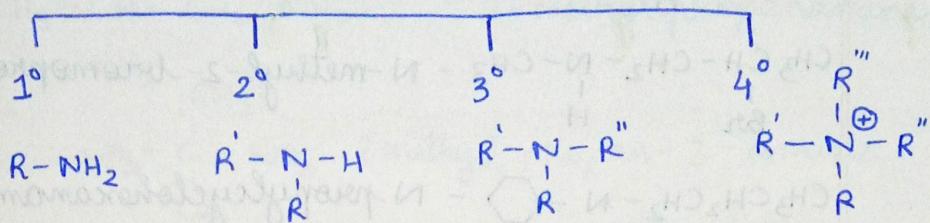


## Chapter - 13

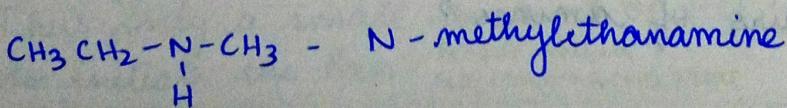
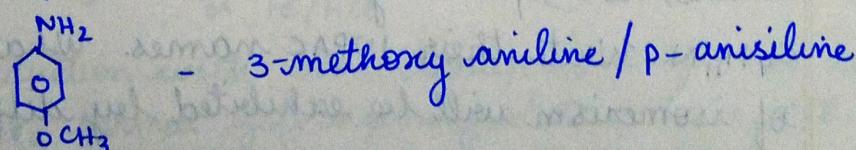
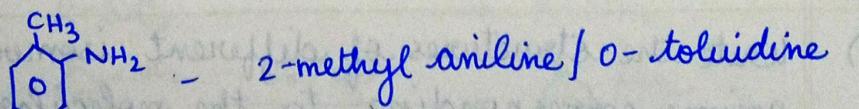
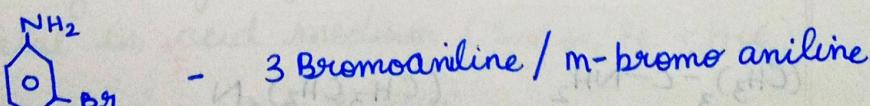
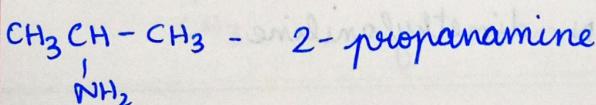
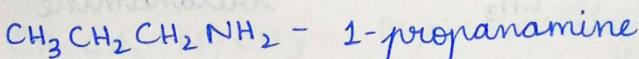
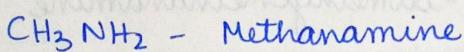
### AMINES

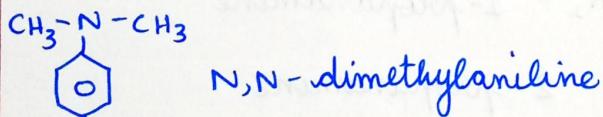
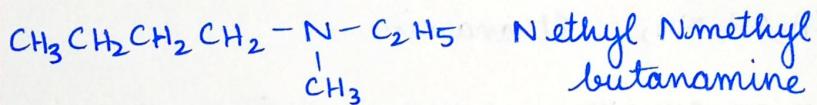
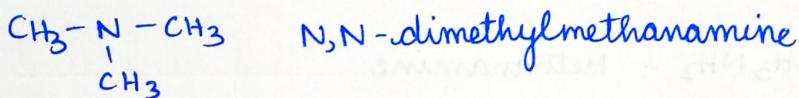
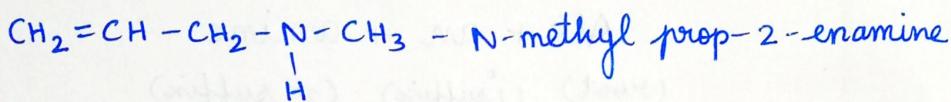
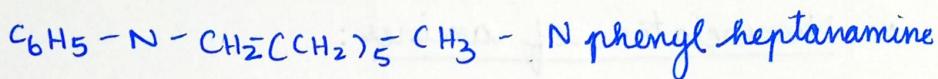
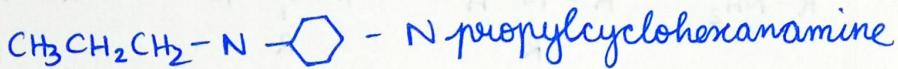
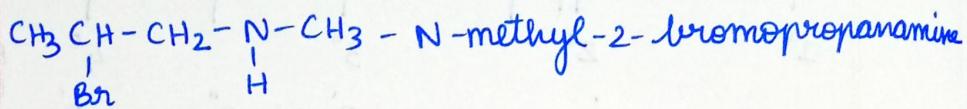
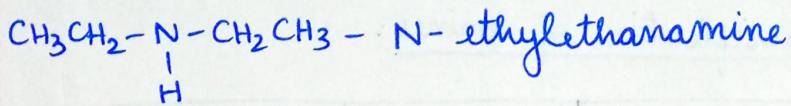
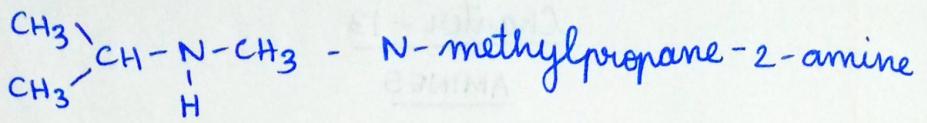
- Classification of Amines:



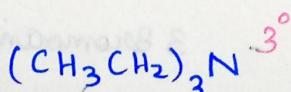
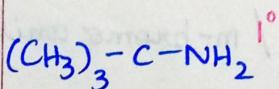
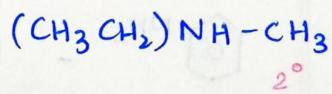
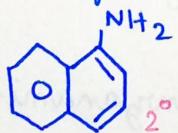
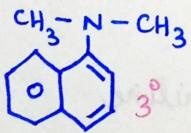
- Nomenclature of amines:

Alk + an + amine  
 (root)    ( $1^\circ$  suffix)    ( $2^\circ$  suffix)

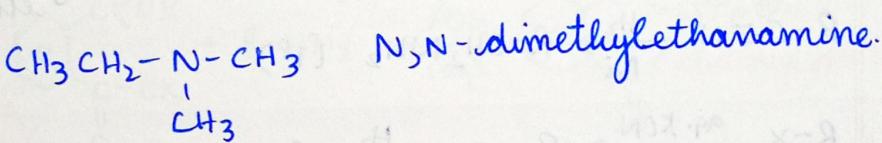
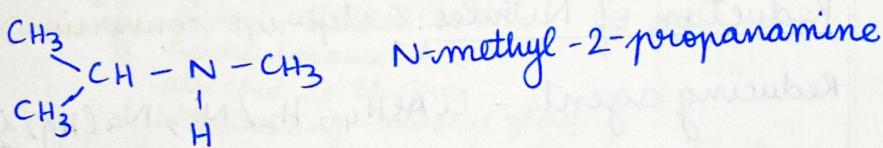
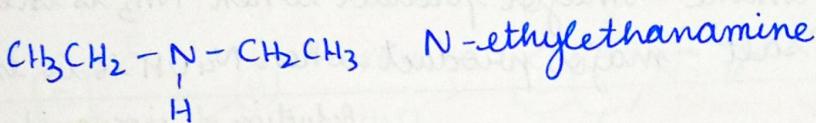
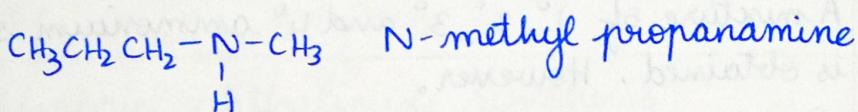
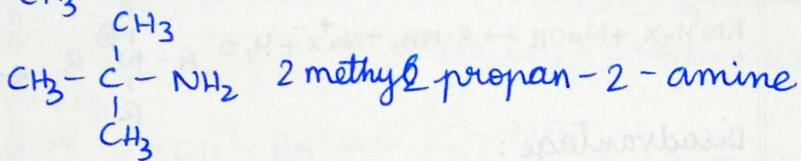
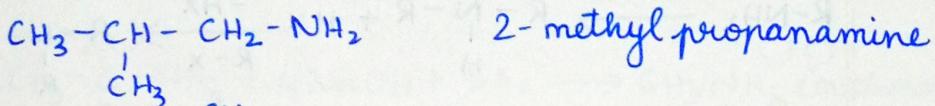
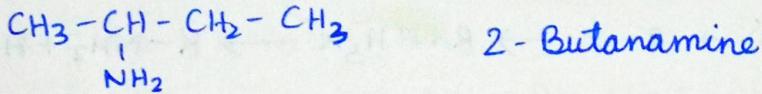
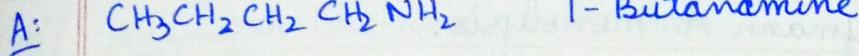




• Classify the following as  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ .



Q) Write the structures of different isomeric amines corresponding to the molecular formula  $\text{C}_4\text{H}_{11}\text{N}$ . Write their IUPAC names. What types of isomerism will be exhibited by different pairs of amines?

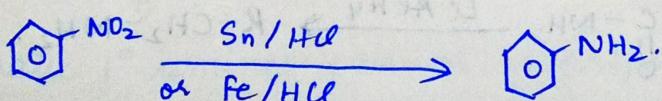
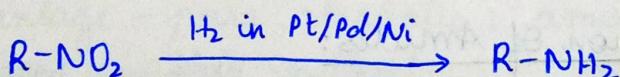


### Preparation of Amines:

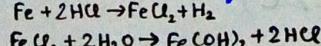
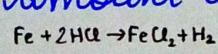
#### 1) Reduction of nitro compounds:

Catalytic hydrogenation ( $\text{H}_2$  in Pt/Pd/Ni)

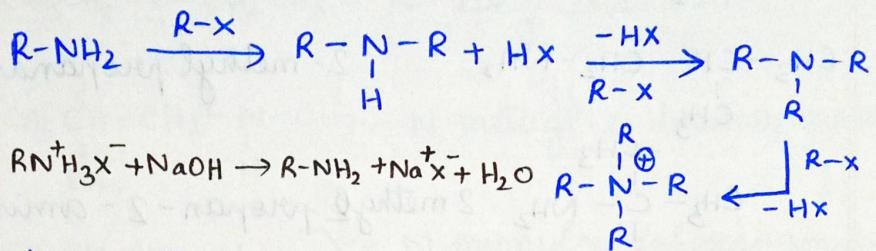
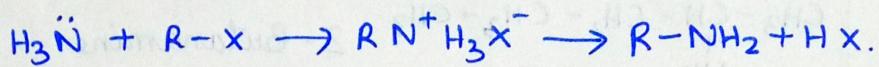
Metal in acid medium (Sn/Zn/Fe + HCl)



Reduction with iron scrap is preferred as  $\text{FeCl}_2$  formed gets hydrolysed to release  $\text{HCl}$ . Thus only a small amount of  $\text{HCl}$  is needed to initiate the Rxn.



## 2) Hoffmann Ammonolysis:



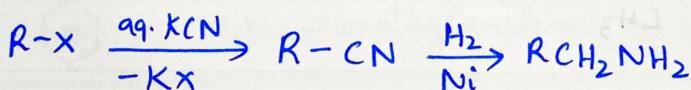
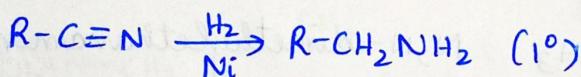
Disadvantage:

A mixture of  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$  and  $4^\circ$  ammonium salt is obtained. However,

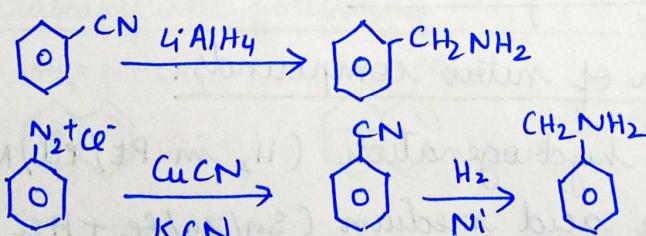
$1^\circ$  amine - major product when  $\text{NH}_3$  is in excess.  
 $4^\circ$  salt - major product when  $\text{NaOH}$  is in excess.

## 3) Reduction of Nitriles: (step-up conversion) Reduction of isocyanides,

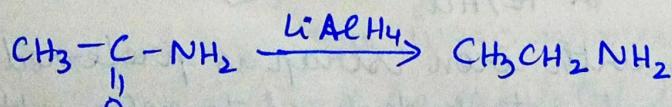
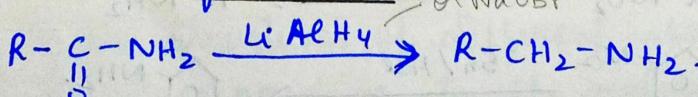
Reducing agents -  $\text{LiAlH}_4$ ,  $\text{H}_2/\text{Ni}$ ,  $\text{Na}(\text{Hg})$  in ethanol.



e.g.



## 4) Reduction Of Amides:

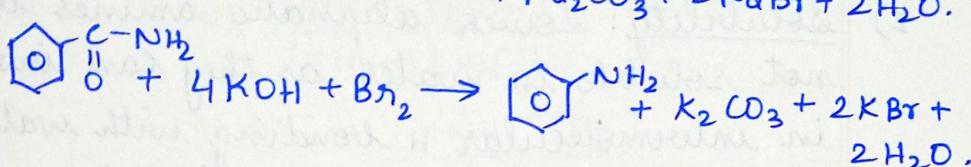
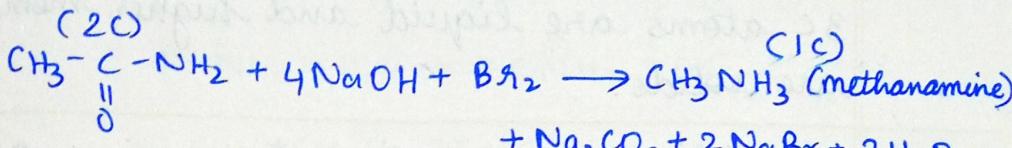
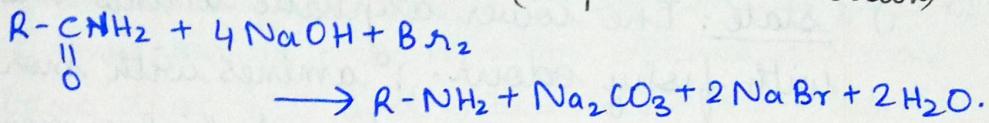


ethanamide  
(2C)

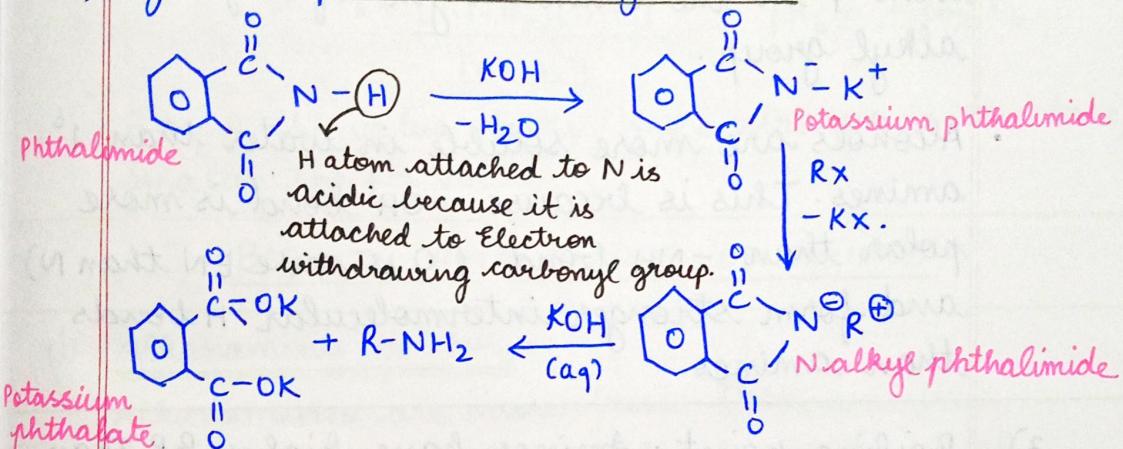
ethanamine (2C)

5) Hoffmann Bromamide Reaction:

(step-down conversion)



6) Laybourn phthalimide synthesis:



Note:

- 1) Hydrolysis is not done in acidic medium as the product formed is phthalic acid which will react with  $\text{R}-\text{NH}_2$  (base) to give back salt.
- 2) Advantage - pure aliphatic  $1^\circ$  amines can be prepared by this method.
- 3) Aromatic  $1^\circ$  amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution even with phthalimide ion.

## Physical properties:

- 1) State: The lower aliphatic amines are gases with fishy odour.  $1^\circ$  amines with more than 3c atoms are liquid and higher members are solids.
- 2) Solubility: Lower aliphatic amines are soluble in water as they can involve in intermolecular H bonding with water molecules. However, the solubility decreases with  $\uparrow$  in the chain length of hydrophobic alkyl group.
  - Alcohols are more soluble in water than  $1^\circ$  amines. This is because -OH bond is more polar than -NH bond ( $O$  is more EN than  $N$ ) and form stronger intermolecular H bonds than amines.
- 3) Boiling point: Amines have higher BP than hydrocarbons, haloalkanes, hydrocarbons and carbonyl compounds of comparable molar mass. This is because amines can involve in intermolecular H bonding and exist as associated molecules.
  - However, BP of amines are lesser than alcohols.
  - Among isomeric amines, the boiling point order is  $3^\circ < 2^\circ < 1^\circ$ . (Extent of H bond)
  - $3^\circ$  amines don't have intermolecular H bonding due to the absence of H atom available for H bond formation, whereas this intermolecular association is more in  $1^\circ$  amines as there are 2 H atoms available for H-bond formation.

## BASICITY OF AMINES

Amines are basic in nature due to the presence of lone pair of  $e^-$  on N atom. Amines are more basic than  $H_2O$  and gets easily protonated.



$$K = \frac{[R\overset{+}{N}H_3^+][OH^-]}{[RNH_2][H_2O]}$$

$$K_{H_2O} = \frac{[R\overset{+}{N}H_3^+][OH^-]}{[RNH_2]}$$

$$K_b = \frac{[R\overset{+}{N}H_3^+][OH^-]}{[RNH_2]} ; \quad pK_b = -\log K_b.$$

Larger the value of  $K_b$ , more stronger is the base, smaller the  $pK_b$  value.

## BASICITY RELATIONSHIP OF AMINES

### (i) Alkanamines vs $NH_3$ :

Alkanamines are more basic than ammonia because of the ERG (+I) Alkyl group which will increase the  $e^-$  density of N atom, thereby gets protonated easily in presence of an acid.

### (ii) $1^\circ, 2^\circ, 3^\circ$ amines:

a) In gas phase / non-polar solvents:  $3^\circ > 2^\circ > 1^\circ$   
The basic strength is expected to increase from  $1^\circ$  to  $3^\circ$  amines because of the presence of more ERG on  $3^\circ$  amines.

### b) In aqueous phase:

- Hydration / solvation effect: Hydration effect refers to stabilisation of protonated amines by water molecules. Water molecules form H bonds with protonated amines and release energy called hydration energy.

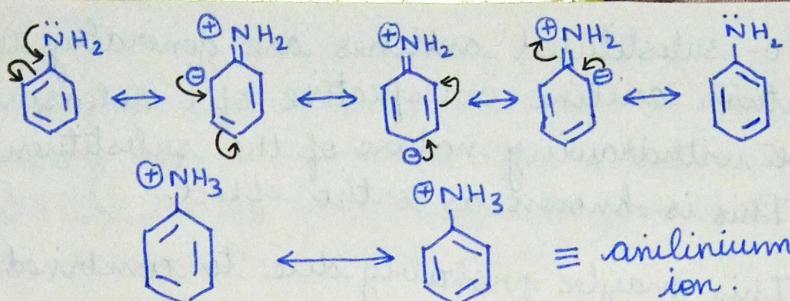
greater the extent of H bonding in protonated amines, more will be the stabilisation.

Consequently, greater will be the basic strength of protonated amines -  $1^\circ > 2^\circ > 3^\circ$

- Steric effect: It refers to the crowding of alkyl groups around N, which causes hindrance to protonation of amines. Steric effect  $\uparrow$  with  $\uparrow$  in no. of alkyl groups around N atom and consequently, the basic strength of amines due to steric factor should be  $1^\circ > 2^\circ > 3^\circ$ .
- The basic strength of amines in aqueous phase can be decided by the overall combined effect of +I effect, hydration effect and steric factors. All these factors favour the highest basic strength of  $2^\circ$  amines.
- If the alkyl group is small like methyl, then steric hindrance to H-bond is least, which predominates over the stability due to +I effect.  
 $[2^\circ > 1^\circ > 3^\circ (-CH_3)]$
- On the other hand, if the alkyl groups are bulkier like ethyl, there will be considerable steric hindrance to H-bonding. Thus in this case, +I effect predominates over stability due to H bond. Therefore, the order of basicity will be  $[2^\circ > 3^\circ > 1^\circ (-C_2H_5)]$

### (iii) Aryl amines vs Ammonia:

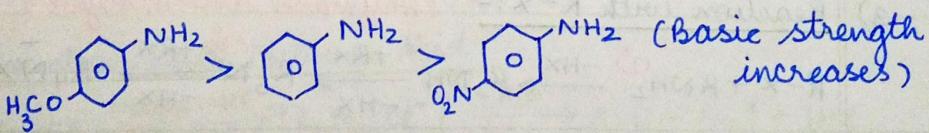
- Aromatic amines such as aniline are less basic than ammonia. The less basic character of aniline can be explained on the basis of resonance. The lp of  $e^-$  on N atom is withdrawn away from it. Therefore the  $e^-$  donating capacity of N for protonation is considerably decreased.



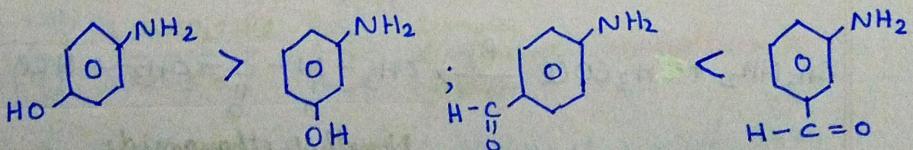
- Anilinium ion is less stabilised by resonance (lesser the no. of resonating structures, lesser the stability). So when aniline accepts a proton, it leads to the formation of less stabilised anilinium ion.
- Hence it is difficult for aniline to accept a proton and hence it is less basic.

### Effect of substituents on the basic nature of aromatic amines:

- ERG like  $-R$ ,  $-OR$ ,  $-OH$ ,  $-NH_2$  ↑ the basic strength because they tend to stabilise the cation formed by protonation of amines.
- EWG, like  $-X$ ,  $-NO_2$ ,  $-C(=O)-$ ,  $-C(=O)OH$  decreases the basic strength. They tend to destabilise the protonated amines.

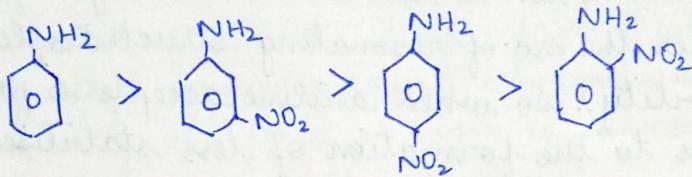


The base weakening effect of EWG and the base strengthening effect of ERG is more pronounced at para position than at meta.

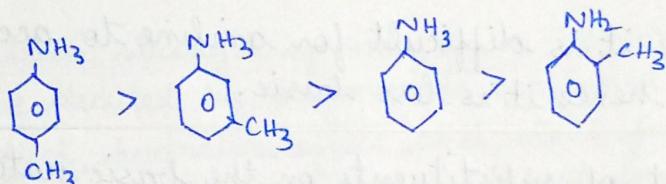


o-substituted anilines are generally weaker than aniline irrespective of e<sup>-</sup> releasing or e<sup>-</sup> withdrawing nature of the substituent. This is known as ortho effect.

This maybe probably due to combined electronic and steric factors.

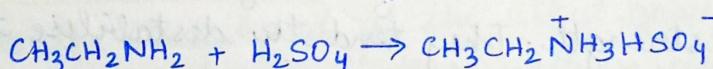
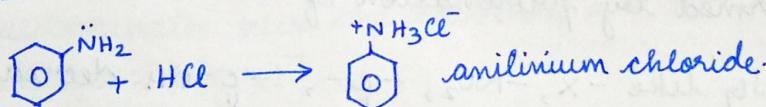
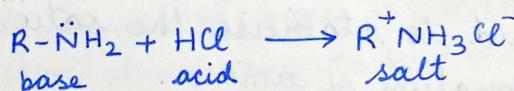


Basic character decreases →

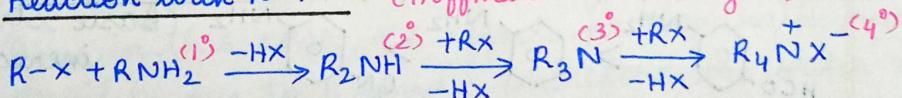


### Chemical Properties

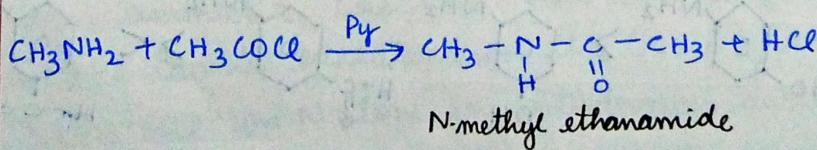
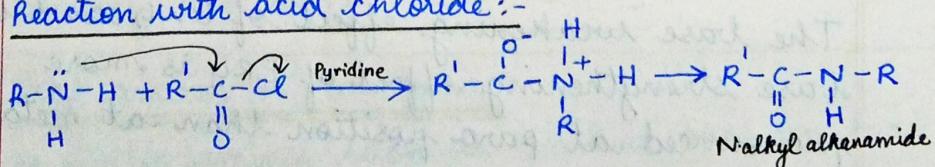
#### 1) Reaction with acids :-



#### 2) Reaction with R-X :- (Hoffmann ammonolysis)

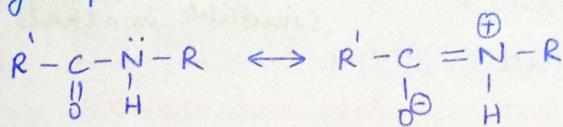


#### 3) Reaction with acid chloride :-



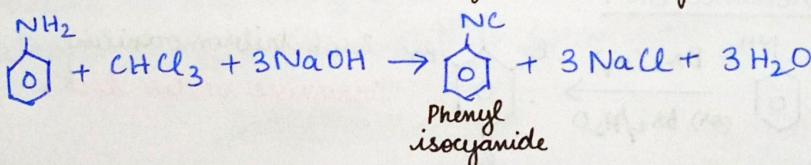
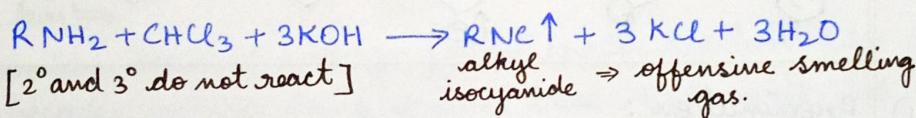
### Note:

- (i) Reaction with acid chloride takes place in the presence of strong base like pyridine. This is because the base neutralises the by-product acid to form salt and hence favours the forward rxn.
- (ii) The N-alkyl alkanamide formed will not further react with acid chloride because the lp of  $e^-$  on N atom is involved in resonance with the carbonyl group. Hence it is not available for Nu addition.

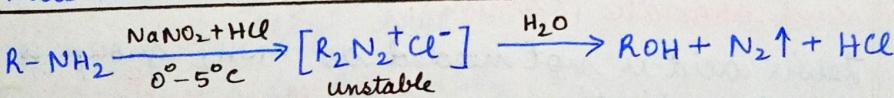


### 4) Carbonylamine reaction:

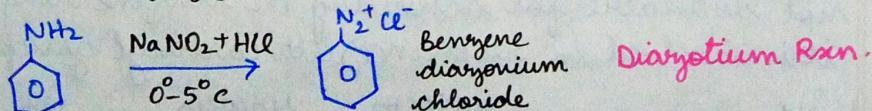
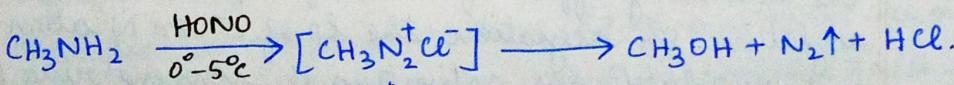
- Both aliphatic and aromatic  $1^\circ$  amines react with chloroform in presence of caustic soda/caustic potash to give iso-cyanides which are offensive-smelling
- This acts as a test to distinguish between  $1^\circ$  and  $2^\circ$  amines.



### 5) Reaction with Nitrous Acid:



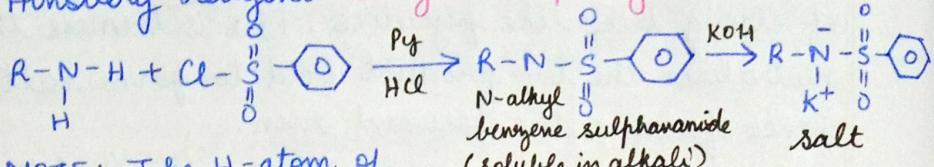
- This rxn is helpful in quantitative estimation of amino acids.



Note: This reaction with HONO is used as a test to distinguish between aliphatic and aromatic  $1^\circ$  amines.

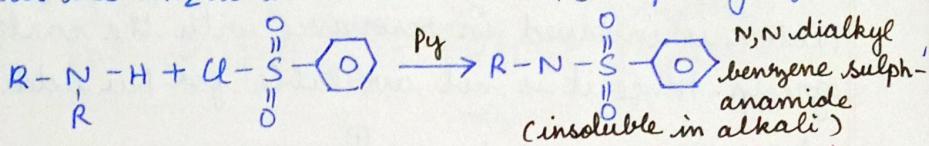
### 6) Hinsberg test:

Hinsberg reagent - Benzene sulphonyl chloride



NOTE: The H-atom of

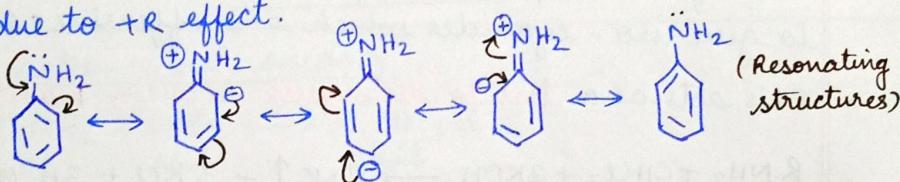
N-alkyl benzene sulphonamide is acidic in nature as the  $\text{NH}_2$  is attached to EWG (sulphonyl group)



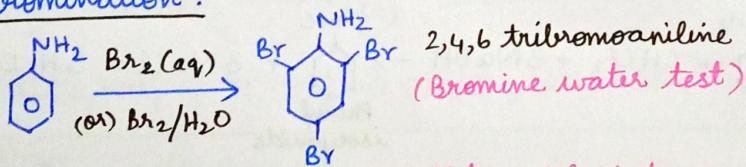
NOTE: This is used as a test to distinguish between  $1^\circ, 2^\circ, 3^\circ$  amines (both aliphatic and aromatic)

### Electrophilic Substitution Reaction

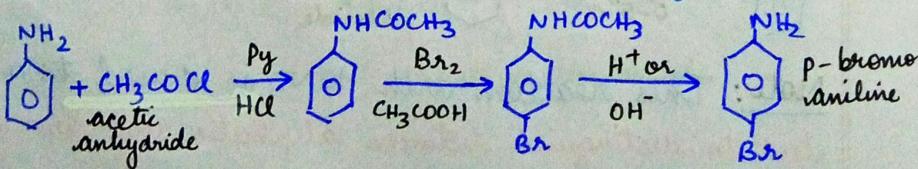
$-\text{NH}_2$  group is highly activating and hence increases the electron density at O and P positions due to  $+R$  effect.



### 1) Bromination:



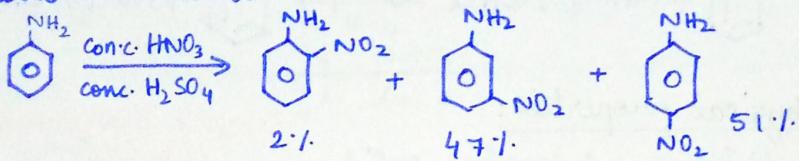
- This acts as a test to distinguish between aliphatic and aromatic  $1^\circ$  amines.
- Lewis acid is not needed as  $-\text{NH}_2$  group is highly activating.
- The activating effect of  $-\text{NH}_2$  group is decreased by acylation. On acylation, the lp of  $e^-$  on N atom is not available for activating the benzene ring (as it is involved in resonance with carbonyl group).



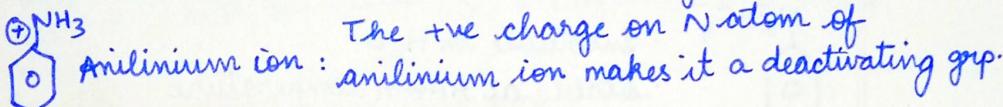
2)

### Nitration:

Aniline on nitration gives tarry oxidation along with nitro derivatives.

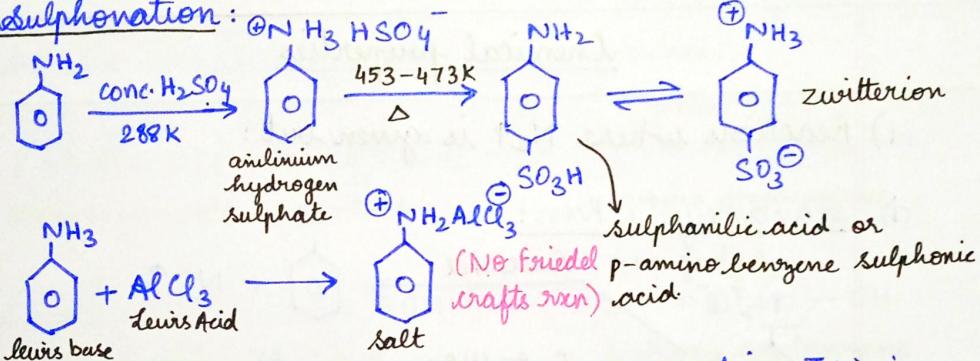


Nitration of aniline gives substantial amount of meta product because in acidic medium, aniline forms anilinium ion which is meta-directing.



3)

### Sulphonation:



Aniline does not undergo Friedel-Crafts reaction. This is because aniline being a lewis base reacts with the catalyst  $\text{AlCl}_3$ , a lewis acid to form salt.

### Diaryonium Salts

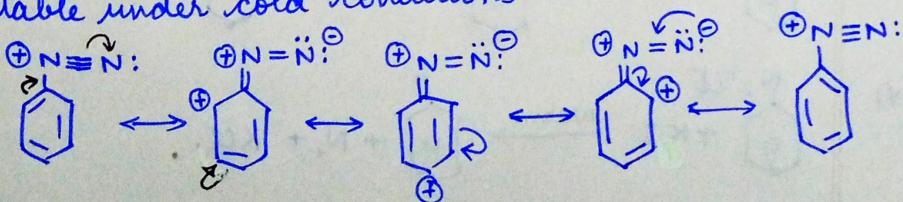
General formula -  $\text{RN}_2^+ \text{X}^-$

R = Alkyl, aryl.

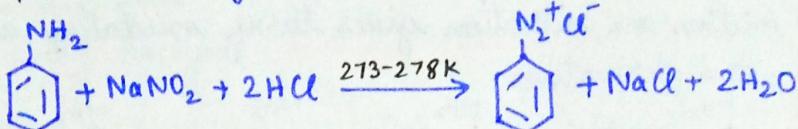
X =  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$ .

Benzene diaryonium salt - more stable than aliphatic diaryonium salt.

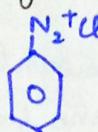
Aliphatic diaryonium salts are unstable and readily decompose in aqueous medium to give alcohol and Nitrogen gas ( $\text{N}_2 \uparrow$ ). Whereas aryl diaryonium salts are stable under cold conditions due to resonance.



Preparation: By diazotisation reaction

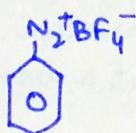


Physical properties:



- colourless solid
- soluble in  $\text{H}_2\text{O}$
- stable at cold temp. ( $0^\circ - 5^\circ\text{C}$ )
- Readily decomposes on warming.

Benzene diazonium chloride



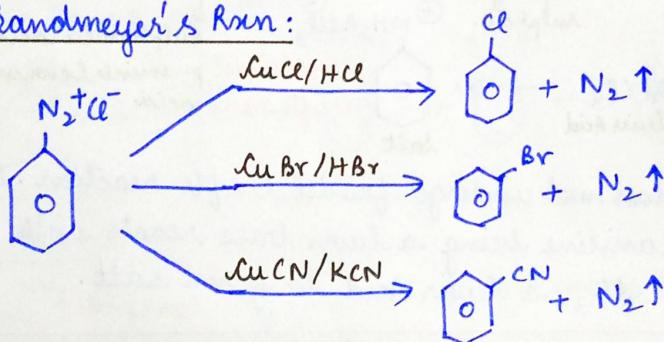
- Insoluble in  $\text{H}_2\text{O}$
- stable at room temperature

Benzene diazonium fluoroborate.

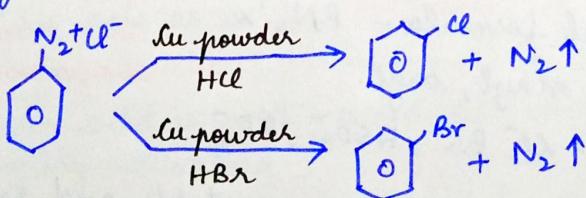
Chemical properties

i) Reactions where  $\text{N}_2\uparrow$  is given out:

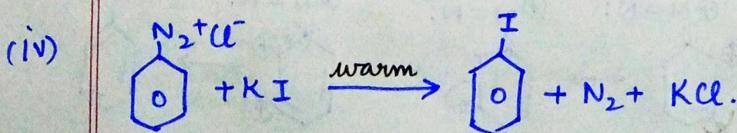
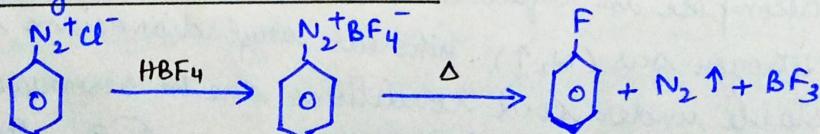
(i) Sandmeyer's Rxn:



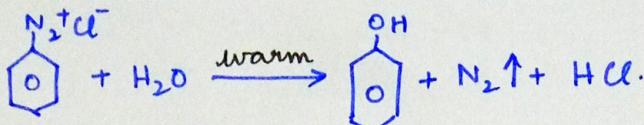
(ii) Gattermann Reaction:



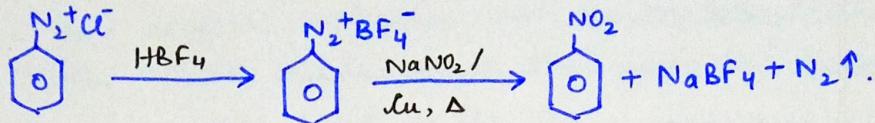
(iii) Baumann-Schiemann Reaction:



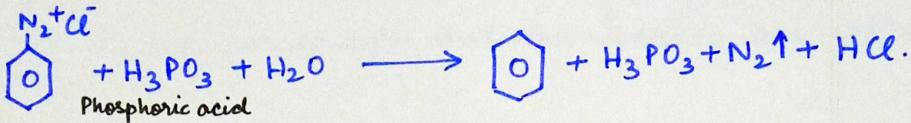
(V)



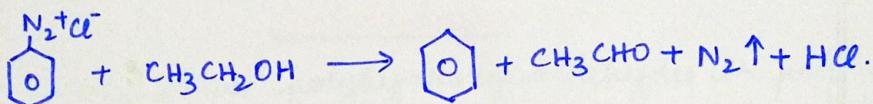
(VI)



(VII)



(VIII)



2) Reactions where N is retained:

Coupling reaction: This test is used to distinguish between aliphatic and aromatic  $1^\circ$  amines.

