

# Fundamentals of Organic Chemistry

## CHEM 109

*For Students of Health Colleges*

Credit hrs.: (2+1)

*King Saud University*

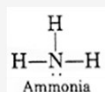
College of Science, Chemistry Department

### CHAPTER 8: Amines

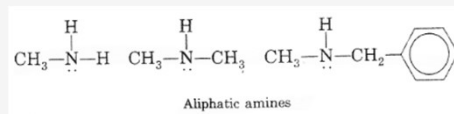
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## Structure and Classification of Amines

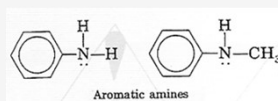
- **Amines** are compounds that derived from **ammonia** by replacement of one, two, or three hydrogens by alkyl or aryl groups.



- **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.



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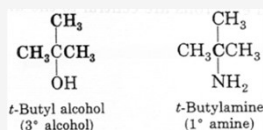
## Classification and Structure of Amines

- 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:**



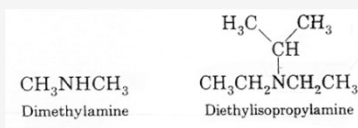
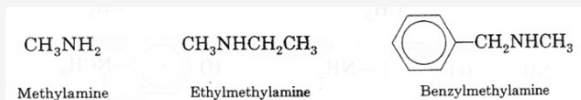
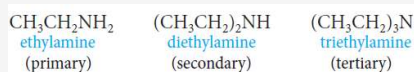
- *t*-butyl alcohol is a **tertiary alcohol** (because three carbons are attached to the carbinol carbon).
- *t*-butyl amine is a **primary amine** (because only one carbon is attached directly to the nitrogen atom).

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## Nomenclature of Amines

### Common Names

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

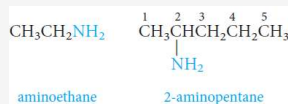


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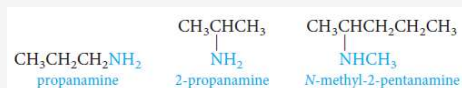
## Nomenclature of Amines

### IUPAC System

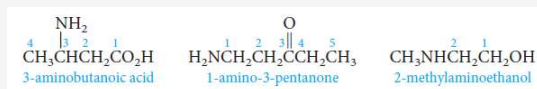
- The amino group,  $\text{-NH}_2$ , is named **as a substituent**.



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



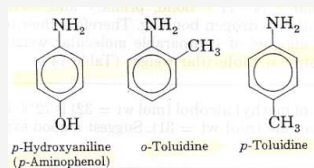
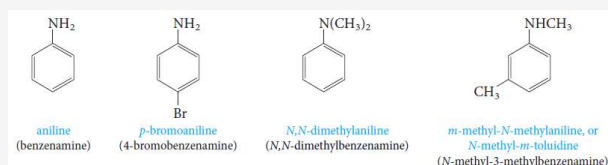
- When **other functional groups** are present, the amino group,  $\text{-NH}_2$ , is named as a substituent.



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## Nomenclature of Amines

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



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## 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 <sub>3</sub> CH <sub>3</sub> (30) bp -88.6°C	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> (44) bp -42.1°C
amine	CH <sub>3</sub> NH <sub>2</sub> (31) bp -6.3°C	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> (45) bp +16.6°C
alcohol	CH <sub>3</sub> OH (32) bp +65.0°C	CH <sub>3</sub> CH <sub>2</sub> 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.*

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## Physical Properties of Amines

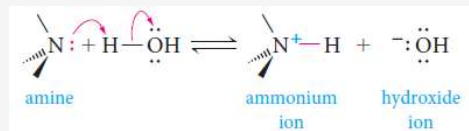
### Solubility in Water

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

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## The Basicity of Amines

- 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:



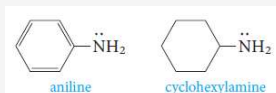
- Electron-donating groups increase the basicity of amines.
- Electron-withdrawing groups decrease their basicity.



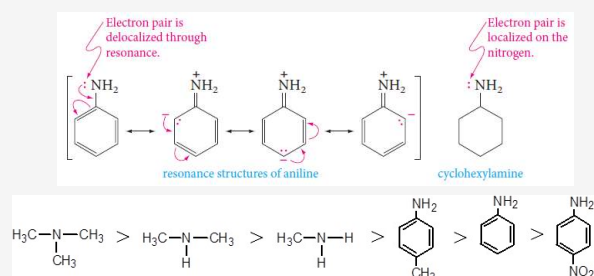
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## The Basicity of Amines

- 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:

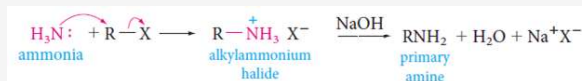


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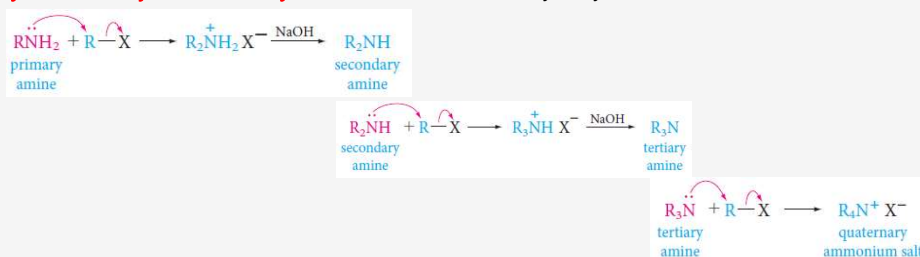
## Preparation of Amines

### 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.

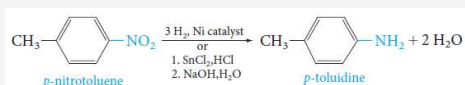


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## Preparation of Amines

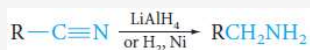
### 2) Reduction of Nitro Groups

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



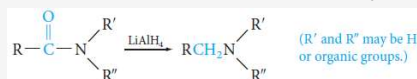
### 3) Reduction of Nitriles

- Reduction of nitriles (cyanides) gives primary amines.



### 4) Reduction of Amides

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

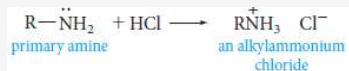


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## Reactions of Amines

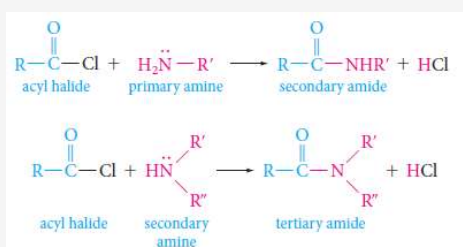
### 1) Reactions with Acids: Salt Formation

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.

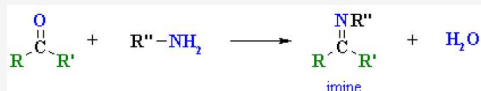


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## Reactions of Amines

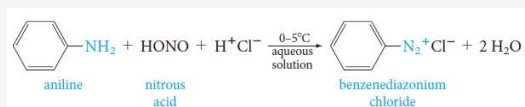
### 3) Imines Formation

**Primary amines, R-NH<sub>2</sub> or ArNH<sub>2</sub>**, 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**.

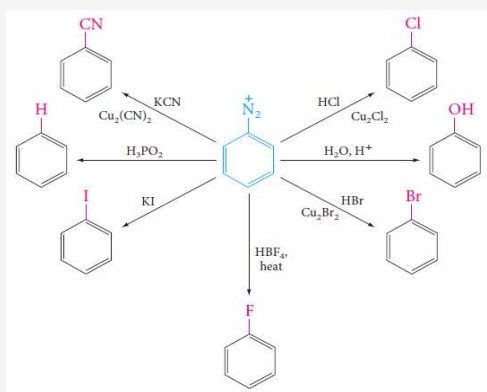


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## Reactions of Amines

### 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.



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