiary is almost the same as that of primary).



amine Aromatic Amines:

Aromatic amines are less basic than aliphatic amines and ammonia. Reason:-

- pK_b value of aniline (pK_b : 9.4) is quite higher than ammonia (pK_b : 4.7). It is because in aniline or other arylamines, the $-\text{NH}_2$ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation (The lone pair of electrons on the nitrogen atom is delocalised into the benzene ring on to the ortho and para positions) with the benzene ring and thus making it less available for protonation.
- In case of arylamines, the reaction is shifted toward the left and makes aniline a weaker base than ammonia or aliphatic amines.
- If we write different resonating structures of aniline, we will find that aniline is a resonance hybrid of the following four structures:



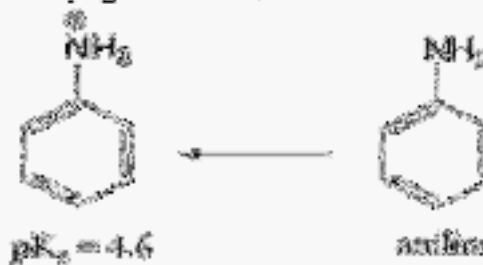
But for anilinium ion no other resonating structures are possible.

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We know that greater the number of resonating structures, greater is the stability. Thus you can infer that aniline is more stable than anilinium ion. Hence, the proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia.

Other factor(s) to consider in comparison is that the greater electron-withdrawing inductive effect of the sp^2 -hybridized carbon of an aromatic amine compared with that of the sp^3 -hybridized carbon of an aliphatic amine.

Aniline is substantially less basic than methylamine, as is evident by looking at the pK_a values for their respective ammonium conjugate acids (remember that the lower the pK_a of the conjugate acid, the weaker the base).



Working Example 1: Compare the basicity of aniline with cyclohexylamine

In Aniline (Arylamines), the lone pair on nitrogen (which is free for protonation in a cyclohexylamines) is present in conjugation with the benzene ring, so aniline can't lose electrons as easily as a cyclohexylamines can. The basicity of amines is due to the nitrogen of the amine donating its lone pair of electrons. So resonance stabilized amines are less basic compared to non-conjugated amines (alkylamines).

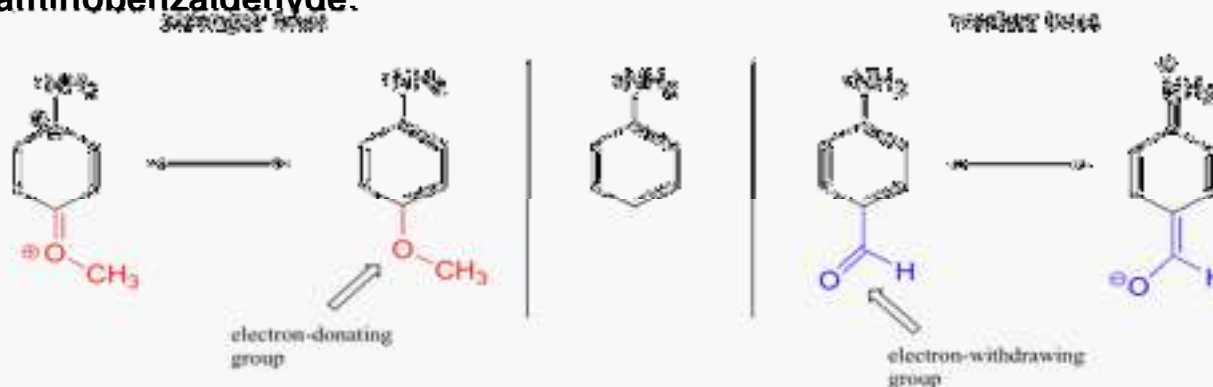


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In case of substituted aniline, it is observed that electron releasing groups like $-\text{OCH}_3$, $-\text{CH}_3$ increase basic strength whereas electron withdrawing groups like $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{CHO}$, & $-\text{X}$ (X:halogen) decrease it by a combination of resonance and inductive effects.

Anything ortho to the amine, no matter whether it is electron donating or withdrawing, will decrease the basicity of the aromatic amine. This is because of the **ortho effect**, which is basically sterics. The protonated amine will have a greater steric interaction with the ortho group, so it will be less stable.

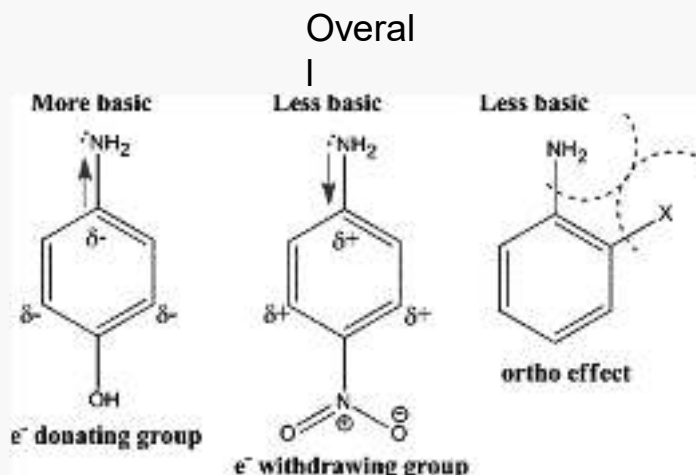
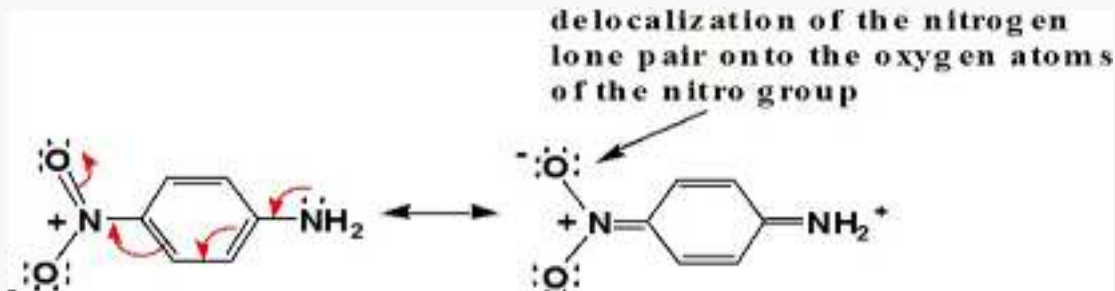
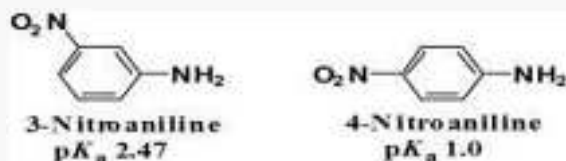
Working Example 2: Compare the basicity of 4-methoxy aniline with 4-aminobenzaldehyde.



In the case of 4-methoxy aniline (the molecule on the left side of the figure above), the lone pair on the methoxy group donates electron density to the aromatic system, and a resonance contributor can be drawn in which a negative charge is placed on the carbon adjacent to the nitrogen, which makes the lone pair of the nitrogen more reactive. In effect, the methoxy group is 'pushing' electron density towards the nitrogen. Conversely, the aldehyde group on the right-side molecule is 'pulling' electron density away from the nitrogen, decreasing its basicity.

These resonance effects are possible when the substituent is located at the ortho or para position, but not at the meta position because cannot do this kind of resonance at the meta position. For example: 3-nitroaniline is a stronger base than 4-nitroaniline due to non-resonance effect lone pair remains with amine for donation/reaction.

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Reactions of Amines:

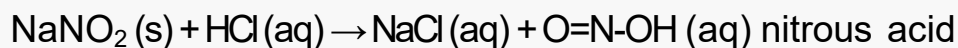
1. Reaction of amines and acid will give amine salt.

Amine salt: - composed of two types of ions: i) the protonated amine cation (an ammonium ion) ii) anion derived from the acid



2. Reaction with nitrous acid:

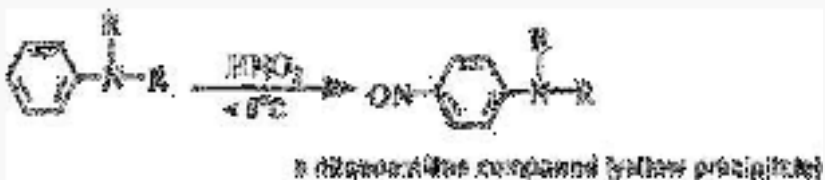
- Nitrous acid (HNO_2) is unstable and is prepared in situ by the reaction of dilute HCl or dilute H_2SO_4 with sodium nitrite in the absence of heat.



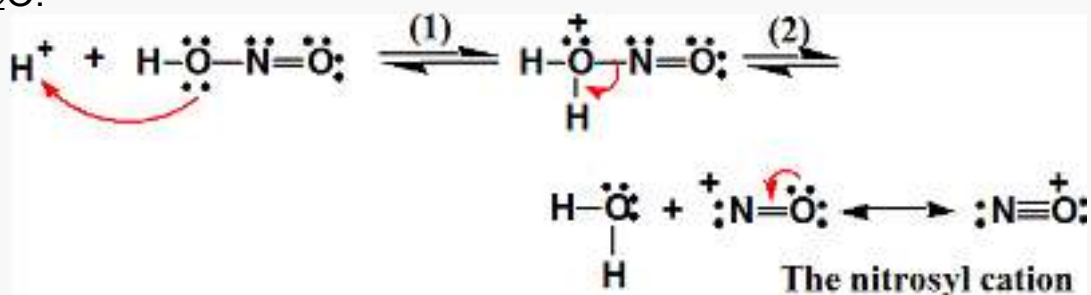
- Nitrous acid can be used to differentiate primary, secondary and tertiary aliphatic amines.
- Primary aromatic amines react with cold HNO_2 and dissolved in dilute HCl at $0-5^\circ \text{C}$ will produce diazonium salt. When this cold salt is heated at room temperature, nitrogen gas will be evolved.



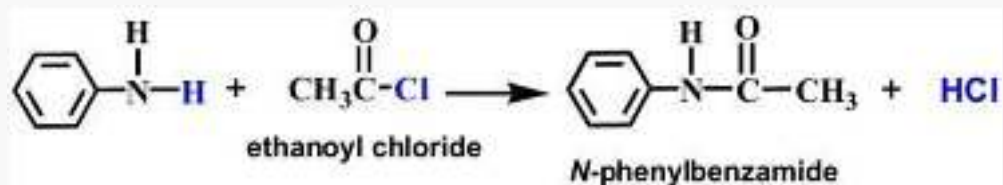
- Tertiary aromatic amines react with nitrous acid by undergoing substitution at the para position of the benzene ring to form nitrosoaniline, which is a yellow precipitate. Here, NO^+ is a weak electrophile and participates in Electrophilic Aromatic Substitution.



Formation of NO^+ from HNO_2 : Step 1: Protonation of HNO_2 & Step 2: Loss of H_2O .



3. Acylation: Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. You can consider this reaction as the replacement of hydrogen atom of $-NH_2$ or $>N-H$ 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.



Note: The amide is a less powerful activating group than the simple amino group,

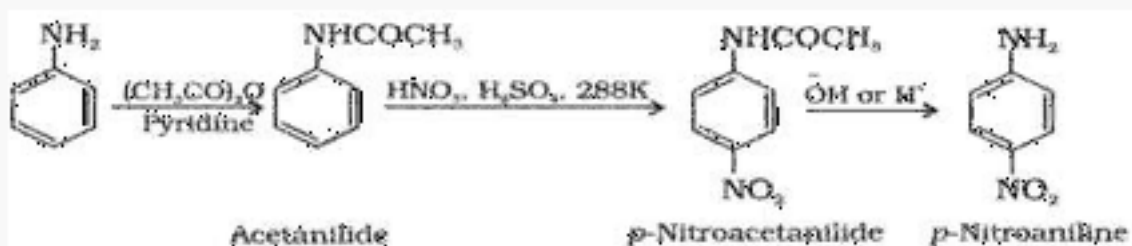
$-NH_2$ since resonance within the N-acetyl group of the amide competes with delocalization of the N lone pair into the ring and Steric effects in the amide also

often lead to a dec

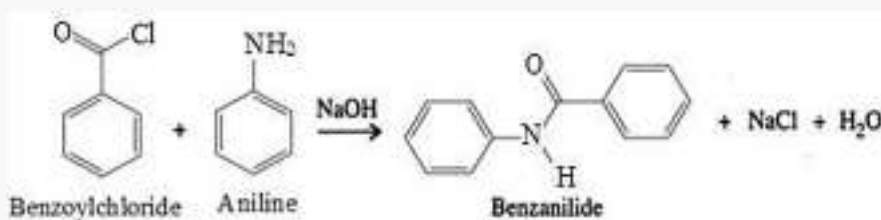


The group $-NHCOCH_3$ is less powerful ortho and para director because of the electron-withdrawing character of oxygen makes nitrogen a poor source of electrons. This fact is made use in preparing mono substituted aniline. The $-NH_2$ group is such a powerful activator, that substitution occurs at all available ortho and para positions of aniline. If, however, $-NH_2$ group is converted to $-NHCOCH_3$, the molecule becomes less powerful activator. Hence only mono substitution products are obtained. Finally $-NHCOCH_3$ is converted back to $-NH_2$ by hydrolyzing with acid. This technique is especially used while nitrating aniline as strong oxidizing agent destroys the highly reactive ring.

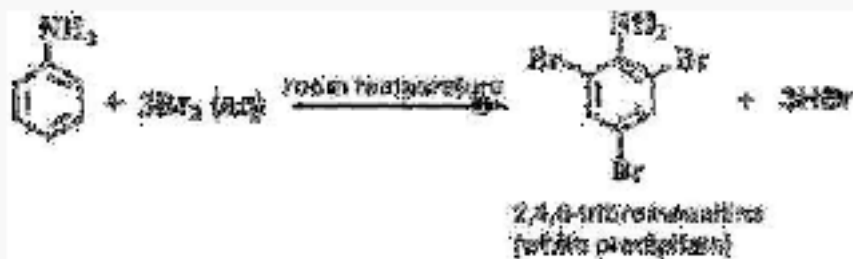
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Amines also react with benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$). This reaction is known as benzoylation.



- 4. Ring halogenation of phenyl amine:** When bromine water is added to phenylamine (aniline) at room temperature, decolorisation of the bromine water occurs and a white precipitate of 2,4,6-tribromoaniline is obtained. This reaction is used as a test for aniline.



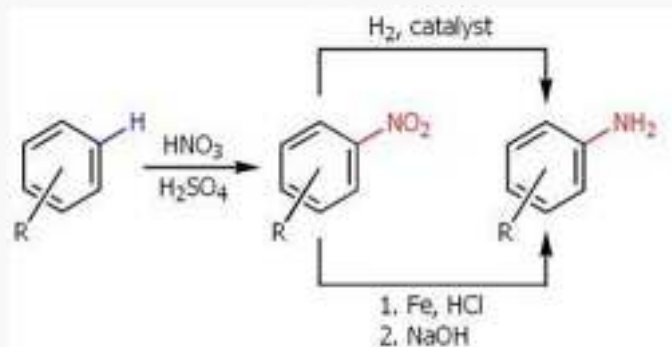
Preparation of Aromatic Amines:

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.
- Nitroalkanes 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.

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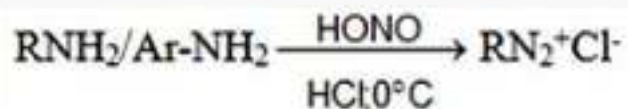
Thus, only a small amount of hydrochloric acid is required to initiate the reaction.



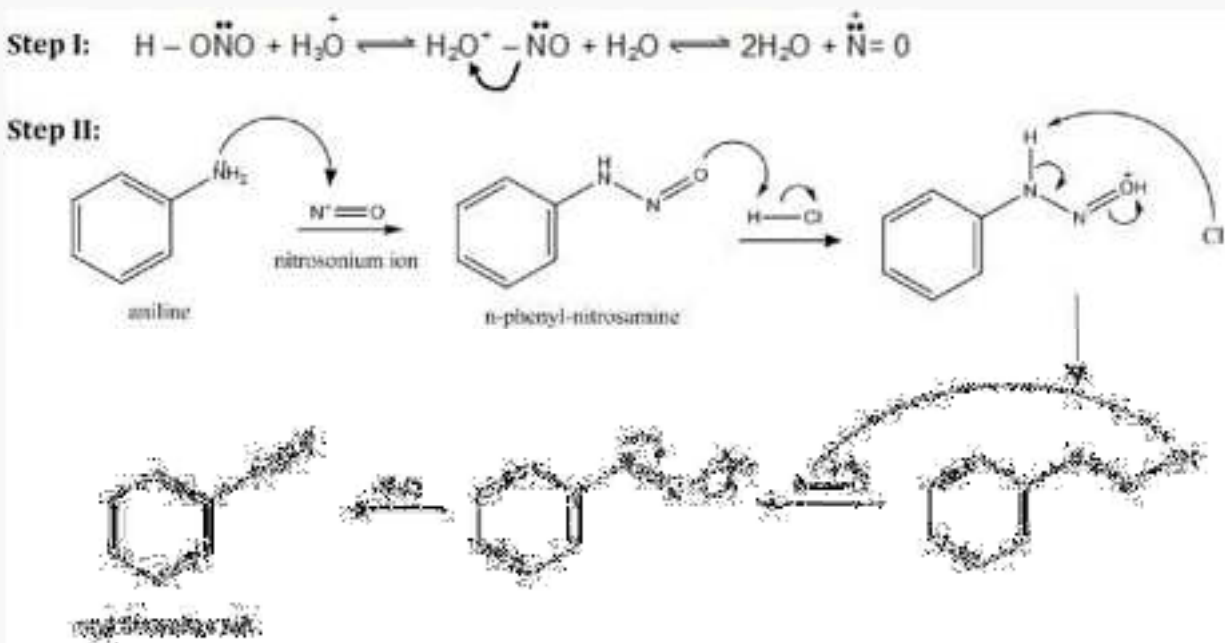
Synthesis and Synthetic uses of Aryl Diazonium Salts:

These Aryl diazonium salts are prepared by treating a primary amine with NaNO_2 in presence of con. HCl ; the temperature being $0-5^\circ\text{C}$. (Here the temperature has to be taken care of and if the temperature exceeds 5°C , the reaction will not take place.)

General Reaction:



Mechanism:



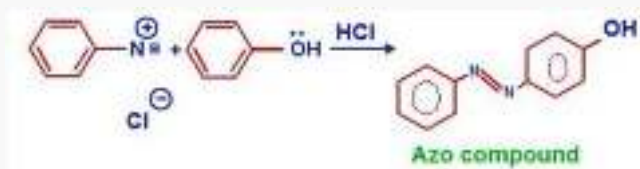
Primary aromatic amines are used as a starting material for the manufacture of azo dyes.

- Azo compounds: - compounds bearing the functional group $\text{R-N=N-R}'$, in which R and R' can be either aryl or alkyl.
- N=N group is called an azo group
- HNNH is called diimide

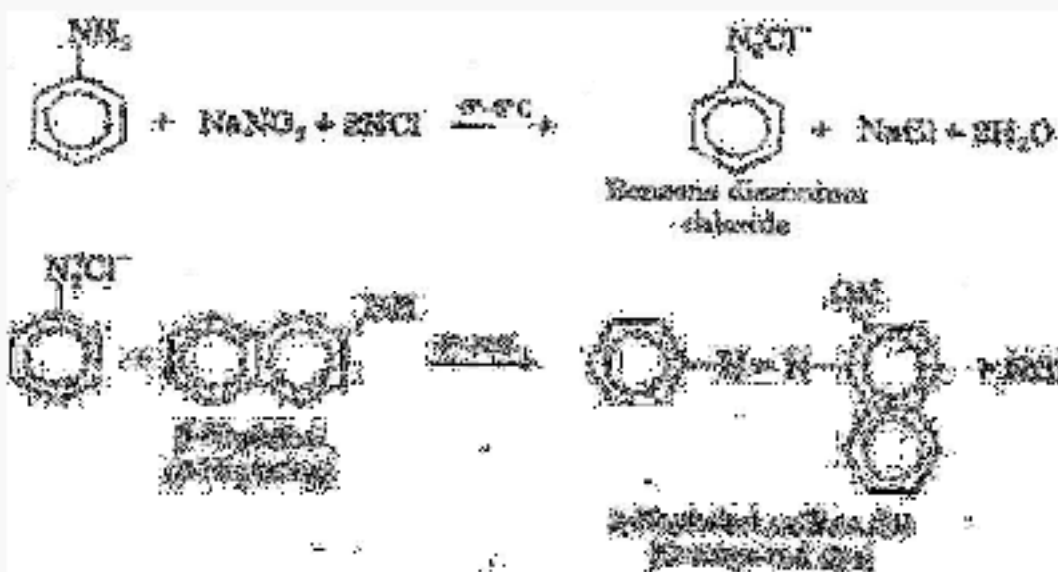
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- Aryl azo compounds have vivid colors, especially reds, oranges, and yellows
- Amines react with sodium nitrite or nitric(III) acid to form diazonium salt, which can undergo coupling reaction to form azo compound (colored compounds).

Example 1:



Example
2:



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Uses:

- Azo-compounds are highly coloured, they are widely used in dyeing industries, such as: i) Methyl orange ii) Direct brown 138 iii) Sunset yellow FCF
- Methyl orange - used as acid-base indicators due to the different colors of their acid and salt forms
- Artist's paints – clays, yellow to red range
- Dye in food and textiles Uses and important of azo dye
- **EXAMPLES OF AZO DYES USED IN FOOD:**
E102: Tartrazine, E107 : Yellow 2G, E110 : Sunset Yellow, E122 : Azorubine,
E123: Amaranth, E124 : Ponceau 4R, E129 : Allura Red & E151 : Brilliant Black.