

Fundamentals of Organic Chemistry

CHEM 108

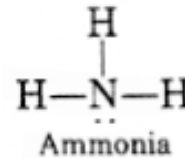
King Saud University

College of Science, Chemistry Department

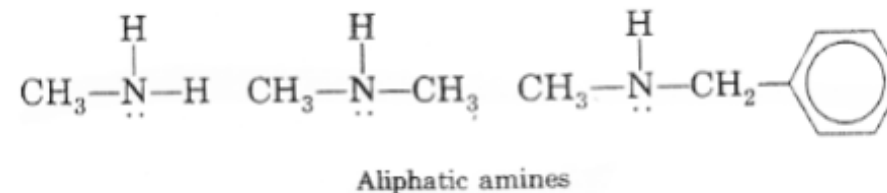
Structure and Classification of Amines

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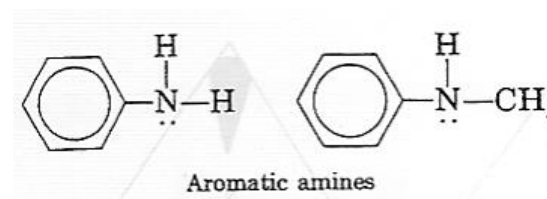
- **Amines** are compounds that derived from **ammonia** by replacement of one, two, or three hydrogens by alkyl or aryl groups.



- **Aliphatic amines** contain *only alkyl* groups bonded directly to the nitrogen atom.

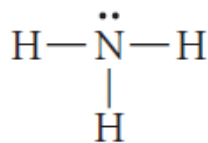


- **Aromatic amines** are those in which one or more aryl groups are bonded directly to nitrogen.

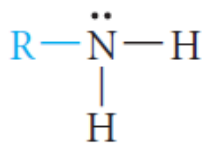


Classification and Structure of Amines

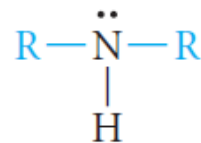
- The relation between **ammonia and amines** is illustrated by the following structures:



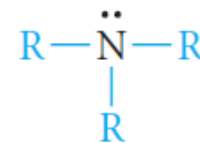
ammonia



primary amine



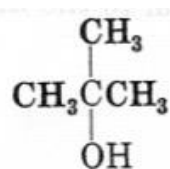
secondary amine



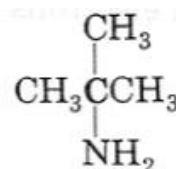
tertiary amine

- Amines** are classified as **primary**, **secondary**, or **tertiary**, depending on whether one, two, or three organic groups are attached to the nitrogen.

- NOTE:**



t-Butyl alcohol
(3° alcohol)



t-Butylamine
(1° amine)

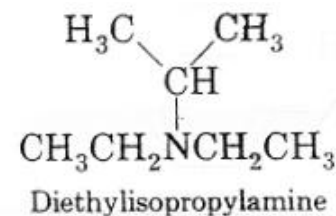
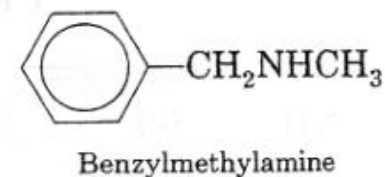
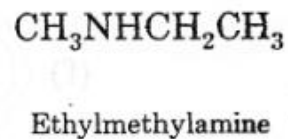
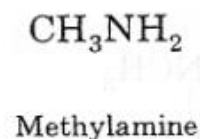
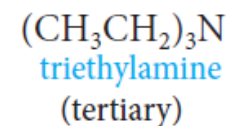
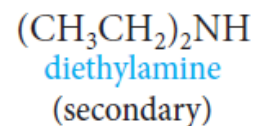
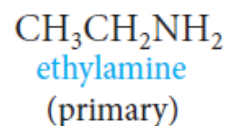
- t*-butyl alcohol is a **tertiary alcohol** (because three carbons are attached to the carbinol carbon).
- t*-butyl amine is a **primary amine** (because only one carbon is attached directly to the nitrogen atom).

Nomenclature of Amines

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Common Names

- **Amines** are named by specifying the alkyl groups attached to the nitrogen and adding the suffix *-amine* (*Alkylamine*).

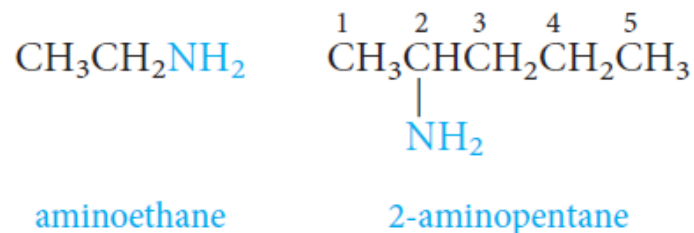


Nomenclature of Amines

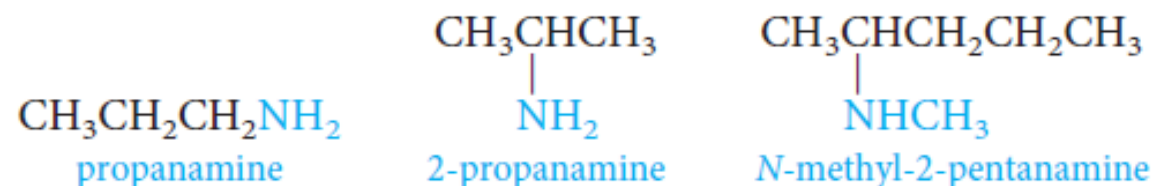
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IUPAC System

- The amino group, -NH_2 , is named **as a substituent**.



- Amines can be named as **alkanamines**.

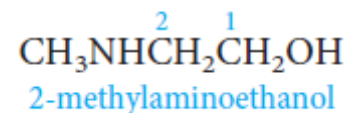
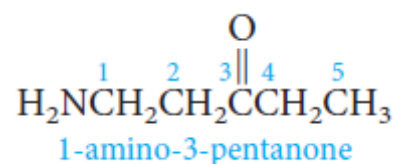
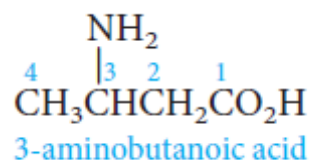


Nomenclature of Amines

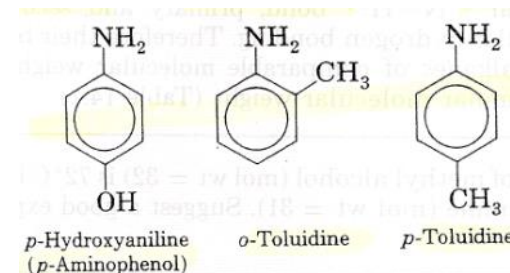
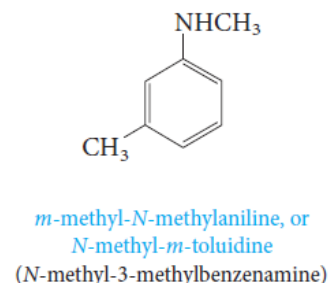
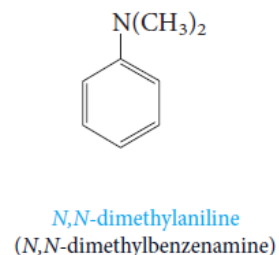
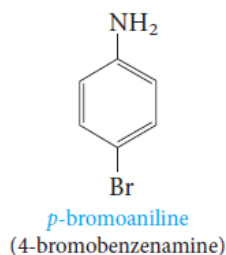
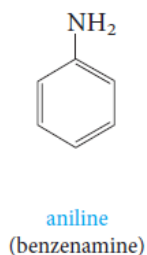
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IUPAC System

- When **other functional groups** are present, the amino group, -NH_2 , is named as a substituent.



- Aromatic amines** are named as derivatives of aniline.
- In the CA system, aniline is called benzenamine.



Physical Properties of Amines

Boiling Point

- **Methylamine and ethylamine are gases**, but primary amines with three or more carbons are liquids.
- **Primary amines** boil well above alkanes with comparable molecular weights, but below comparable alcohols.

Intermolecular N-H ···N hydrogen bonds are important and raise the boiling points of primary and secondary amines but are not as strong as the O-H ···O bonds of alcohols. The reason for this is that nitrogen is not as electronegative as oxygen.

alkane	CH ₃ CH ₃ (30) bp −88.6°C	CH ₃ CH ₂ CH ₃ (44) bp −42.1°C
amine	CH ₃ NH ₂ (31) bp −6.3°C	CH ₃ CH ₂ NH ₂ (45) bp +16.6°C
alcohol	CH ₃ OH (32) bp +65.0°C	CH ₃ CH ₂ OH (46) bp +78.5°C

Physical Properties of Amines



Boiling Point

- **Tertiary amines** are also polar compounds, but because hydrogen is not bonded to nitrogen, these amines are incapable of **intermolecular hydrogen bonding**.

Their boiling points are Lower than primary and secondary amines of identical molecular weights and Higher than those of alkanes of similar molecular weight.

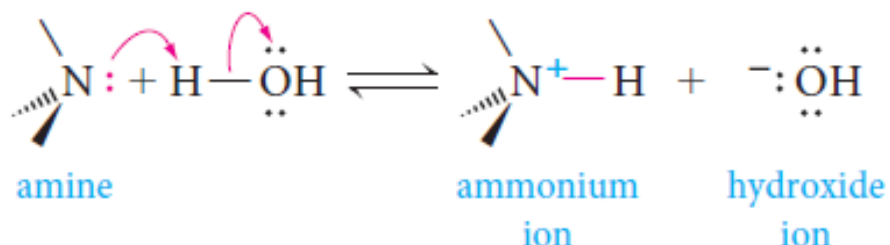
Solubility in Water

- **All three classes of amines** can form hydrogen bonds with the -OH group of water (that is, $\text{O}-\text{H} \cdots \text{N}$).
- **Primary and secondary amines** can also form hydrogen bonds with the oxygen atom in water: $\text{N}-\text{H} \cdots \text{O}$.
- **Amines** with up to six carbons show appreciable solubility in water.

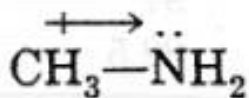
The Basicity of Amines

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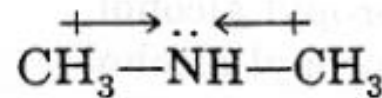
- The **unshared pair of electrons** on the nitrogen atom dominates the chemistry of amines.
- Because of this electron pair, **amines are both basic and nucleophilic**.
- Aqueous solutions of amines are basic because of the following equilibrium:



- Electron-donating groups increase the basicity of amines.
- Electron-withdrawing groups decrease their basicity.



One electron-donating group

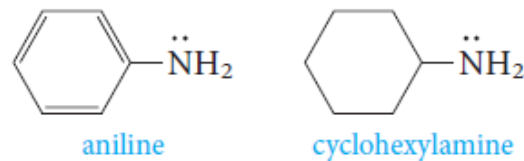


Two electron-donating groups

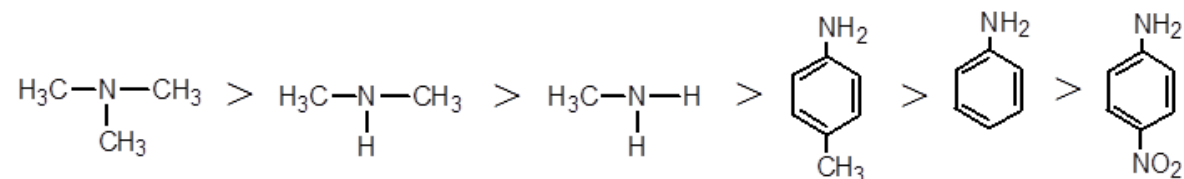
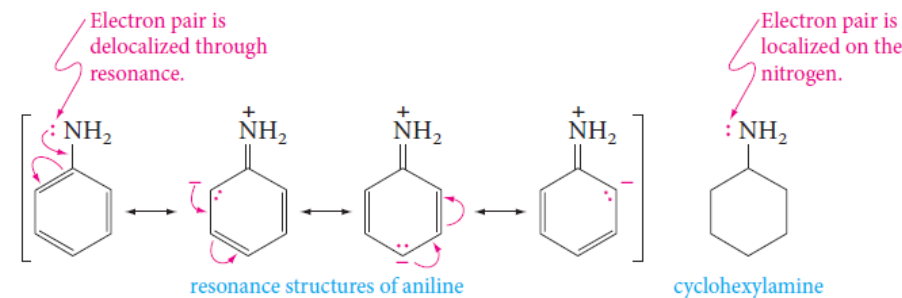
The Basicity of Amines

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- **Aromatic amines are much weaker than aliphatic amines or ammonia.**
 - **Example:** aniline is less basic than cyclohexylamine.



The reason is the resonance delocalization of the unshared electron pair that is possible in aniline, but not in cyclohexylamine:

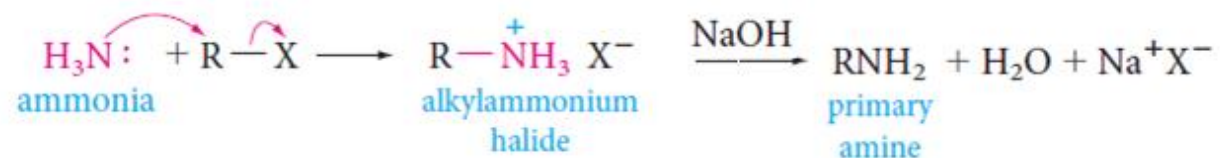


1) Alkylation of Ammonia

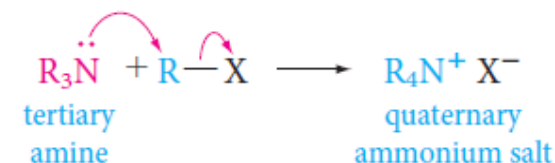
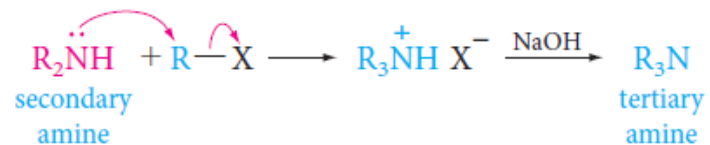
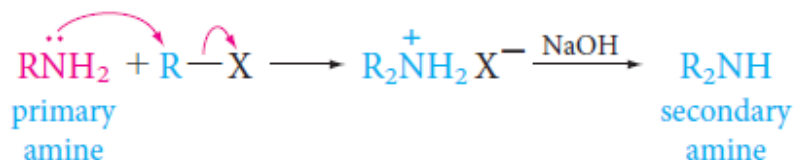
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- **Ammonia** reacts with alkyl halides to give amines via a two-step process.

The first step is a nucleophilic substitution reaction. *The free amine* can then be obtained from its salt by treatment with a strong base



- **Primary, secondary, and tertiary amines** can be similarly alkylated.

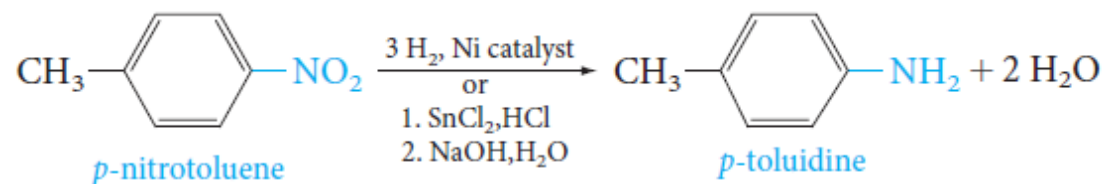


2) Reduction of Nitro Groups

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- The best route to **aromatic primary amines** is by reduction of the corresponding nitro compounds.

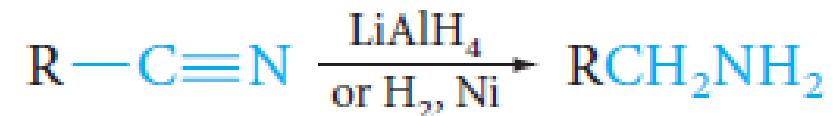
The nitro group is easily reduced, either catalytically with hydrogen or by chemical reducing agents.



3) Reduction of Nitriles

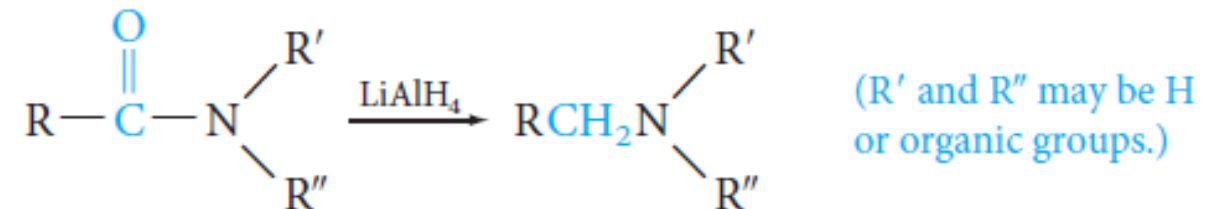
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- **Reduction of nitriles** (cyanides) gives primary amines.



4) Reduction of Amides

- **Amides** can be reduced to amines with lithium aluminum hydride.

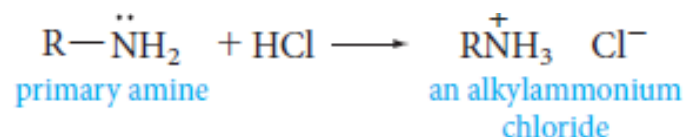


Reactions of Amines

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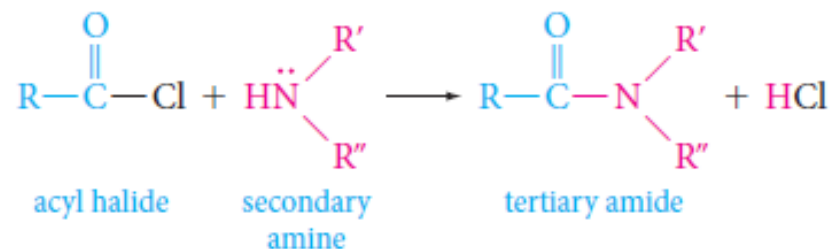
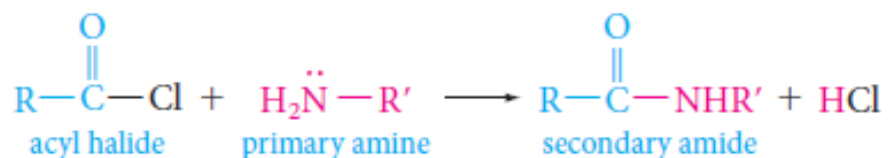
1) Reactions with Acids: Salt Formation

Amines react with strong acids to form **alkylammonium salts**.



2) Acylation of Amines: Amides Formation

Primary and secondary amines react with acyl halides to form amides.

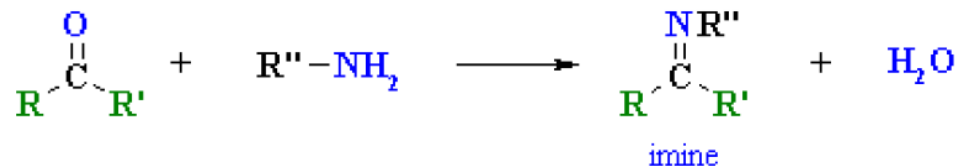


Reactions of Amines

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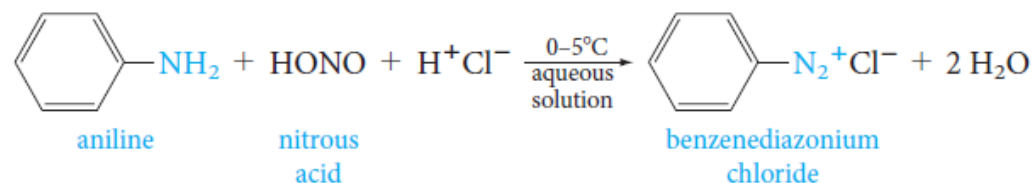
3) Imines Formation

Primary amines, $R-NH_2$ or $ArNH_2$, undergo nucleophilic addition with aldehydes or ketones in an acidic buffer to give substituted imines.



4) Aromatic Diazonium Salts

- Primary aromatic amines react with nitrous acid at 0°C to yield aryl diazonium ions. The process is called **diazotization**.



Reactions of Amines

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4) Aromatic Diazonium Salts

- They are useful in synthesis because the diazonio group ($-N_2^+$) can be **replaced by nucleophiles**; the other product is nitrogen gas.

