# Unit :- Amines

⇒ Amines are considered as derivative of ammonia in which one or more hydrogen from ammonia is replaced by Hydrocarbon group.

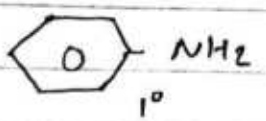
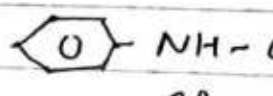
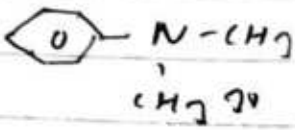
$R-NH_2$ (1°) $\quad R-NH-R$ (2°) $\quad R-\underset{R'}{\overset{|}{N}}-R$ (3°)

# classification of amines :-

On the basis of number of Hydrogen replaced from ammonia by Hydrocarbon group, amines are classified as primary, second & tertiary amine.

Eg :- primary amine $CH_3-NH_2$ (1°); Secondry amine $CH_3-NH-CH_3$ (2°); tertiary amine, $CH_3-\underset{CH_3}{\overset{|}{N}}-CH_3$ (3°)

$CH_3-CH_2-NH_2$ (1°) $\quad CH_3-CH_2-NH-CH_3$ (2°) $\quad CH_3-CH_2-\underset{CH_3}{\overset{|}{N}}-CH_3$ (3°)

 (1°)  (2°)  (3°)

Secondry & tertiary amine can be further divided into two class;

(a) Simple amine :-

These are secondry or tertiary amine containing same hydrocarbon group.

Eg:- Secondry amine

$CH_3-CH_2-\underset{2^\circ}{NH}-CH_2-CH_3$

Tertiary amine.

$CH_3-\underset{\substack{| \\ CH_3}}{\overset{3^\circ}{N}}-CH_3$

(b) Mixed amine:-

These are secondry or tertiary amine not containing same hydrocarbon group.

Eg:- $CH_3-CH_2-\underset{2^\circ}{NH}-CH_3$

$CH_3-CH_2-\underset{\substack{| \\ CH_3}}{\overset{3^\circ}{N}}-CH_3$

Besides these class of amine there is one more class of amine in which Nitrogen is quatrnary and is considered as derivative of ammonium salt.

$[R_4N]^+$ = Tetra alkyl ammonium ion.

$[(CH_3)_4N]^+$ = Tetramethyl ammonium ion.

$[(CH_3)_4N]Cl$ = Tetra methyl ammonium chloride.

# Nomenclature.

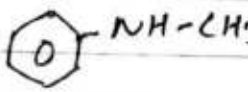
→ common system:- primary amines are named as <u>alkyl amine</u>

simple amines are named as dialkyl amine or trialkyl amine.

Mixed amine are named by writing the name of alkyl group in alphabetical order before the word amine

→ IUPAC System:-

prefix + wordroot + pri. suffix + amine.

| Eg | Formula | common Name | IUPAC Name. |
|---|---|---|---|
| 1) | $CH_3-NH_2$ | Methyl amine | Methanamine. |
| 2) | $CH_3-CH_2-NH_2$ | Ethyl amine. | Ethanamine. |
| 3) | $CH_3-CH_2-CH_2-NH_2$ | N-propyl amine | propan-1-amine. |
| 4) | $CH_3-NH-CH_3$ | Dimethyl amine. | N-methylmethanamine |
| 5) | $CH_3-CH_2-NH-CH_3$ | Ethylmethylamine. | N-Methylethanamine |
| 6) | $CH_3-CH_2-CH_2-\overset{CH_3}{\underset{\vert}{N}}-CH_2-CH_3$ | Ethylmethyl-n-propylamine. | N-ethyl-N-Methyl propan-1-amine |
| 7) | $CH_3-CH_2-CH_2-N(CH_3)_2$ | Dimethyl-n-propylamine. | N,N-Dimethylpropan-1-amine. |
| 8) |  | aniline (phenylamine) | Aniline. |
| 9) |  | Methylphenylamine | N-methylaniline |

# General method of preparation.

(1) From Haloalkane (Read property of Haloalkane):-

$$R-X + NH_3 \longrightarrow R-NH_2 + HX.$$

(2) From alcohol (Read property of alcohol):-

$$R-OH + NH_3 \longrightarrow R-NH_2 + H_2O$$

③ By reduction of alkanenitrile.

$$R-CN + 2H_2 \xrightarrow[\Delta]{Ni} R-CH_2-NH_2.$$

④ By reduction of Nitroalkane.

$$R-NO_2 + 3H_2 \xrightarrow[\Delta]{Ni} R-NH_2 + 2H_2O$$

⑤ From amide.

① By reduction:-

$$R-CONH_2 + 2H_2 \xrightarrow[\Delta]{Ni} R-CH_2-NH_2 + H_2O.$$

ii By Hoffman's bromide reaction (Decarbonylation reaction):-

When amide is heated with bromine an alkyl like KOH, it undergoes decarbonylation reaction producing amine with one carbon atom less than amide. This reaction is called Hoffman's bromide reaction.

$$R-CONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} R-NH_2 + K_2CO_3 + 2KBr + H_2O$$

$$CH_3-CONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} CH_3-NH_2 + K_2CO_3 + 2KBr + H_2O$$

# physical properties of amine.

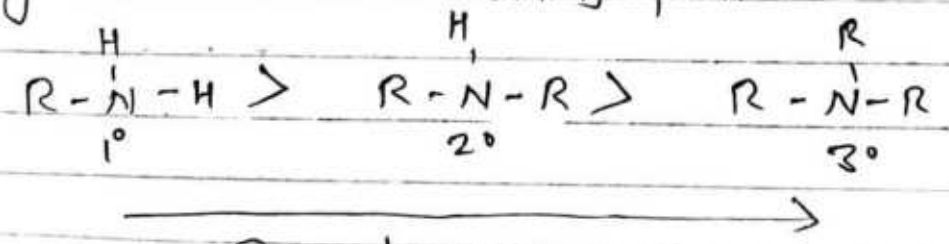
(i) physical state:-

Lower member of amines are colourless gas & higher members are liquid. methyl amine & Ethylamine have ammonical smell & other amine have fishy smell

(ii) Boiling point:-

Expect tertiary amine other amines can form inter-molecular hydrogen bond so they have high boiling point than alkane, Haloalkane, ether, aldehyde & ketone having comparable molecular mass.

Different degree of amine show following order of B.P. boiling point.




Amine have less boiling point than alcohol & carboxylic acid having comparable mass because N-H bond is less polar than O-H bond. So, inter molecular H-bond so, inter molecular hydrogen bond formed by amine is weaker than alcohol and carboxylic acid.

iii] Solubility:-

Lower member of amine are soluble in water because they can form inter-molecular hydrogen bond with water but as molecular mass increases solubility decreases due to increase in hydrophobic interaction.

# Chemical properties.

1. Basic Nature:-

Amines are basic in Nature because they can donate lone pair of $e^-$ present on nitrogen.

Aq. solution of amine is alkaline in Nature because amine reacts with water producing $OH^-$ ion.

$$R-NH_2 + H_2O \rightleftharpoons [R-NH_3]^+ + OH^-$$

→ Action with acid: Amine combines with acid producing salt:

$$R-NH_2 + HCl \longrightarrow [RNH_3]Cl$$

Alkylammonium chloride

→ Comparison of Basic Strength.

$$R-\ddot{N}H_2 < R \rightarrow \underset{\uparrow R}{\ddot{N}H} < R \rightarrow \underset{\uparrow R}{\ddot{N}} \leftarrow R$$

Basic strength increasing →

Different degree of amines shows above order of their basic strength in vapour state.

Tertiary amine is more basic than secondry amine because tertiary amine contains 3 electron releasing alkyl group where as secondry amine contains 2 electron releasing alkyl group so, electron density is comparatively higher in tertiary amine. similarly, Secondry amine is more basic than primary amine.

② Alkylation = Reaction with Haloalkane:-
Lower degree of amine reacts with Haloalkane to form higher degree of amine.

$$CH_3-NH_2 + CH_3Cl \xrightarrow[-HCl]{} (CH_3)_2NH \underset{2^\circ}{} \xrightarrow[-HCl]{CH_3-Cl} (CH_3)_3N \underset{3^\circ}{}$$

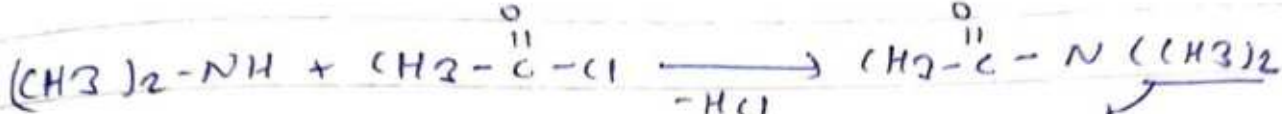
or

$$CH_3-N(CH_3)-CH_3$$

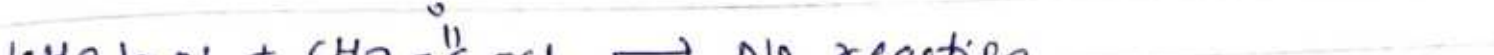
③ Acylation:-
Reaction with acid halide or acid anhydride
primary & secondry amines react with acid halide or acid anhydride producing substituted amide. But, tertiary amine doesn't react due to absence of replacable hydrogen.

$$CH_3-CH_2-NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-HCl]{} CH_3-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_3$$

N-Ethylethanamide.



N-N-Dimethylethanamide.



# Nitrous acid test reaction

Nitrous acid reacts with different degree of amine producing different compound so it is used as test reagent for amines.

Nitrous acid reacts with primary amine producing alcohol and releasing Nitrogen gas.

(1) $R-NH_2 + HNO_2 \xrightarrow[0°c \text{ to } 5°c]{NaNO_2 + HCl} R-OH + N_2\uparrow + H_2O$

Nitrous acid reacts with secondry amine producing yellow coloured oily dialkyl nitrosoamine

$R_2NH + HNO_2 \xrightarrow[0° \text{ to } 5°c]{NaNO_2 + HCl} R_2-N-NO + H_2O$

Dialkylnitrosoamine
yellow

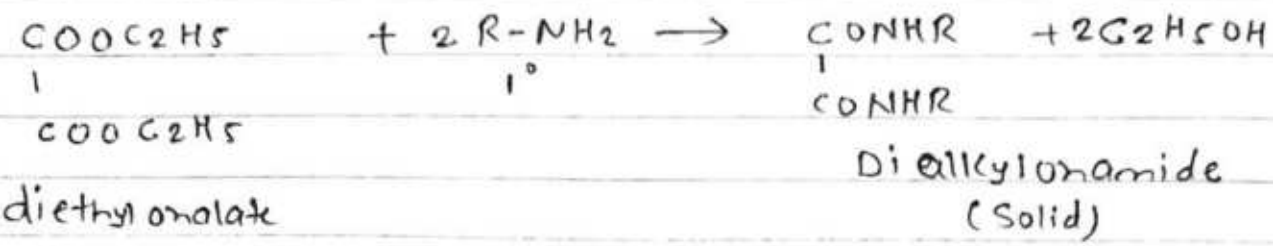
Nitrous acid reacts with tertiary amine producing water soluble trialkylammonium nitrite.

$R_3N + HNO_2 \xrightarrow[0° \text{ to } 5°c]{NaNO_2 + HCl} [R_3NH]NO_2$

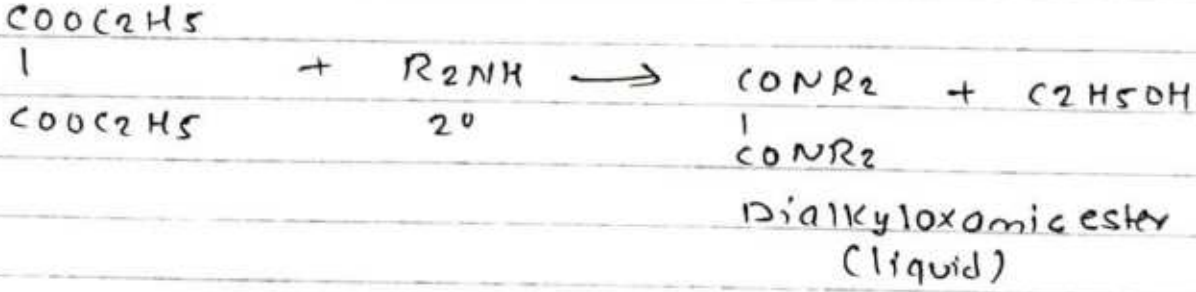
* Seperation of 1°, 2° and 3° - amine by Hoffman's method

To seperate primary secondry tertiary amine from their mixture, it is treated with diethyl oxalate.

primary amine reacts with diethyl oxalate producing solid dialkyloxamide.



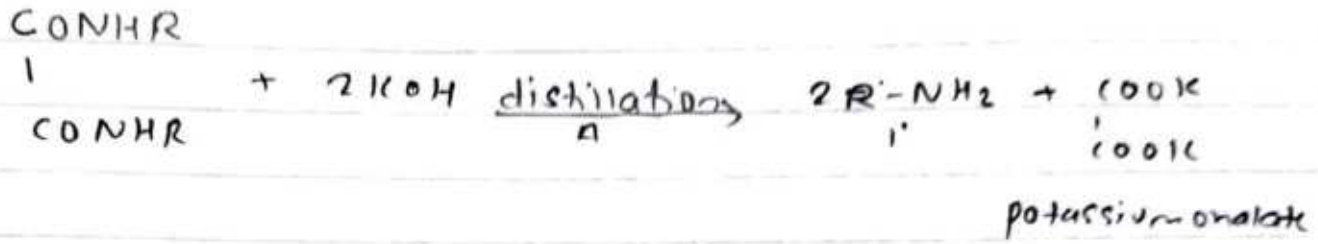

Secondry amine reacts with diethyl oxalate producing liquid dialkyloxamic ester

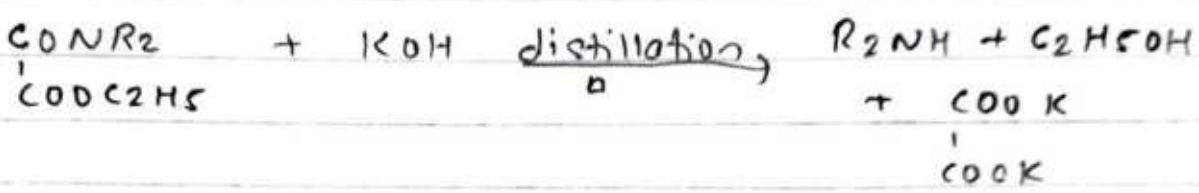



Tertiary amine doesnot react with diethyl oxalate due to absence of replaceable Hydrogen.

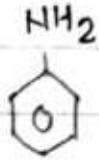
The whole mixture is subjected to fractional distillation as a result tertiary amine seprate out first followed by alcohol. Solid oxamide and liquid oxamic ester remains as residue which are seperated by filtration and seperately treated with aqueous KOH to generate amines and finally distilled

to get pure amines :



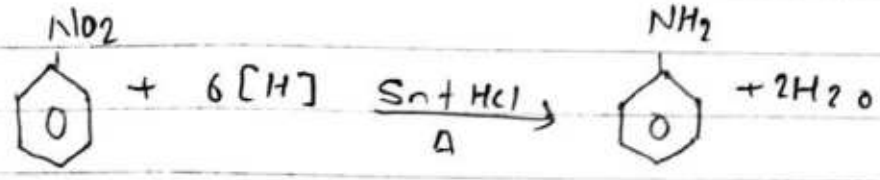



# Aniline :

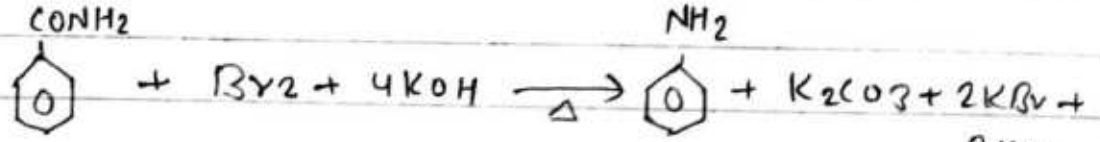
Aniline :- 

# General method of preparation.

(i) From nitrobenzene :-




(ii) From benzamide :-




# physical properties of aniline :-

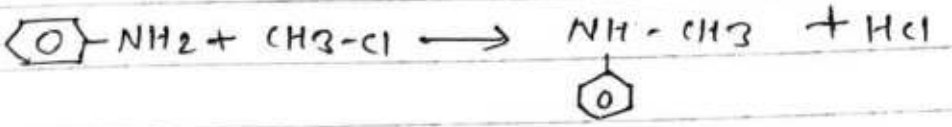
(1) It is colourless liquid with unpleasant smell. But sometime dark brown colour appears due to slow oxidation of aniline in air in presence of sunlight.

2. It is insoluble in water.
3. It's boiling point is 184°C.

4. Basic Nature:-

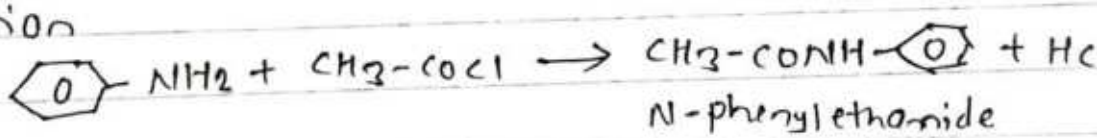
Aniline is basic in Nature because it contains donatable lone pair of electron on Nitrogen. It is less basic that amine and even ammonia because it's lone pair of electron is involved in resonance and not easily available for donation.

(ii) Alkylation :-



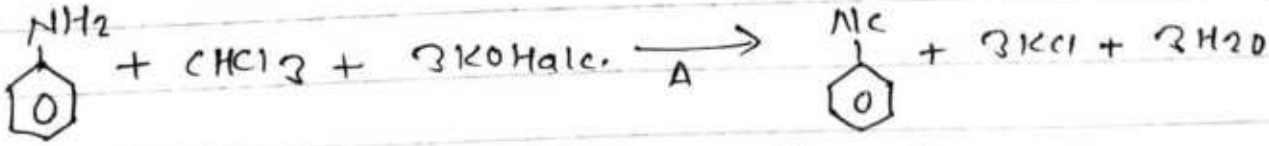
N-methylaniline.

(iii) Acylation



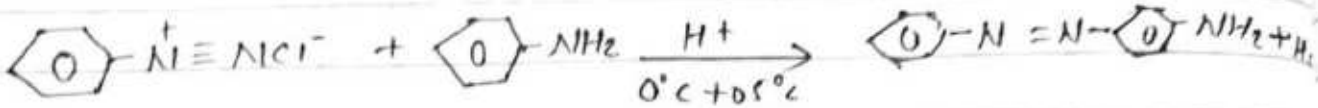
N-phenylethanamide

(iv) carbylamine reaction ( Isocyanide Test reaction)



phenyl Isocyanide

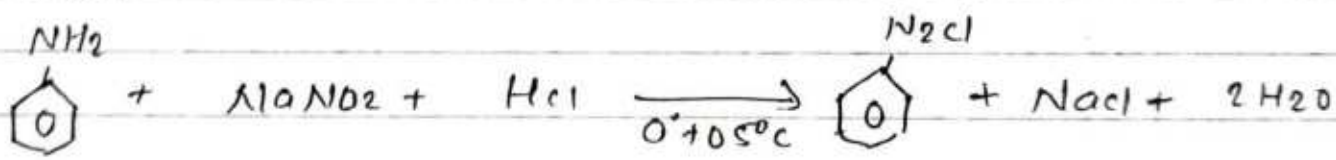
(vii) // coupling reaction.



p-aminoazobenzene.
(orange red)

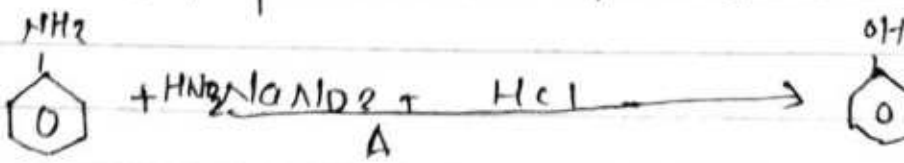
(iii) // Diazotisation reaction (Diazo reaction) :-

When aniline is treated with sodium Nitrite and Hydrochloric acid at 0°C to 5°C temperature, Benzenediazonium chloride is formed. This reaction is called Diazotisation reaction.



Benzendiazonium chloride.

If this reaction is carried out at ordinary, phenol is formed.



# Electrophilic substitution reaction :

In Aniline electrophilic substitution reaction takes place at ortho and para position because resonance caused by amino group increases electron density at ortho and para position so, amino group in aniline is called ortho para directing group

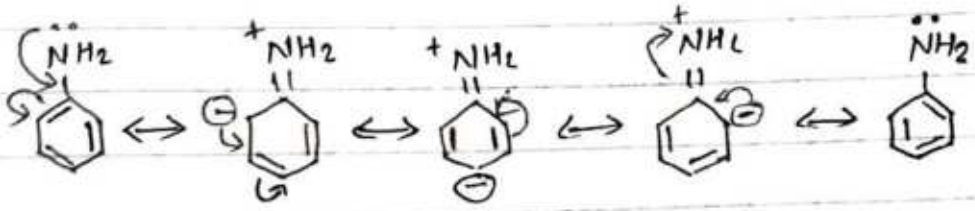
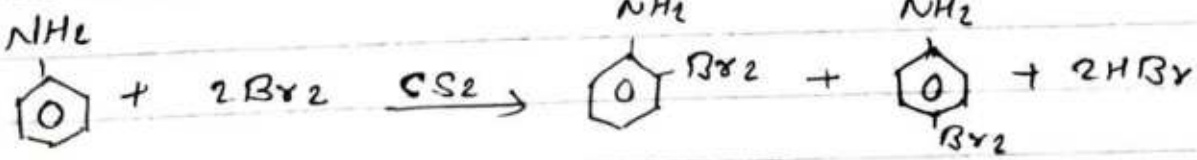
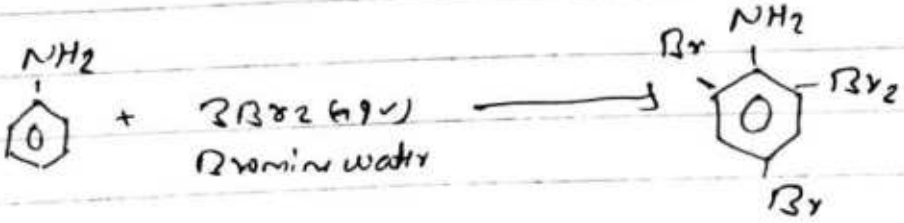


Fig :- Resonance str. of ~~Anitri~~ Aniline.

# Reaction.

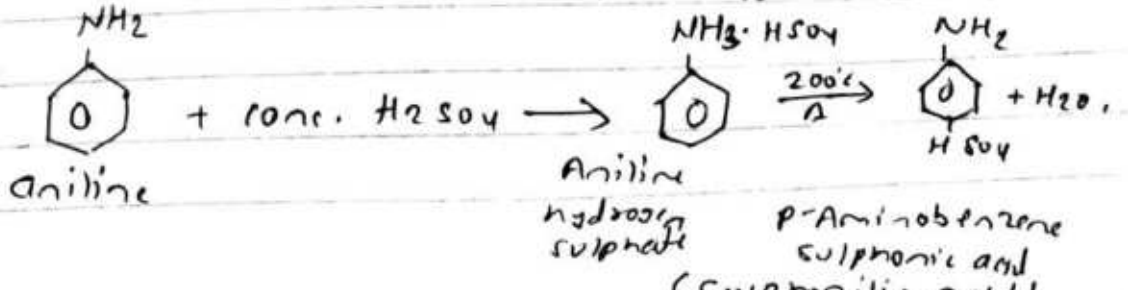
(a) Halogenation





2,4,6 tri Bromoaniline.

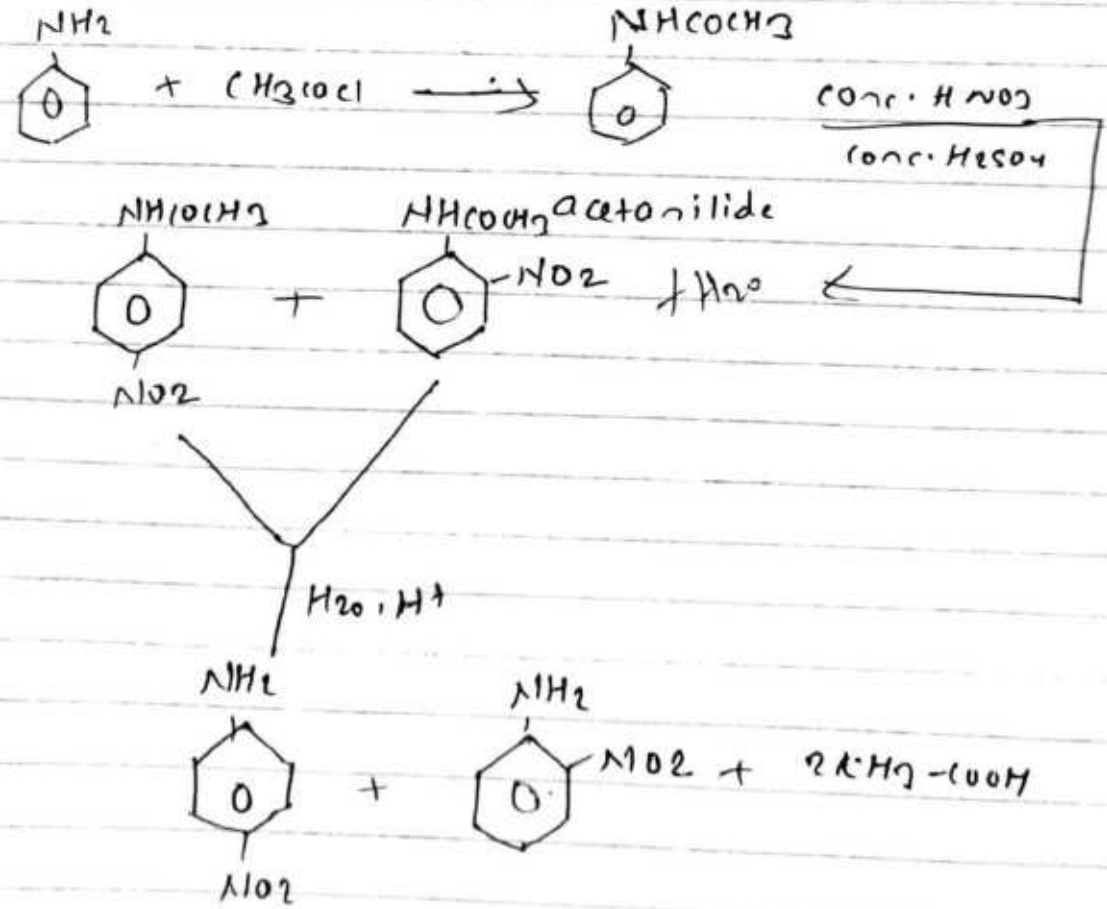
(b) Sulphonation :-



© Nitration:

Conc. Nitric acid is not only Nitrating agent but also an oxidizing agent which oxidize aniline to complex oxidation product (tarry) so direct Nitration of aniline is not possible.

Therefore, Before Nitration amino group is protected by acylation with acetyl chloride which gives acetanilide then nitration is done followed by Hydrolysis to get ortho and para Nitro substituted aniline.



Aniline doesnot undergo friedal craft alkylation and acylation because it is lewis base and the catalyst used in these reaction ($AlCl_3$) is lewis acid so, they combine to form salt.