

Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

College of Science, Chemistry Department

Learning Objectives



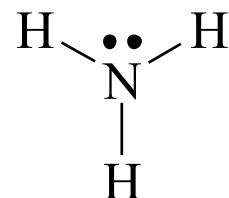
At the end of this chapter, students will able to:

- Recognize and name amines.
- Predict the reactivity of amines as bases and nucleophiles
- Recognize the basic properties (structure, physical and chemical properties) of amines.
- know the different methods for the preparation of amines.
- Know the chemical reactions of amines.

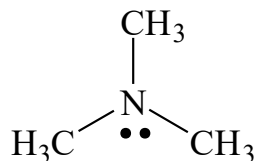
Structure and Classification of Amines



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



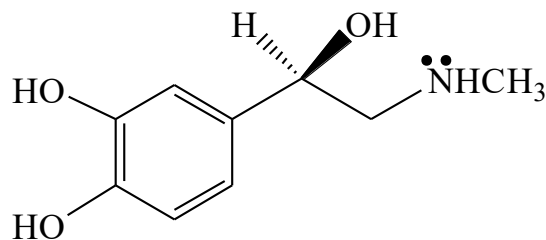
Ammonia



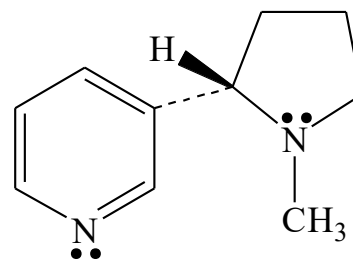
Trimethyl amine

Nitrogen atom with a lone pair of electrons, making amines both basic and nucleophilic

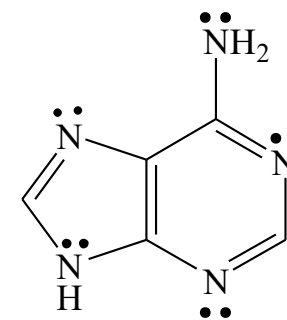
- **Amines** occur naturally in plants and animals.



Adrenaline
(Epinephrine)

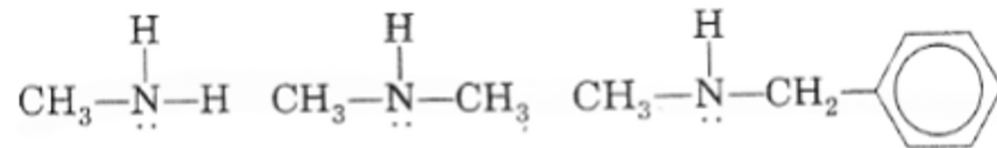


Nicotine



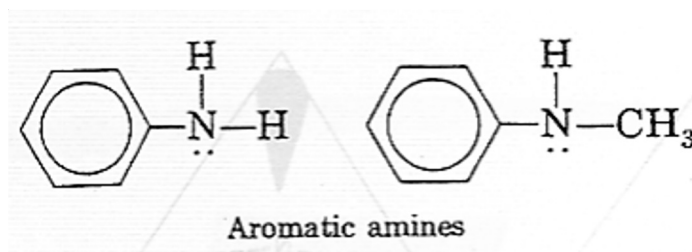
Adenine
(Vitamin B4)

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



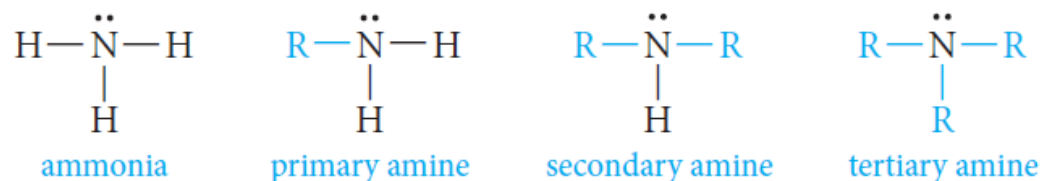
Aliphatic amines

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



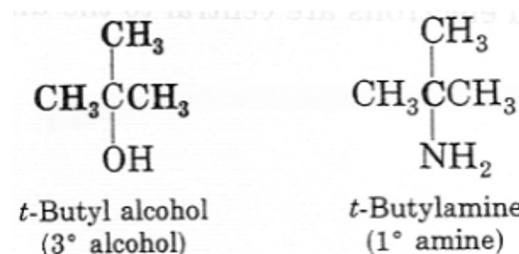
Aromatic amines

- 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.

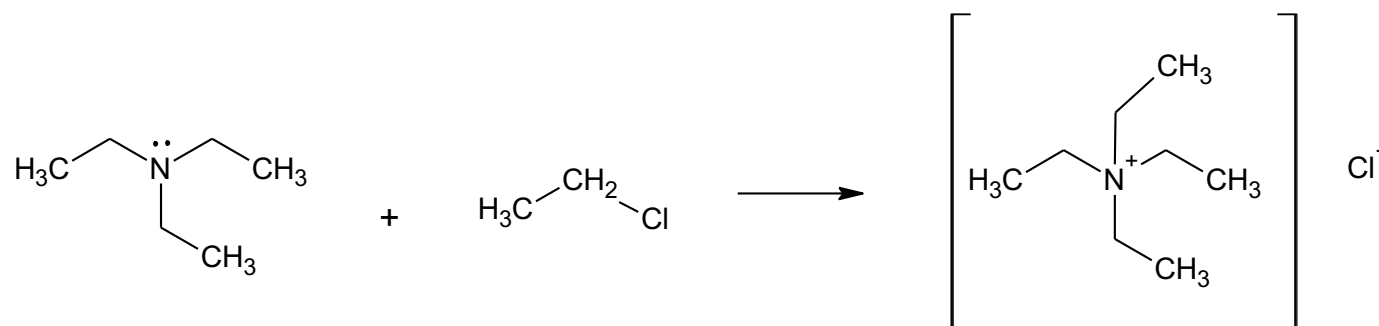
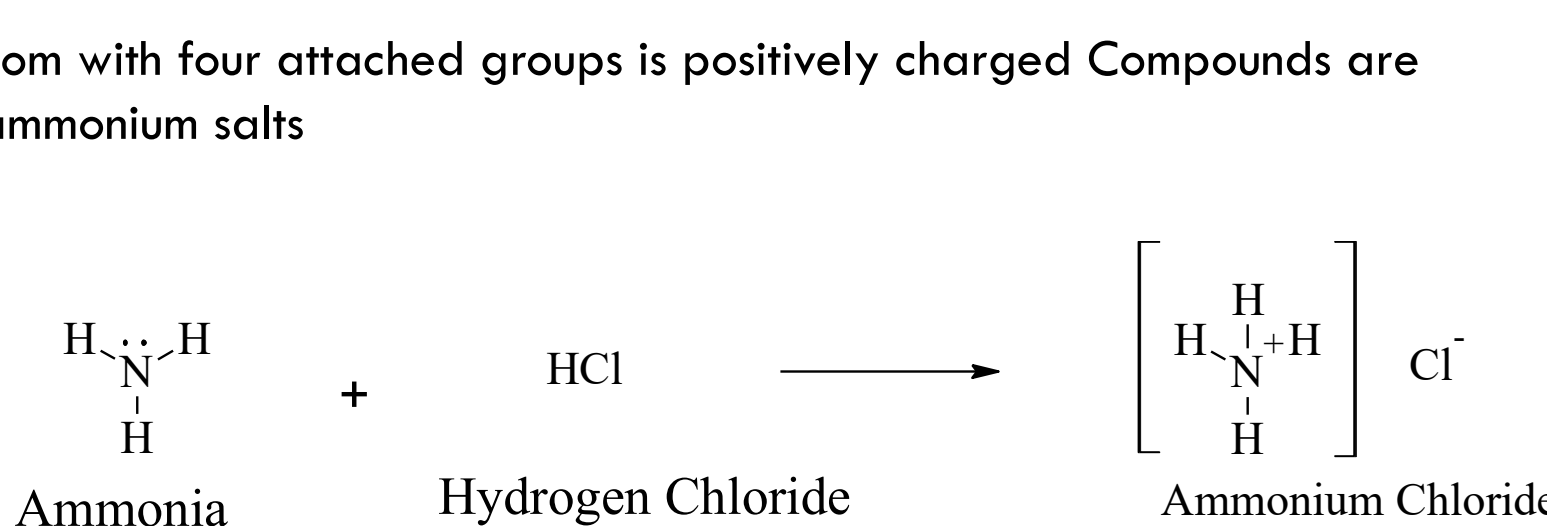
- NOTE:**



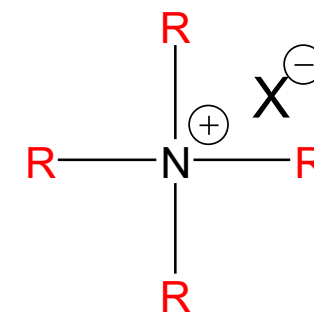
- t-butyl alcohol** is a **tertiary alcohol** (because three carbons are attached to the carbinol carbon).
- t-butyl amine** is a **primary amine** (because only one carbon is attached directly to the nitrogen atom).

○ Quaternary Ammonium Ions:

A nitrogen atom with four attached groups is positively charged. Compounds are quaternary ammonium salts



Tetraethyl Ammonium Chloride

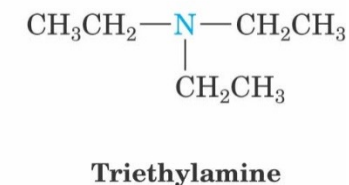
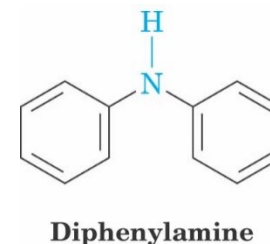
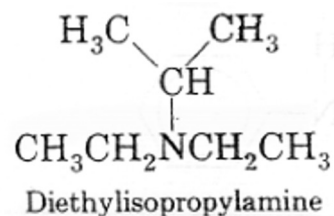
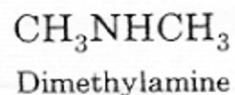
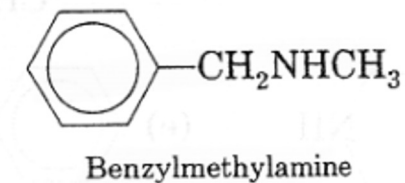
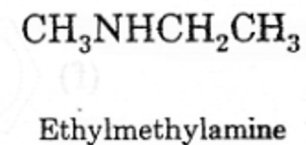
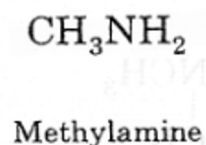
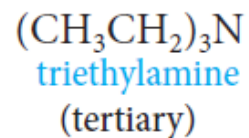
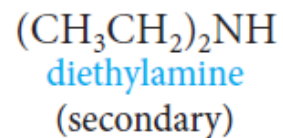
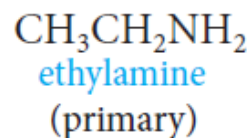


Nomenclature of Amines

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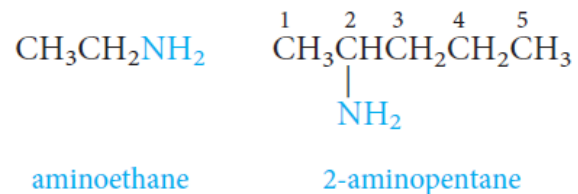
Common Names

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

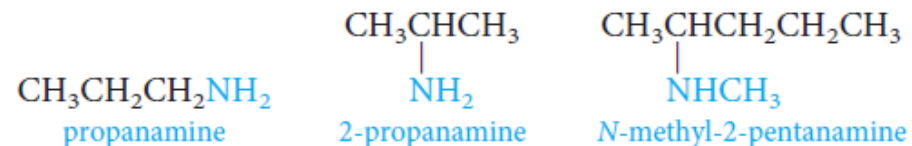


IUPAC Names

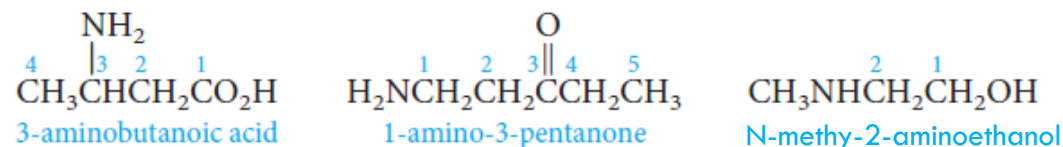
- The amino group, -NH_2 , is named **as a substituent**.



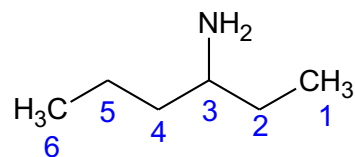
- Amines can be named as **alkanamines**.



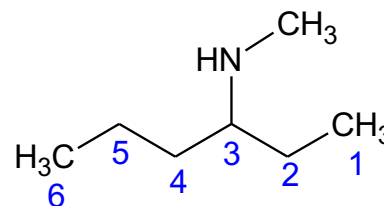
- When **other functional groups** are present, the amino group, -NH_2 , is named as a substituent.



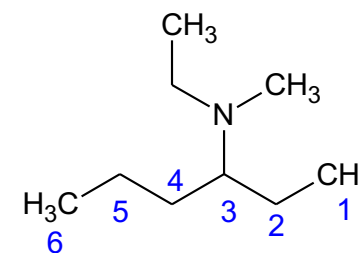
- When different alkyl groups are attached to the nitrogen; they are named in alphabetical order



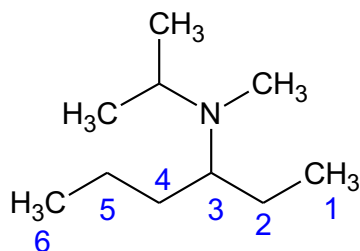
3-Hexanamine



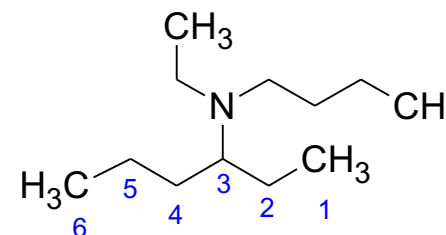
N-Methyl-3-hexanamine



N-Ethyl-*N*-methyl-3-hexanamine



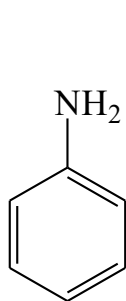
N-Isopropyl-*N*-methyl-3-hexanamine



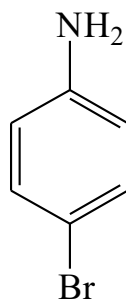
N-butyl-*N*-ethyl-3-hexanamine

○ **Aromatic amines** are named as derivatives of aniline.

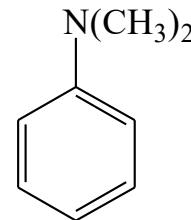
- Aniline is called benzenamine.



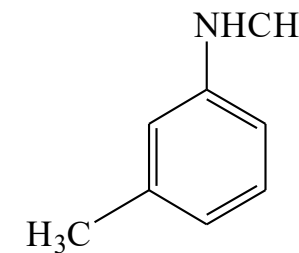
Aniline
(Benzenamine)



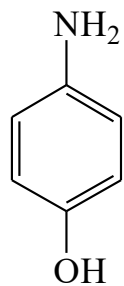
p-Bromoaniline
(4-Bromobenzenamine)



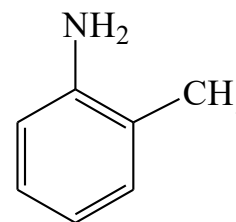
N,N-Dimethylaniline
(4-Dimethylbenzenamine)



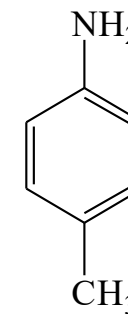
m-Methyl-*N*-methylaniline
OR: *N*-Methyl-*m*-toluidine
(*N*-methyl-3-methylbenzenamine)



p-Aminophenol
p-Hydroxyaniline
(4-Aminophenol)



o-Toluidine

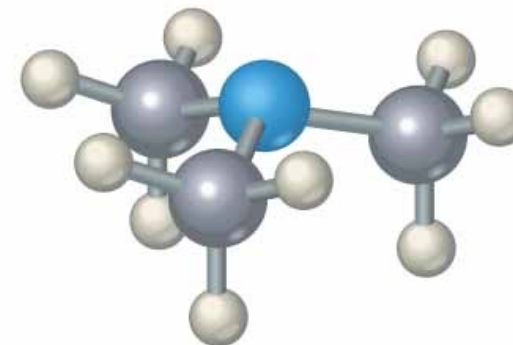
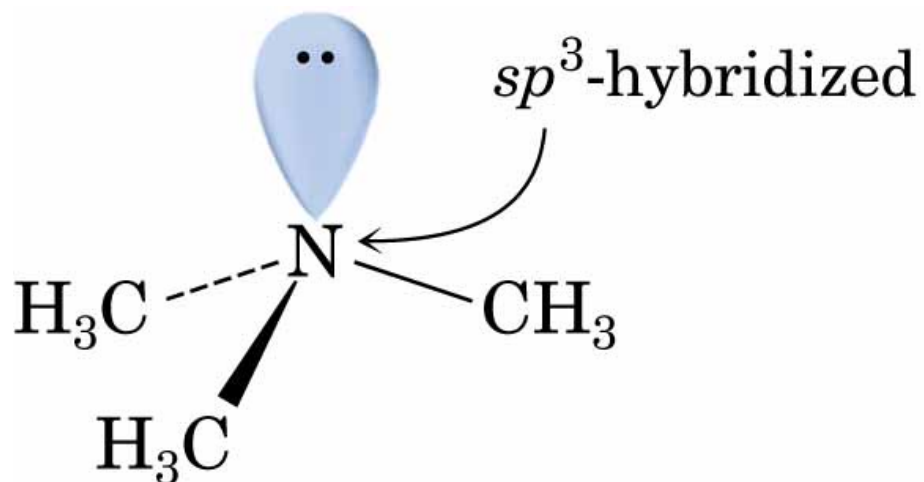


p-Toluidine

Structure and Bonding in Amines



Bonding to N is similar to that in ammonia: N is sp^3 -hybridized C–N–C bond angles are close to 109° tetrahedral value



Trimethylamine

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.

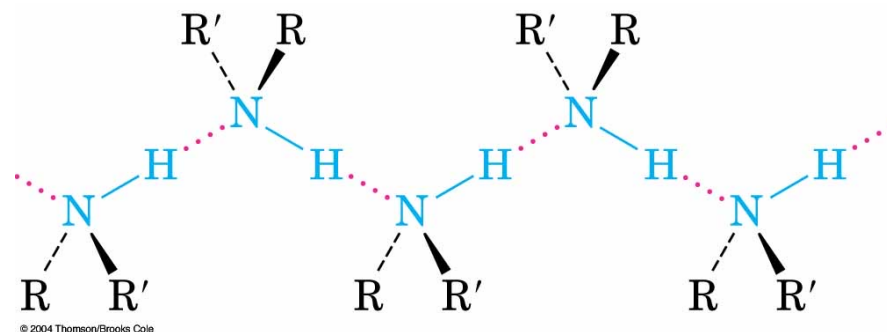
alkane	CH ₃ CH ₃ (30) bp -88.6°C	CH ₃ CH ₂ CH ₃ (44) bp -42.1°C
amine	CH ₃ NH ₂ (31) bp -6.3°C	CH ₃ CH ₂ NH ₂ (45) bp +16.6°C
alcohol	CH ₃ OH (32) bp +65.0°C	CH ₃ CH ₂ OH (46) bp +78.5°C

- **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

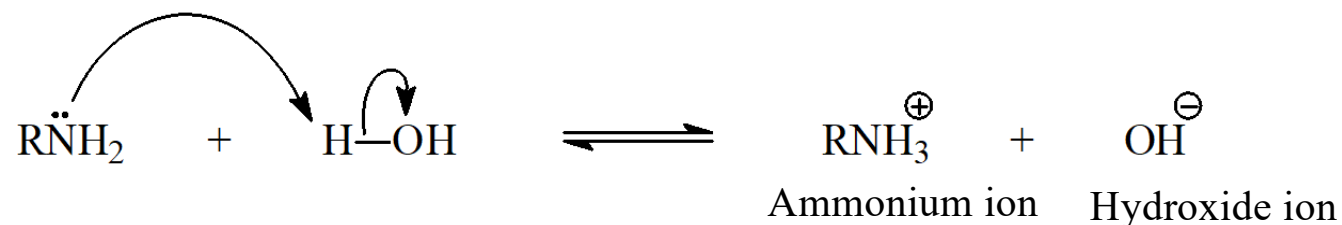
- **All three classes of amines** can form hydrogen bonds with the -OH group of water (that is, $\text{O}-\text{H} \cdots \text{N}$).
- **Primary and secondary amines** can also form hydrogen bonds with the oxygen atom in water: $\text{N}-\text{H} \cdots \text{O}$.
- **Amines** with up to six carbons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



- The most convenient way to measure the basicity of an amine (RNH₂) is to look at the acidity of the corresponding ammonium ion (RNH₃⁺)

$$K_b = \frac{[\text{RNH}_3^{\oplus}][\text{OH}^{\ominus}]}{[\text{RNH}_2]} \qquad \text{p}K_b = -\log K_b$$

- Typical amines have K_b values = 10^{-3} to 10^{-4}

	K_b
Aliphatic amines	$10^{-3} - 10^{-4}$
Ammonia	1.8×10^{-5}
Aniline	10^{-9} or less

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

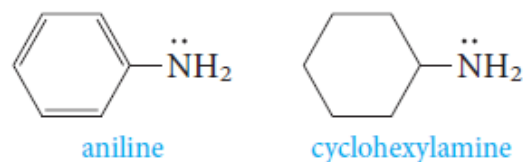


- Amines are stronger bases than alcohols, ethers, or water

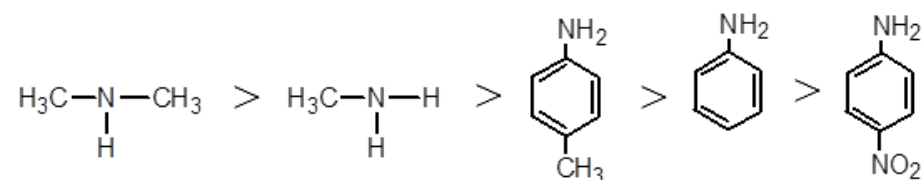
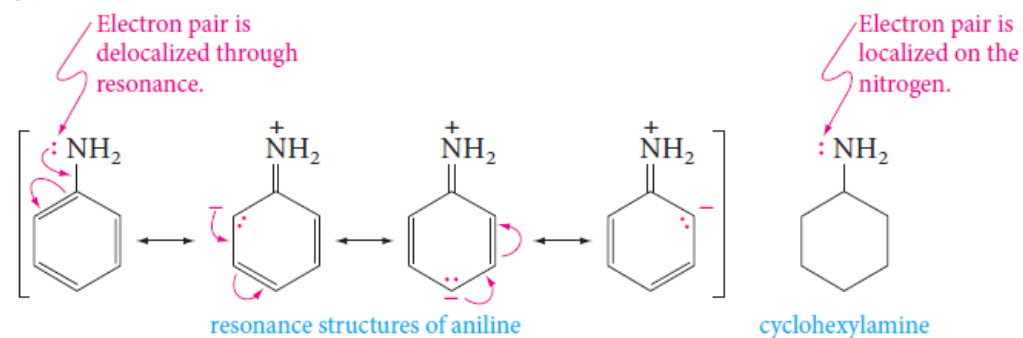
	Structure	Basicity	Acidity of conjugate acid
compound		pK_b	pK_a
Ammonia	NH_3	4.7	9.3
Primary Amines			
Methylamine	CH_3NH_2	3.4	10.6
Ethylamine	$CH_3CH_2NH_2$	3.2	10.8
Isopropylamine	$(CH_3)_2CHNH_2$	3.4	10.6
tert-Butylamine	$(CH_3)_3CNH_2$	3.6	10.4
Aniline	$C_6H_5NH_2$	9.4	4.6
Secondary amines			
Dimethylamine	$(CH_3)_2NH$	3.3	10.7
Diethylamine	$(CH_3CH_2)_2NH$	2.9	11.1
N-Methylaniline	$C_6H_5NHCH_3$	9.2	4.8
Tertiary amines			
Trimethylamine	$(CH_3)_3N$	4.3	9.7
Triethylamine	$(CH_3CH_2)_3N$	3.2	10.8
N,N-Dimethylaniline	$C_6H_5N(CH_3)_2$	8.9	5.1

○ **Aromatic amines are much weaker than aliphatic amines or ammonia.**

▪ **Example:** aniline is less basic than cyclohexylamine.



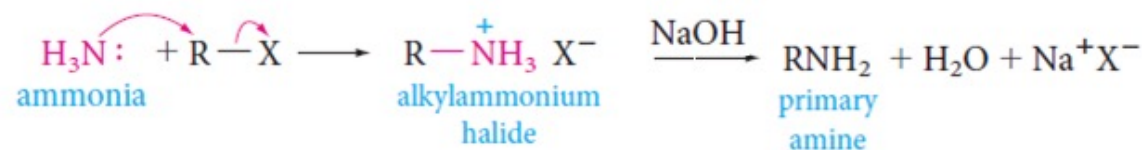
The reason is the resonance delocalization of the unshared electron pair that is possible in aniline, but not in cyclohexylamine:



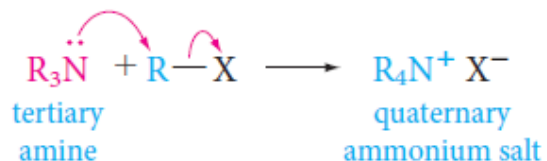
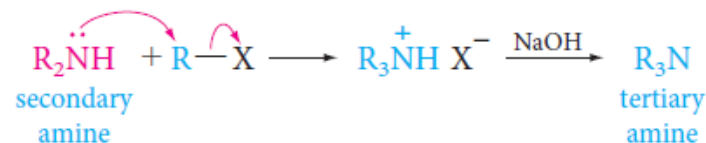
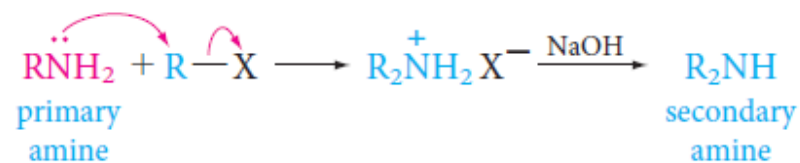
Preparation of Amines

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*

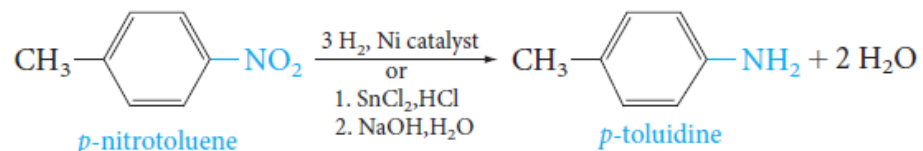


- **Primary, secondary, and tertiary amines** can be similarly alkylated.



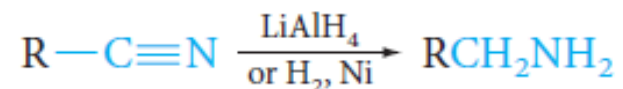
2) Reduction of Nitro Groups

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



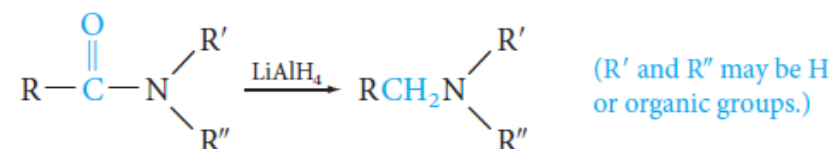
3) Reduction of Nitriles

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



4) Reduction of Amides

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

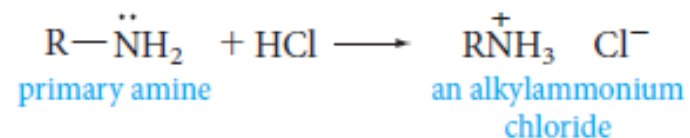


Reactions of Amines

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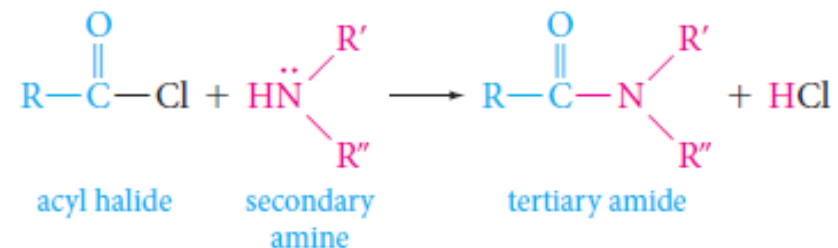
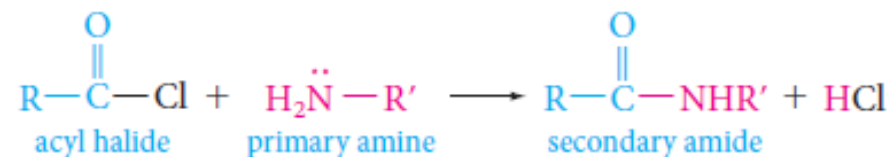
1) Reactions with Acids: Salt Formation

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



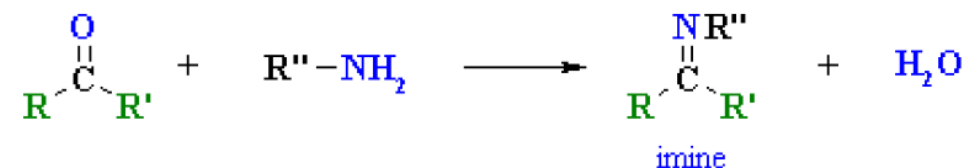
2) Acylation of Amines: Amides Formation

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



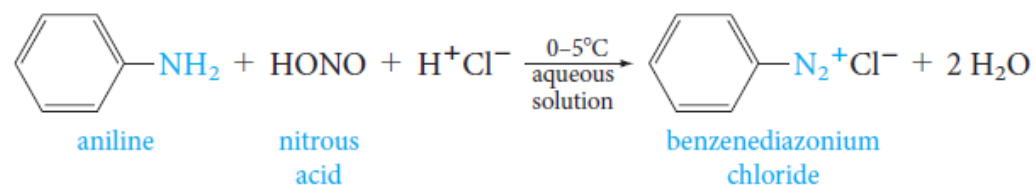
3) Imines Formation

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

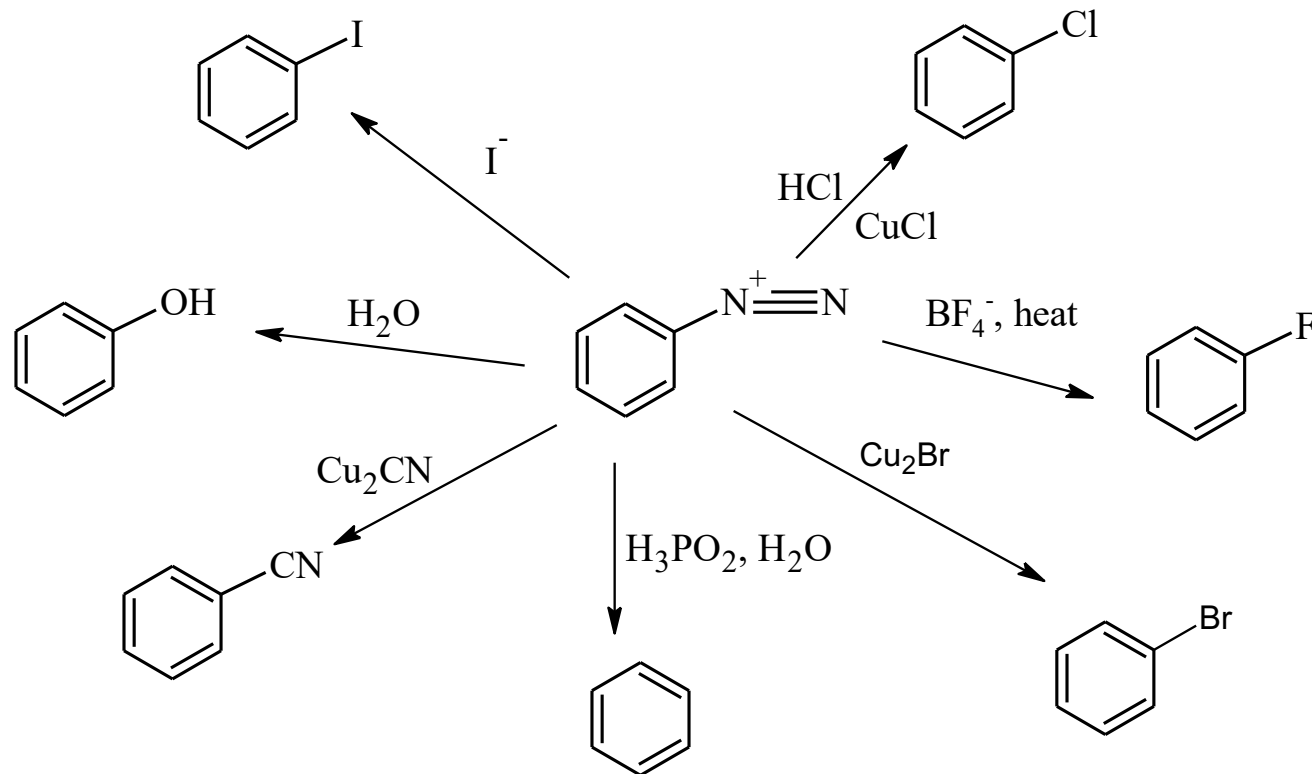


4) Aromatic Diazonium Salts

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



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



Uses of Amines

- **Amines** are largely used in pharmaceutical industry.
- **Morphine** and **Demerol** are used as analgesics that are pain killers.
- **Novocaine** is used as anesthetic and Ephedra is a very common decongestant.
- We use **tetramethyl ammonium iodide** for disinfecting drinking water.
- They find large applications in man-made dyes.