

## Amines

Bases , Substituted ammonia

Biologically significant : ammonia acids , DNA , RNA bases , alkaloids

### General formula

Primary amine  $R-NH_2$

Secondary amine  $R_2-NH$

Tertiary amine  $R_3-N$

Quaternary amine  $R_4-N^+ X^-$

Nitrogen compounds they are very important in chemistry and biology.

Nitrogen is very electronegative results in :

N-H bond being very polar

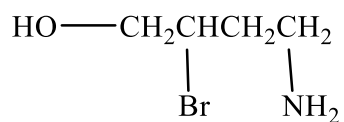
Hydrogen bonding being possible

High boiling points

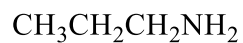
Amines being organic bases

### Nomenclature of amines

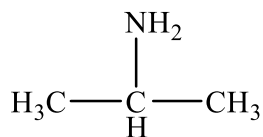
When a primary amine present with another functional group : Use same approach as with any branch or substituent .



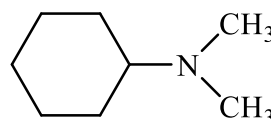
4-amino-2-bromo-1-butanol



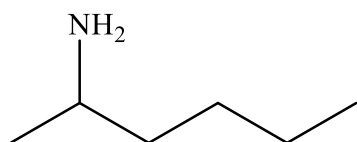
1-amino propane  
propyl amine



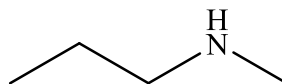
2-amino propane  
isopropyl amine



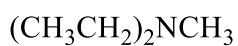
*N,N*-dimethylaminocyclohexane



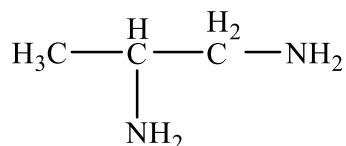
2-aminohexane



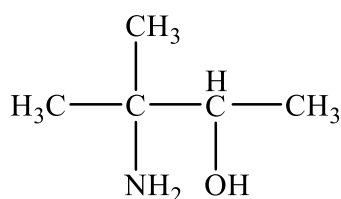
1-methylaminopropane  
*N*-methyl-1-aminopropane



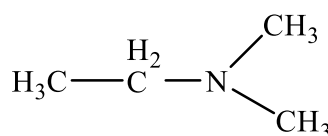
1-ethylmethylaminoethane  
*N*-ethyl-*N*-methyl-1-aminoethane



1,2-diaminopropane



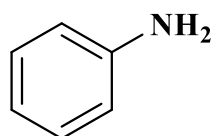
3-amino-3-methyl-2-butanol



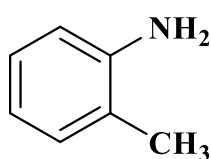
1,1-dimethylaminoethane

## Nomenclature of aromatic amines

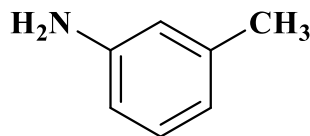
Many aromatic amines have special names that have been accepted as IUPAC names.



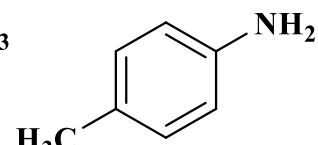
aniline



*o*-toluidine



*m*-toluidine



*p*-toluidine

## Some Common Names

Common approach is to give alkyl name with amine extension .

methylamine	$\text{H}_3\text{C}-\text{NH}_2$		
dimethylamine	$\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{C}-\text{N}-\text{CH}_3 \end{array}$		
ethylamine	$\text{H}_3\text{C}-\text{CH}_2-\text{NH}_2$		
ethylmethylamine	$\begin{array}{c} \text{H}_3\text{C} \\   \\ \text{H}-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$		
	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}-\text{NH}_2 \\   \\ \text{CH}_3 \end{array}$	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{N}(\text{H})-\text{CH}_3$
<b>IUPAC name</b>	1-amino butane	2-amino-2-methyl propane	1-methylaminopropane
<b>CA name</b>	butanamine	2-methyl-2-propanamine	1-methylpropanamine
<b>Common name</b>	n-butylamine	tert-butylamine	methylpropylamine

## Physical properties of amines

the boiling points of some common amines. 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, as shown in Table 2. 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.

Table (1) :- The boiling points of some sample amines

Name	Formula	b.p C°
ammonia	NH <sub>3</sub>	-33.4
Methyl amine	CH <sub>3</sub> NH <sub>2</sub>	-6.3
dimethyl amine	(CH <sub>3</sub> ) <sub>2</sub> NH-	7.4
trimethylamine	(CH <sub>3</sub> ) <sub>3</sub> N-	2.9
ethylamine	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	16.6
propyl amine	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	48.7
butyl amine	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	77.8
aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	184

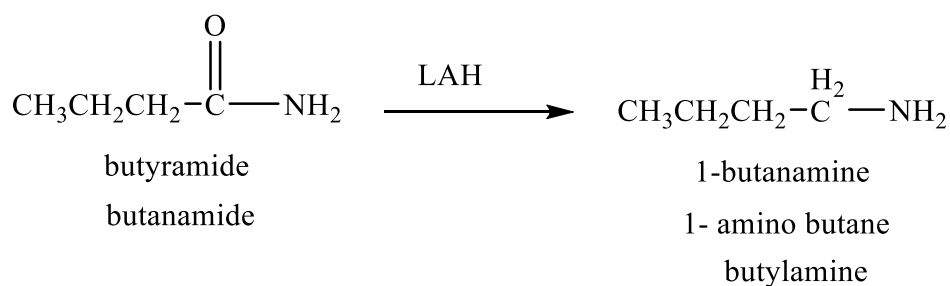
Table (2) :- A composition of Alkane , Amine and alcohol of boiling points

Family name	Comp. name	structure	M. wt	b.p C°	Comp. name	structure	M. wt	b.p C°
alkane	ethane	CH <sub>3</sub> CH <sub>3</sub>	30	-88.6	propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	44	-42.1
amine	methylamine	CH <sub>3</sub> NH <sub>2</sub>	31	-6.3	ethylamine	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	45	-16.6
alcohol	methanol	CH <sub>3</sub> OH	32	65.0	ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	46	78.5

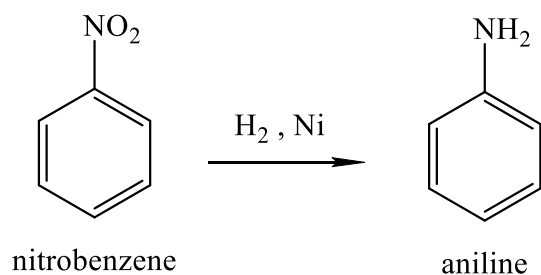
## Production of amines

### Laboratory Sources

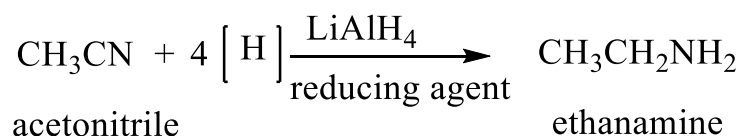
#### 1- from amide



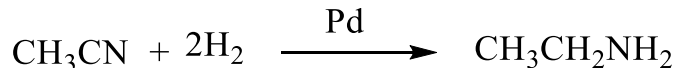
2- from nitro compounds



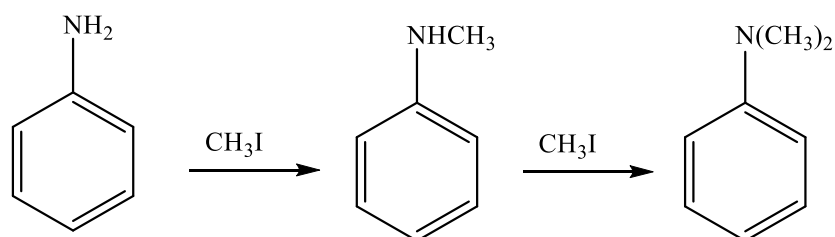
3- (a) The carbon- Nitrogen triple bond is reduced using hydrides to give a primary amine . For example, with ethane nitrile you get ethylamine.



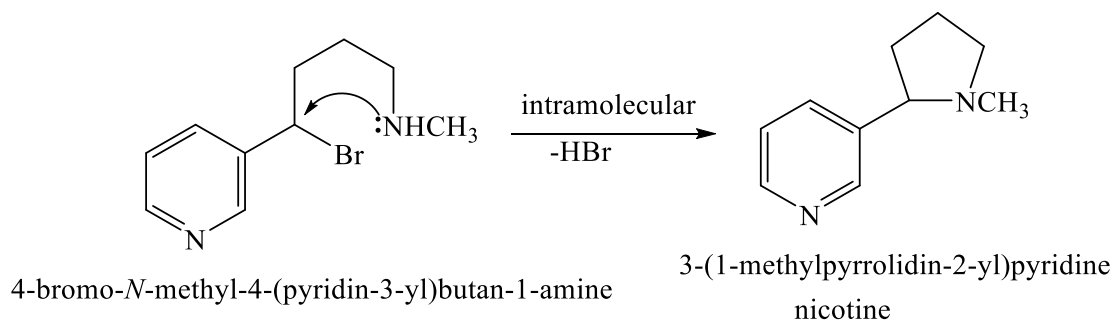
3- (b) The reduction of nitriles using hydrogen and a metal catalyst.



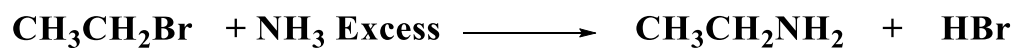
Aromatic amines can often be alkylated selectively



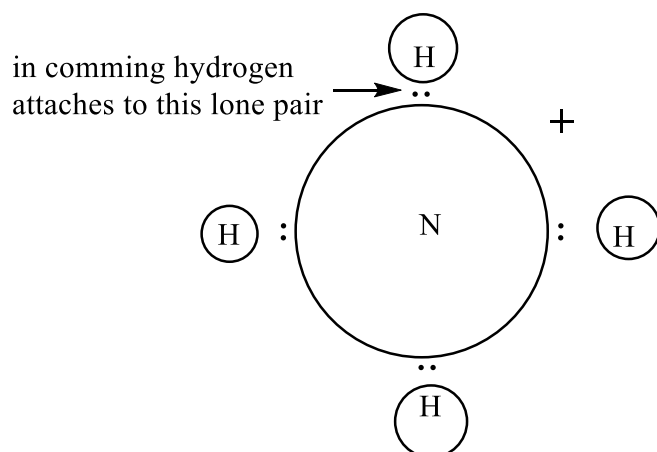
The alkylation can be intermolecular, as in the following final step in a laboratory synthesis of nicotine.



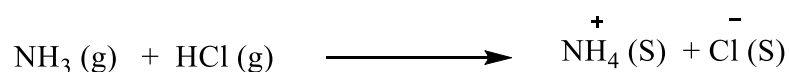
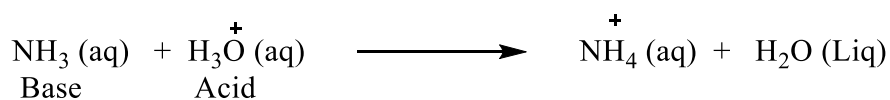
4- The more ammonia there is in the mixture the more the forward reaction is favored.



### Amines as Bases



### Formation of ammonium ion

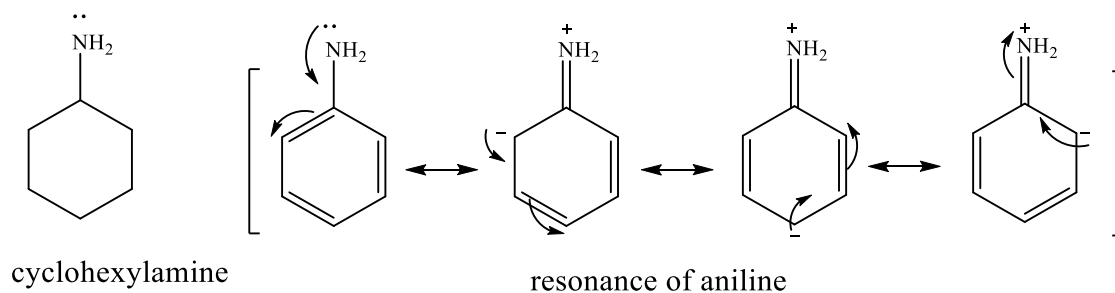


Amines are and the ammonia are considered bases.

Table (3) :- Basicity of some Common Amines , Expressed As Pka of the Corresponding Ammonium ions

Name	Amine	Ammonium ion	Pka of the ion	Pkb
ammonia	NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>	9.30	4.7
Methyl amine	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	10.84	
Di methyl amine	(CH <sub>3</sub> ) <sub>2</sub> NH	(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	10.71	
Tri methyl amine	(CH <sub>3</sub> ) <sub>3</sub> N	(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	9.77	
Ethyl amine	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	10.67	
Propyl amine	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	10.58	
aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	4.67	9.3

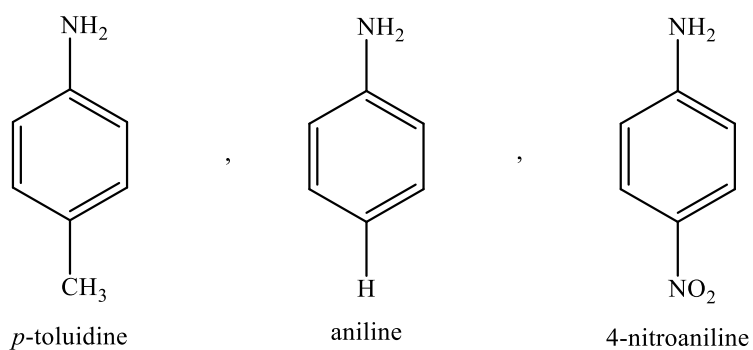
Aliphatic amines are stronger bases than aromatic amines **because of the resonance in aromatic amines.**



Electron donating groups increase the basicity of amines, and electron withdrawing groups decrease their basicity. Moreover, amines are stronger bases than amides.

CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> is **stronger base** than CH<sub>2</sub>(Cl)CH<sub>2</sub>NH<sub>2</sub>

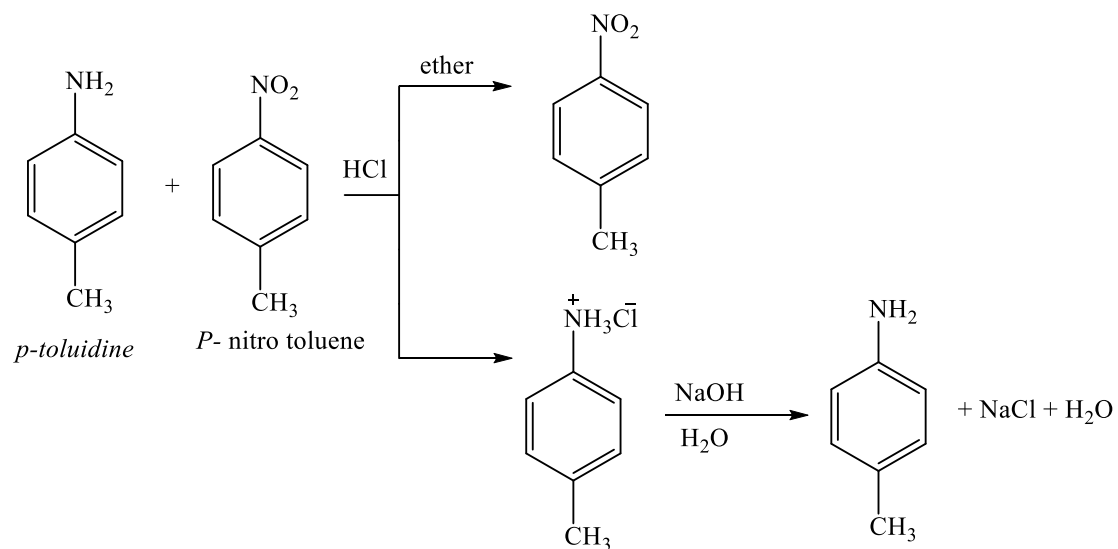
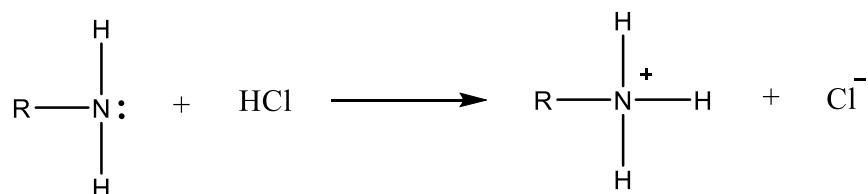
However, when comparing several aromatic amines, any of these amines is more basic as in the following example:-



The *p*-toluidine is **more basic** than the aniline and the 4-nitro aniline.

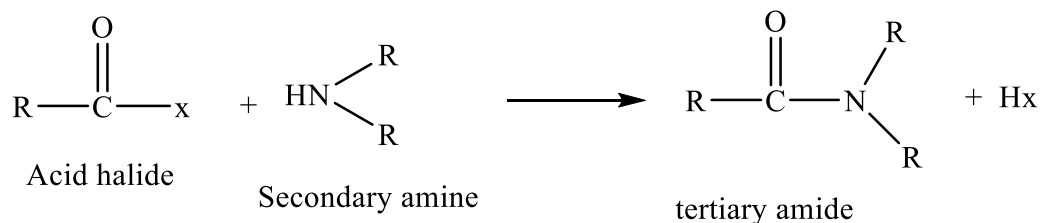
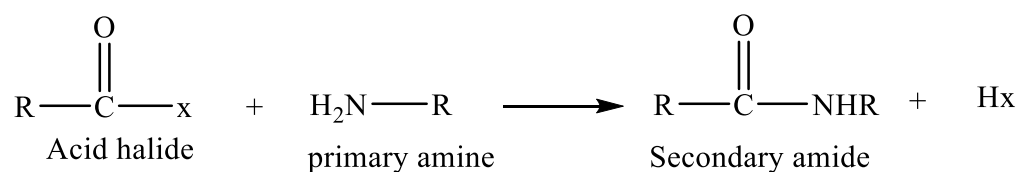
### Basicity of Amines

Amines react with acids product the ammonium ion.

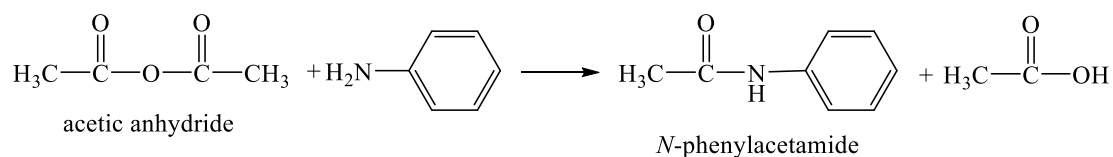




## Some Amines Reactions

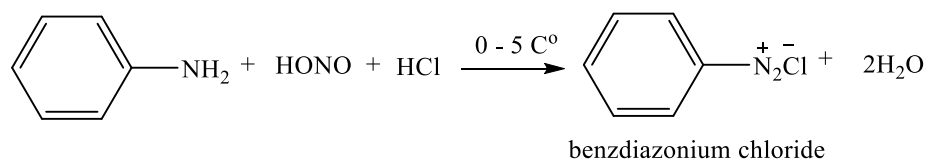


x = Cl, Br, I

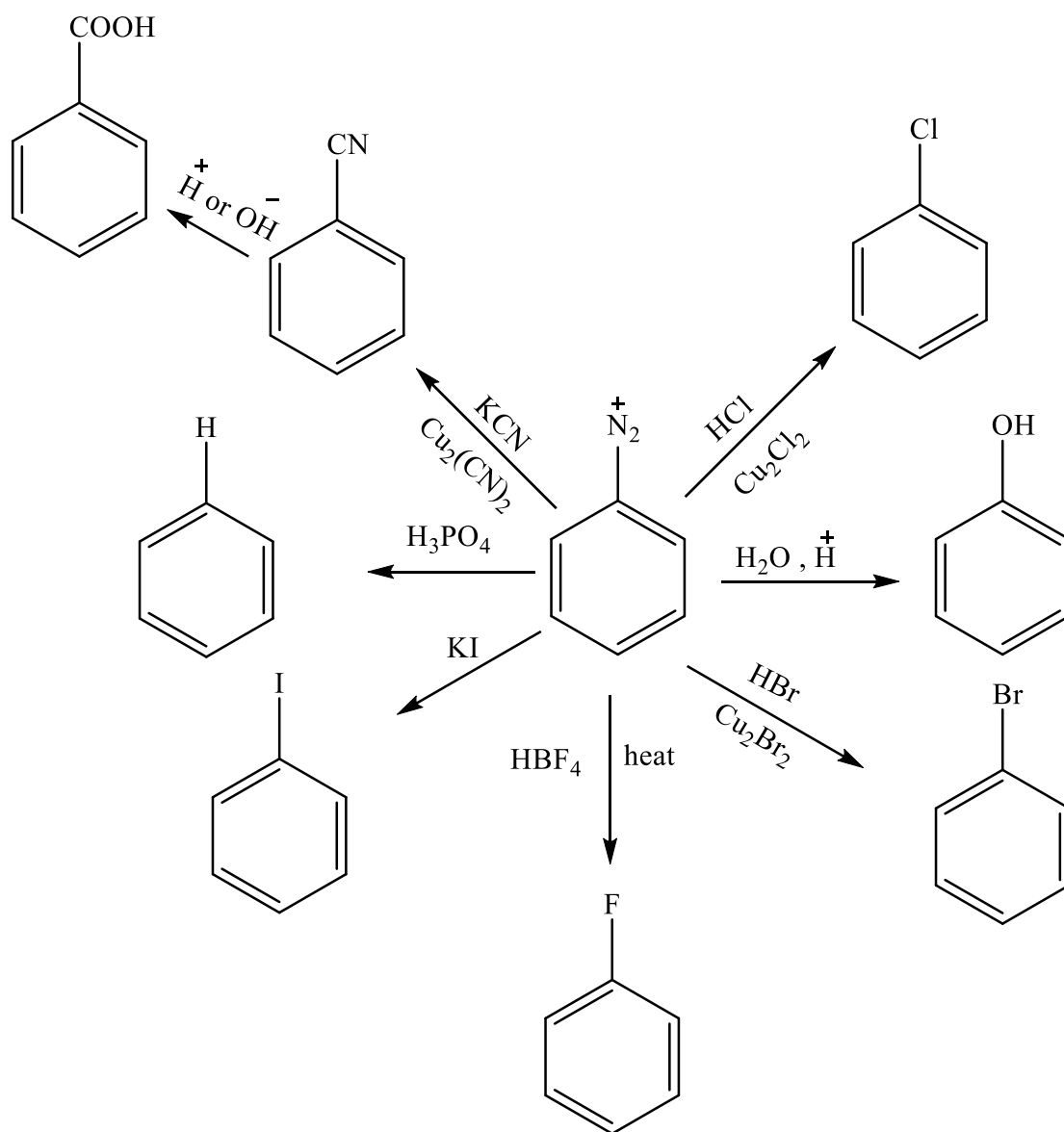


## Aromatic Diazonium Compounds

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



All these compounds are prepared from Diazonium salts



## Diazo Dyes

