

CHAPTER 11

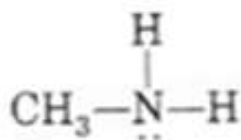
Amines

and Related

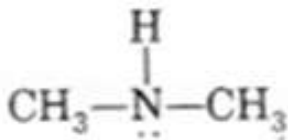
Nitrogen Compounds

Amines are derived from **ammonia** by replacing one H, or more, by alkyl- or by aryl group(s).

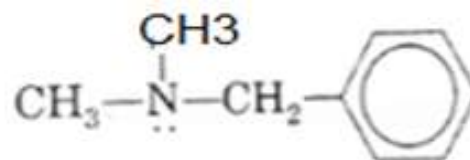
Classification : a) Aliphatic amines and Aromatic amines
b) Primary, secondary, and tertiary amines



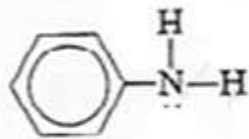
primary aliphatic



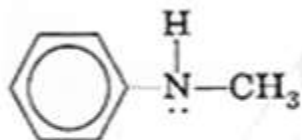
secondary aliphatic



tertiary aliphatic

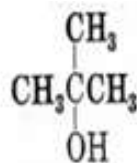


primary aromatic

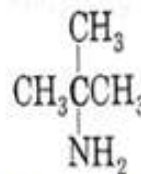


secondary aromatic

compare alcohols :



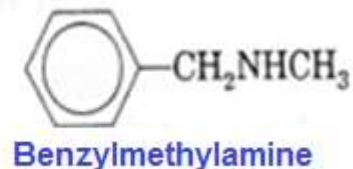
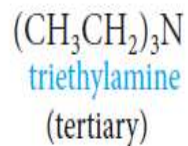
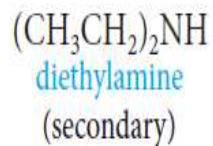
tertiary butyl alcohol
(tertiary)



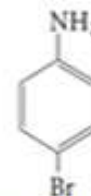
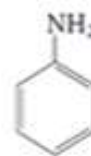
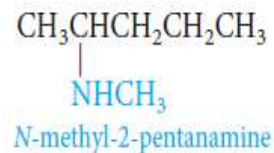
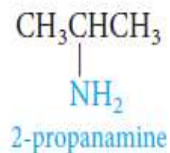
tertiary butyl amine
(primary)

Nomenclature :

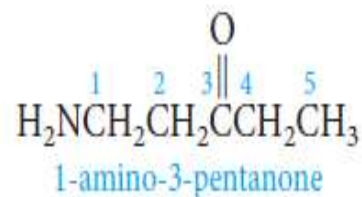
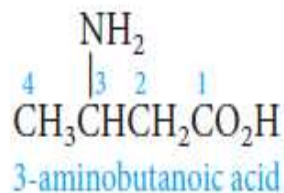
1- Common names: Alkylamines



2- IUPAC : Alkanamines:



If other functional groups present, amino group as substituent :



Physical Properties :

Boiling point : higher than alkanes, but lower than alcohols, aldehydes, ketones, etc.

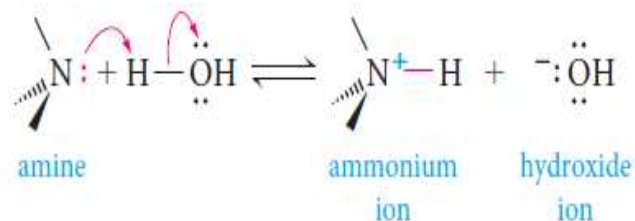
Primary and secondary amines have H-bonds, but weaker than those in alcohols.

Tertiary amines have no H-bonds, lower boiling points than primary or secondary amines :

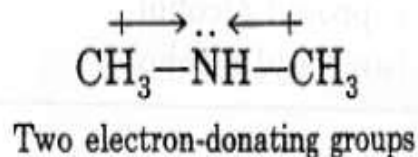
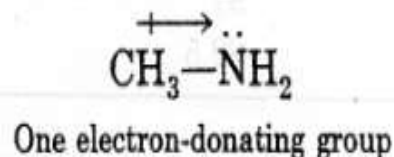
alkane	CH ₃ CH ₃ (30) bp -88.6°C	CH ₃ CH ₂ CH ₃ (44) bp -42.1°C
amine	CH ₃ NH ₂ (31) bp -6.3°C	CH ₃ CH ₂ NH ₂ (45) bp +16.6°C
alcohol	CH ₃ OH (32) bp +65.0°C	CH ₃ CH ₂ OH (46) bp +78.5°C

Solubility : all amines can form hydrogen bonds with the -OH of water through Nitrogen lone pair. So they are soluble up to 5C-atoms.

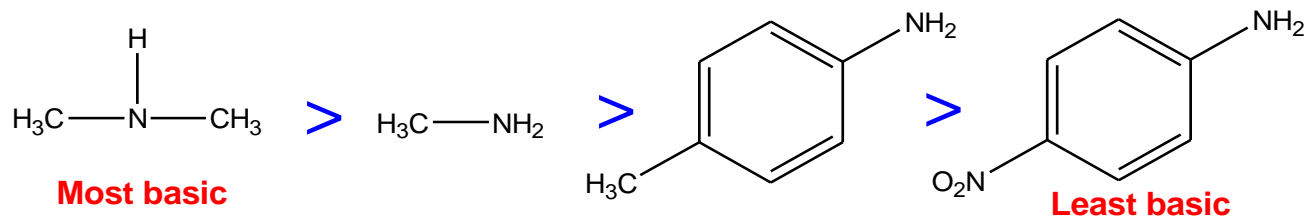
Basicity of Amines : Amines are Basic and Nucleophilic (like ammonia)



- Electron-donating groups increase basicity.
- Electron-withdrawing groups decrease basicity.

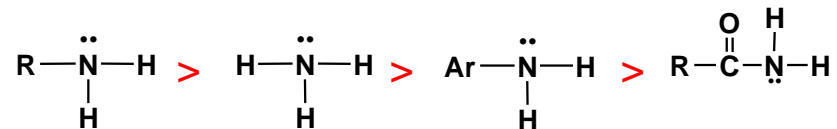


Aromatic ring decreases basicity through delocalization of the N-lone pair over ortho- and para-positions of the ring :

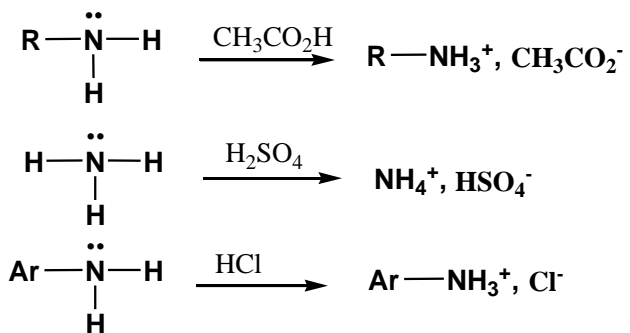


Relative basicity : any aliphatic amine > ammonia > aromatic amines >> amides

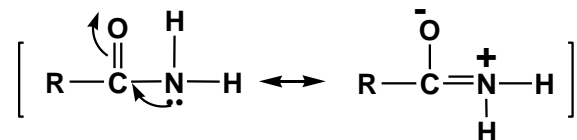
secondary, tertiary amines > primary amines > ammonia



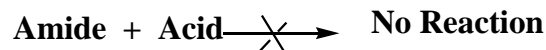
Reaction with acids : All amines react with all acids to form ammonium salts :



Amides are **not basic** because of the electron-withdrawing effect of the C=O group which causes delocalization of the lone pair of N atom by resonance as follows:



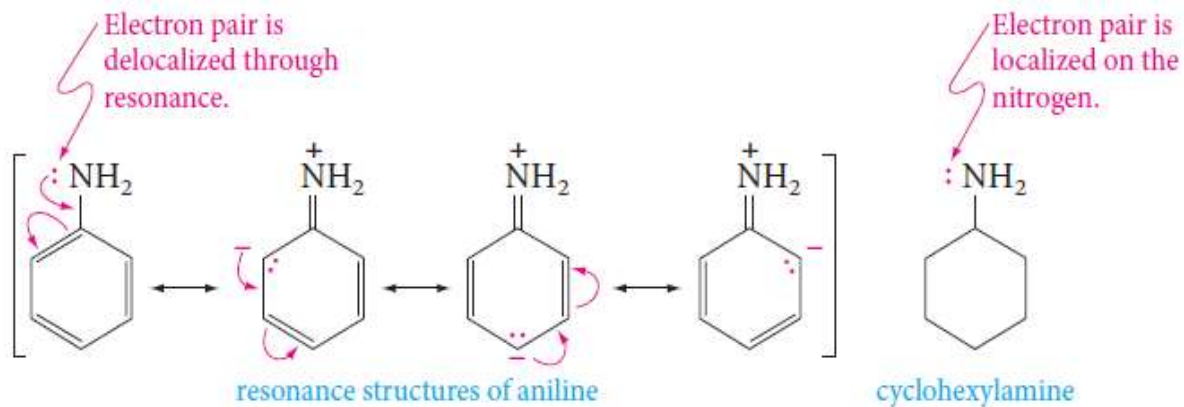
Amides do **not** form ammonium salts with acids:



The amide linkage occurs in **peptides** and **proteins**, linking amino acids to each other.

Aromatic amines are weaker bases than ammonia or aliphatic amines.

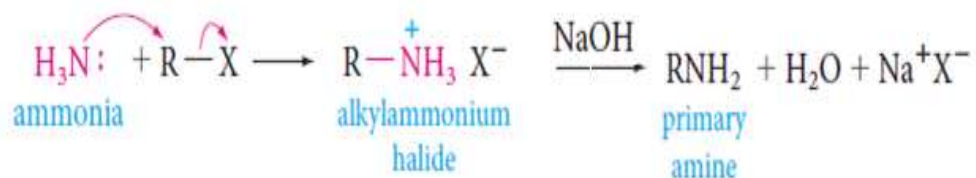
Reason : delocalization of lone pair:



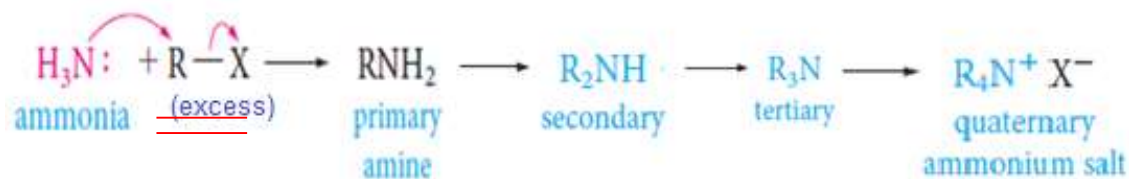
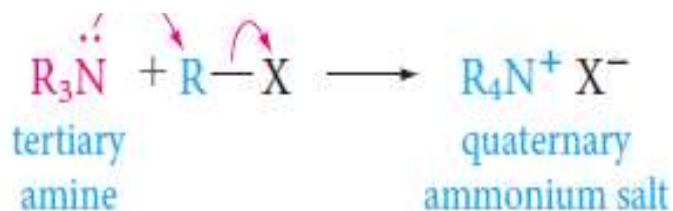
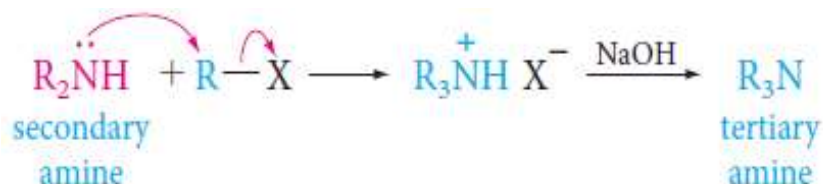
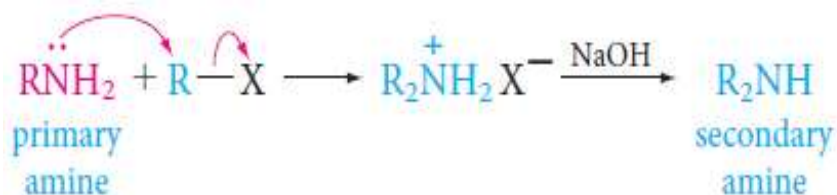
aniline is **less basic** than cyclohexylamine

Preparation of Amines :

1) Alkylation of Ammonia :

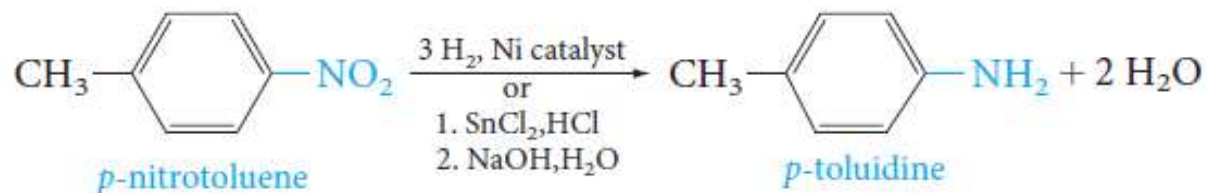


Other amines can be similarly alkylated :

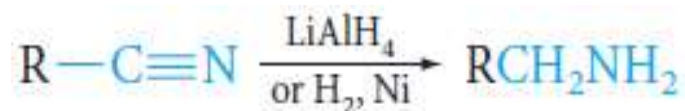


2) Reduction of other nitrogen-containing compounds :

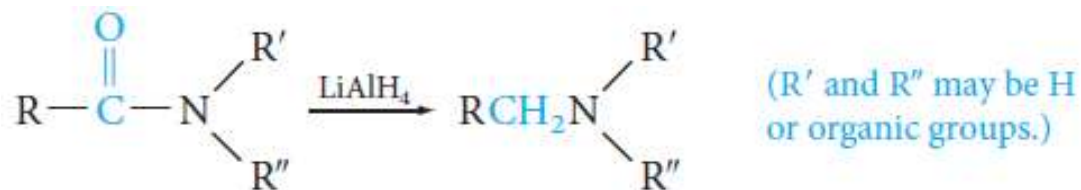
A- Nitro Compounds :



B- Nitriles :

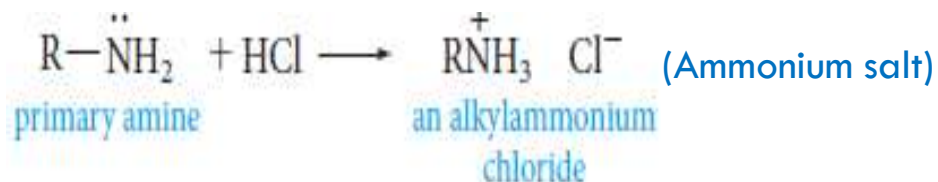


C- Amides :



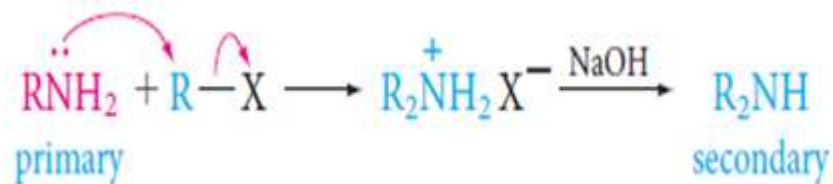
Reactions :

1) With Acids (amines as bases: give ammonium salts) :

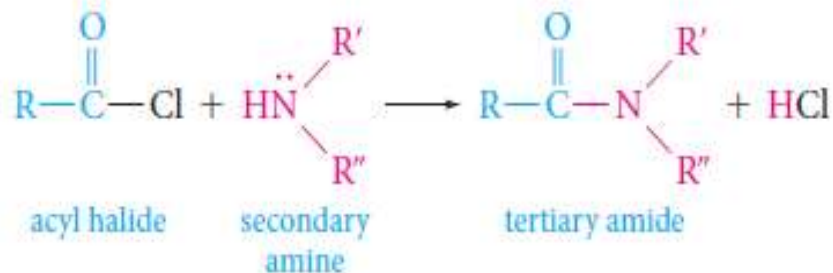
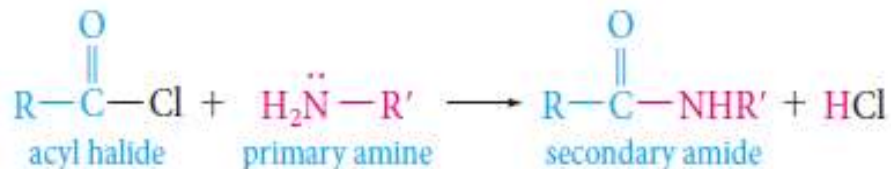


2) Alkylation and Acylation (amines as nucleophiles) :

with alkyl halides:

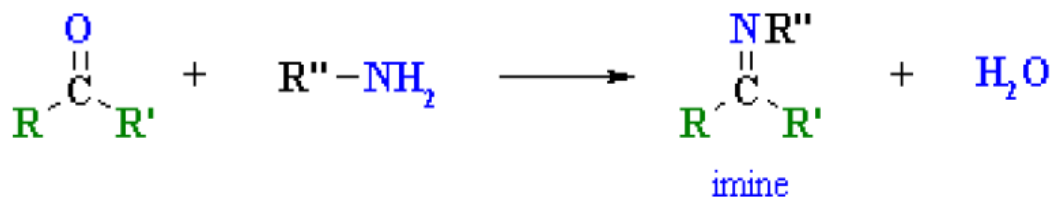


with acyl halides:

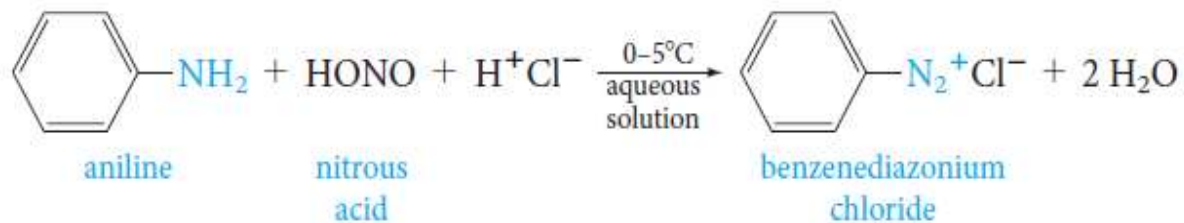


3) Imine Formation

with aldehydes
Or ketones:

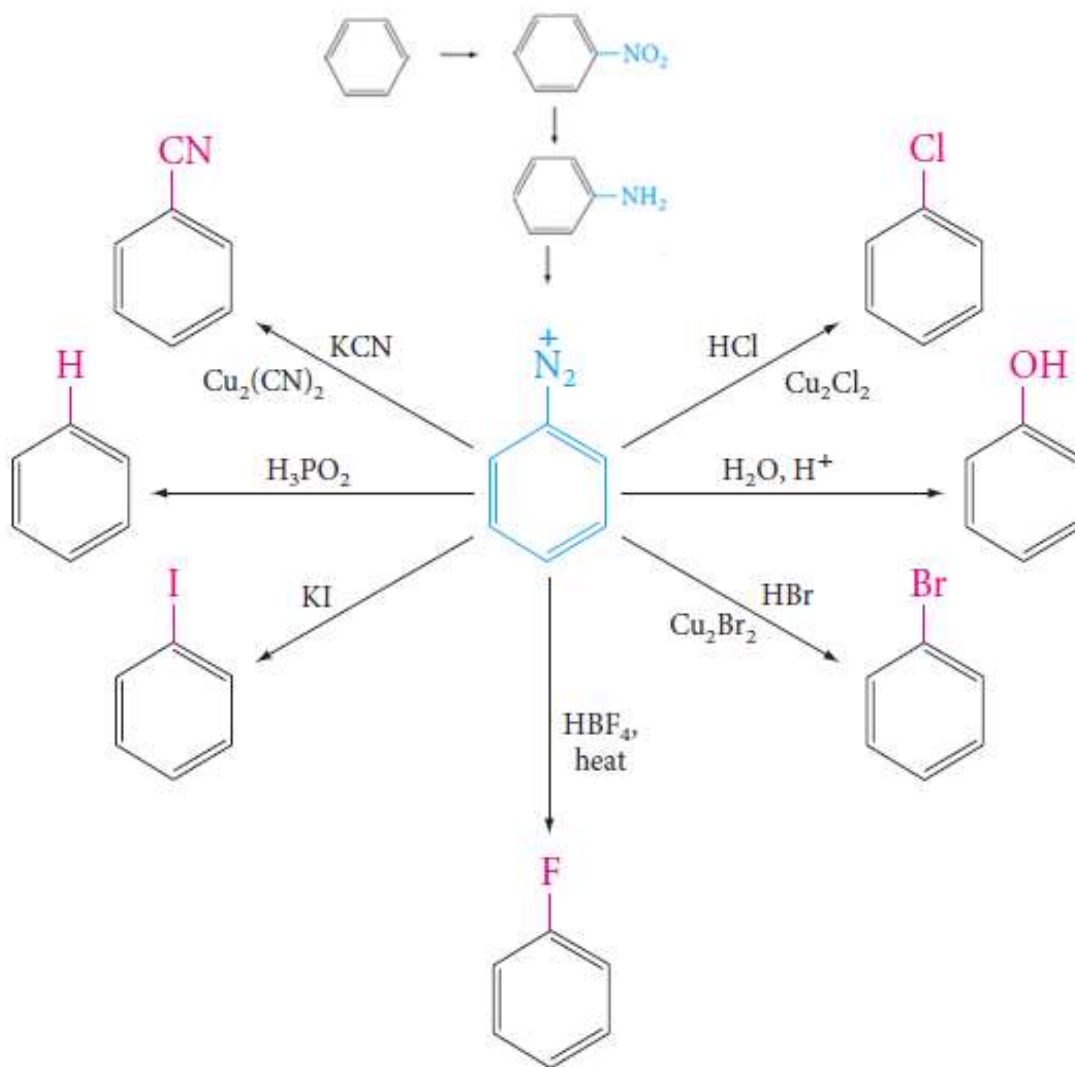


4) Aromatic Diazonium Salts (only primary aromatic)



Reactions of diazonium salts :

The (-N₂⁺) is good leaving group, can be replaced by **Nucleophiles** (**Nucleophilic Aromatic Substitution**)



Diazonium ions act as **Electrophiles** in **azo-coupling reactions**:

Azo-coupling of diazonium salts with activated aromatic compounds (for example phenols) to give azo-dyes :

