# AMINES

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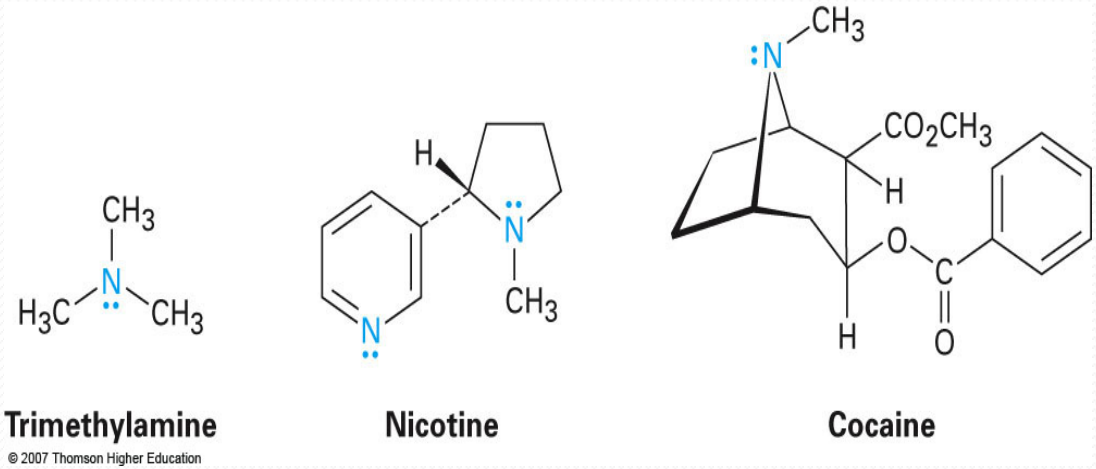
- Amines are composed of nitrogen atoms bearing alkyl or aromatic groups.
- Amines occur widely in both plants and animals.
- Amines are bioactive as they produce biological responses like mood alterations.
- Amines are of wide importance.
- Trimethylamine occurs in animal tissues, responsible for the odor in fish.
- Nicotine in tobacco.
- Cocaine a stimulant.

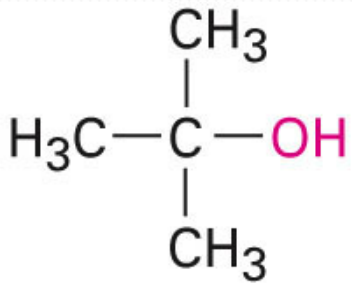



Trimethylamine Nicotine Cocaine

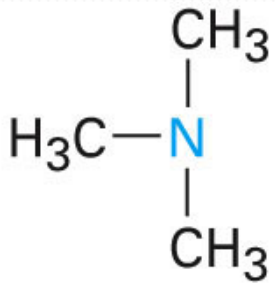
# Classification Of Amines

Amines are classified depending upon the number of substituent's attached to nitrogen.

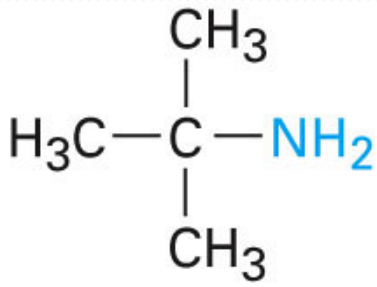
- Primary amines – $RNH_2$
- Secondary amines- $R_2NH$
- Tertiary amines- $R_3N$
- Compounds with four groups attached to nitrogen are known as quaternary ammonium salts ($R_4N^+ X^-$).



***tert*-Butyl alcohol**
**(a tertiary alcohol)**



**Trimethylamine**
**(a tertiary amine)**

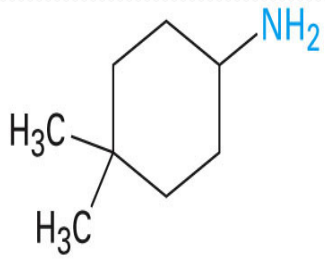


***tert*-Butylamine**
**(a primary amine)**

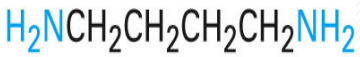
# Naming Amines

- Primary amines are named by adding the suffix –amine to the name of the organic substituent.
- Amines that have additional functional groups are named by adding $–NH_2$ group as an amino substituent on the parent molecule.
- Symmetrical secondary and tertiary amines are named by adding the prefix *di-* or *tri-* to the alkyl group.
- Unsymmetrically substituted secondary and tertiary amines are named as *N*-substituted primary amines. The largest group is chosen as parent, and other substituent's as *N*-substituent's on the parent chain.
- Aromatic amines – $C_6H_5NH_2$
- Heterocyclic amines- compound in which the nitrogen atom occurs as a part of ring.

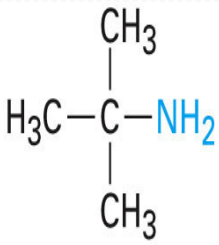
# Naming Amines




4,4-Dimethylcyclohexanamine

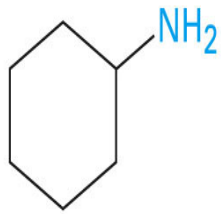



1,4-Butanediamine

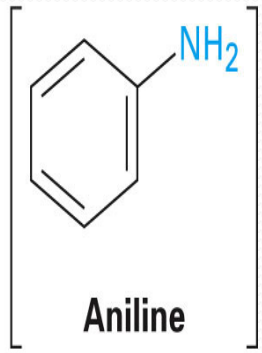



*tert*-Butylamine

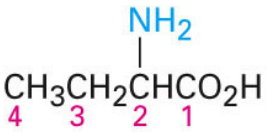




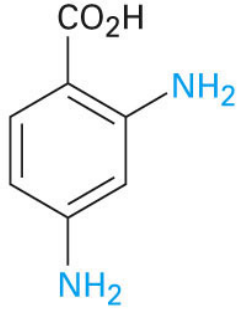

Cyclohexylamine



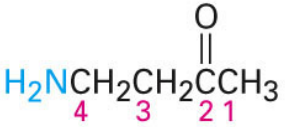

Aniline




2-Aminobutanoic acid

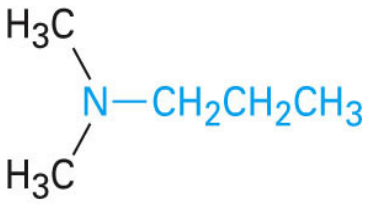



2,4-Diaminobenzoic acid

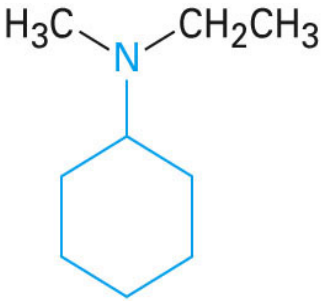



4-Amino-2-butanone



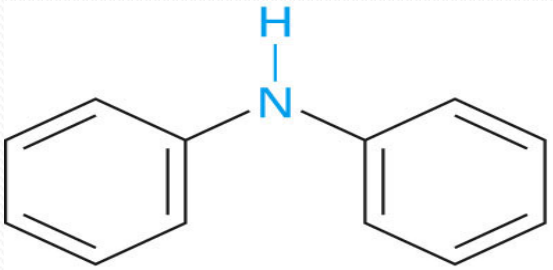



*N,N*-Dimethylpropylamine

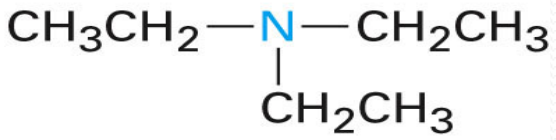



*N*-Ethyl-*N*-methylcyclohexylamine

# Naming Amines

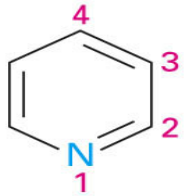


**Diphenylamine**

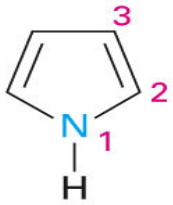


**Triethylamine**

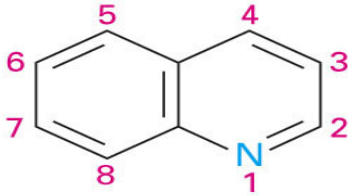




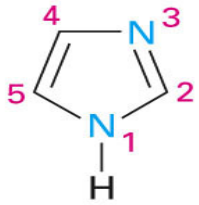
**Pyridine**



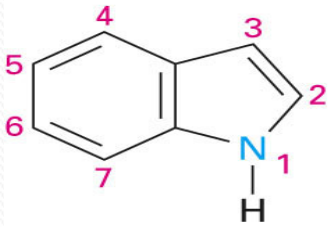
**Pyrrole**



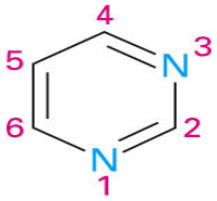
**Quinoline**



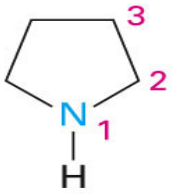
**Imidazole**



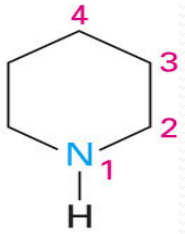
**Indole**



**Pyrimidine**



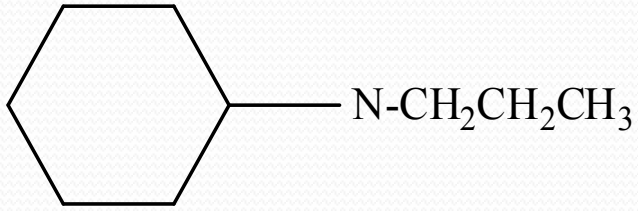
**Pyrrolidine**



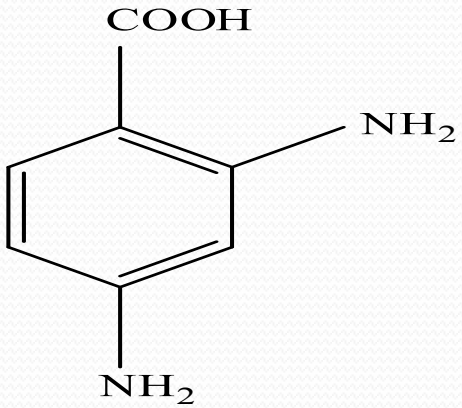
**Piperidine**

# Name the following compounds

1. $CH_3NHCH_2CH_3$

2. 


3. 


4. 


5. 

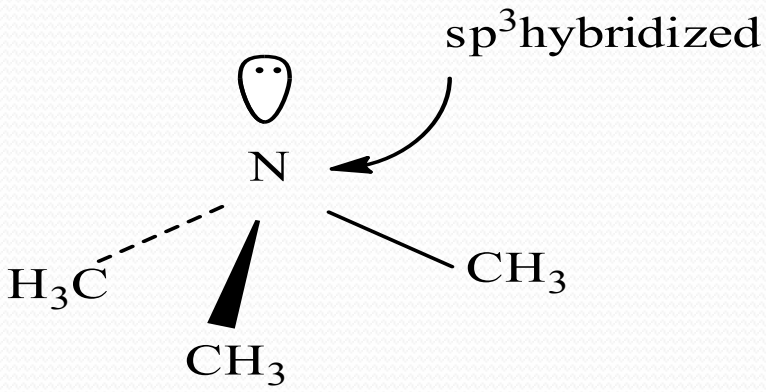
# Draw the structures of the following IUPAC names:

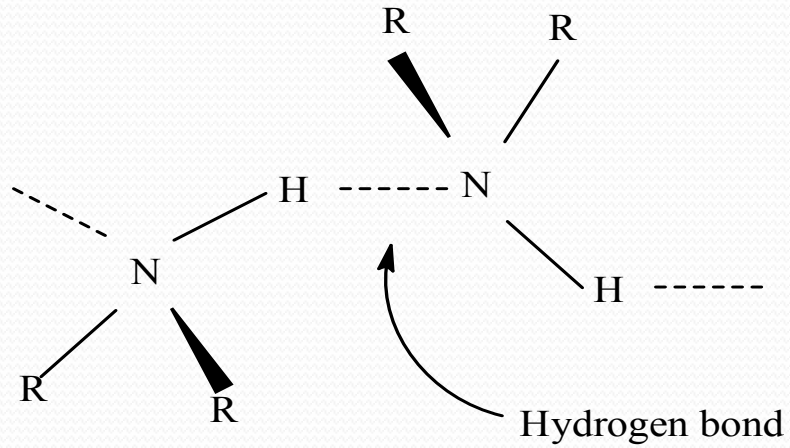
1. Triethylamine
2. *N*-Methylaniline
3. *p*-Bromoaniline
4. *N*-ethyl-*N*-methylcyclopentylamine
5. *N*-methyl pyrrole
6. 2-Aminobutanoic acid
7. 2-methyl propan-1-amine
8. *N*,*N*-diethyl amine
9. Trimethylamine

# Structure And Properties Of Amines

- The bonding in amines is similar to ammonia.
- The nitrogen atom is $sp^3$ hybridized, with lone pair of electrons on the nitrogen atom. C-N-C bond angle is very close to 109°.
- Like alcohols, amines are highly polar.
- Also like alcohols, primary and secondary amines form hydrogen bonds and therefore have higher boiling points.
- One other characteristic of amines is odor.

  Example: Trimethylamine has fishlike aroma.



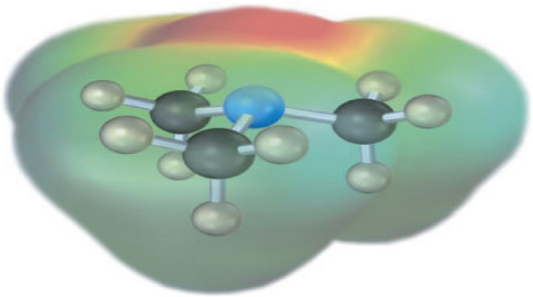



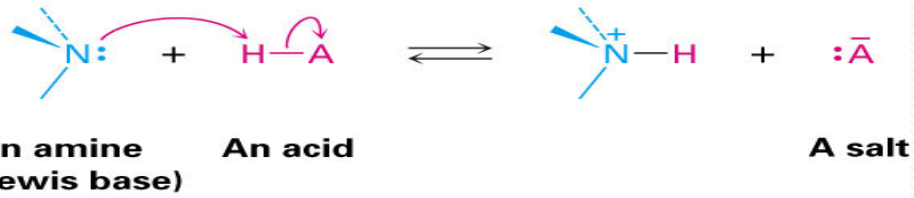
# Basicity Of Amines

- Amines are both basic and nucleophillic, because of the presence of lone pair of electrons on the nitrogen atom.
- Amines are much stronger bases than alcohols, ethers or water.
- When an amine is dissolved in water, water acts as an acid and donates $H^+$ to the amine.

$$RNH_2 + H_2O \longleftrightarrow RNH_3^+ + OH^-$$

- Smaller the $pK_b$ value, stronger is the base.
- Larger the $pK_b$ value, weaker is the base.
- Aryl amines are weaker bases than alkyl amines.





# Basicity of Some Common Amines

| Name | Structure | $pK_b$ |
|---|---|---|
| Triethylamine | $(CH_3CH_2)_3N$ | 2.99 |
| Ethylamine | $CH_3CH_2NH_2$ | 3.19 |
| Dimethylamine | $(CH_3)_2NH$ | 3.27 |
| Methylamine | $CH_3NH_2$ | 3.34 |
| Diethylamine | $(CH_3CH_2)_2NH$ | 3.51 |
| Trimethylamine | $(CH_3)_3N$ | 4.19 |
| Ammonia | $NH_3$ | 4.74 |
| Aniline | $C_6H_5NH_2$ | 9.37 |

More Basic

Less Basic

# Basicity Of Amines

1. Why are alkylamines more basic than ammonia?

The alkyl group, -R, is an electron donating group. The donation of electrons helps to stabilize the ammonium ion by decreasing the positive charge, lowering the $\Delta H$, shifting the ionization farther to the right and increasing the basicity.

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

$$R\text{-}NH_2 + H_2O \leftrightarrows R\text{-}NH_3^+ + OH^-$$

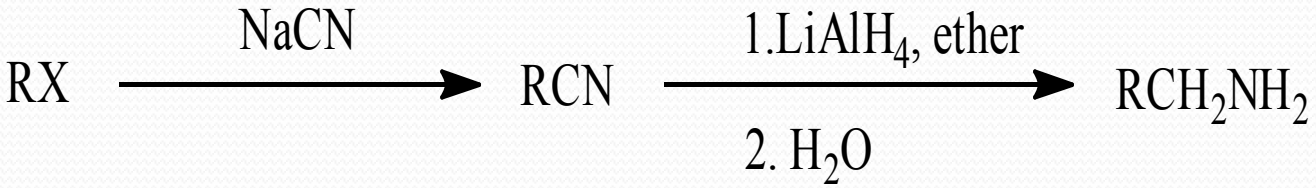
2. Why are arylamines less basic than alkylamines?

The nitrogen lone-pair electrons in aryl amine are shared with the π orbitals of the aromatic ring and are less available for bonding to an acid.

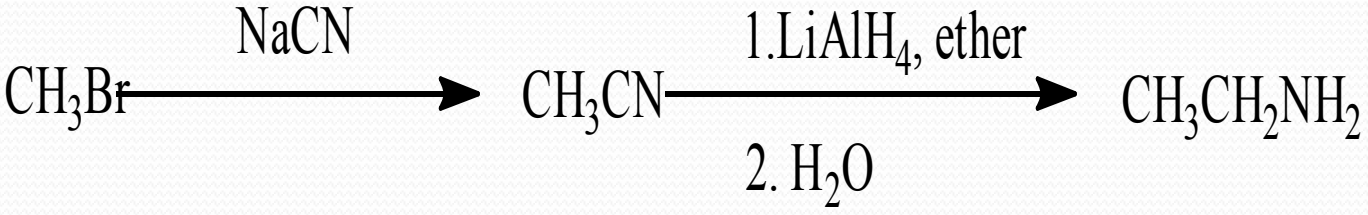
# Synthesis Of Amines

Reduction of nitriles and amides:

- Alkyl halides react with cyanide ion following $S_N2$ reaction to form nitriles, followed by reduction to form primary amines.



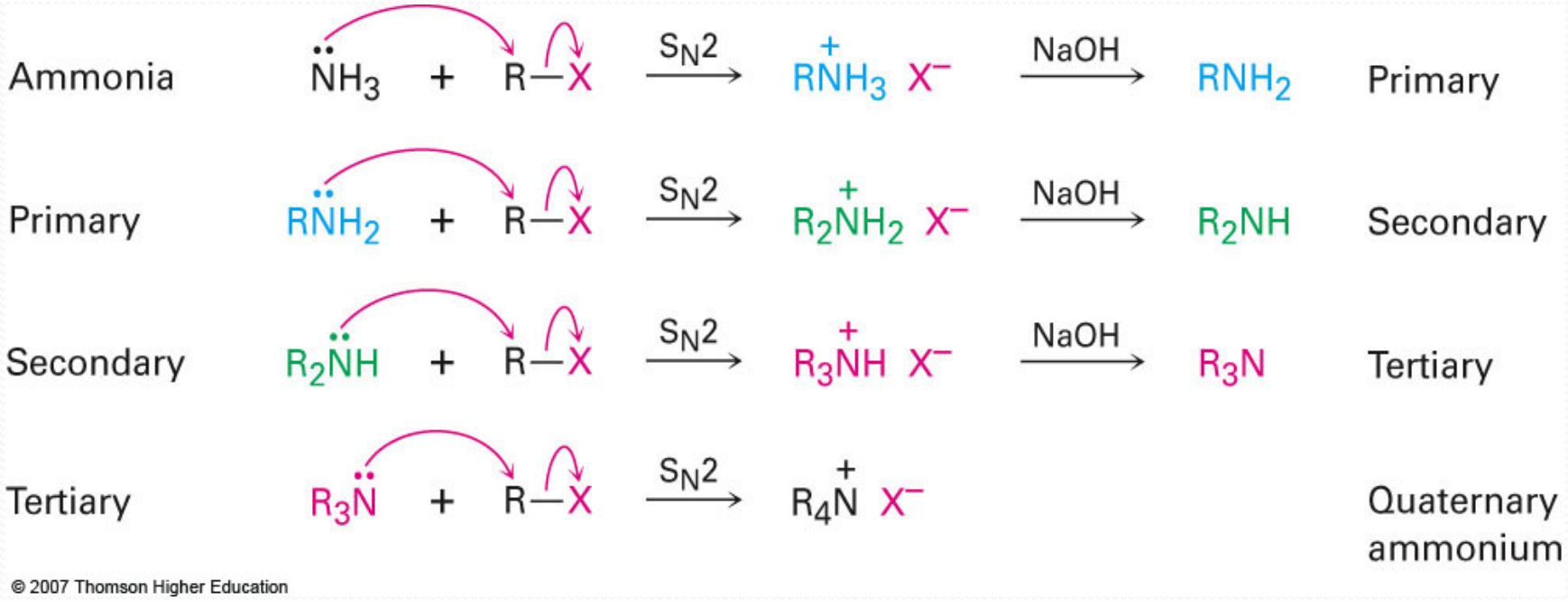

Alkyl halide  Nitrile  Alkyl amine




Methyl bromide  Methyl cyanide  Methyl amine

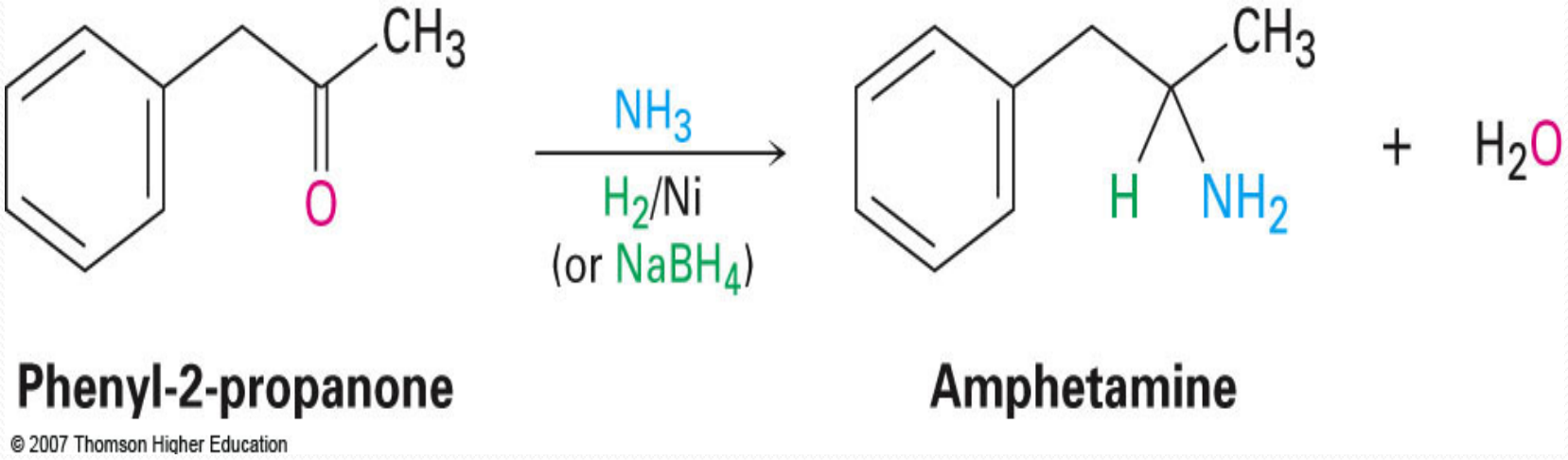
# $S_N2$ Reactions of Alkyl Halides

- The simplest method to prepare amines is by $S_N2$ alkylation of ammonia or an alkyl amine with alkyl halides.
- If ammonia is reacts with R-X, a primary amine is formed.
- If a primary amine reacts with R-X, a secondary amine is obtained; and so on.



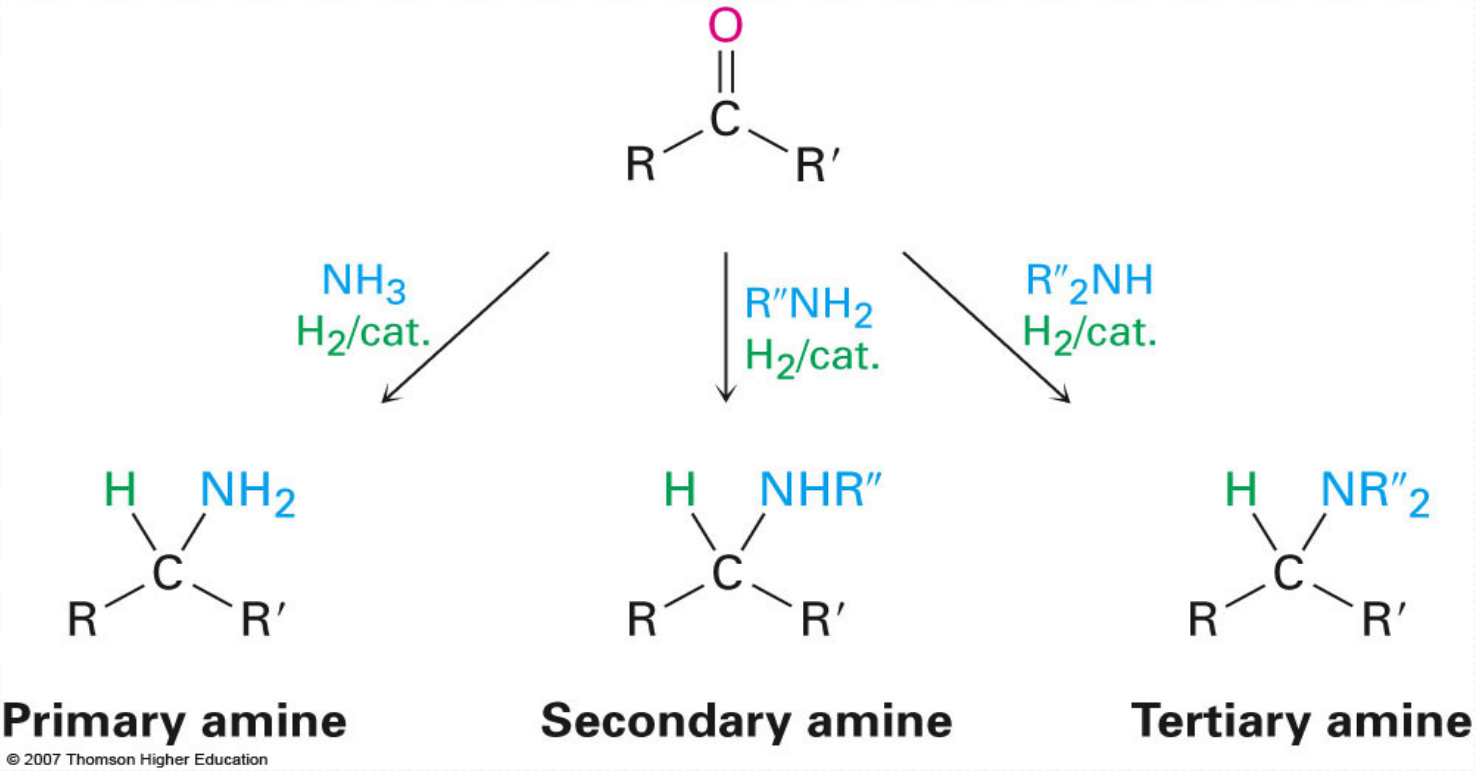
# Reductive Amination of Aldehydes And Ketones

- Treatment of an aldehyde or ketone with ammonia or an amine in the presence of a reducing agent



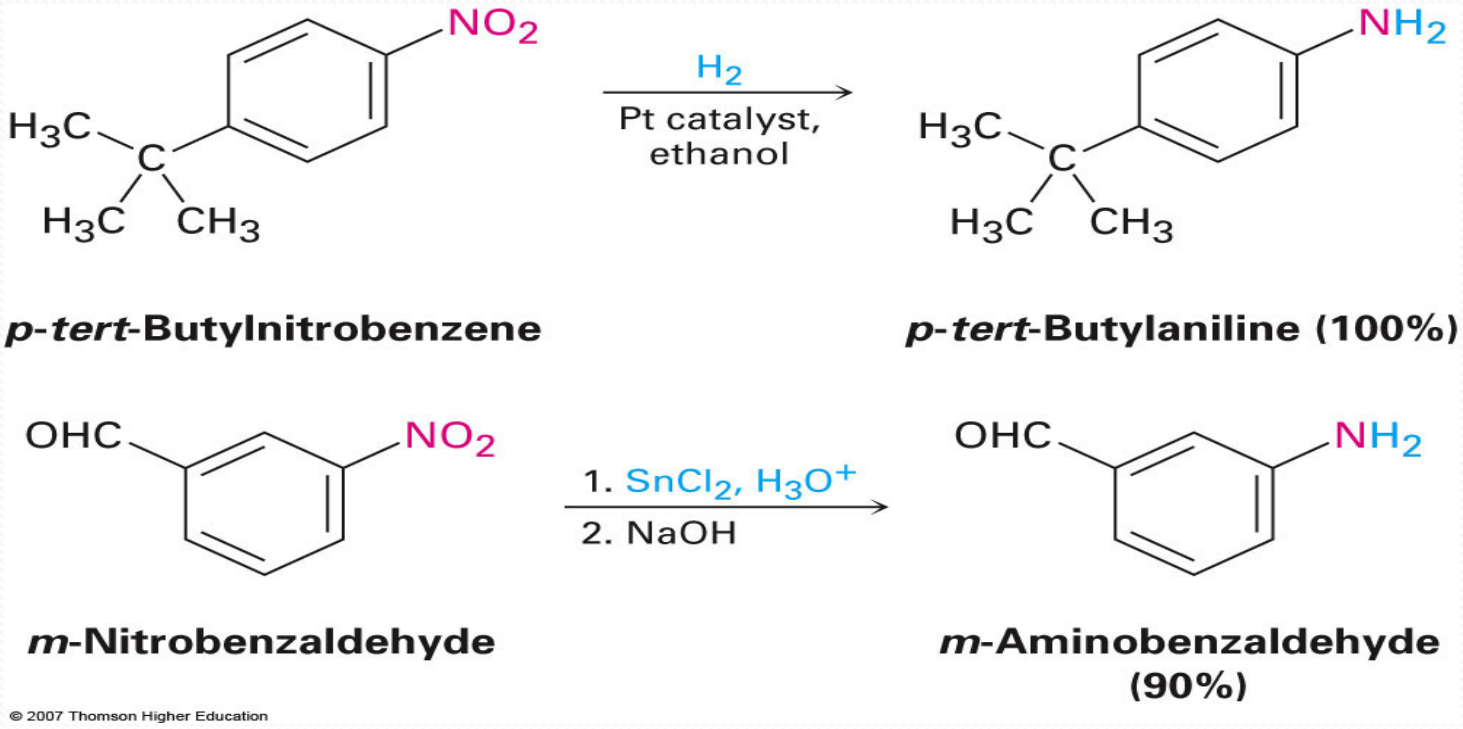
# Reductive Amination

Ammonia, primary amines, and secondary amines yield primary, secondary, and tertiary amines, respectively.



# Reduction Of Nitrobenzenes

- Arylamines are prepared from nitration of an aromatic compound and reduction of the nitro group.
- Reduction by catalytic hydrogenation over platinum is suitable if no other groups can be reduced.
- Iron, zinc, tin, and tin(II) chloride are effective in acidic solution.

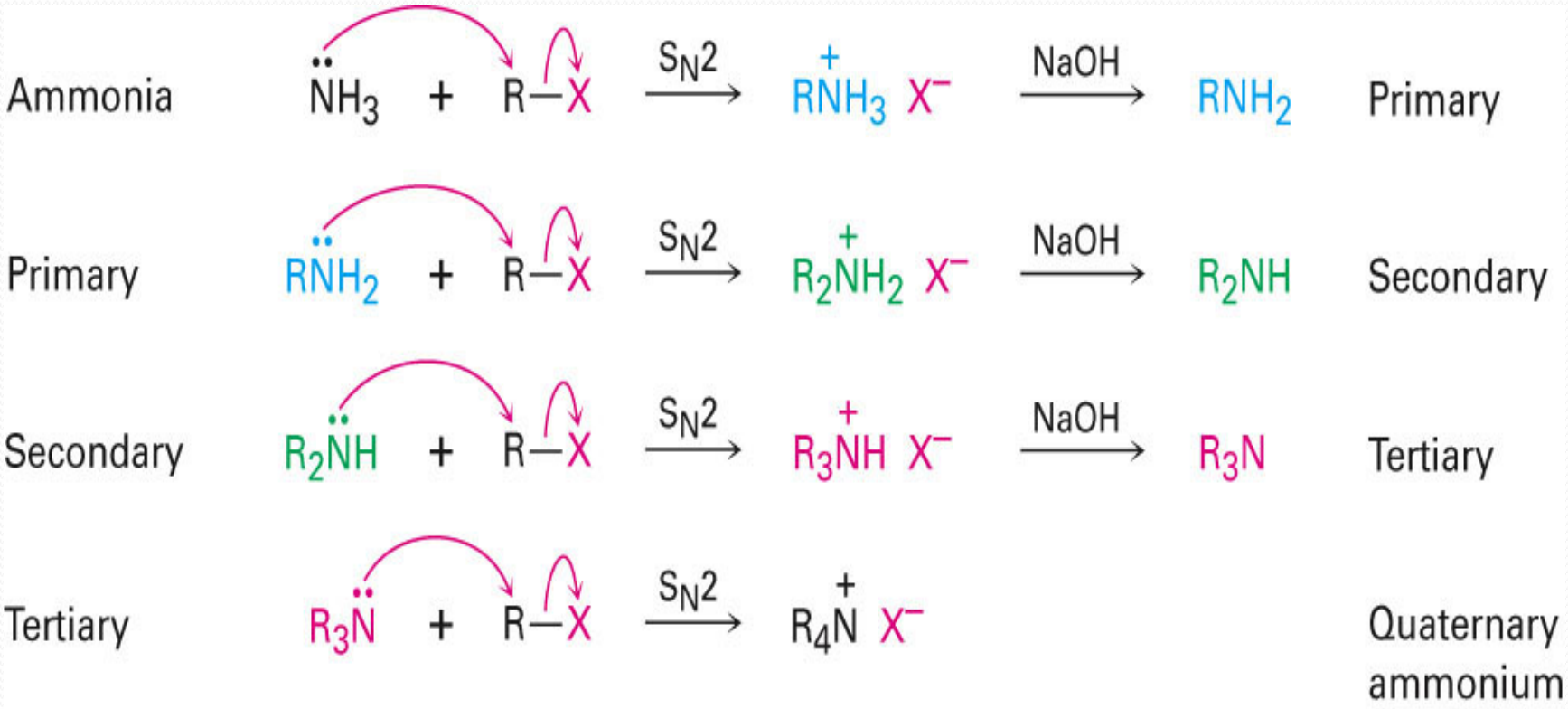


# Reactions Of Amines

Alkyl amines undergo alkylation and acylation reaction.

- Alkylation of Amines:

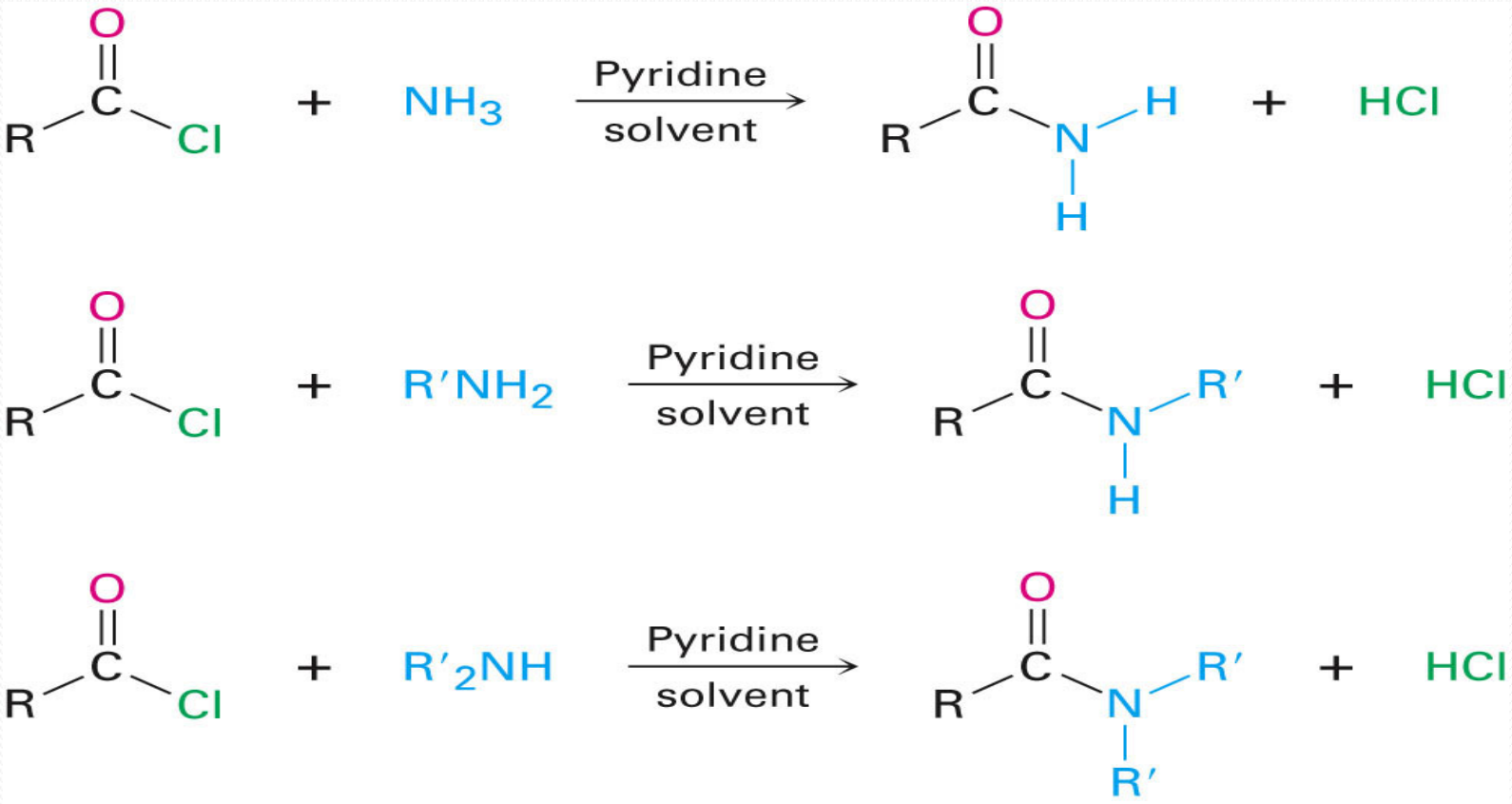
  Primary, secondary and tertiary amines can be alkylated by the reaction with alkyl halides.



# Reactions Of Amines

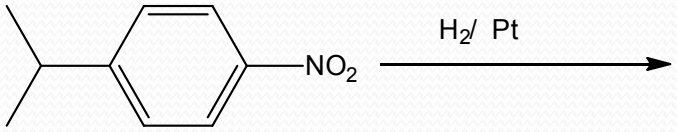
- Acylation of alkyl amines:

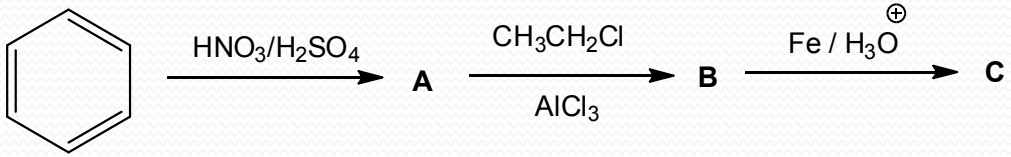
  Primary and secondary(but not tertiary) amines can also be acylated by nucleophilic acyl substitution reactions with acid chlorides.



# Practice Examples

1. Which compound is more basic, triethylamine or aniline?

2. 


3. 


4. How do you synthesize *m*-aminobenzoic acid from benzene?
5. How do you prepare dibutylamine from 1-bromobutane?