



# 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



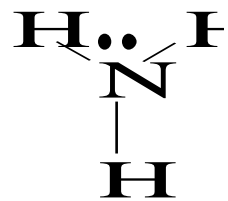
## At the end of this chapter, students will able to:

- 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.

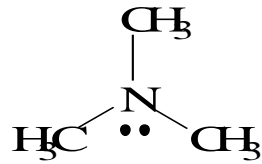
# Structure and Classification of Amines

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



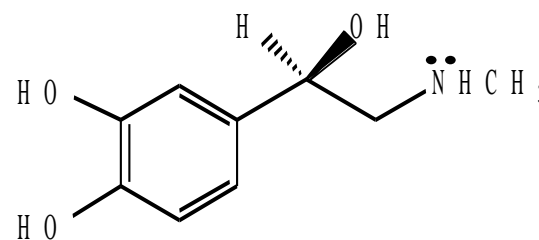
Ammonia



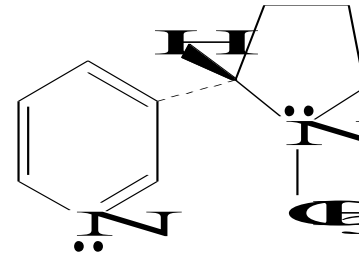
Trimethylamine

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

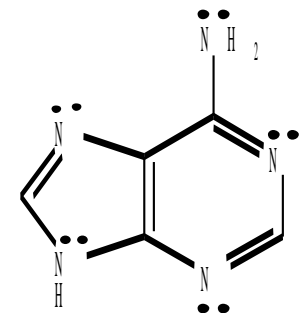
- **Amines** occur naturally in plants and animals.



Adrenaline  
(Epinephrine)



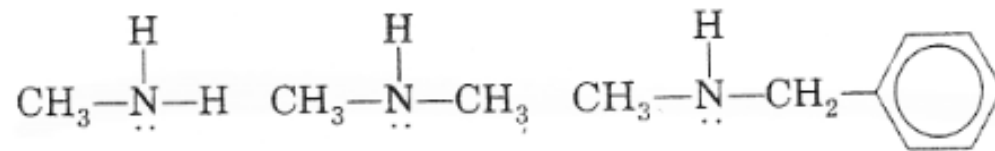
Histamine



Adenine  
(Vitamin B4)

# Structure and Classification of Amines

- **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.

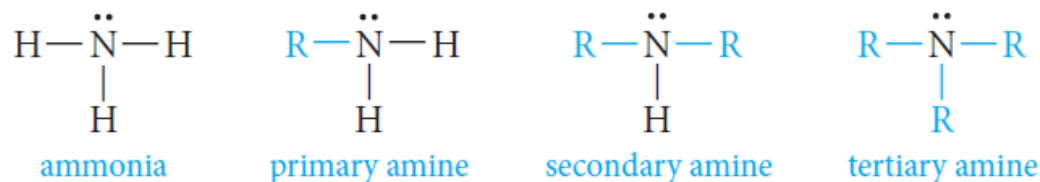


Aromatic amines

# Classification and Structure of Amines

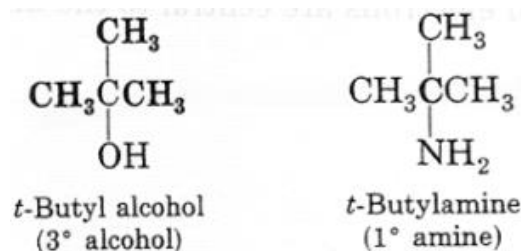
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- The relation between **ammonia and amines** is illustrated by the following structures:



- 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).

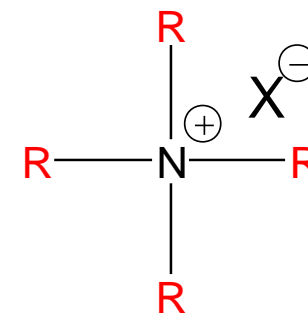
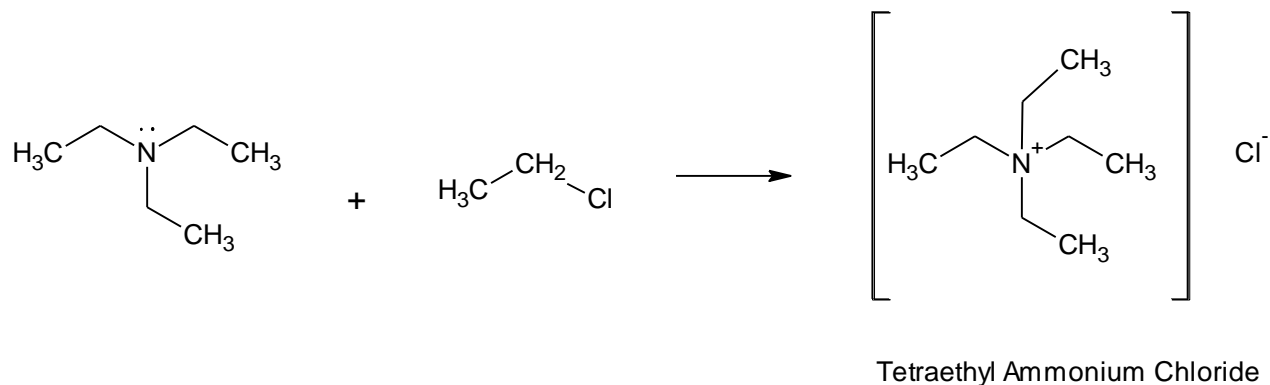
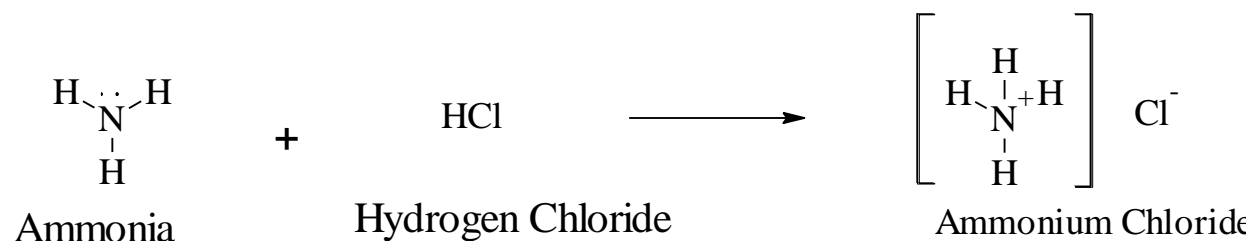
# Classification and Structure of Amines



## ○ Quaternary Ammonium Ions:

A nitrogen atom with four attached groups is positively charged

Compounds are quaternary ammonium salts

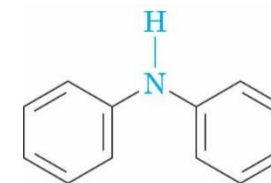
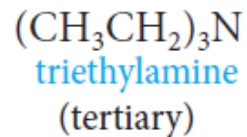
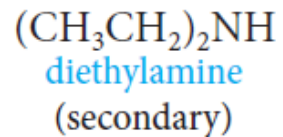
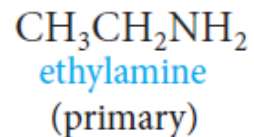


# Nomenclature of Amines

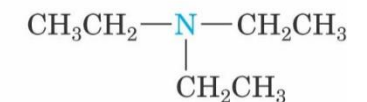
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## Common Names

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



Diphenylamine  
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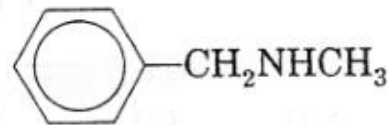
Triethylamine



Methylamine



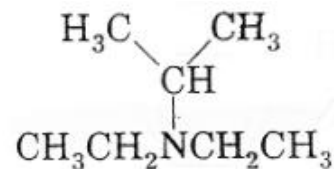
Ethylmethylamine



Benzylmethylamine

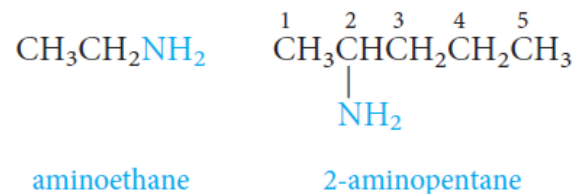


Dimethylamine

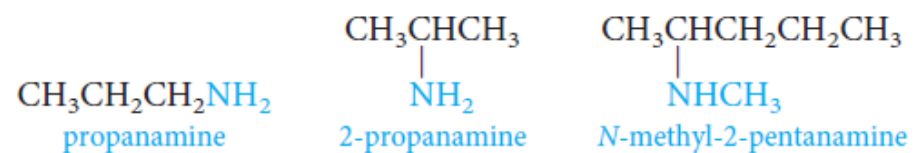


Diethylisopropylamine

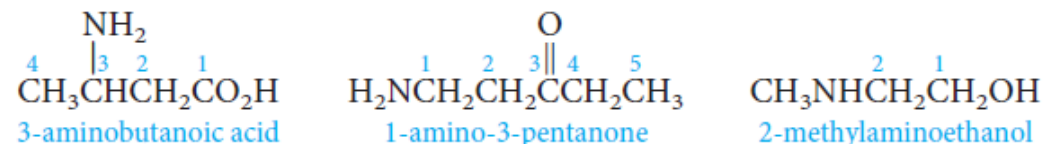
- The amino group,  $\text{-NH}_2$ , is named **as a substituent**.



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



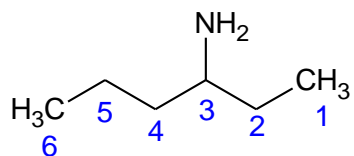
- When **other functional groups** are present, the amino group,  $\text{-NH}_2$ , is named as a substituent.



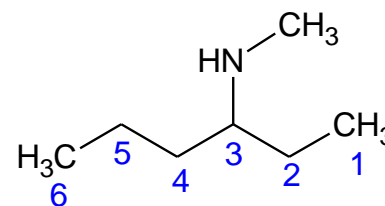




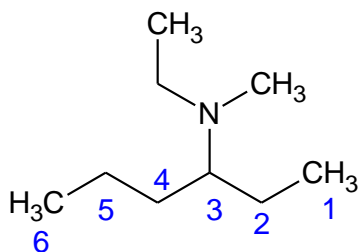
When different alkyl groups are attached to the nitrogen; they are named in alphabetical order



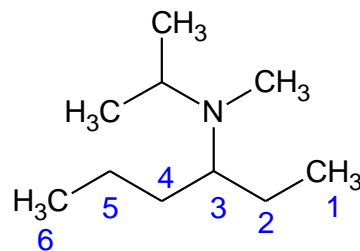
3-Hexanamine



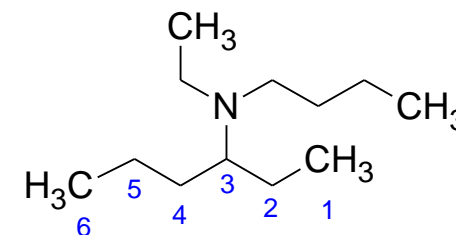
N-Methyl-3-hexanamine



N-Ethyl-N-methyl-3-hexanamine



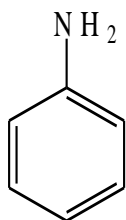
N-Ethyl-N-isopropyl-3-hexanamine



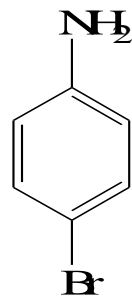
N-butyl-N-ethyl-3-hexanamine



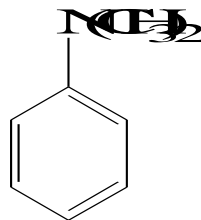
- **Aromatic amines** are named as derivatives of aniline.
- In the CA system, aniline is called benzenamine.



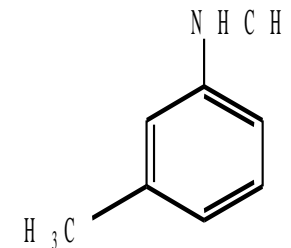
Aniline  
(Benzenamine)



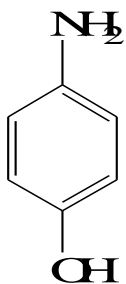
*p*-Bromaniline  
(4-Bromobenzenamine)



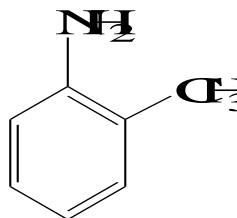
~~N,N-Dimethylaniline~~  
~~(4-Dimethylaniline)~~



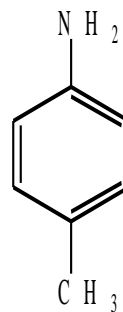
*m*-Methyl-N-methylaniline  
O R : N-Methyl-*m*-toluidine  
(N-methyl-3-methylbenzenamine)



*p*-Aminophenol  
*p*-Hydroxylaniline  
(4-Aminophenol)



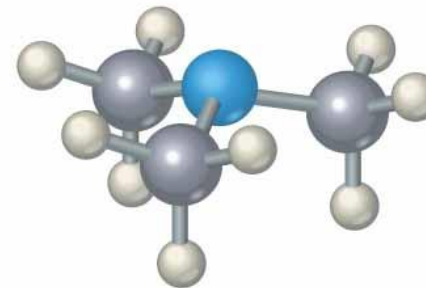
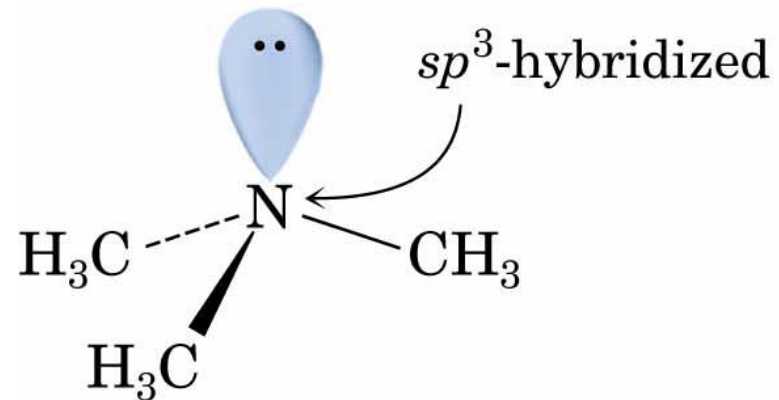
*o*-Toluidine



*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  $109^\circ$  tetrahedral value



**Trimethylamine**



- **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.*

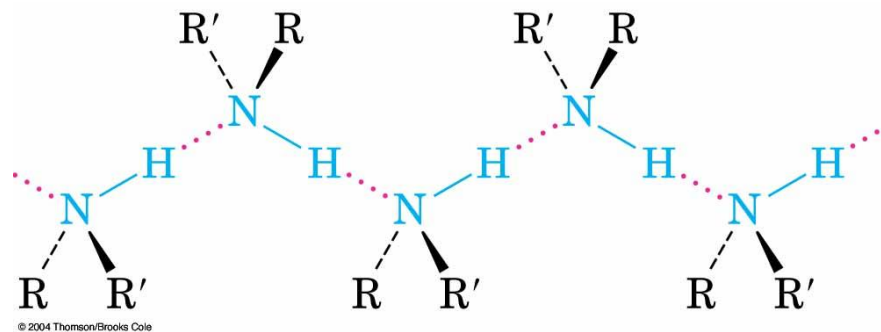
*The reason for this is that nitrogen is not as electronegative as oxygen.*

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.*

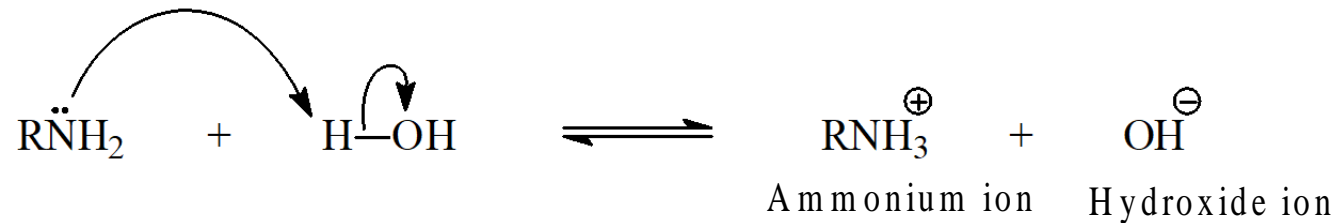
- **All three classes of amines** can form hydrogen bonds with the -OH group of water (that is, O-H ··· N).
- **Primary and secondary amines** can also form hydrogen bonds with the oxygen atom in water: N-H ··· O.
- **Amines** with up to six carbons show appreciable solubility in water.



# 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 (RNH<sub>2</sub>) is to look at the acidity of the corresponding ammonium ion (RNH<sub>3</sub><sup>+</sup>)

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

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

# The Basicity of Amines



	$K_b$
Aliphatic amines	$10^{-3} - 10^{-4}$
Ammonia	$1.8 \times 10^{-5}$
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

# The Basicity of Amines



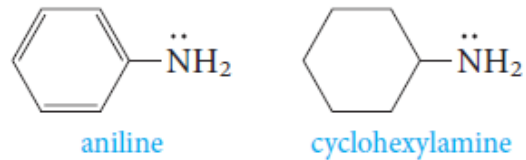
	Structure	Basicity	Acidity of conjugate acid
compound		$pK_b$	$pK_a$
Ammonia	$NH_3$	4.7	9.3
<b>Primary Amines</b>			
Methylamine	$CH_3NH_2$	3.4	10.6
Ethylamine	$CH_3CH_2NH_2$	3.2	10.8
Isopropylamine	$(CH_3)_2CHNH_2$	3.4	10.6
tert-Butylamine	$(CH_3)_3CNH_2$	3.6	10.4
Aniline	$C_6H_5NH_2$	9.4	4.6
<b>Secondary amines</b>			
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
<b>Tertiary amines</b>			
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



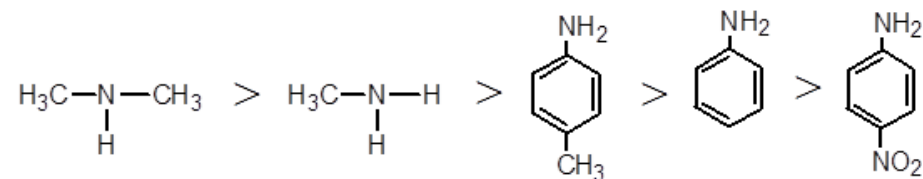
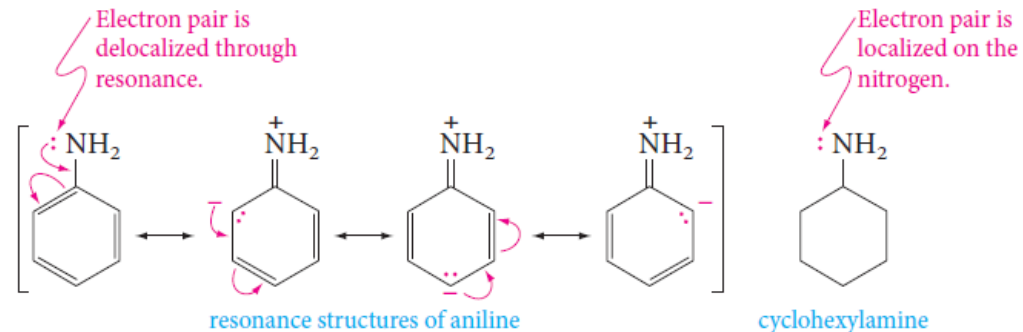
# The Basicity of Amines

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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:

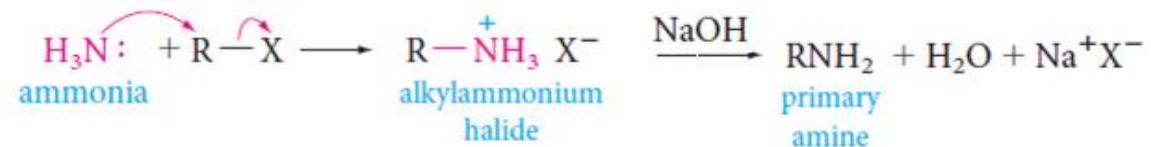


# Preparation of Amines

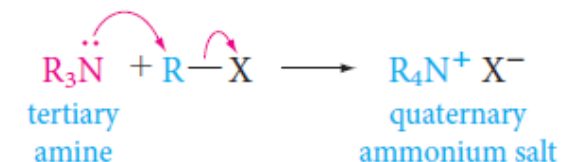
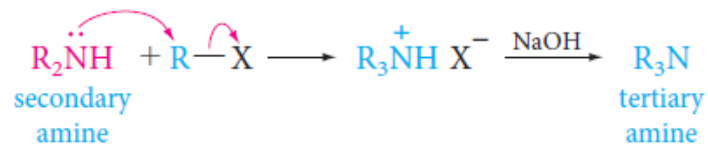
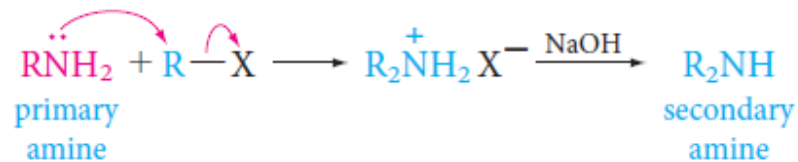
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## 1) Alkylation of Ammonia

- **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.

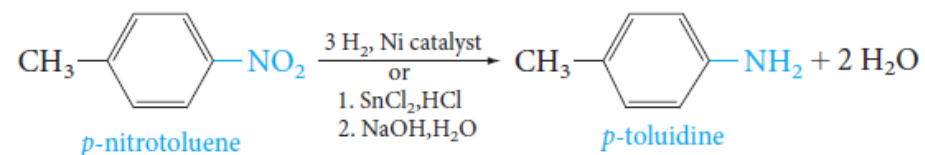


# Preparation of Amines

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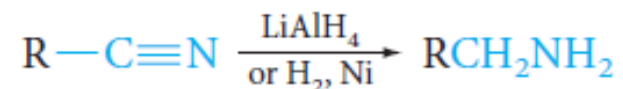
## 2) Reduction of Nitro Groups

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



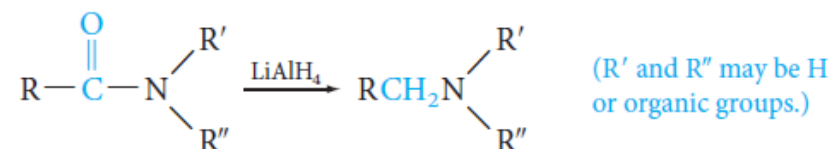
## 3) Reduction of Nitriles

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



## 4) Reduction of Amides

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

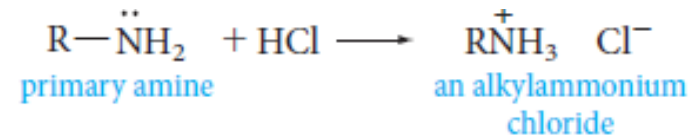


# Reactions of Amines

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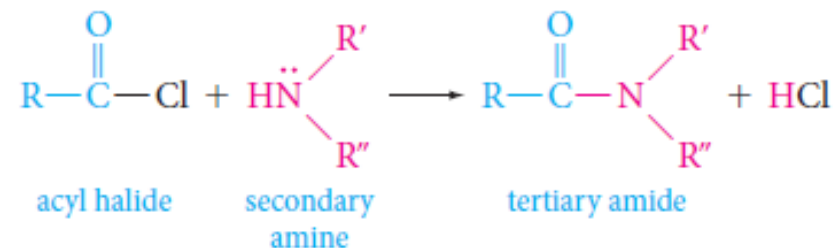
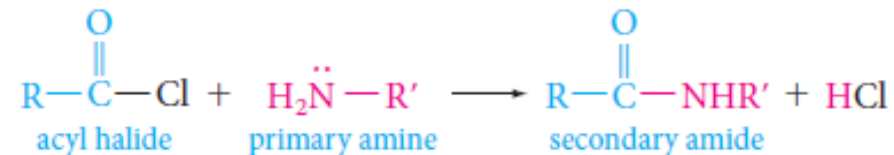
## 1) Reactions with Acids: Salt Formation

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.

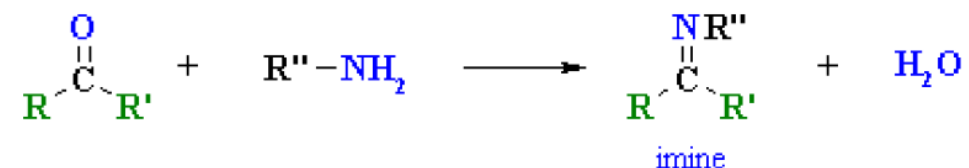


# Reactions of Amines

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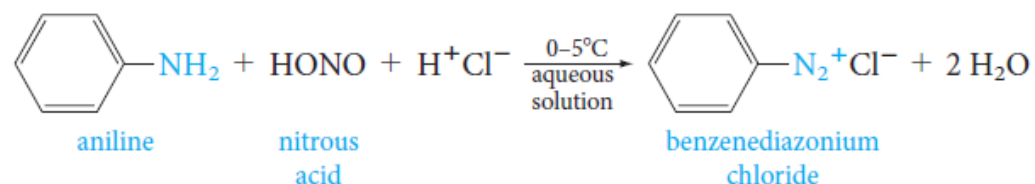
## 3) Imines Formation

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

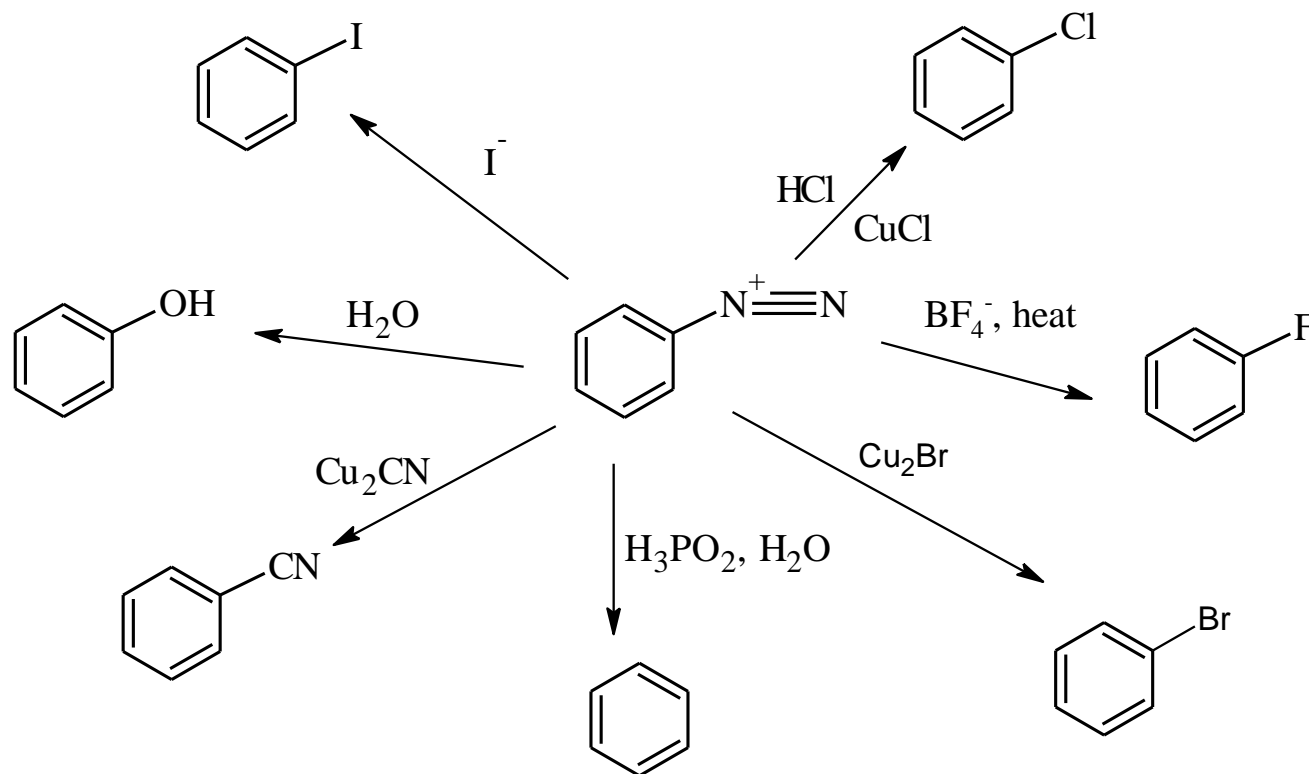
- Primary aromatic amines react with nitrous acid at  $0^\circ\text{C}$  to yield aryldiazonium ions. The process is called **diazotization**.



# 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.



# 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.