

Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

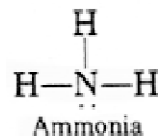
King Saud University

College of Science, Chemistry Department

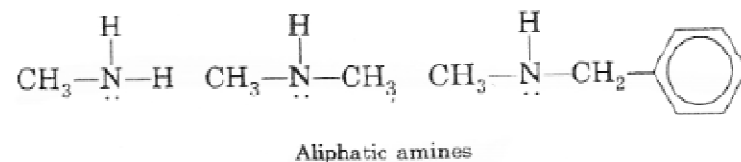
Structure and Classification of Amines

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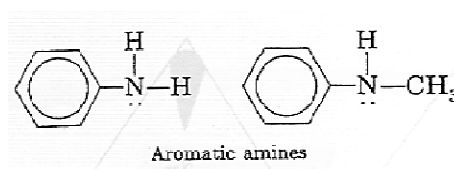
- **Amines** are compounds that derived from **ammonia** by replacement of one, two, or three hydrogens by alkyl or aryl groups.



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



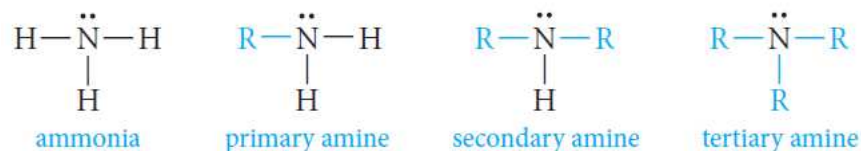
- **Aromatic amines** are those in which one or more aryl groups are bonded directly to nitrogen.



Classification and Structure of Amines

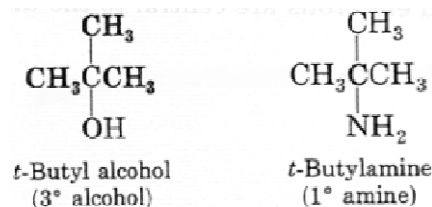
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- The relation between **ammonia and amines** is illustrated by the following structures:



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

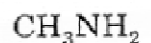
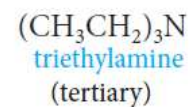
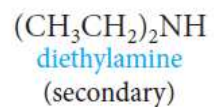
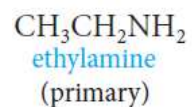
- NOTE:**



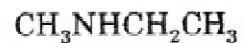
- t-butyl alcohol** is a **tertiary alcohol** (because three carbons are attached to the carbinol carbon).
- t-butyl amine** is a **primary amine** (because only one carbon is attached directly to the nitrogen atom).



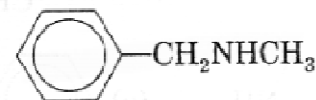
Amines are named by specifying the alkyl groups attached to the nitrogen and adding the suffix – *amine* (*Alkylamine*).



Methylamine



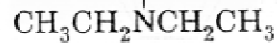
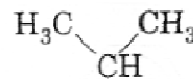
Ethylmethylamine



Benzylmethylamine



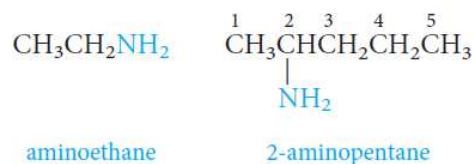
Dimethylamine



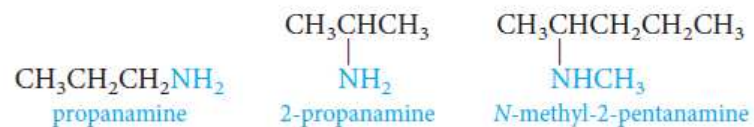
Diethylisopropylamine



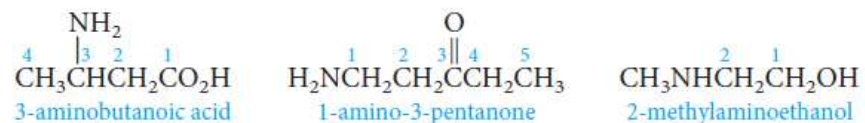
- The amino group, -NH_2 , is named **as a substituent**.



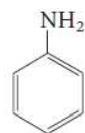
- Amines can be named as **alkanamines**.



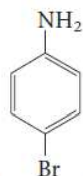
- When **other functional groups** are present, the amino group, -NH_2 , is named as a substituent.



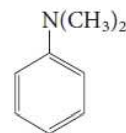
- **Aromatic amines** are named as derivatives of aniline.
- In the CA system, aniline is called benzenamine.



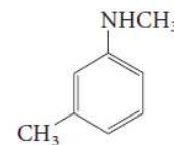
aniline
(benzenamine)



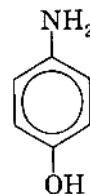
p-bromoaniline
(4-bromobenzenamine)



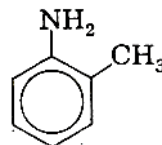
N,N-dimethylaniline
(*N,N*-dimethylbenzenamine)



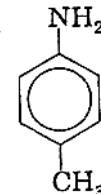
m-methyl-*N*-methylaniline, or
N-methyl-*m*-toluidine
(*N*-methyl-3-methylbenzenamine)



p-Hydroxyaniline
(*p*-Aminophenol)



o-Toluidine



p-Toluidine



- **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

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

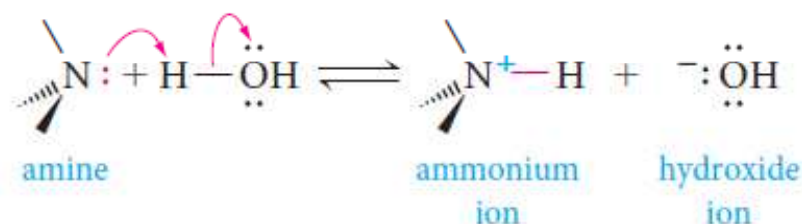
Their boiling points are Lower than primary and secondary amines of identical molecular weights and Higher than those of alkanes of similar molecular weight.

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

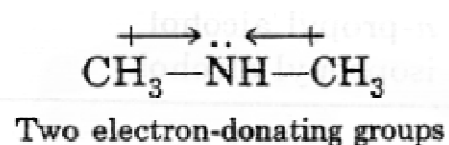
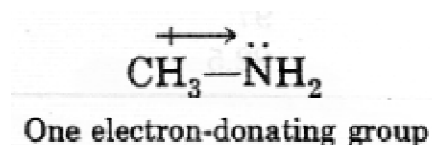
The Basicity of Amines

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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:



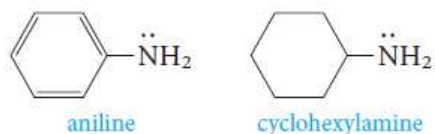
- Electron-donating groups increase the basicity of amines.
- Electron-withdrawing groups decrease their basicity.



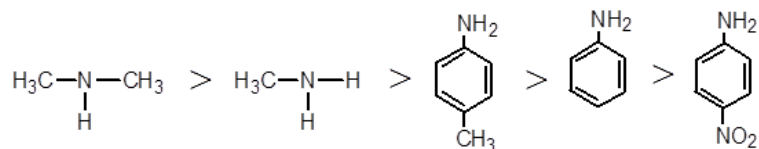
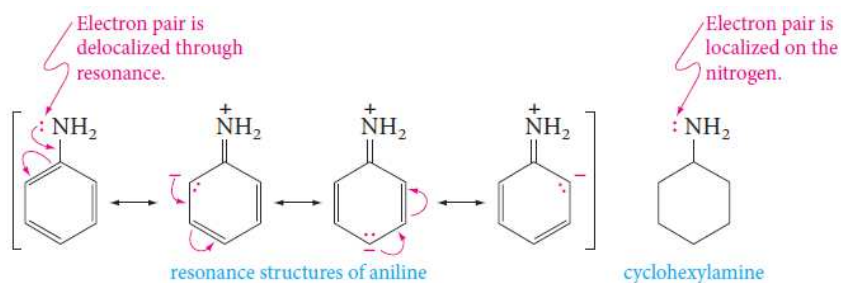
The Basicity of Amines

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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:

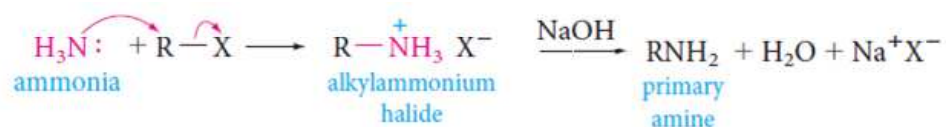


Preparation of Amines

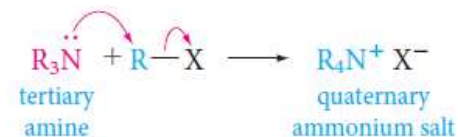
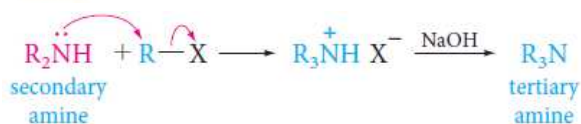
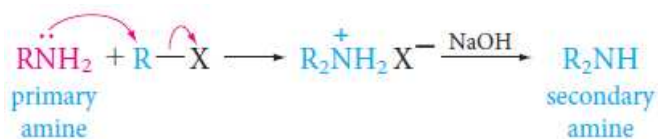
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1) Alkylation of Ammonia

- **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*



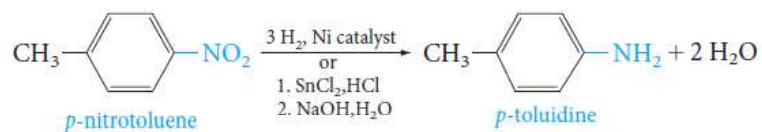
- **Primary, secondary, and tertiary amines** can be similarly alkylated.



Preparation of Amines

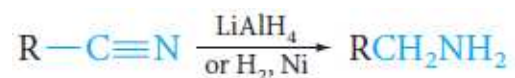
2) Reduction of Nitro Groups

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



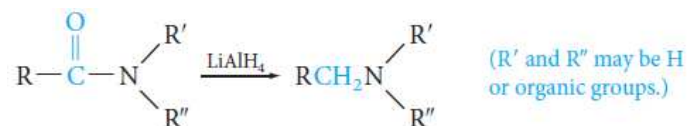
3) Reduction of Nitriles

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



4) Reduction of Amides

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

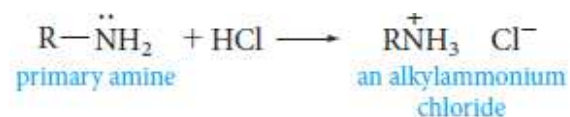


Reactions of Amines



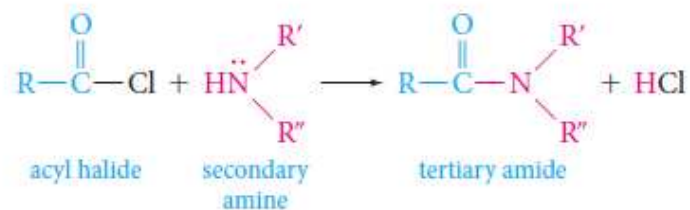
1) Reactions with Acids: Salt Formation

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



2) Acylation of Amines: Amides Formation

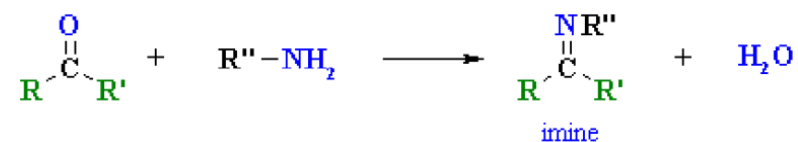
Primary and secondary amines react with acyl halides to form amides.



Reactions of Amines

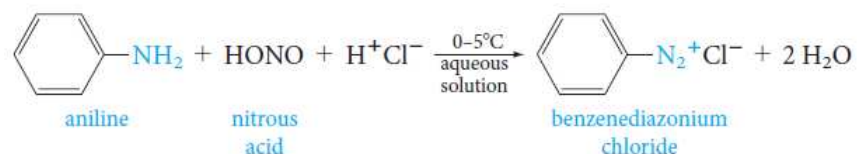
3) Imines Formation

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 aryldiazonium ions. The process is called **diazotization**.



Reactions of Amines

5) Aromatic Diazonium Salts

- They are useful in synthesis because the diazonio group ($-\text{N}_2^+$) can be **replaced by nucleophiles**; the other product is nitrogen gas.

