CHEM 108

FUNDAMENTALS OF ORGANIC CHEMISTRY

FOR B.Sc. PROGRAMS OF SCIENTIFIC COLLEGES

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 4 (3+1)

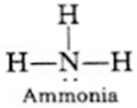
Chemistry Department, College of Science, King Saud University

CHAPTER 8

AMINES

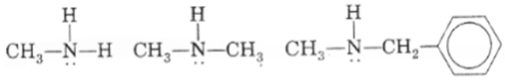
Structure and Classification of Amines

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



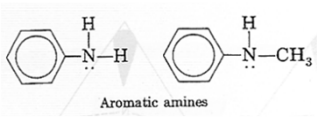
Ammonia

- 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

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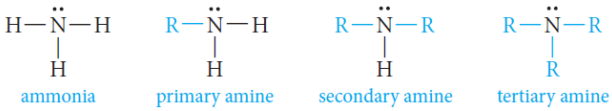
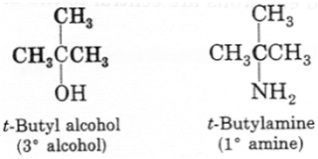
Classification and Structure of Amines

- 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).

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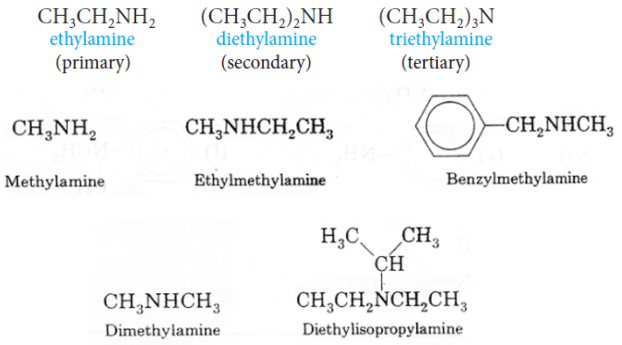
Nomenclature of Amines

Common Names

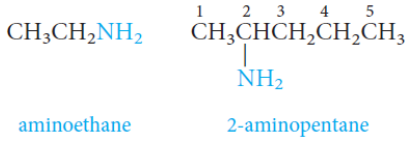
- Amines are named by specifying the alkyl groups attached to the nitrogen and adding the suffix *–amine (Alkylamine)*.



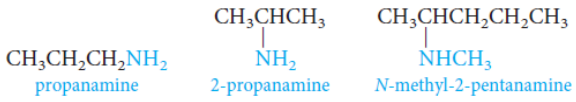
Nomenclature of Amines

IUPAC System

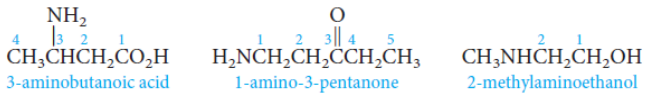
- The amino group, -NH_2, is named as a substituent.



- Amines can be named as alkanamines.



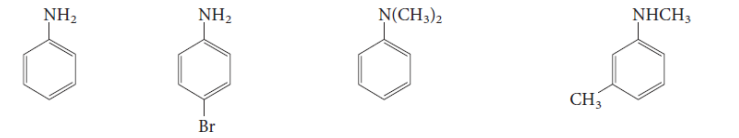
- When other functional groups are present, the amino group, -NH_2, is named as a substituent.



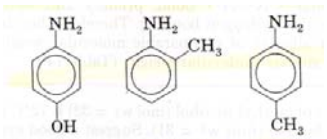
Nomenclature of Amines

IUPAC System

- 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

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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_3CH_3 (30) bp −88.6°C	$CH_3CH_2CH_3$ (44) bp −42.1°C
amine	CH_3NH_2 (31) bp −6.3°C	$CH_3CH_2NH_2$ (45) bp +16.6°C
alcohol	CH_3OH (32) bp +65.0°C	CH_3CH_2OH (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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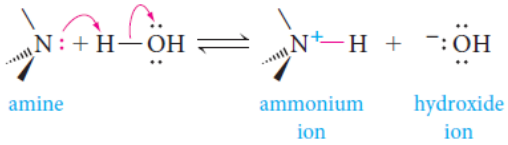
Physical Properties of Amines

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.

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:



amine — ammonium ion — hydroxide ion

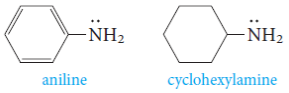
- Electron-donating groups increase the basicity of amines.
- Electron-withdrawing groups decrease their basicity.

One electron-donating group — Two electron-donating groups

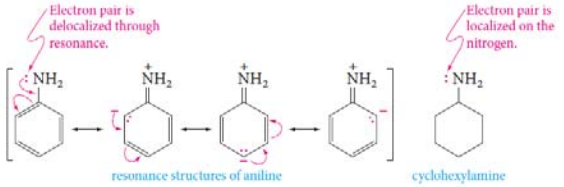
The Basicity of Amines

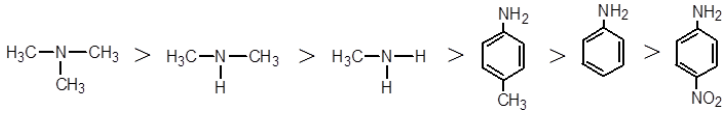
- Aromatic amines are much weaker than aliphatic amines or ammonia.

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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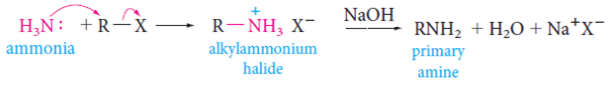
Preparation of Amines

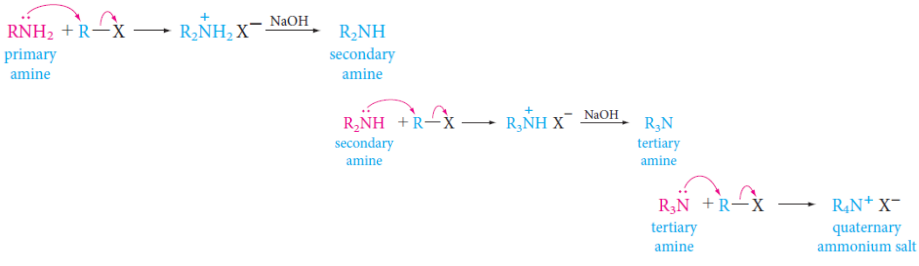
1) Alkylation of Ammonia

- 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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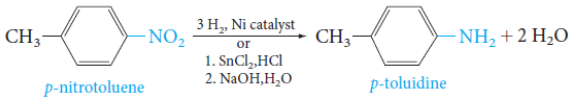
Preparation of Amines

2) Reduction of Nitro Groups

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

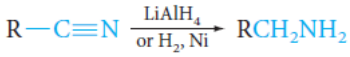
The nitro group is easily reduced, either catalytically with hydrogen or by chemical reducing agents.



p-nitrotoluene — *p*-toluidine

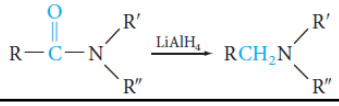
3) Reduction of Nitriles

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



4) Reduction of Amides

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

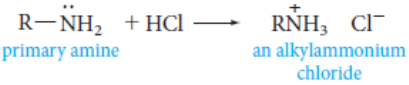


(R′ and R″ may be H or organic groups.)

Reactions of Amines

1) Reactions with Acids: Salt Formation

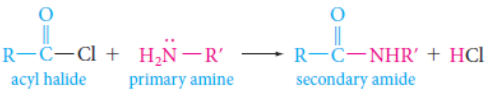
Amines react with strong acids to form alkylammonium salts.



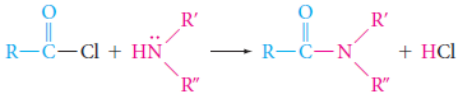
primary amine — an alkylammonium chloride

2) Acylation of Amines: Amides Formation

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



acyl halide — primary amine — secondary amide

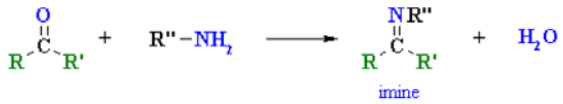


acyl halide — secondary amine — tertiary amide

Reactions of Amines

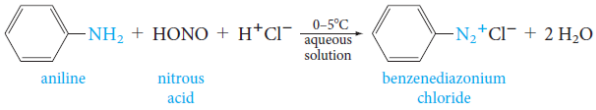
3) Imines Formation

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 amices react with nitrous acid at 0°C to yield aryldiazonium ions.
The process is called diazotization.



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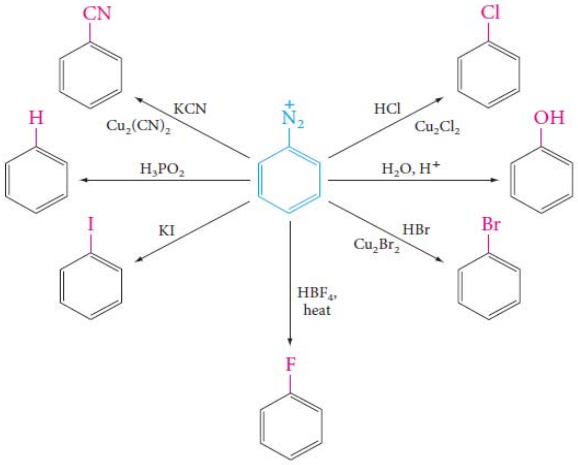
Reactions of Amines

4) Aromatic Diazonium Salts

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



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