241 Chem

CH-8

Amines

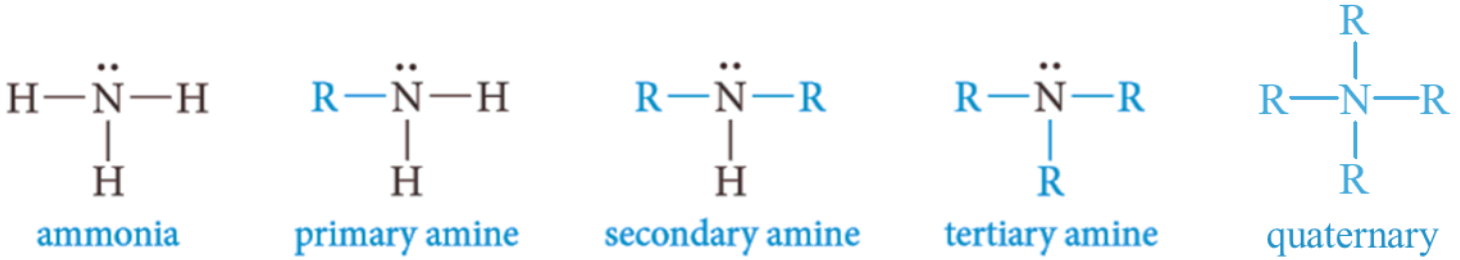
Learning Objectives

By the end of this chapter the student will know:

- Structure and Classification of amines
- Nomenclature of amines
- Physical Properties of amines
- Preparation of amines
- Reaction of amines

Structure and Classification of Amines

- Amines are organic derivatives of ammonia in which one or more hydrogens are replaced with alkyl or aryl groups.
- It has high degree of biological activity, many amines are used as drugs and medicines.
- Amines are classified as primary, secondary, or tertiary, depending on the number of carbon atoms bonded directly to nitrogen.
- In a heterocyclic amine, the nitrogen atom is part of an aliphatic or aromatic ring.



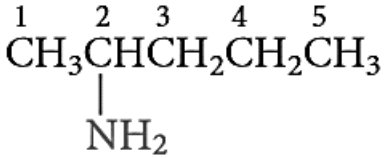
Nomenclature of Amines

- Common names are formed from the names of the alkyl groups bonded to nitrogen, followed by the suffix *-amine*.
- The prefixes *di-*, *tri-*, and *tetra-* are used to describe two, three, or four identical substituents.
- The IUPAC system, the *amino* group, $-NH_2$, is named as a substituent.
- In this system, secondary or tertiary amines are named by using a prefix that includes all but the longest carbon chain.
- Recently, Chemical Abstracts (CA) introduced a system for naming amines that is rational and easy to use. In this system, amines are named as *alkanamines*, the *-e* ending in the alkane name is changed to *-amine*, and a number shows the position of the amino group along the chain.
- Other substituents on the carbon chain are given numbers, and the prefix *N-* is used for each substituent on nitrogen.

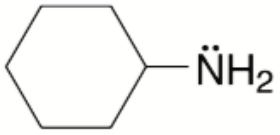
IUPAC name:

Common name:

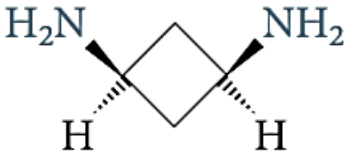
aminoethane
ethanamine
ethylamine



2-aminopentane
2-pentanamine
sec-butylamine

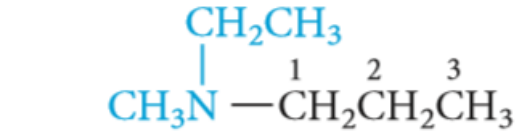


aminocyclohexane
cyclohexanamine
cyclohexylamine

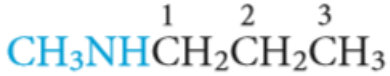


cis-1,3-diaminocyclobutane
cis-cyclobutane-1,3-diamine
1,3-cyclohexyldiamine

1-(ethylamino)ethane
N-ethylethanamine
diethylamine

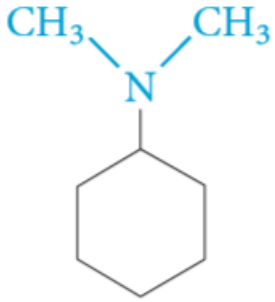


1-(ethylmethylamino)propane
N-ethyl-*N*-methyl-1-propanamine
Ethylmethylpropylamine

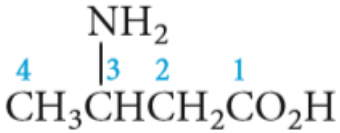


1-(methylamino)propane
N-methyl-1-propanamine
methylpropylamine

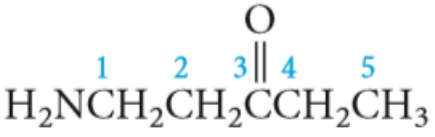
1-(diethylamino)ethane
N,N-diethylethanamine
triethylamine



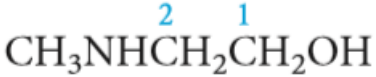
1-(dimethylamino)cyclohexane
N,N-dimethylcyclohexanamine
cyclohexyldimethylamine



3-aminobutanoic acid



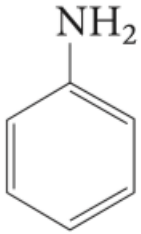
1-amino-3-pentanone



2-(methylamino)ethanol
2-(*N*-methylamino)ethanol

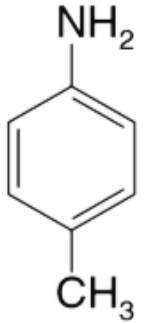
Nomenclature of Amines

- Aromatic amines are named as derivatives of aniline. In the CA system, aniline is called benzenamine; these CA names are shown in parentheses.

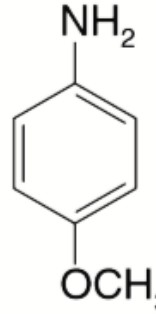


Aniline
benzenamine

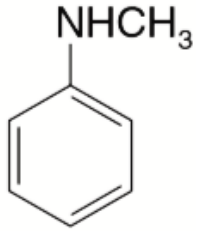
4-bromoaniline
p-bromoaniline



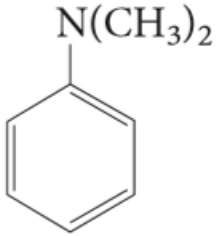
4-methylaniline
p-Toluidine



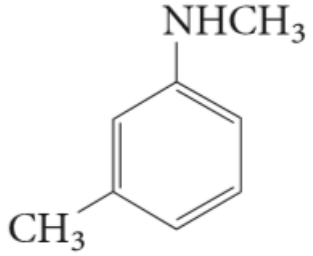
4-methoxyaniline
p-Anisidine



N-Methylaniline



N,N-dimethylaniline



N-methyl-3-methylaniline
N-methyl-*m*-toluidine

Physical Properties of Amines

Solubility

- 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. Thus, most simple amines with up to five or six carbon atoms are either completely or appreciably soluble in water.

Boiling point

- Amines are moderately polar substances; they 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.
- Molecules of tertiary amines cannot form hydrogen bonds to each other, as a result, tertiary amines generally boil at lower temperatures than primary and secondary amines of comparable molecular weight.

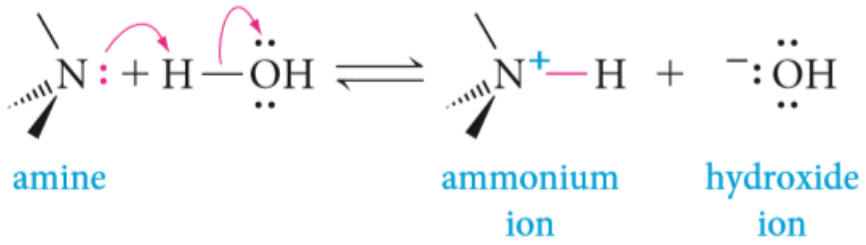
$CH_3CH_2CH_3$	$CH_3CH_2NH_2$	CH_3CH_2OH
Propane	Ethylamine	Ethanol
bp −42°C	bp 17°C	bp 78°C

$CH_3CH_2CH_2NH_2$	$CH_3CH_2NHCH_3$	$(CH_3)_3N$
Propylamine (a primary amine)	*N*-Methylethylamine (a secondary amine)	Trimethylamine (a tertiary amine)
bp 50°C	bp 34°C	bp 3°C

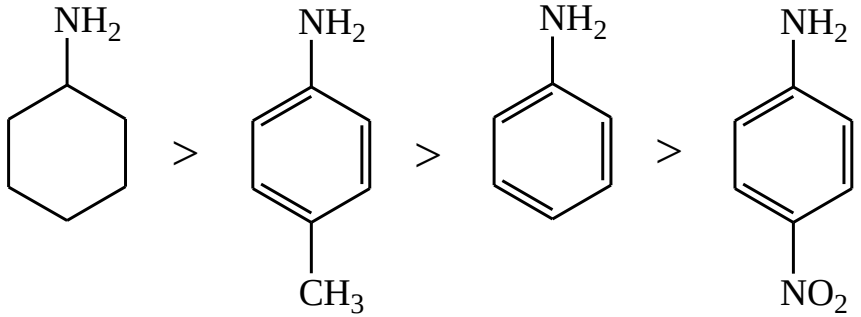
Physical Properties of Amines

Basicity of Amines: Amine Salts

- 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:

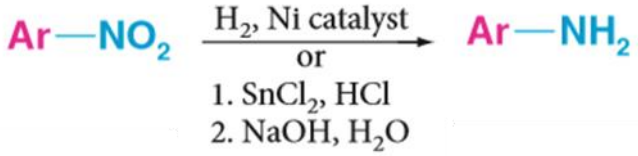


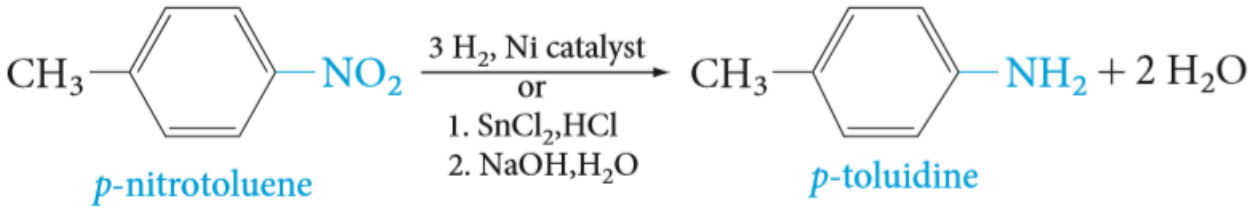
- Amines are relatively weak bases. Most are stronger bases than water but are far weaker bases than hydroxide ions, alkoxide ions, and alkanide anions.
- Alkylamines are approximately 10 times as basic as ammonia. Recall that alkyl groups are electron-donating relative to hydrogen.
- Aromatic amines less basic than aliphatic amines.
- Electron-donating groups increase the basicity of amines, and electron-withdrawing groups decrease their basicity.



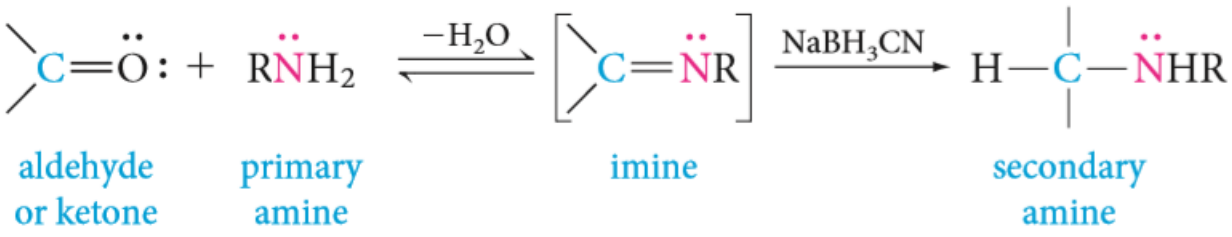
Preparation of Amines

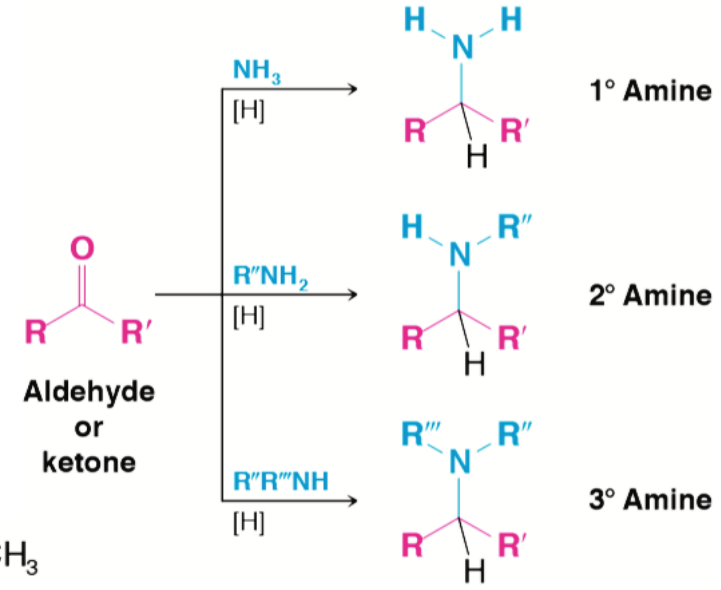
1- Reduction of nitro compounds

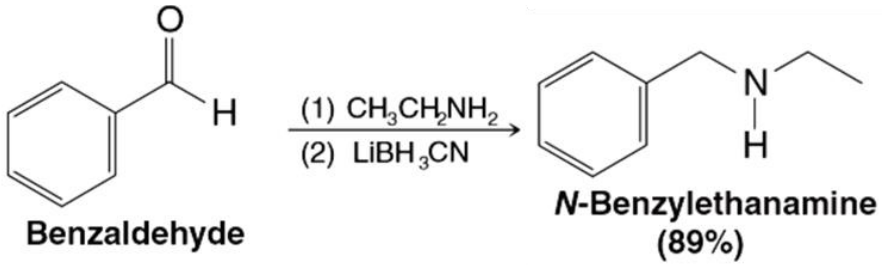


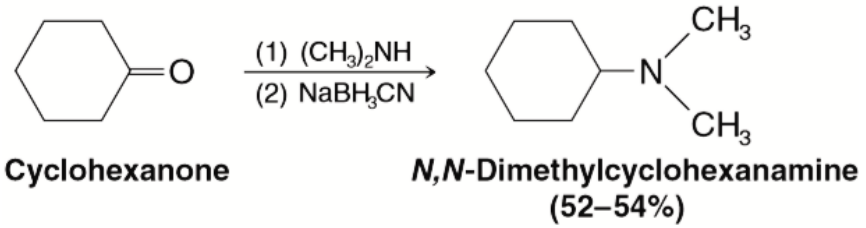


2- Reductive Amination of Aldehydes and Ketones



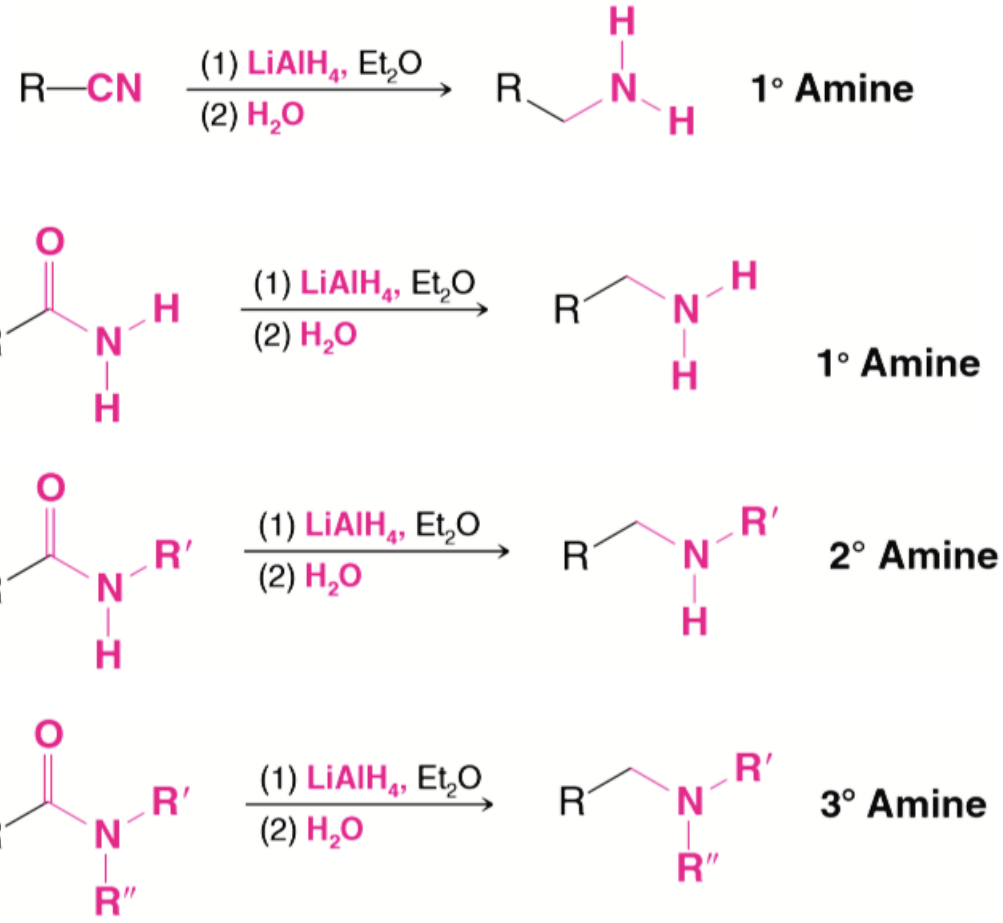


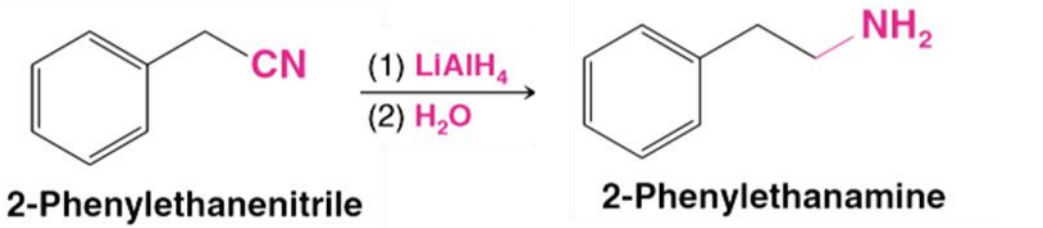


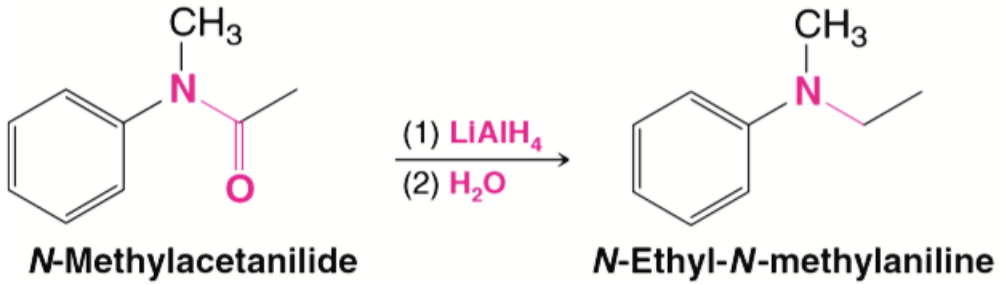


Preparation of Amines

3- Hydride Reduction of Amides and Nitriles

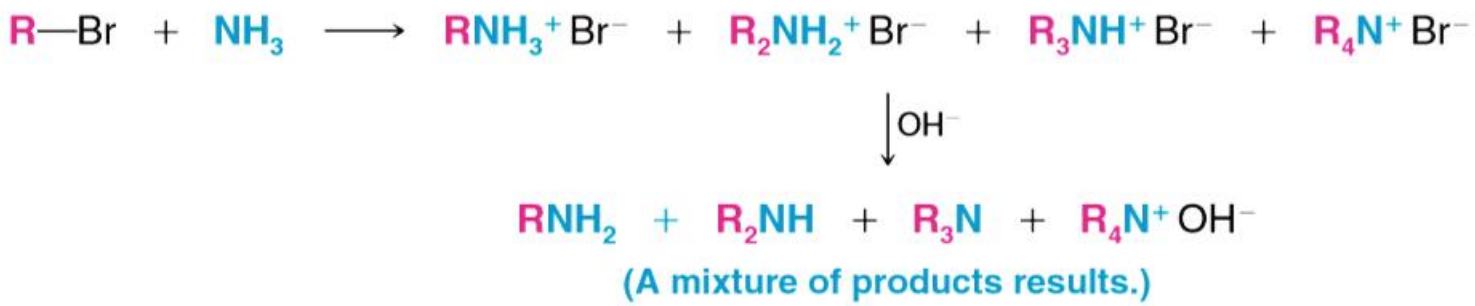




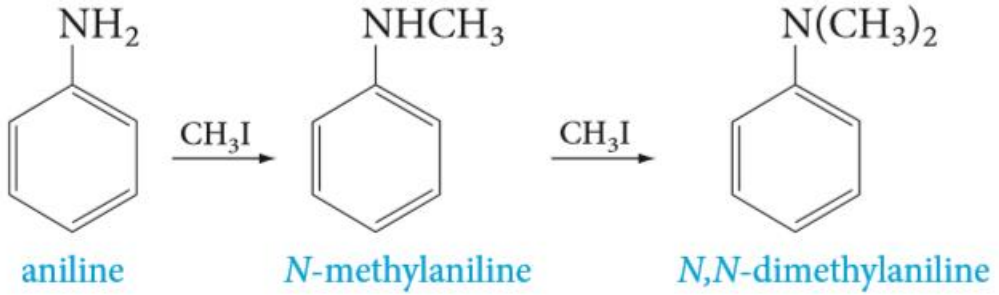


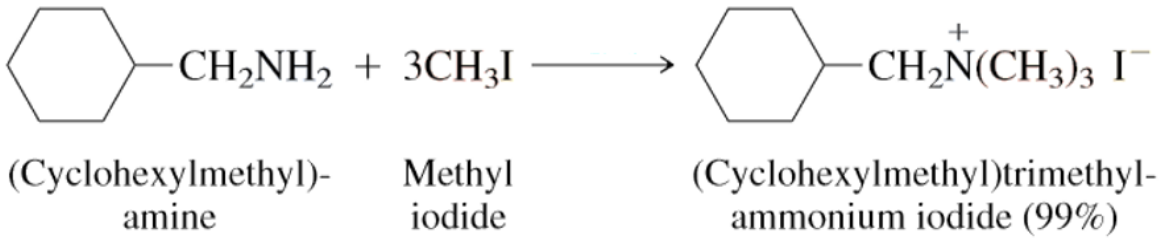
Preparation of Amines

4- Alkylation of Ammonia and amines



(R = a 1° alkyl group)

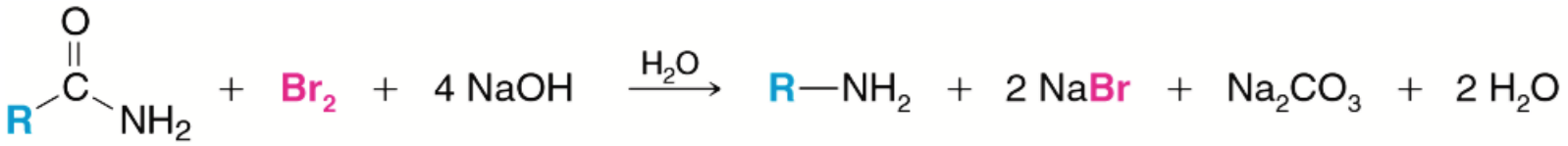


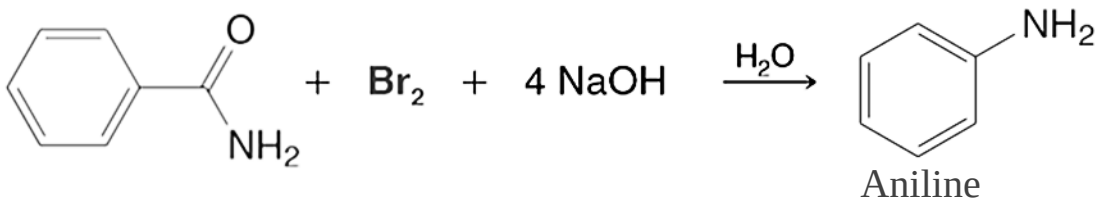


Preparation of Amines

5- Preparation of Primary Amines through the Hofmann and Curtius Rearrangement

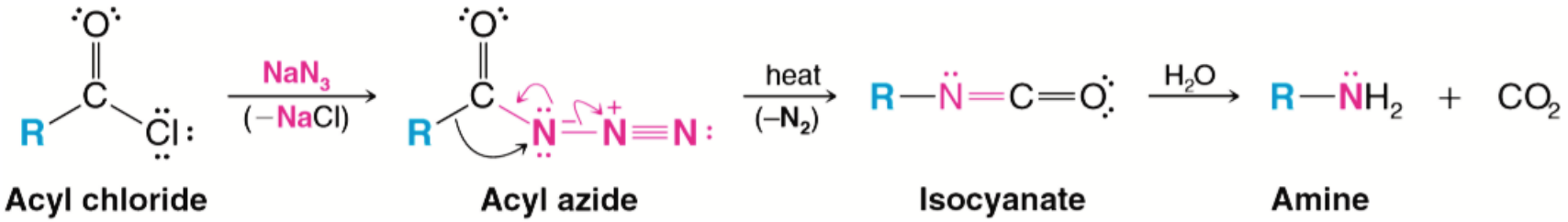
Hofmann Rearrangement



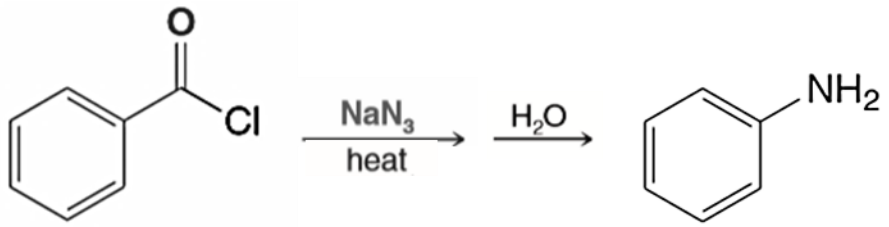


Aniline

Curtius Rearrangement



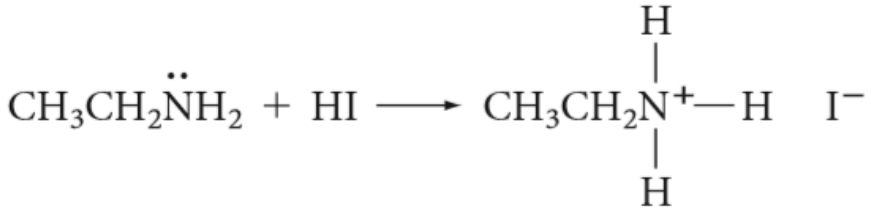
Acyl chloride **Acyl azide** **Isocyanate** **Amine**



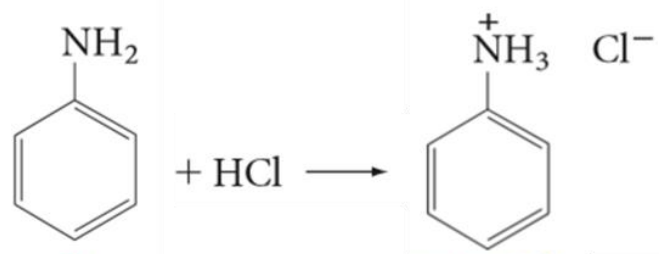
Reactions of Amines

1- Acid–Base Reactions

(R, R′, and/or R″ may be alkyl, H, or Ar)

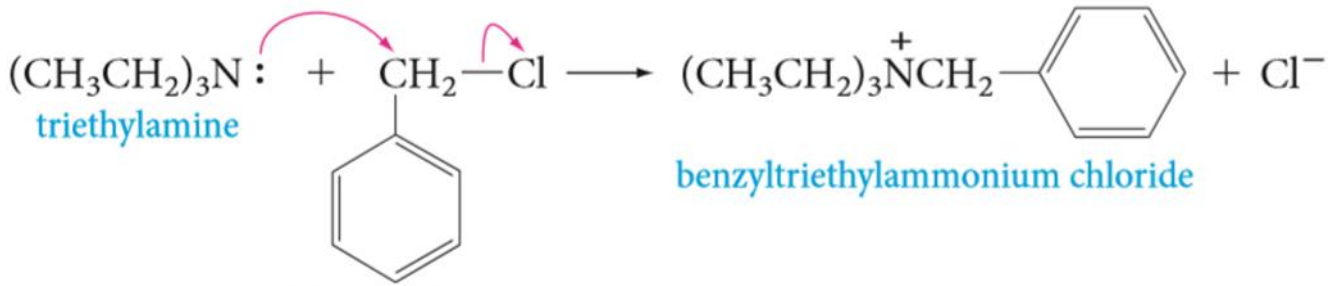


ethylamine — ethylammonium iodide



aniline — amine salt

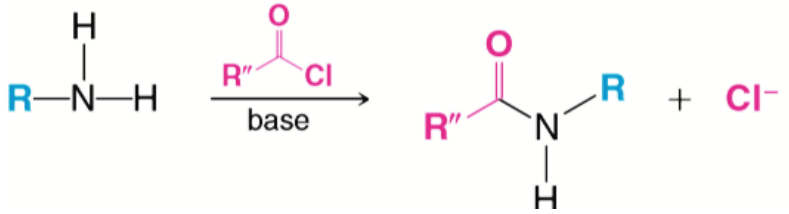
2- Alkylation of Amines: Quaternary Ammonium Salts (Amines as Nucleophiles)

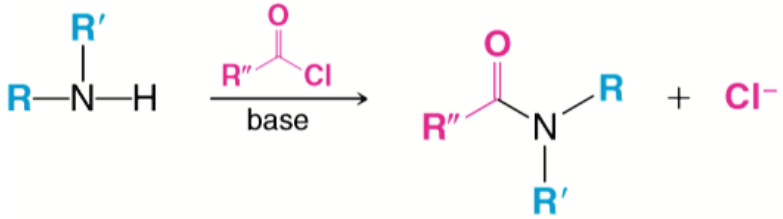


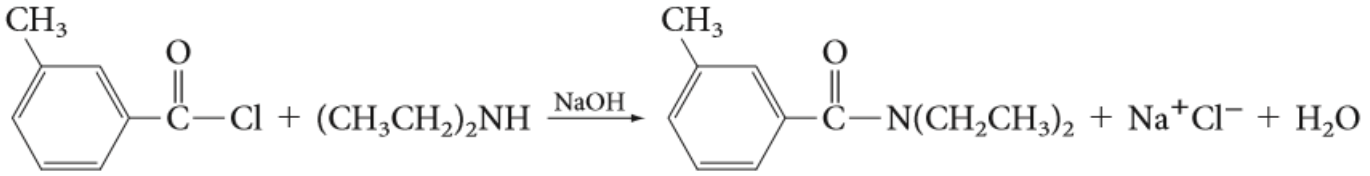
triethylamine — benzyl chloride — benzyltriethylammonium chloride

Reactions of Amines

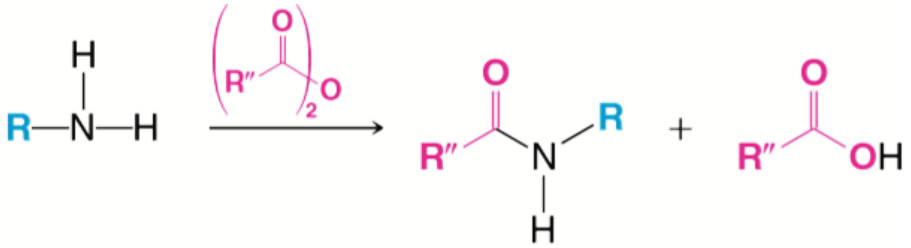
3- Acylation of Amines with Acid Derivatives (Amines as Nucleophiles)

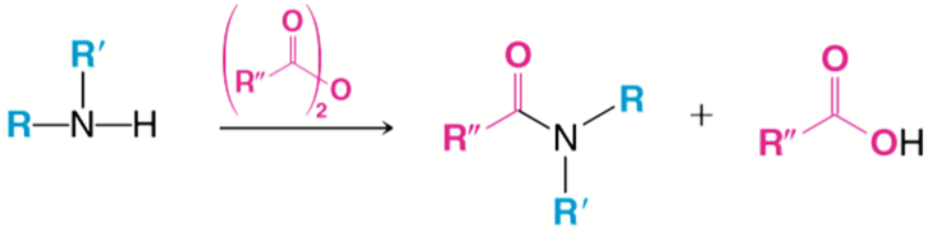


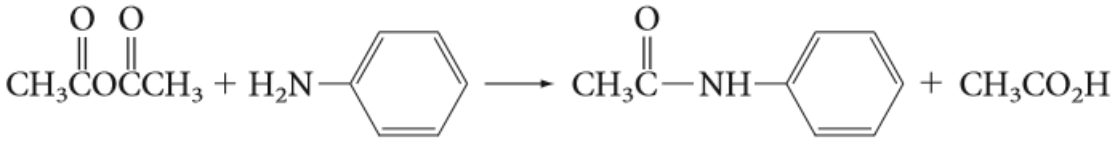




m-toluyl chloride — diethylamine — *N,N*-diethyl-*m*-toluamide (the insect repellent OFF®)



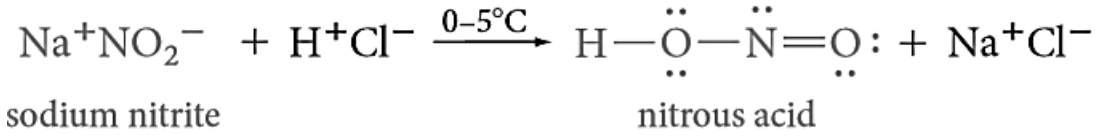




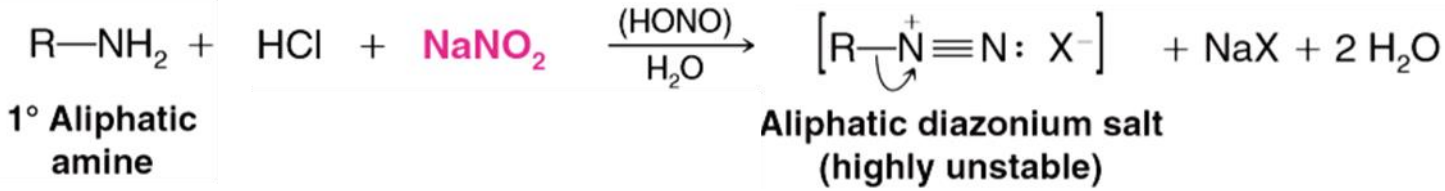
acetic anhydride — aniline — acetanilide

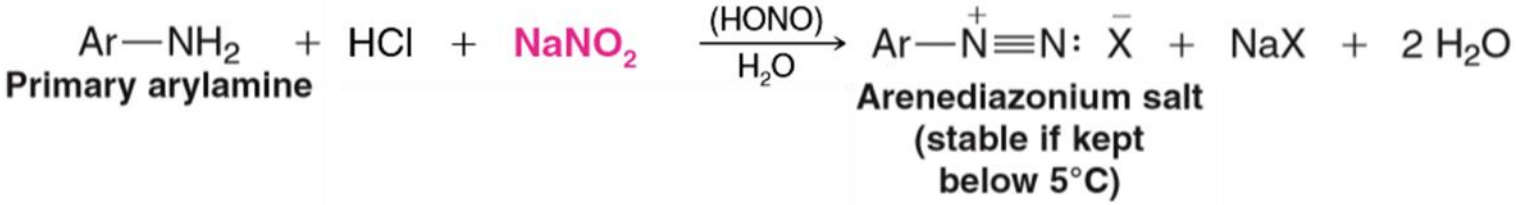
Reactions of Amines

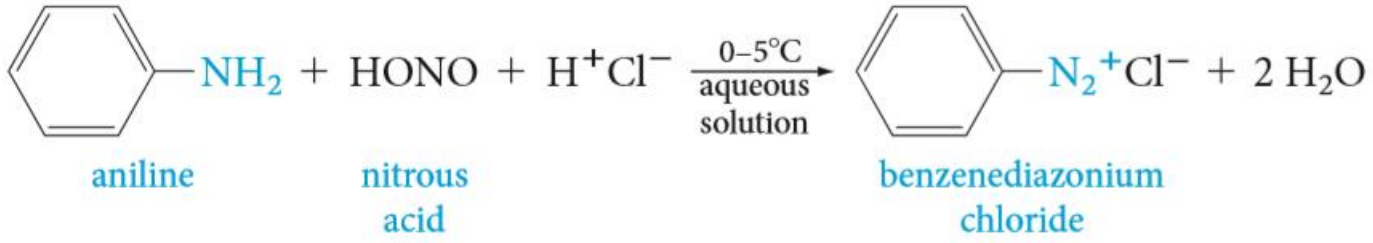
4- Reactions with Nitrous Acid



- Primary aliphatic amines react with nitrous acid through a reaction called diazotization to yield highly unstable aliphatic diazonium salt.



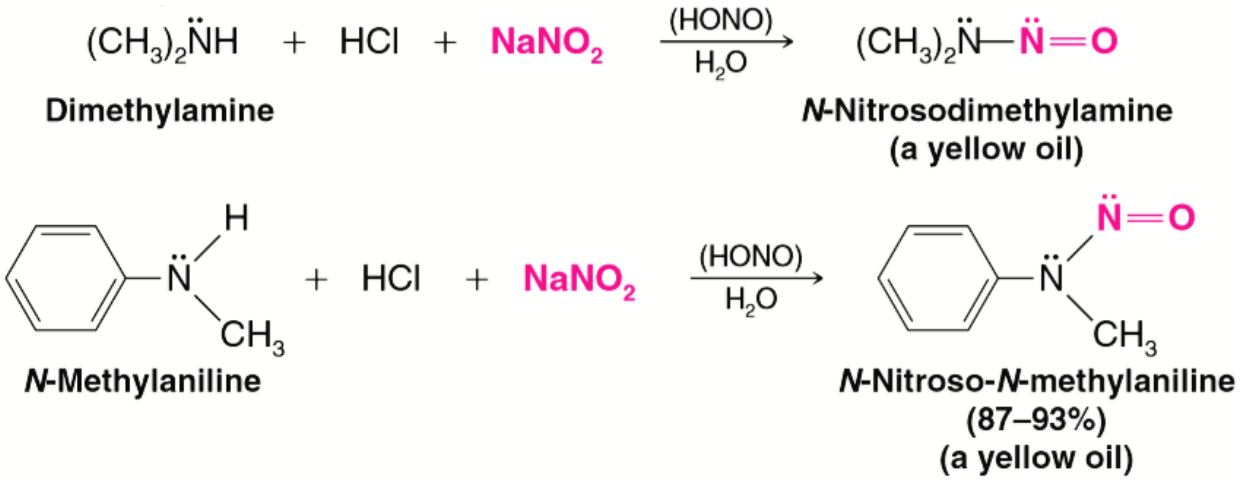




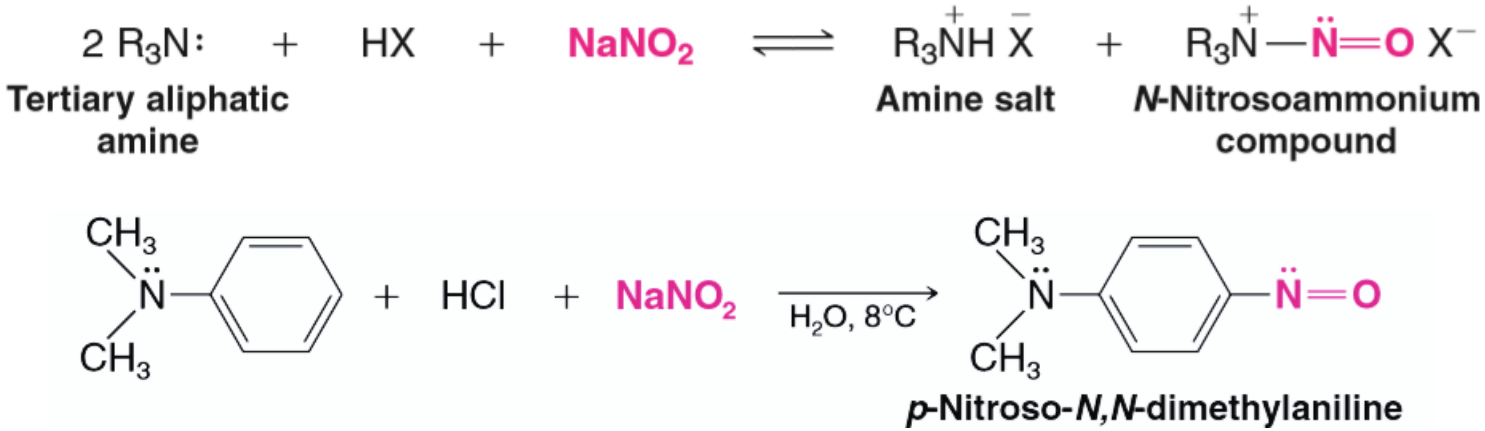
Reactions of Amines

4- Reactions with Nitrous Acid

- Secondary amines react with nitrous acid to yield N-nitrosoamines.

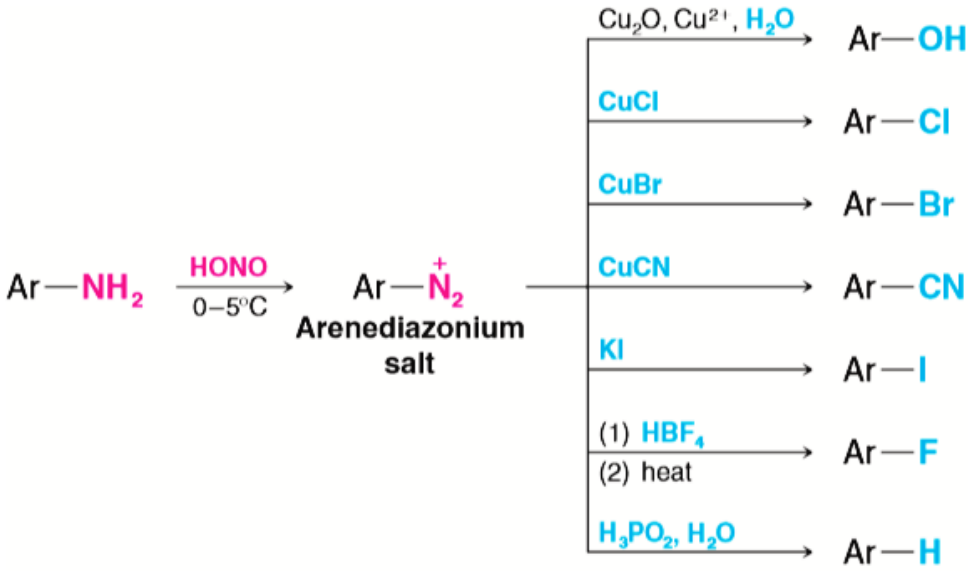


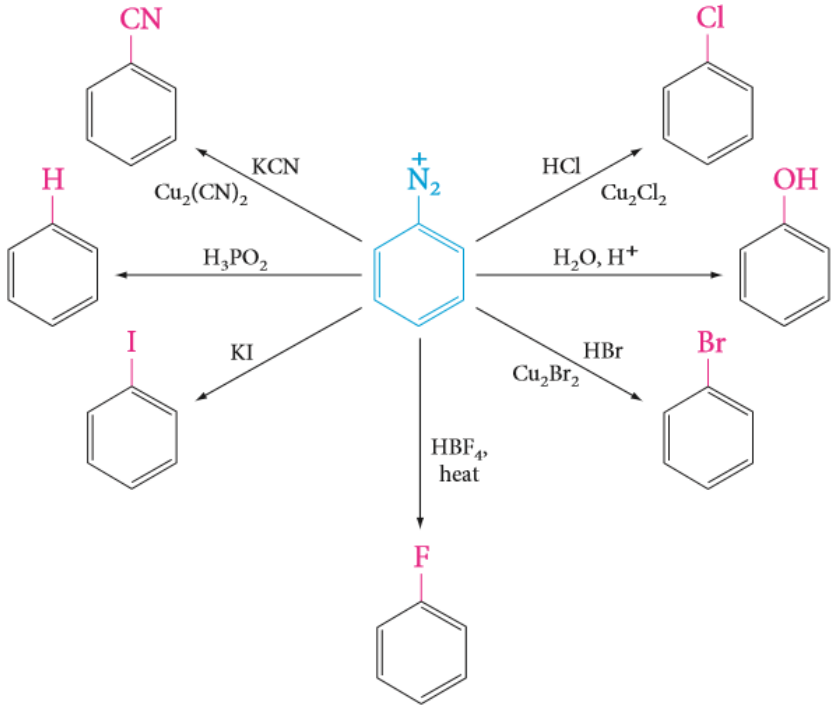
- Tertiary aliphatic amine react with nitrous acid to form the tertiary amine salt and N-nitrosoammonium compound.
- Tertiary arylamines react with nitrous acid to form C-nitroso aromatic compounds.



Reactions of Amines

5- Syntheses Using Diazonium Salts





6- Diazo Coupling; Azo Dyes