

AMINES

①

(ORGANIC CHAPTER-4)

Alkyl or aryl derivatives of ammonia are regarded as amines.

IUPAC:- Alkanamine

Common name:- Alkylamine

Thus, characteristic functional groups for 1° , 2° or 3° amines are:-

$-\text{NH}_2$:- **primary**. Eg:- CH_3NH_2
Methanamine

$-\text{NH}-$:- **secondary**. Eg:- $\text{CH}_3-\text{NH}-\text{CH}_3$
N-Methylmethanamine

$-\text{N}-$:- **tertiary**. Eg:- $\text{CH}_3-\text{N}(\text{CH}_3)_2$
N,N-Dimethylmethanamine

STRUCTURE OF AMINES:-

In amines, nitrogen is sp^3 hybridized and the molecule have pyramidal shape like that in NH_3 . Therefore, in 1° and 2° amines, the bond angle is 107° . However, in 3° amines, the bond angle is 108° due to presence of three bulky alkyl groups around N atom (due to steric hindrance)

IUPAC name of some amines that were asked in board examination:-

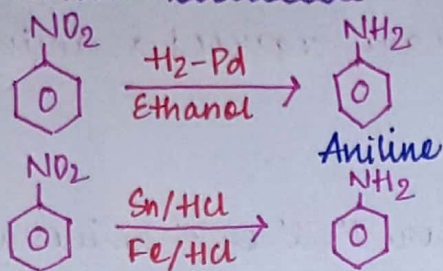
STRUCTURE	IUPAC name
1. $\text{CH}_3-\text{NH}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	N-methyl-2-methylpropanamine
2. $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$	N-Ethyl-N-methylethanamine
3. $\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{N}(\text{CH}_3)_2$	N,N-Dimethylbutanamide
4. $\text{NH}-\text{COCH}_3$ 	N-Phenyl ethanamide
5.	2,4-Dibromoaniline
6. $(\text{CH}_3)_2\text{N}-\text{CH}_2\text{CH}_3$	N,N-Dimethyl ethanamine

(JM)

PREPARATION OF AMINES:-

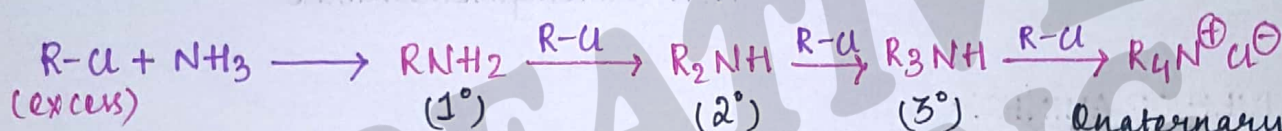
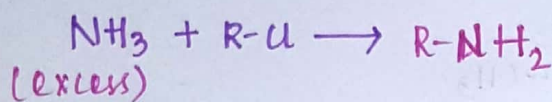
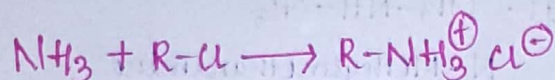
(2)

① Reduction of nitro compounds:-



The reaction with Iron scrap and HCl is preferred because the FeCl_2 get hydrolysed to form Hydrochloric acid. Thus, a little amount of HCl is required to initiate the reaction.

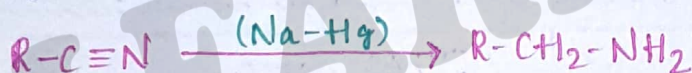
② Ammonolysis of alkyl halide:-



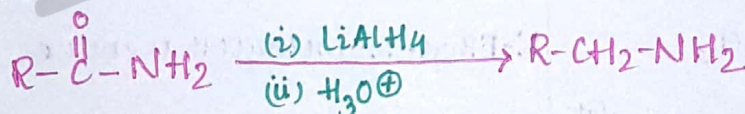
Quaternary Ammonium salt

It forms a mixture of 1°, 2°, 3° and quaternary ammonium salt. So, yield of product is less.

③ From nitriles:-

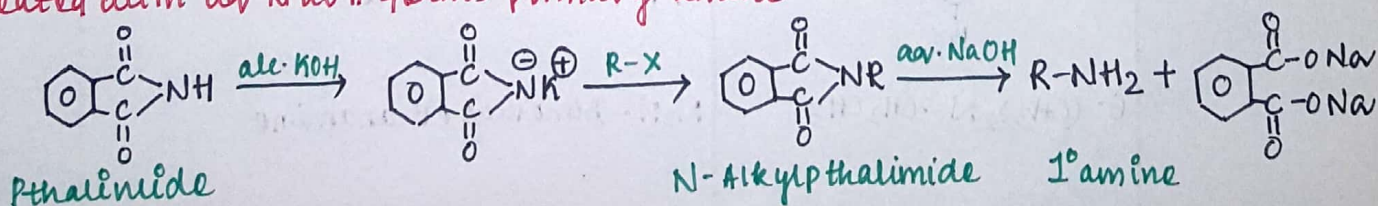


④ From amides:-



⑤ Gabriel Pthalimide Synthesis:-

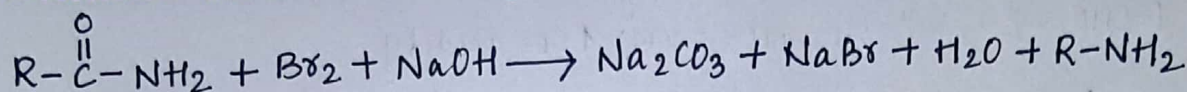
When phthalimide is treated with alc. KOH, it forms potassium phthalimide which on treating with suitable alkyl halide, forms N-alkene when treated with aq. NaOH forms primary amine.



It will attack from the backside of R-X following S_N2 mechanism. (3)
So, R must be primary.

Haloarenes (Aniline) do not undergo nucleophilic substitution reaction, so they cannot be prepared by Gabriel Phthalimide synthesis.

⑥ Hoffmann bromamide degradation reaction:-



The 1° amine contains one C less than the parent amide.

PHYSICAL PROPERTIES:-

① Solubility:-

They are soluble in water as they are able to form hydrogen bonding with water molecules.

Aniline is soluble in organic solvent like ether, benzene and alcohol. Alcohol are more polar than amine because of intermolecular hydrogen bonding with water molecules.

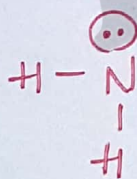
The order of solubility of amine is $1^\circ > 2^\circ > 3^\circ$

② Boiling Point:-

Carboxylic Acid > Alcohol > Amine > Aldehyde > Ketone > Ether > Alkane
The boiling point of alcohol is greater than amine because of more electronegativity of oxygen than ammonia.

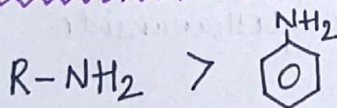
CHEMICAL REACTIONS:-

① BASICITY OF AMINES:-



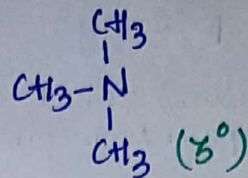
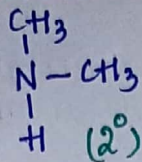
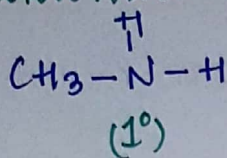
Due to presence of lone pair of e^- in the benzene ring, it can able to donate a pair of electron. So, it act as a Lewis base.

② Alkyl amine vs Aryl amine:-



The lone pair of electrons are delocalised over the benzene ring due to resonance. So Aniline is a weak base.

③ On the basis of degree of amine:-

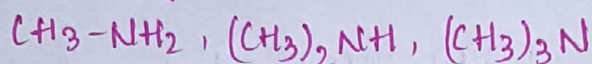


- EDG ($-\text{CH}_3$, $-\text{OH}$, etc) ↑ basicity
- EWG ($-\text{CHO}$, $-\text{C}=\text{O}$, $-\text{C}=\text{O}-\text{OH}$, $-\text{NO}_2$, $-\text{CN}$) ↑ acidity

Order of basicity is $3^\circ > 2^\circ > 1^\circ$.

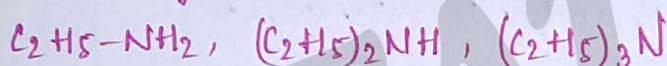
④ In aqueous phase,

- If R is a CH_3 group then,



Trick:- (i) 1st write solvation order. i.e $1^\circ > 2^\circ > 3^\circ$
 (ii) Keeping the last one fixed, interchange the positions i.e $2^\circ > 1^\circ > 3^\circ$

- If R is any other group then,

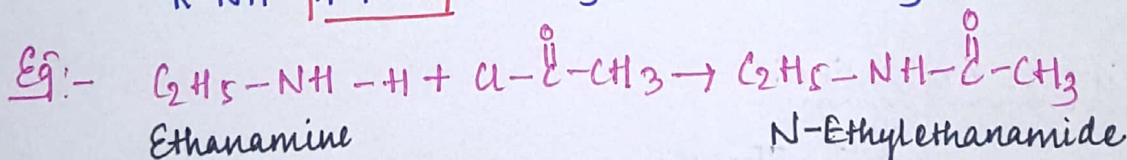
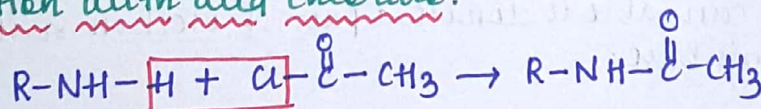


Trick:- (i) 1st write +I order. i.e $3^\circ > 2^\circ > 1^\circ$
 (ii) Keeping the last one fixed, interchange the positions. i.e $2^\circ > 3^\circ > 1^\circ$

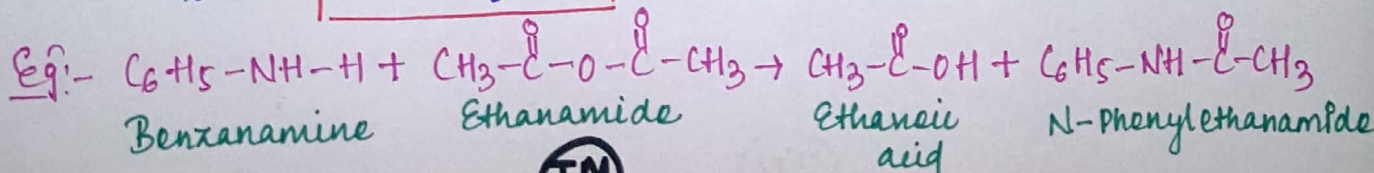
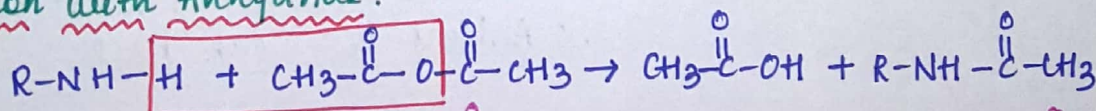
⑤ In gaseous phase, the order is $3^\circ > 2^\circ > 1^\circ$.

⑥ ACYLATION:- The aliphatic and aromatic, 1° and 2° amine react with acid chloride, anhydride and ester. This reaction is known as acylation & the product formed are known as amide.

(a) Reaction with acid chloride:-



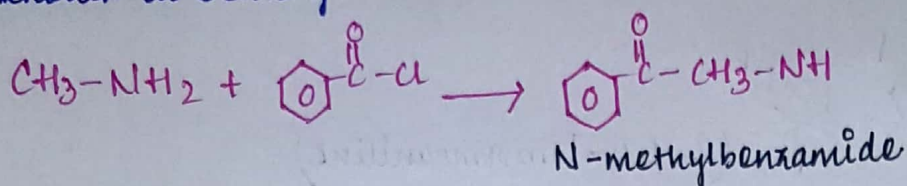
(b) Reaction with Anhydride:-



(JM)

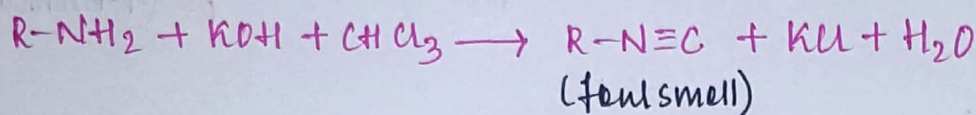
⑦ Benzoylation:-

When amines react with benzoyl chloride (C_6H_5COCl). This reaction is known as benzoylation.



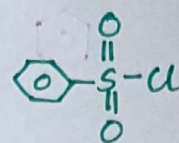
⑧ Carbylamine reaction:-

- used for the distinction of primary amines from others.



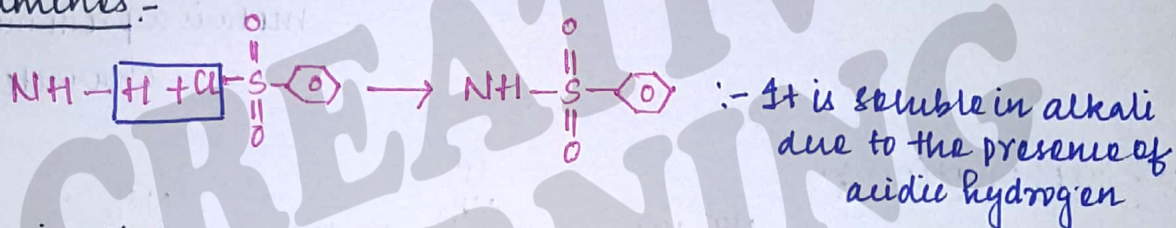
⑨ Hinsberg's Test:-

- Hinsberg reagent is benzene sulphonyl chloride. i.e.

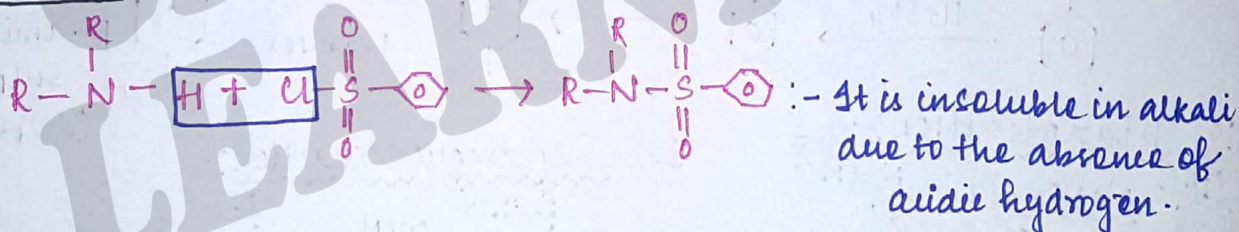


- used for the distinction of 1° , 2° and 3° amines.

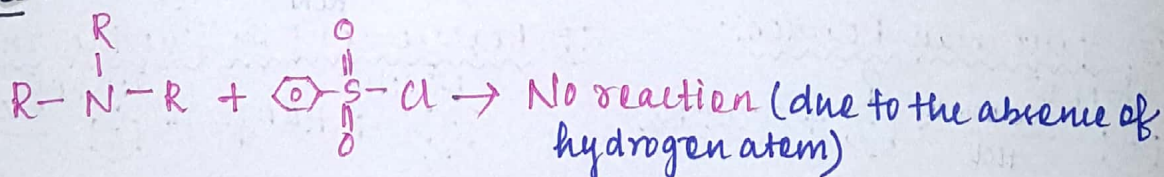
(a) 1° amines:-



(b) 2° amines:-

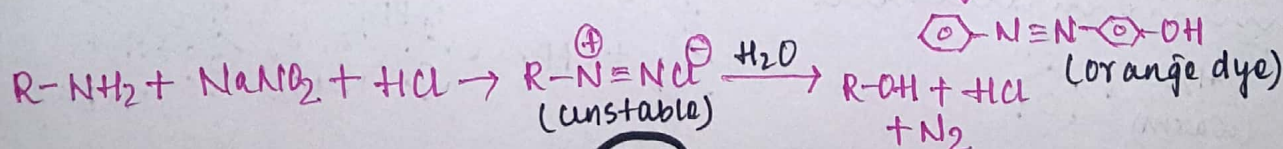
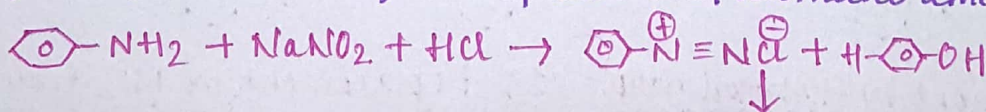


(c) 3° amines:-



⑩ AZODYE TEST/COUPLING TEST:-

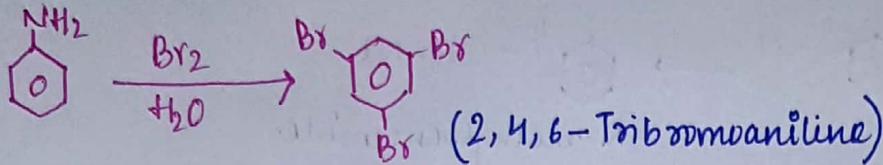
- used for the distinction of 1° aliphatic and aromatic amine.



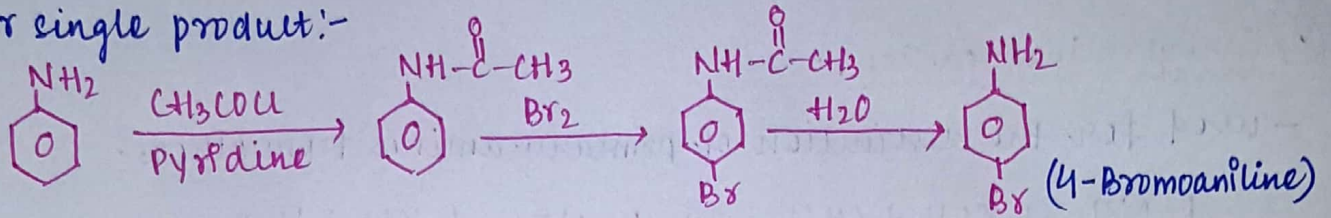
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(11) ELECTROPHILIC SUBSTITUTION REACTION:-

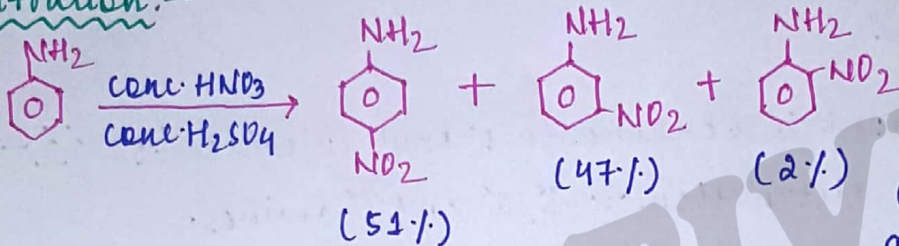
(a) Bromination:-



for single product:-

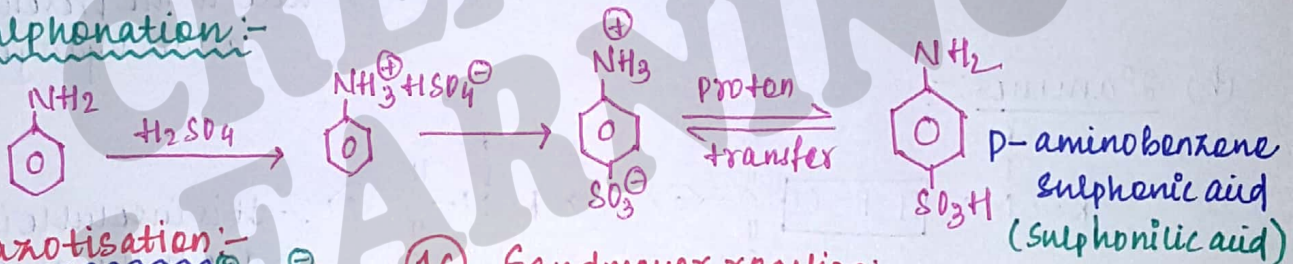


(b) Nitration:-

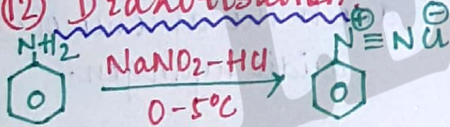


Aniline when treated with H_2SO_4 forms anilinium ion where as NH_3^+ act as a strong EWG. So meta is a predominant character

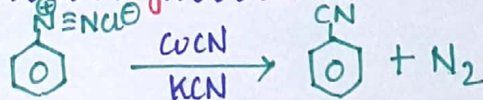
(c) Sulphonation:-



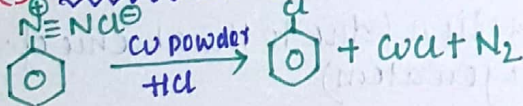
(12) Diazotisation:-



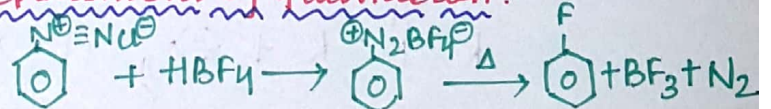
(16) Sandmeyer reaction:-



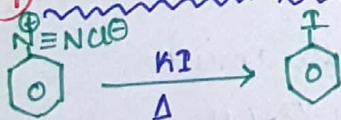
(13) Gatterman Reaction:-



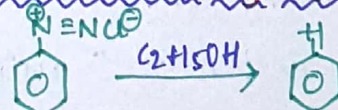
(17) Replacement by fluoride ion:-



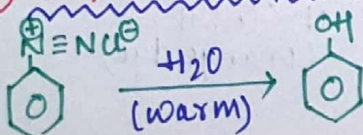
(14) Replacement by Iodine:-



(18) Replacement by hydroxyl:-



(15) Replacement by Hydroxyl group:-



(19) Replacement by NO₂ group:-

