

Chemical Reactions of Amines

Have you ever wondered how different clothes get different colours? There is various type of dyes that colour your clothes beautifully. However, do you know what these are? These are **Amino acids**. You must have heard that **proteins** are made up of amino acids. In **Organic chemistry**, you will often see the Amino group in many compounds. The **chemical reactions** of amines are super awesome and at times super useful also. The nitrogen derivatives of **hydrocarbons** make up many crucial compounds. These include dyes and drugs. Let us find out more!

Amines

There are organic compounds and functional groups containing a nitrogen atom with a lone pair of electrons. Amines are one of them. Amines are the derivatives of ammonia. They have one or more hydrogen atoms. We can replace these hydrogen atoms with an alkyl or aryl group.

Here, we will discuss the chemical reactions of amines. So we will know some interesting facts which are associated with chemical reactions of amines.

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Classification of Amines

On the basis of the presence of replaceable hydrogen atoms, we can classify amines into three types:

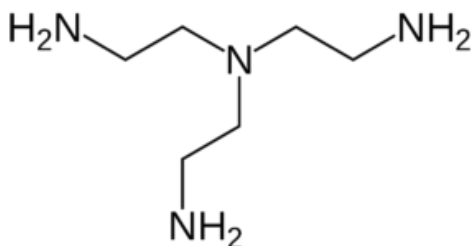
- **Primary Amines:** The amine is primary amine when an alkyl or Aryl group replaces one of three [hydrogen atoms](#).
- **Secondary Amines:** It is a secondary amine when the alkyl or aryl group replaces two hydrogen atoms.

- Tertiary Amines: The amine is a tertiary amine when total three hydrogen atoms are replaced by alkyl or aryl group.

Normally, secondary or tertiary amines form a cyclic structure.

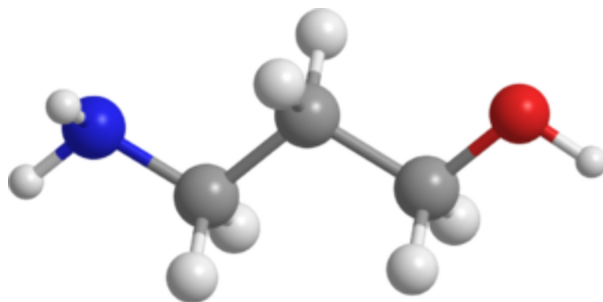
Chemical Reactions of Amines

Amines can act as both bases and nucleophiles due to the unshared electron pair.

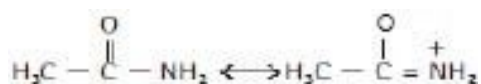


Basic Nature of Amines

In this section, we will look at the basic nature of some common amines.



- Aniline is less basic than ammonia. The phenyl group exerts an inductive effect, i.e., it withdraws electrons. This results in the lower availability of electrons on nitrogen for protonation.
- Ethylamine and acetamide both contain an amino group. However, acetamide does not show its basic nature. This is because lone pair of electrons on nitrogen is delocalized by resonance with the carbonyl group which makes it less available for protonation.



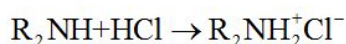
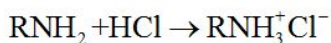
- The compound with least 's' character (sp³ hybridized) is most basic and with more 's' character (sp-hybridized) is least basic. Examples in decreasing order of basicity are :



Electron withdrawing ($\text{C}_6\text{H}_5\text{—}$) groups cause a decrease in the electron density on the nitrogen atom. Thus, they result in a decrease in the basicity.



Amines being basic in nature, react with acids to form corresponding salt.

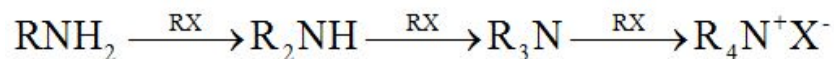


These are all about the basic nature of amines. Now, we move on to the important segment: Preparation of amines.

Preparation of Amines

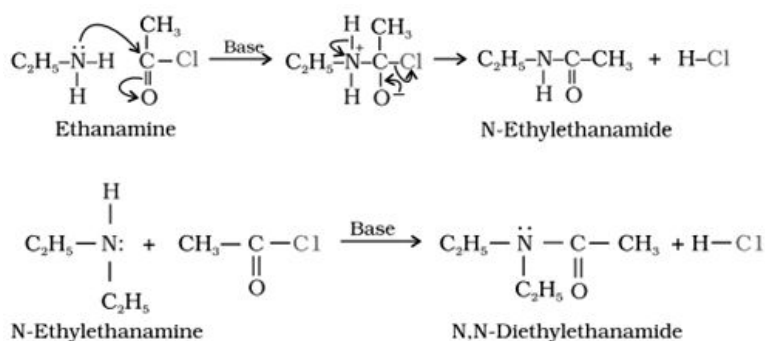
1) Alkylation

Alkylation of 1^o amine generates 2^o amine, 3^o amine and finally the quaternary salts.



2) Acylation

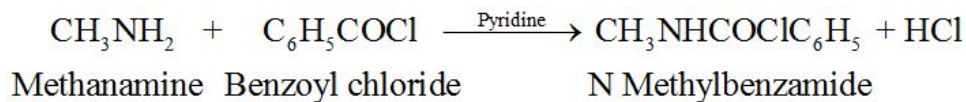
Acylation is the reaction with acid chlorides, anhydrides and esters. These occur by nucleophilic **substitution reactions**. The reaction is proceeded by the replacement of hydrogen atom of -NH_2 or $>\text{N-H}$ group by the acyl group (RCOX).



We cannot acylate Tertiary (3°) amine. This is because there is no Hydrogen bonded to nitrogen.

3) Benzoylation

Here, methenamine reacts with benzoyl chloride. The products are hydrochloric acid and N Methylbenzamide.

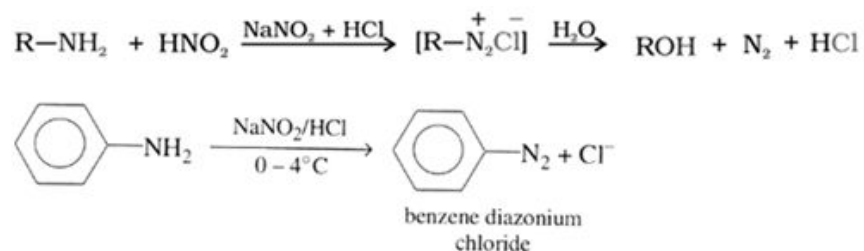


Chemical Reactions of Amines

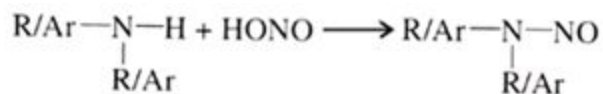
1) Reaction with Nitrous Acid, HNO₂

Three classes of amines react differently with nitrous acid as follows:

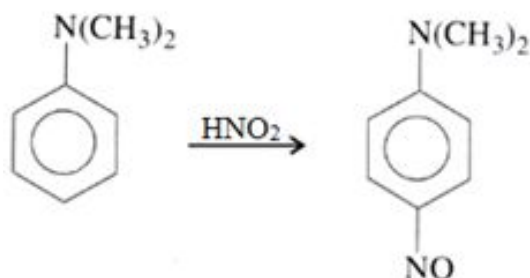
(a) The Reaction of 1^o Amines



(b) The Reaction of 2^o Amines

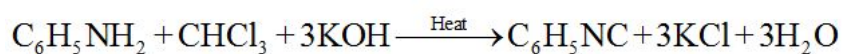


(c) The Reaction of 3^o Amines



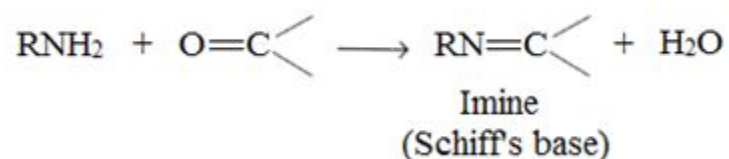
2) Carbylamine Reaction

Primary amine reacts with $CHCl_3/KOH$ to form isocyanides (carbylamines). You get a very unpleasant smell with the products. Both aliphatic and aromatic amines take part in this reaction. This reaction is as follows:



3) Reaction with Aldehyde and Ketones

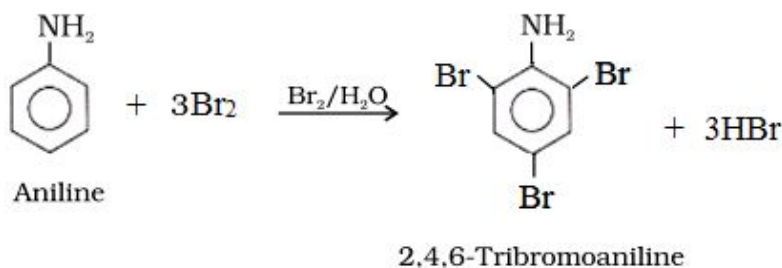
1^o amines react with aldehydes and ketones to form Schiff's bases. The reaction is given below.



4) Electrophilic Substitution Reactions

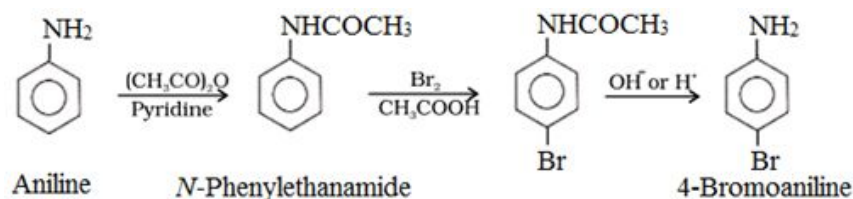
Aniline is ortho and para directing towards electrophilic substitution reaction. This is because of high electron density at ortho and para-positions. Some of the electrophilic substitution reactions of aniline are as follows:

(a) Bromination

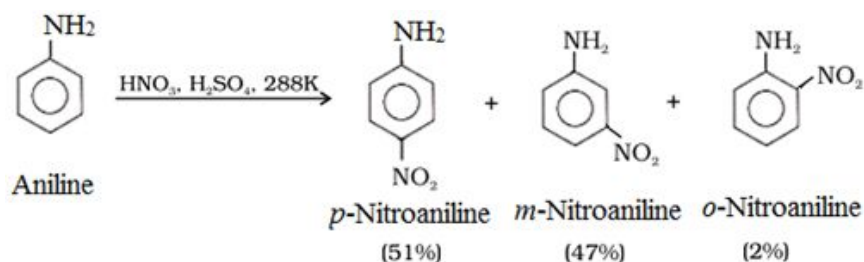


To prepare monosubstituted aniline derivative:

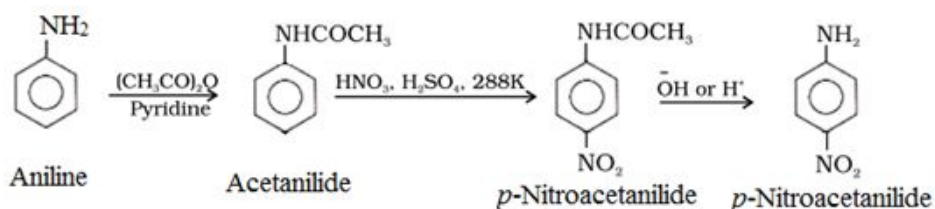
- You have to carry out the first acetylation of aniline with acetic anhydride.
- You would have to follow this by the desired substitution of the substituted amide.
- This is then hydrolyzed. We thus, obtain the monosubstituted amine.



(b) Nitration



To get *p*-nitro derivative as the major product, you have to carry the acetylation of aniline with acetic anhydride. Then, you should carry out the desired substitution of anilide. After this, you must carry out hydrolysis of the substituted anilide to the substituted amine.



Solved Example for You

Q: How can we convert secondary amine into nitrosoamine?

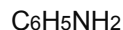
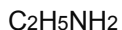
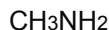
Ans: We can convert secondary amine into nitrosoamine by treating the amine with the nitrous acid.

Classification of Amines

You have heard of [Ammonia](#). Haven't you? But, it is not the only nitrogen product that is popular. There are so many other products of ammonia that are derived by altering the [hydrogen](#) atoms. We give them names like Primary amine or Secondary amine etc. In this chapter, we will look at the classification of amines in details. We will also have a brief look at the nomenclature of the classification of amines.

What are Amines?

Amines are the organic compounds derived from ammonia (NH_3). They are derived by replacing its one or more hydrogen atoms by alkyl or aryl group. For example:



Methyl Amine

Ethyl Amine

Aniline

Classification of Amines

On the basis of the number of hydrogen atoms replaced in NH_3 molecule, amines are categorized into three types:

1° or the Primary Amines

In 1° amine, one hydrogen atom of NH_3 is replaced by an alkyl or aryl group. For example:

- CH_3NH_2
- Methyl Amine

2° or the Secondary Amines

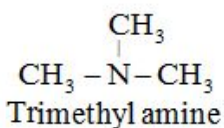
In 2° amine, two hydrogen atoms of NH_3 are replaced by alkyl or aryl groups. For example: CH_3NHCH_3 or Dimethyl Amine

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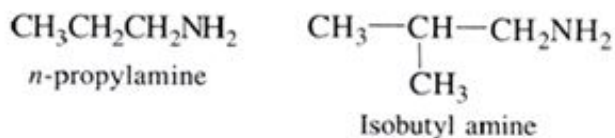
3° or Tertiary Amines

In tertiary amine, all the three hydrogen atoms of NH_3 are replaced by alkyl or aryl groups. For example:

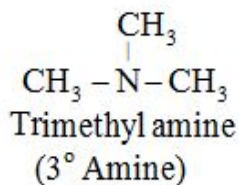
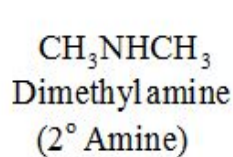


Nomenclature of Amines

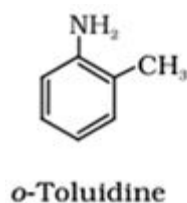
- In the common naming system, we name aliphatic amines by prefixing an alkyl group to a mine, i.e. alkylamine. For example:



- Secondary and tertiary amines, having two or more similar groups are named by adding prefix 'di' or 'tri' before the name of the alkyl group. For example:



- Aromatic amines are named as derivatives of the parent member, aniline ($\text{C}_6\text{H}_5\text{NH}_2$). For example:



Solved Examples for You

Question: Write a detailed note on the nomenclature of amines.

Answer: In organic chemistry, the names of the **compounds** that are globally accepted are given according to the guidelines given by IUPAC for the nomenclature of organic compounds. The naming of aliphatic amines is done by prefixing the alkyl group to amines and thus the names of aliphatic amines are of the form of an alkylamine.

For examples, CH_3NH_2 is named as methylamine (alkyl part + amine =methylamine). Prefixes such as di and tri are appended before the names of the alkyl group when two or more identical groups are present. If more than one amino group is present in the amine then the parent chain and the position of amino groups is identified by numbering the carbon atoms in the parent chain.

The numbering is done in such a way that the carbon atom bearing the $-\text{NH}_2$ groups get the lowest numbers. Prefixes along with the numbers are then used to denote the number of amino groups and their position in the molecule. For example, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ is named as ethane 1, 2-diamine. If $-\text{NH}_2$ group is attached to a benzene ring then it is called as arylamines.

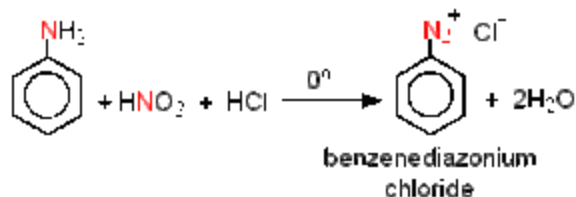
One of the simplest examples of arylamine is $\text{C}_6\text{H}_5\text{NH}_2$. It is commonly known as aniline which is also an accepted IUPAC name. When we name arylamines according to the guidelines given by IUPAC then 'e' of the arene is replaced by an amine, for example, $\text{C}_6\text{H}_5-\text{NH}_2$ is named as benzenamine.

Diazonium Salts

Diazonium salts are a group of **organic compounds** which share one common functional group $R-N_2^+X^-$. In $R-N_2^+X^-$, R is an organic group. For example, alkyl or aryl group. And X is organic or inorganic anions. For example **Halogen**, **Chlorine**, Bromine, etc. Diazonium salts are also known as Diazonium compounds. By heating it in the **water** we can make Phenols. And azo compounds can also be formed by reacting diazonium salts with other aromatic compounds. Let us learn about a different class of organic compounds that have Amine group.

What are Diazonium Salts?

The diazonium salts or diazonium compounds are the class of organic compounds with general **formula** $R-N_2^+X^-$. Here, X is an organic or inorganic anion (for example, **Cl⁻**, **Br⁻**, **BF₄⁻**, etc.) and R is an alkyl or aryl group. The term is derived from two words. ‘*di*’ refers to ‘two’, *azo* is indicative of ‘**nitrogen**’ and *ium* implies that it is cationic in **nature**.



Hence, they have two nitrogen atoms with one being charged.

Benzenediazonium chloride ($\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$), benzene diazonium hydrogen sulfate ($\text{C}_6\text{H}_5\text{N}_2^+\text{HSO}_4^-$), etc. are some of the examples of the diazonium salt.

Now, we look at the properties of diazonium salts. You can learn them as they are important from the exam point of view.

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Properties of Diazonium Salts

- They are ionic in nature.

- They are water soluble.
- Aryl diazonium salts are colourless **crystalline** solids.
- Benzenediazonium chloride is soluble in water. But, it reacts with it only when warmed.
- Benzenediazonium fluoroborate is not soluble in water. It is pretty stable at room **temperature**. So, where do we use these salts? Do you know about its applications? Let us see below.

Importance of Diazonium Salts

- We use diazonium salts in the dye and pigment industries. They play a major role to produce dyed fabrics.
- You can use them in document reproduction. This is because they have a property of breaking down in ultraviolet light.
- They are useful in the synthesis of a large variety of organic compounds, especially aryl derivatives.
- Direct halogenation is not a suitable method for preparing aryl iodides and fluorides. Nucleophilic substitution of chlorine in chlorobenzene by a cyano group is not possible. However, we can use diazonium salts to produce cyanobenzene easily.

- It is not possible to prepare substituted aromatic compounds by direct substitution in benzene. For these compounds, we use replacement of diazo group in diazonium salts.
- They are essential as intermediates for introducing $-F$, $-Br$, $-Cl$, $-I$, $-NO_2$, $-OH$ and $-CN$ groups into the aromatic ring.

Solved Example For You

Q: Write down the method for preparation of diazonium salts.

Ans: Diazotization or dissociation is the process of converting an organic compound, generally primary aromatic amines into diazonium salts. Diazonium groups are very unstable and therefore, we can't store them. Thus, we normally use them immediately after preparation. One of the most common methods of preparation of diazonium salt is by the reaction of nitrous acid with aromatic amines.

The reaction of aniline (aromatic amine) with nitrous acid results in the formation of the diazonium salt. This salt is the benzene diazonium chloride. Nitrous acid is a highly toxic gas. Therefore, it is

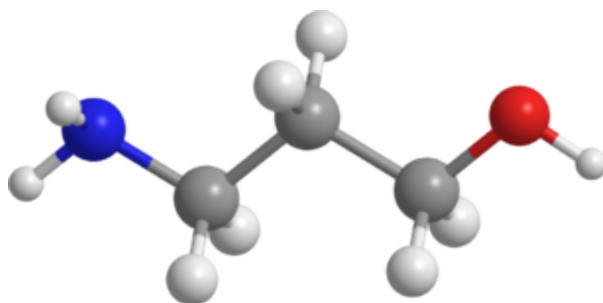
generally prepared during the reaction itself by reacting NaNO_2 with a mineral acid.

Nomenclature of Amines

Have you ever wondered how things get their names? Well, we can't decode all of it. But, we can certainly study about how various [hydrocarbons](#) get their names! Doesn't that sound interesting? In this chapter, we will look at the nomenclature of Amines. First, we will take a quick revision of the definition of Amino group and [classification of amines](#). Let's begin.

What are Amines?

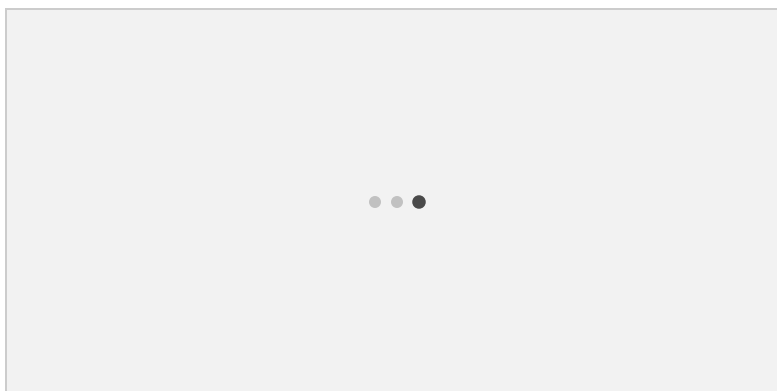
Amines are one of the most important classes of [organic compounds](#). We get them by replacing one or more hydrogen atoms by an alkyl or aryl group in a molecule of [ammonia](#). They are commonly found in [vitamins](#), [proteins](#), [hormones](#), etc. They are extensively used in the manufacturing of many [drugs](#) and detergents.



Classification of Amines

Depending upon the number of hydrogen atoms that can be replaced by an alkyl or aryl group in ammonia, amines are classified as primary (1^o), secondary (2^o) and tertiary (3^o).

If only one **hydrogen atom** is replaced then amines of the form $R-NH_2$ or primary amines (1^o) are obtained. In case, two of the three hydrogen atoms are replaced by alkyl/aryl groups then secondary amines are formed. When all the three hydrogen atoms are replaced by alkyl/aryl group then tertiary amines are obtained.



We have already seen this concept in the previous chapters. Now, that our memories are refreshed, let us move on to the next most important segment: the nomenclature of amines.

Nomenclature of Amines

In the branch of [organic chemistry](#), the names of the compounds that are globally accepted are given according to the guidelines given by IUPAC for the nomenclature of organic compounds. Let us have a look at some of the rules for nomenclature of amines.

Rules of Nomenclature of Amines

- The naming of aliphatic amines is done by prefixing the alkyl group to the amines. Therefore, the names of aliphatic amines are of the form of an alkylamine. For example, CH_3NH_2 is named as methylamine (alkyl part + amine = methylamine).
- Prefixes such as di and tri are attached before the names of the alkyl group when two or more identical groups are present.
- If more than one amino group is present in the amine, a different rule is followed. Here, the parent chain and the position of amino groups is identified by numbering the [carbon atoms](#) in the parent chain. The numbering is done in such a way that the carbon atom bearing the $-\text{NH}_2$ groups get the lowest numbers.
- Prefixes along with the numbers are then used to denote the number of amino groups and their position in the molecule. For

example, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ is named as ethane 1, 2-diamine.

- If $-\text{NH}_2$ group is attached to a benzene ring then it is called as arylamines.
- When we name arylamines according to the guidelines given by IUPAC then 'e' of the arene is replaced by the amine, for example, $\text{C}_6\text{H}_5-\text{NH}_2$ is named as benzenamine.

Solved Examples for You

Q1: Give an example of arylamine.

Ans: An example of arylamine is $\text{C}_6\text{H}_5\text{NH}_2$. It is commonly known as aniline which is also its IUPAC name.

Q2: The number of possible structures of amine ($\text{C}_7\text{H}_9\text{N}$) having one benzene ring is:

- A) 5 B) 3 C) 4 D) 6

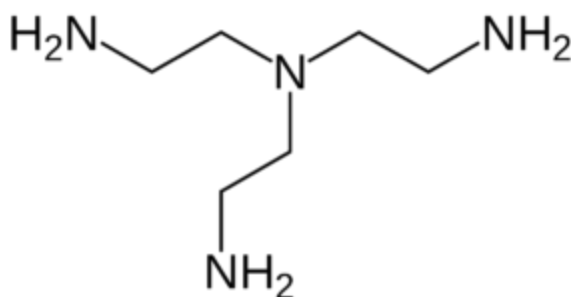
Solution: A) The five possible structures of C_7H_9N are phenylemethanamine, N-methyl aniline, o-toluidine, m-toluidine, p-toluidine.

Physical Properties of Amines

An important class of organic compounds are the Amines. The study of Amines is very interesting in many ways. Amine chemistry is very important in biology. It plays a vital role in all life forms. Here we will study the Amine structure and their physical properties.

The Amine Structure

Amines contain a nitrogen atom with a lone pair of electrons. They are basically the derivatives of ammonia. If we replace one or more hydrogen atoms by substituent groups such as alkyl or aryl in Ammonia, we get a new class of organic compounds called Amines. Examples of significant amine structure include Amino acids, biogenic amine, trimethylamine, and aniline.



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Classification of Amines

Amines are classified into four categories namely, primary, secondary, tertiary and cyclic. A primary amine is one when you can replace one of the three hydrogen atoms by an alkyl or aryl group. When you can replace two out of three hydrogen atoms, we get secondary amine.

Similarly, when all the three hydrogen atoms are replaced tertiary amines are formed. Only secondary or tertiary amines can be cyclic. The 3 – member ring aziridine is an example of cyclic amine. Let us now look at the physical properties of amines in brief.

Physical Properties of Amines

- The lower aliphatic amines are gaseous in nature. They have a fishy smell.

- Primary amines with three or four carbon atoms are liquids at room temperature whereas higher ones are solids.
- Aniline and other arylamines are generally colourless. However, they get coloured when we store them in open due to atmospheric oxidation.
- Lower aliphatic amines can form hydrogen bonds with water molecules. Therefore, such amines are soluble in water.
- Increase in the size of hydrophobic alkyl part increases the molar mass of amines. This usually results in a decrease in its solubility in water.
- Higher amines are insoluble in water. Organic solvents like alcohol, benzene and ether readily dissolve amines.
- Alcohols have higher polarity as compared to amines and hence, they form stronger intermolecular hydrogen bonds.
- Primary and secondary amines are often engaged in the intermolecular association as a result of hydrogen bonding between the nitrogen of one and hydrogen of the other molecule.
- The intermolecular association is more prominent in case of primary amines as compared to secondary due to the availability of two hydrogen atoms.

- In tertiary amines, there is no intermolecular association due to the absence of free hydrogen atom for bonding.
- The order of boiling point of amines is as follows: Primary > Secondary > Tertiary.

Solved Examples for You

Question 1: Primary amines are less soluble than tertiary amines.

- A. True
B. False

Solution: Option A – True. Primary amines are less soluble than tertiary amines as primary amines can form hydrogen bonds with water but tertiary amines cannot.

Question 2: Arrange the following in the decreasing order of boiling point:

- i) $\text{C}_2\text{H}_5\text{OH}$ ii) $(\text{CH}_3)_2\text{NH}$ iii) $\text{C}_2\text{H}_5\text{NH}_2$

- A. $\text{i} > \text{ii} > \text{iii}$
B. $\text{ii} > \text{i} > \text{iii}$

C. $\text{iii} > \text{i} > \text{ii}$

D. $\text{iii} > \text{ii} > \text{i}$

Solution: Option A – $\text{i} > \text{ii} > \text{iii}$. All the given compounds have intermolecular hydrogen bonding due to which their boiling points are higher. $\text{C}_2\text{H}_5\text{OH}$ possesses the strongest hydrogen bonding because the O is more electron negative than N in other compounds. Therefore it has the highest boiling point. In $(\text{CH}_3)_2\text{NH}$ and $\text{C}_2\text{H}_5\text{NH}_2$, the latter has longer alkyl chain which makes hydrogen bonding weaker. Hence the order of boiling points is $\text{i} > \text{ii} > \text{iii}$.

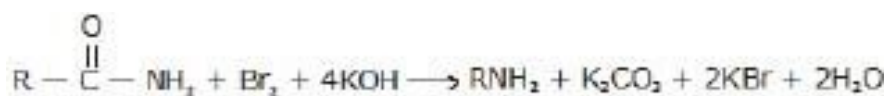
Preparation of Amines

We have discussed all the basics about amines, their physical properties, and [nomenclature](#) in the previous chapter. Are you not interested to know how you can prepare amine? This is a very interesting concept. You will find out when you read it! This is an important subject from the exam point of view as well. Hence, it is important that you take extra care of the [equations](#) and methods. We will now start with the Preparation of Amines.

Methods of Preparation of Amines

Hoffmann's Bromamide Reaction

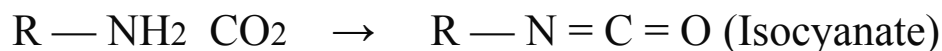
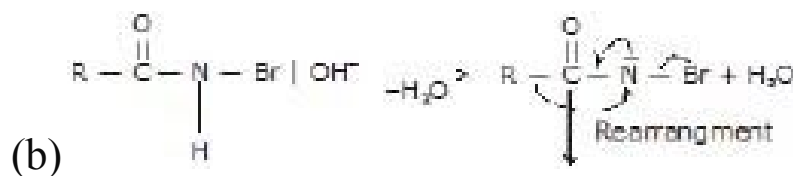
We can also prepare amines (only primary) by Hoffmann degradation. In this method, the amine will have one [carbon atom](#) less than the amide. The reaction proceeds via [formation](#) of nitrene.



Mechanism of above reaction is as given below:



Mechanism



Curtius, Schmidt, and Lossen Rearrangement

These reactions are basically rearrangement reactions in which carbon migrates from carbon to **nitrogen** with the formation of an isocyanate. In these migration processes i.e., 1, 2 shift, migrating group is an alkyl or aryl group and leaving group may be:

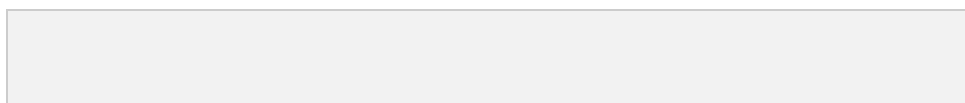
- Br in Hoffmann rearrangement

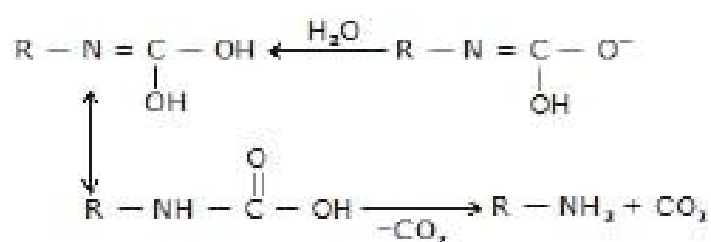
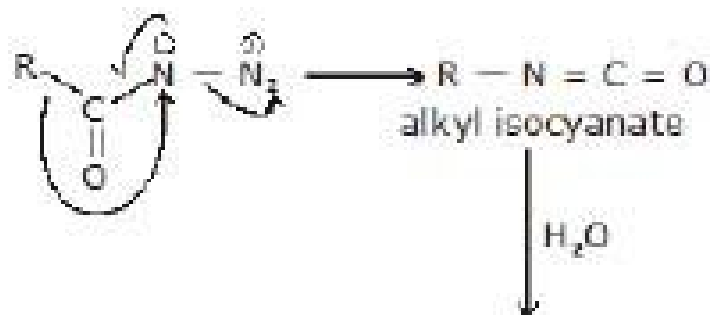
- N₂ in Curtius and Schmidt rearrangement



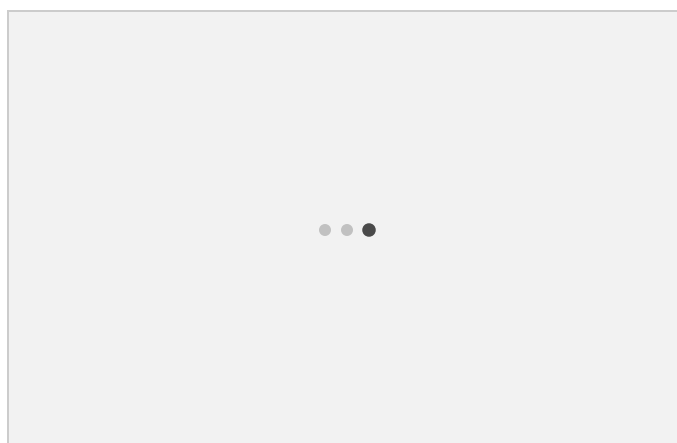
The isocyanate formed on hydrolysis gives amine. Let us now look at these [reactions](#) in greater details.

- Curtius Reaction: Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates. On further hydrolysis, it gives corresponding amines.

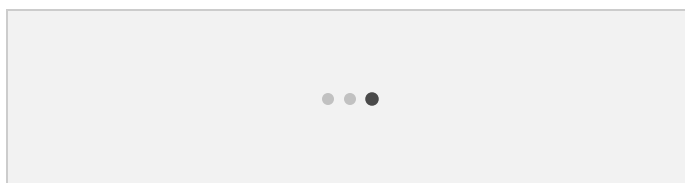
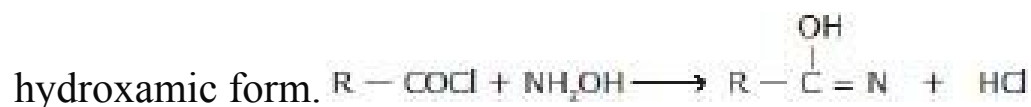




- Schmidt Reaction: Carboxylic acid reacts with the hydrazoic acid in the presence of concentrated H_2SO_4 to give isocyanates.

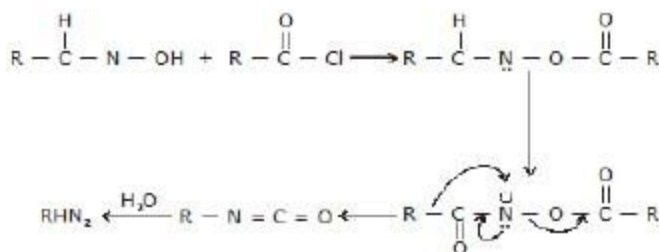


- Lossen Reaction: Hydroxylamine on treatment with acid chloride gives acyl derivatives of hydroxylamine. The acyl derivatives exist in two tautomeric form keto form called hydroxamic form and enol form called hydroximic acid. The



The hydroxamic form

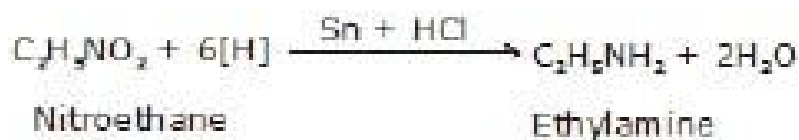
(keto form) forms O-acyl derivatives of hydroxamic form which on heating with bases forms isocyanates and finally amines upon hydrolysis.



Preparation of Amines

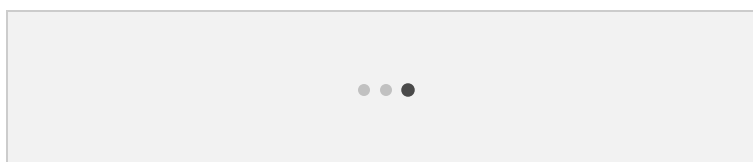
1) By Reduction of Nitroethane

Ethylamine can be obtained by the **reduction** of nitroethane. The reaction is as follows:



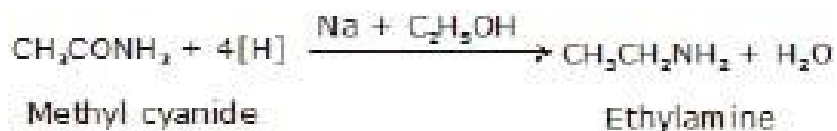
2) By Reduction of Methyl Cyanide

Ethylamine can also be obtained by reducing methyl cyanide. The reaction takes place as below:



3) By Reduction of Acetamide

Ethylamine is obtained by reduction of acetamide with sodium and absolute **alcohol** or LiAlH_4 in ether or hydrogen in presence of nickel catalyst.



4) By Reduction of Aldoxime

Aldoxime on reduction with hydrogen and nickel catalyst or sodium and absolute alcohol or LiAlH_4 in ether yields ethylamine.

...

5) By the Hydrolysis of Ethyl Isocyanate

Ethyl isocyanate on heating with caustic potash [solution](#) undergoes hydrolysis forming ethylamine.



6) By the Acid Hydrolysis of Ethyl Isocyanide

Ethyl isocyanide undergoes hydrolysis with a mineral acid and forms ethylamine.



7) By Schmidt Reaction

In this reaction, the acyl azide $(\text{RCON})_2$ and alkyl isocyanate (R—NCO) are formed as an intermediate.



Solved Example for You

Q: How can we prepare ethylamine in the laboratory?

Ans: We can prepare ethylamine in the laboratory by Hofmann's bromide reaction. Propionamide is heated with bromine and potassium hydroxide solution.