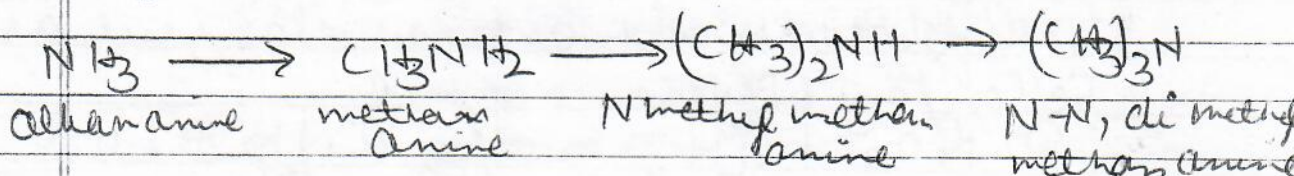
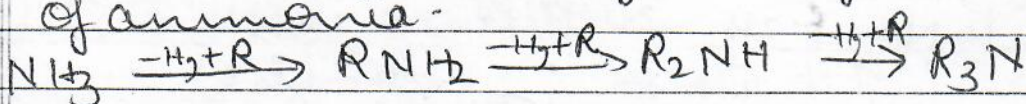


Unit - 13

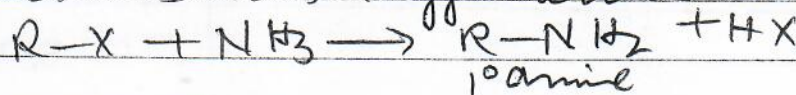
Organic Compounds Containing Nitrogen

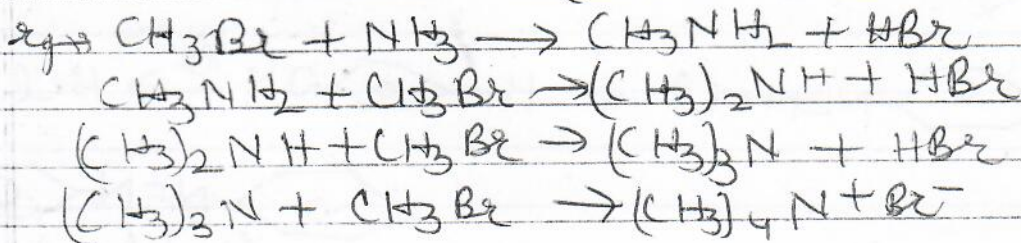
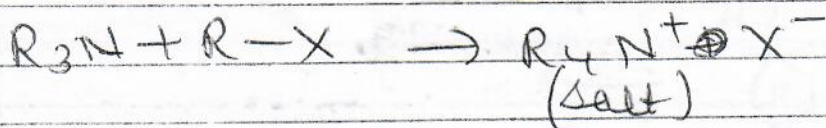
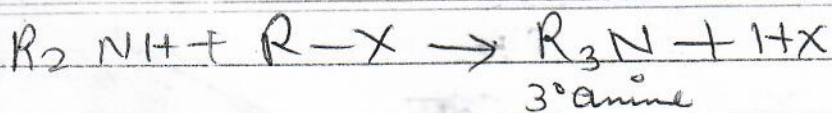
Amines \rightarrow are the alkyl or aryl derivatives of ammonia.



Method of preparations \rightarrow

- 1) From alkyl halide (Hoffmann's ammonolysis) \rightarrow when alkyl halide react with ammonia diff. amines are prepared. This rxn is called Hoffmann's ammonolysis.

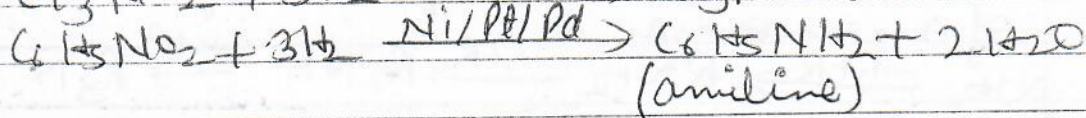
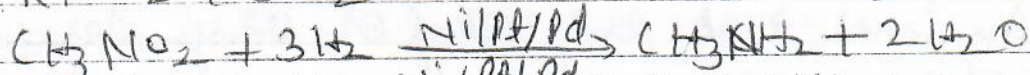
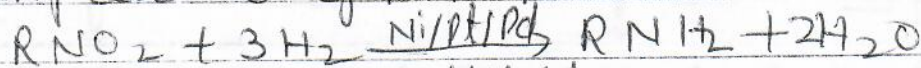




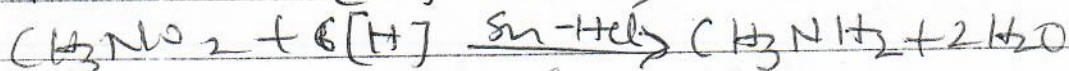
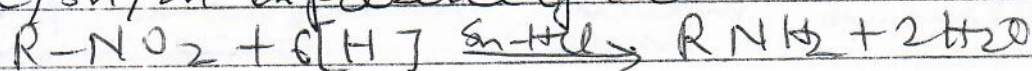
Limitation → In this rxn a mixture of amines are formed as a product.

- 2) From nitro compounds (RNO_2) → Nitro compounds on reduction with ~~red~~ diff. reducing agents forms amines as a product. Reduction of ~~an~~ nitro compounds can be carried out in no. of ways →

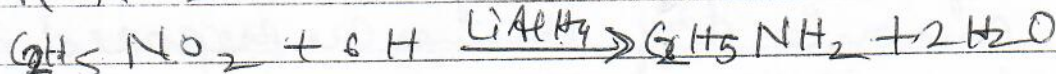
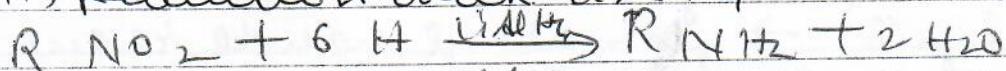
(i) Catalytic reduction → In this reduction nitro compounds react with hydrogen gas in presence of Ni/Pt/Pd.



(ii) Reduction with active metal such as Fe/Sn/Zn in presence of HCl

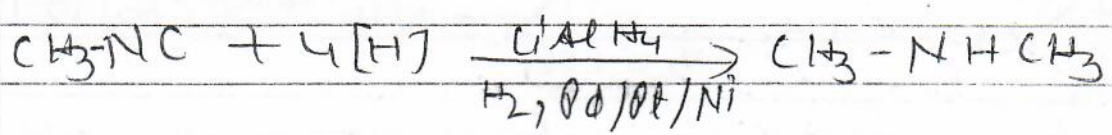
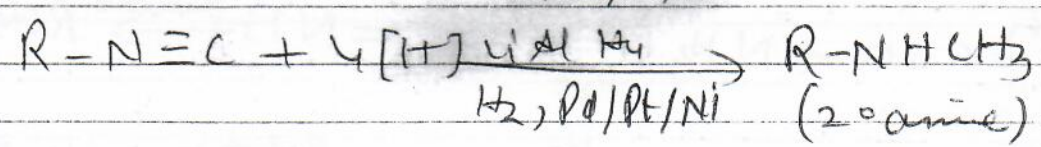
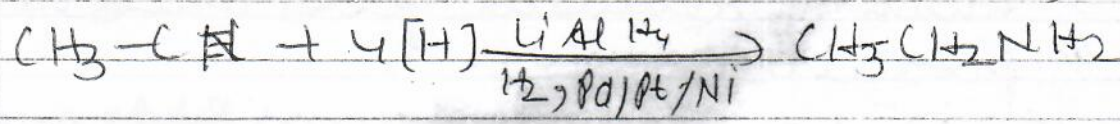
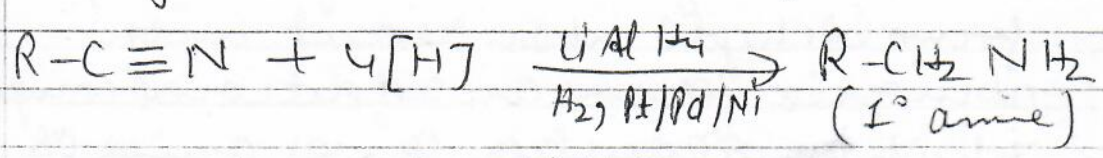


(iii) Reduction with $LiAlH_4$

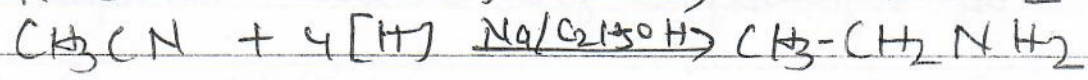
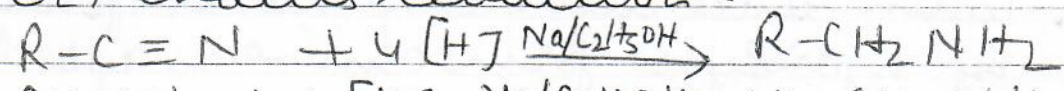


Limitation \rightarrow Aromatic amines cannot be prepared by using $LiAlH_4$ as reducing agent.

- 3) From cyanides (RCN) and isocyanides (RNC) \rightarrow cyanides and isocyanides on reduction in presence of $LiAlH_4$ or H_2 gas in presence of $Pt/Pd/Ni$ forms amines as a product.
- Cyanides on reduction gives 1° amines.
Isocyanides on reduction gives 2° amines.

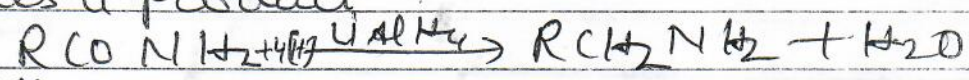


\rightarrow Alkyl cyanide on reduction with Na in ethyl alcohol forms 1° amines as a product. This rxn is called Mendius rxn or Mendius reduction.



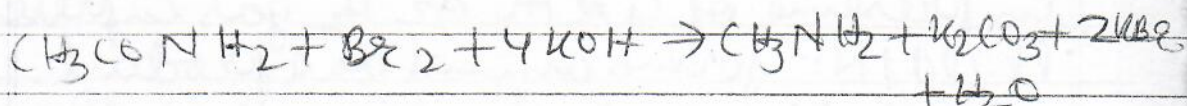
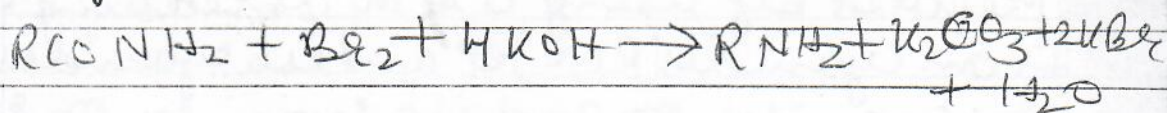
4) From amides \rightarrow

(i) By reduction \rightarrow Amide on reduction with $LiAlH_4$ or Na in C_2H_5OH forms amine as a product.

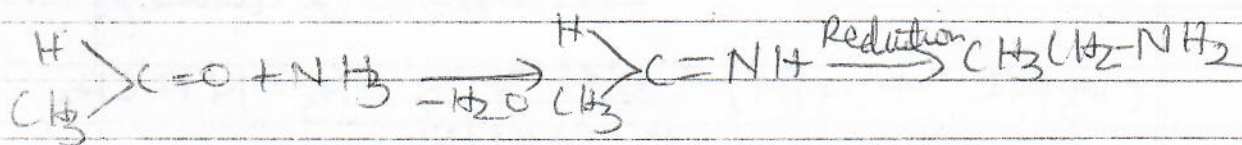
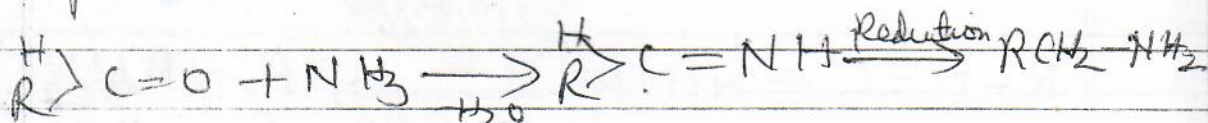


(ii) By Hoffmann's bromamide degradation \rightarrow when amide react with bromine in

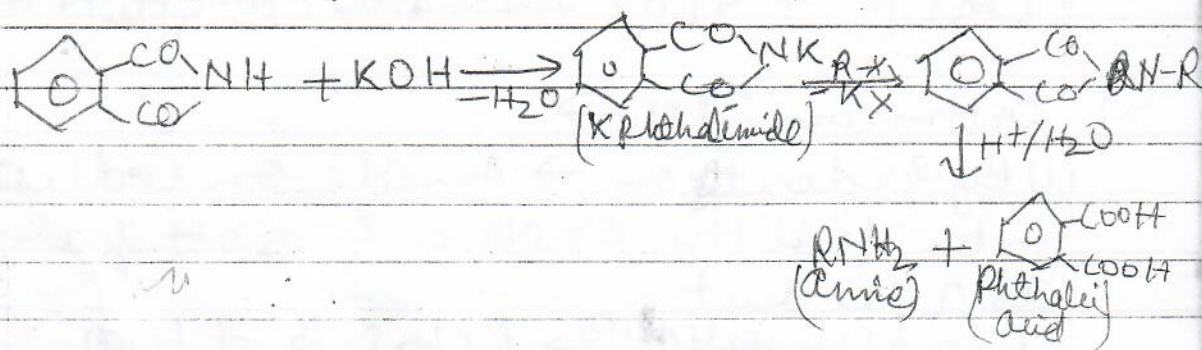
presence of alkali amine is formed as a product containing one carbon less than amide - this rxn is called as Hoffmann's degradation rxn.



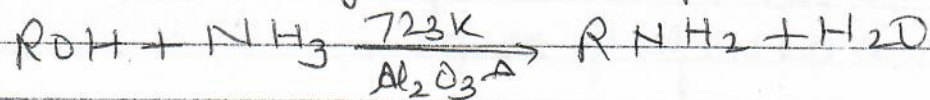
- 5) From aldehyde \rightarrow Aldehyde except formaldehyde when react with ammonia forms an additional compound which on reduction gives amine as a product.



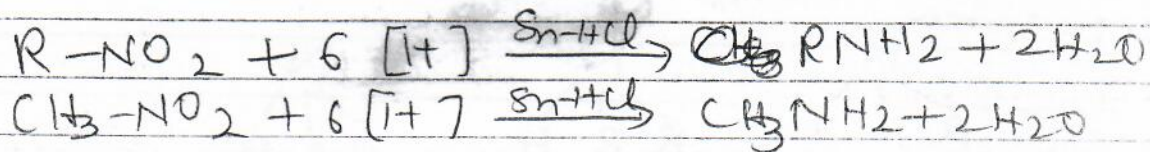
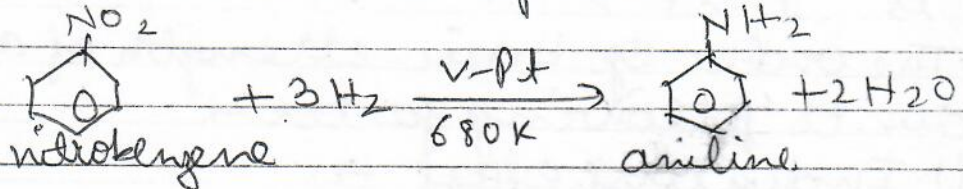
- 6) By Gabriel phthalimide synthesis \rightarrow Phthalimide when react with K hydroxide forms K phthalimide as a product which when react with alkyl halide followed by hydrolysis forms amine as a product.



Industrial method of preparation of amines
 → (1) From alcohol → Alcohol when heated with ammonia at a temp. 723K in presence of Al_2O_3 amines are formed as a product.



(2) From nitro compounds → Nitro compound on reduction with diff. reducing agent forms amines as a product.



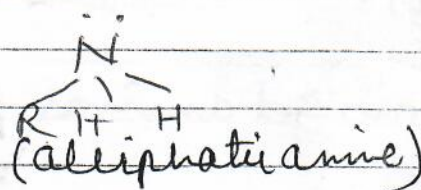
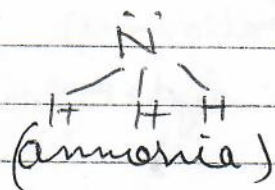
Chemical properties of amines →

(1) Basic nature → Amines contain a lone pair of ~~etc~~ electrons on nitrogen atom due to this they are basic in nature and ~~ben~~ behave as Lewis base.

Amines react with water and gives OH^\ominus ions.



- Aliphatic amines are more basic than ammonia →



It is clear from the structure of aliphatic

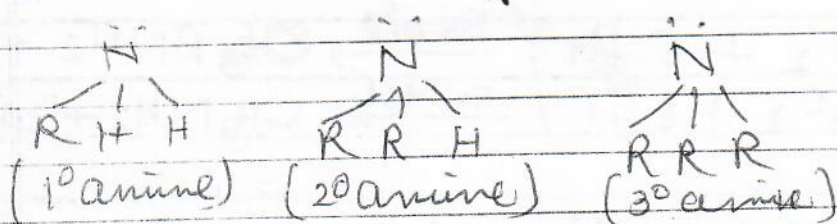
Amine that in aliphatic amine at least one alkyl group is attached to the N atom.

Due to +I effect of alkyl group it increases the e^- density on nitrogen and thus increases its basic nature, whereas in case of ammonia there is no alkyl group.

Basic nature of 1° , 2° & 3° amines \rightarrow
The order of basic strength of amine is $2^\circ > 3^\circ > 1^\circ$

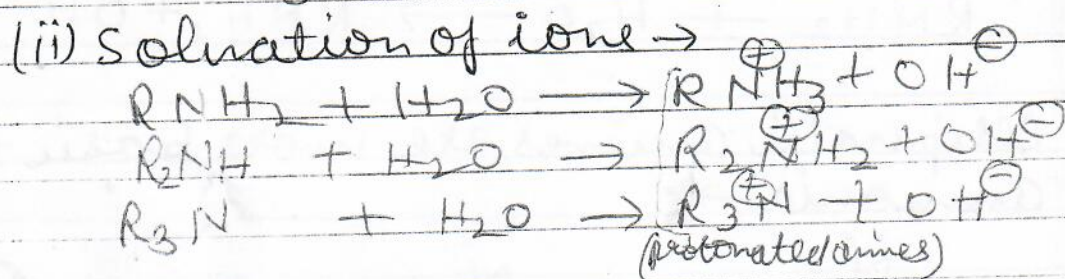
The order of basic strength of amines is due to following factor \Rightarrow

(i) Inductive effect \rightarrow



In 1° amine there is a presence of one alkyl group in 2° amine there is a two alkyl group or in 3° amine there is a three alkyl group.

Due to +I effect of alkyl group the order of basic strength of amine is $3^\circ > 2^\circ > 1^\circ$



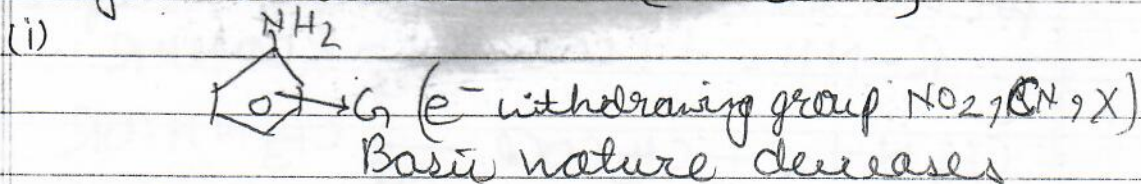
Protonated amines forms hydrogen bonds

with water molecules and release large amount of energy \propto hydration energy and therefore get stabilised.

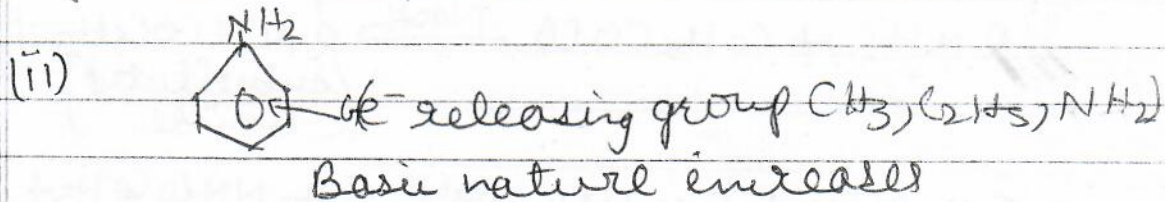
Greater the extent of hydrogen bonding greater be the stability of protonated amine. Thus the order of basic strength of amine is $1^\circ > 2^\circ > 3^\circ$

Thus on combining these two factors the order of basic strength of amines is $2^\circ > 3^\circ > 1^\circ$

Effect of substituent on the basic strength of aromatic amine (aniline) \rightarrow



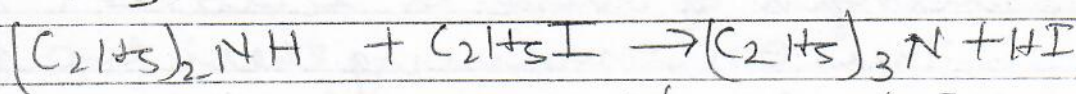
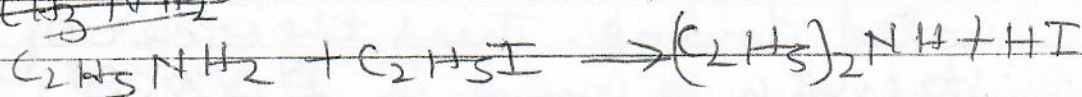
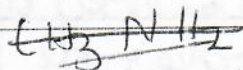
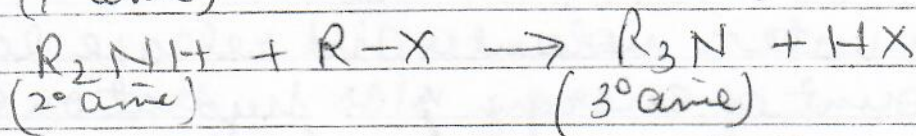
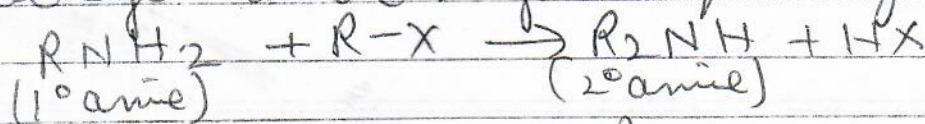
If e^- withdrawing group such as NO_2, CN, X etc. are present at any position in the ring of aromatic amine the basic nature of aromatic amine decreases.



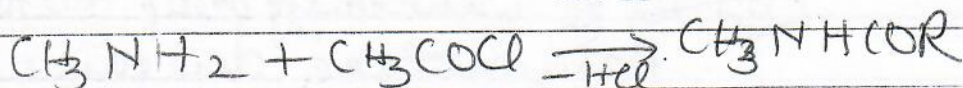
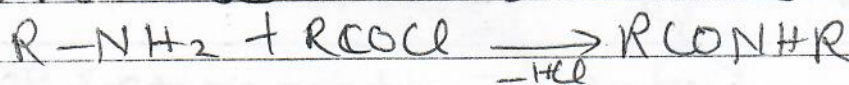
If e^- releasing group such as CH_3, C_2H_5, NH_2 are present at any position in the ring of aromatic amine the basic nature of aromatic amine increases.

(2) Alkylation \rightarrow 1° & 2° amines react with alkyl halide & forms 2° & 3° amines respectively. 3° amines further react with

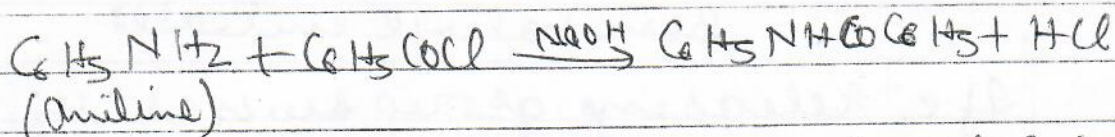
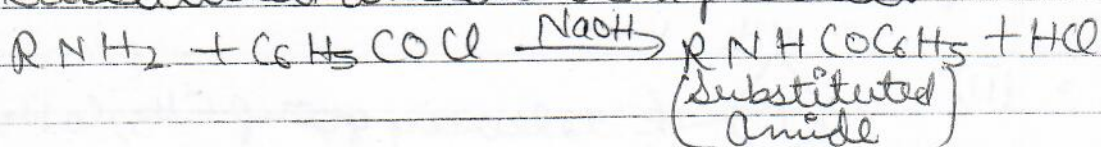
alkyl halide to form quaternary salt -



- (3) Acylation (rxn with acid chloride)
 → Amines react with acid chloride & forms substituted amide as a product



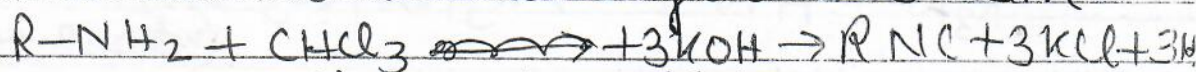
- (4) Benzoylation → Amines react with benzoyl chloride in presence of alkali to form substituted amide as a product -



Aniline when react with benzoyl chloride in presence of a alkali formed substituted amide as a product. This rxn is also known as Schotten Baumann rxn.

Test for 1° amine

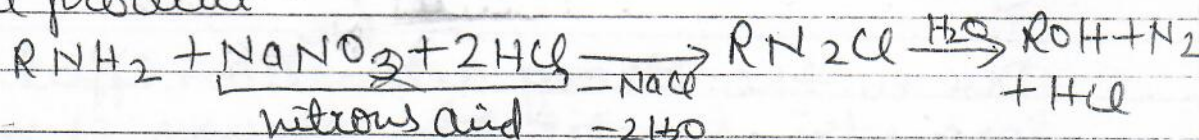
Carbyl amine rxn \rightarrow when 1° amine react with chloroform in presence of alcoholic KOH iso cyanide is formed as a product. This rxn is kias Carbyl amine rxn.



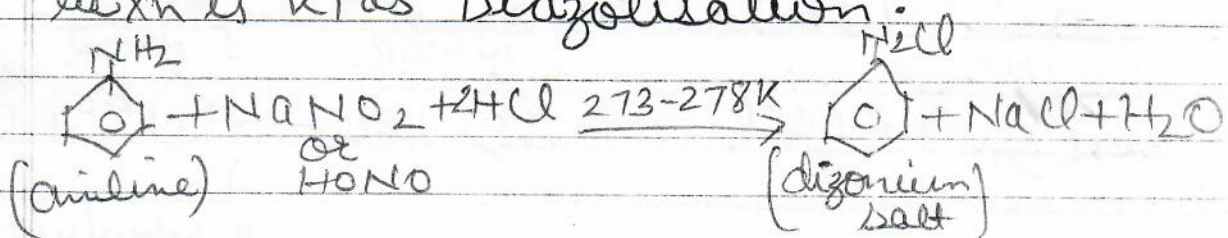
This rxn is used to distinguish 1° amine with other amine.

Rxn with nitrous acid \rightarrow This rxn is used to distinguish 1°, 2° & 3° amines.

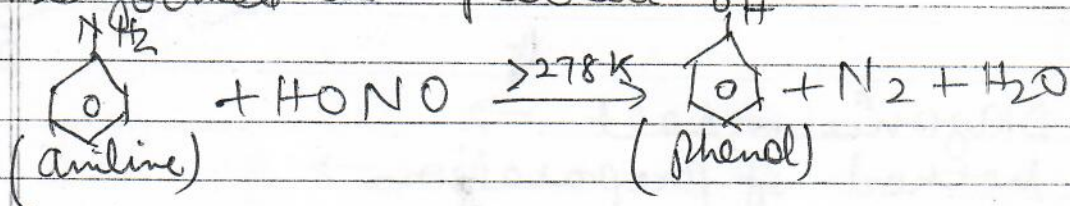
1° aliphatic amines react with nitrous acid and forms diazonium salts which decompose in water to give alcohol as a product -



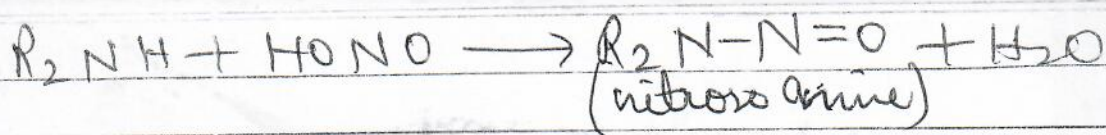
1° aromatic amines react with nitrous acid at temp. 273-278 K to form diazonium salt as a product. This rxn is kias Diazotisation.



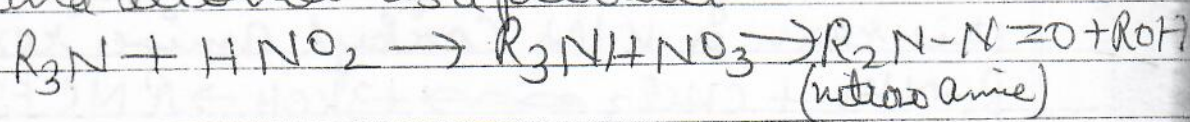
If temp. is increased from 278 K phenol is formed as a product -



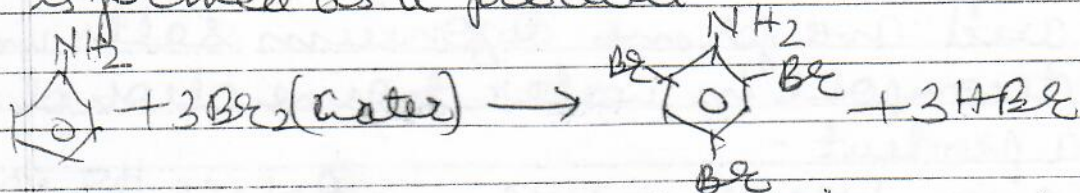
2° amines react with nitrous acid and forms yellow oily nitroso compound as a product.



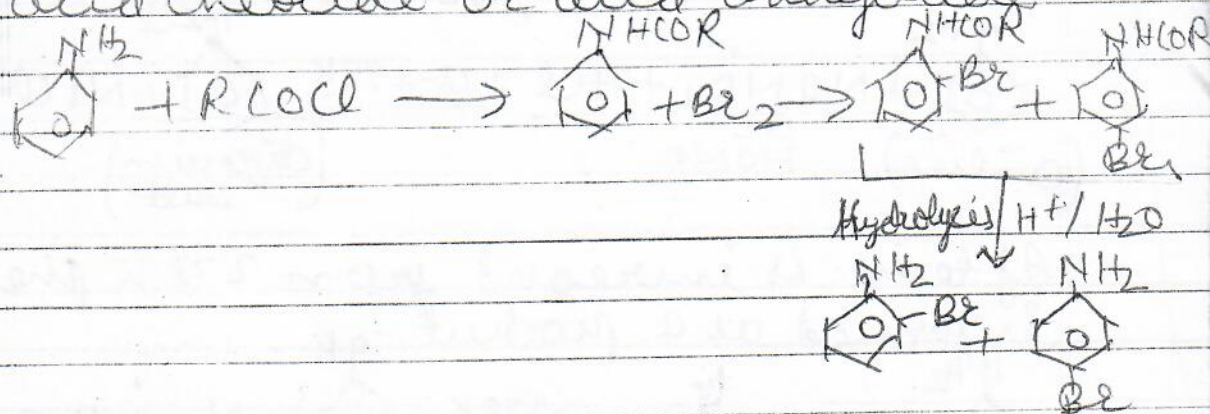
When 3° amines react with nitrous acid forms an additional compound which on decomposition gives nitroso amine and alcohol as a product.



Rexn due to ring in aromatic amines \rightarrow Bromination \rightarrow when aniline react with bromine water tri substitution occurs and 2,4,6 tri bromo aniline is formed as a product.

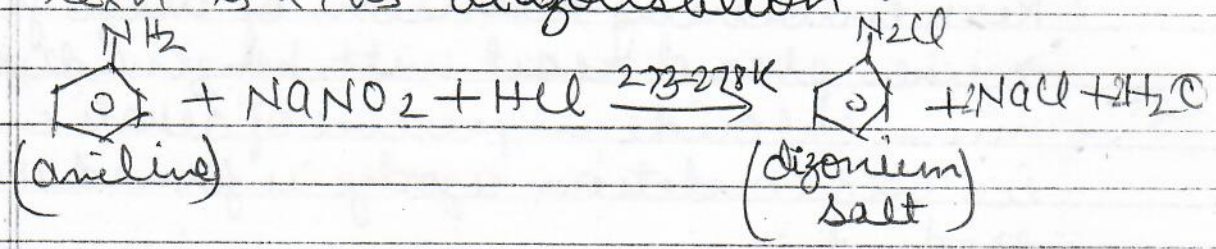


Due to the strong activation effect of NH_2 group tri substitution occurs if mono substitution derivative is to be formed then the NH_2 group in aniline is first deactivated by treating it either with acid chloride or acid anhydride.



Diazonium salt \rightarrow
Method of preparation \rightarrow

From aniline \rightarrow Aniline when react with nitrous acid at a temp. 273-278K diazonium salt is formed as a product. This rxn is called diazotisation.

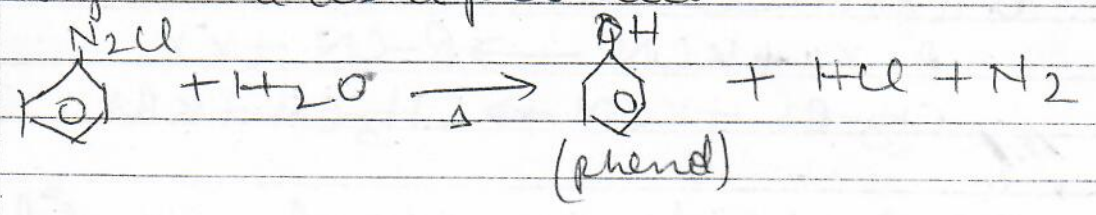


Reactions of diazonium salt \rightarrow

- Diazonium salt gives two types of a rxns \rightarrow
- (i) Rxn involving displacement of diazonium group.
 - (ii) Rxn involving retention of diazo group

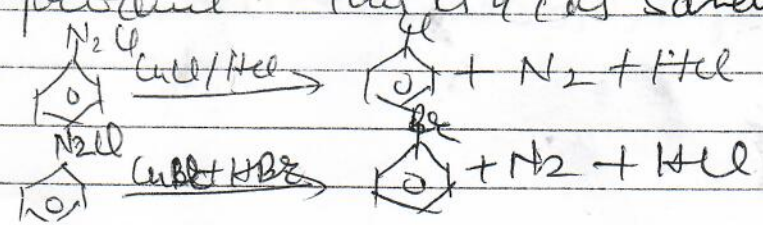
Rxn involving displacement of diazonium group \rightarrow

Displacement by OH group \rightarrow when aqueous solution diazonium salt is heated phenol is formed as a product.

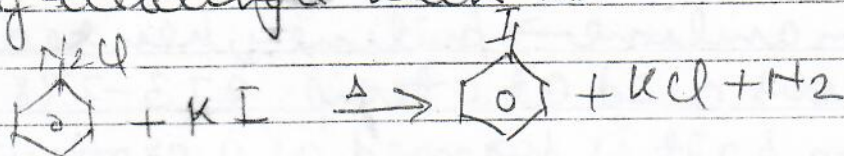


Displacement by Cl or Br \rightarrow

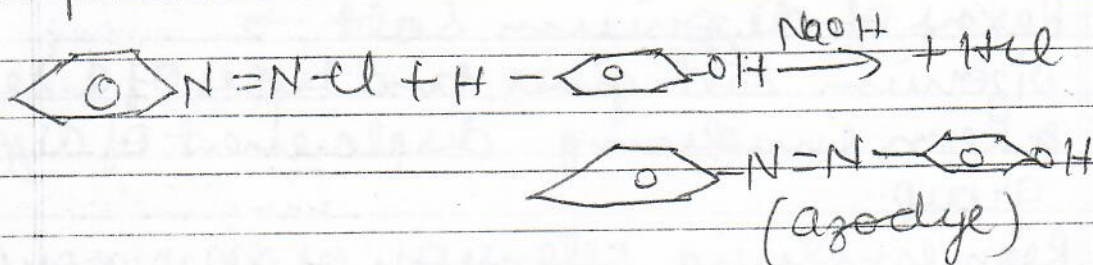
when cuprous chloride or cuprous bromide treated with diazonium salt in presence of corresponding halogen acids chloro or bromo benzene is formed as a product. This is called Sandmeyer rxn.



Displacement by I \rightarrow Iodo benzene can be prepared from benzene diazonium chloride by treating it with KI



Rexn involving release of diazo group \rightarrow when phenol react with benzene diazonium chloride in presence of alkali under ice cold condition azodye is formed as a product.



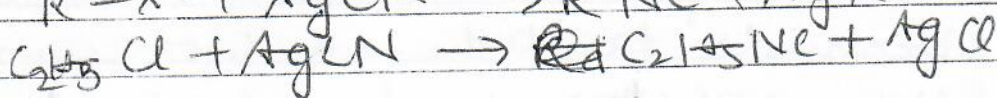
Cyanides or isocyanides \Rightarrow

Method of preparation \rightarrow

(1) From alkyl halide \rightarrow Alkyl halide when react with KCN forms alkyl cyanide as a product -

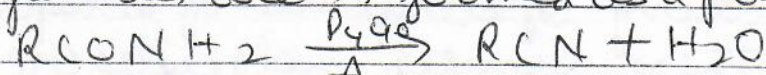


Alkyl halide when react with silver cyanide forms isocyanides as a product -

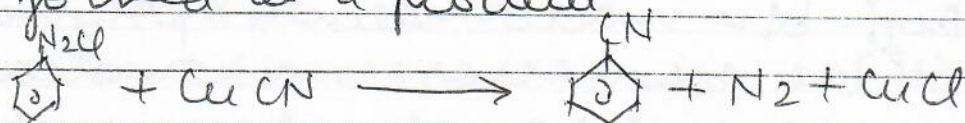


(2) From amides \rightarrow when amide is heated in presence of H_2O dehydration occurs and

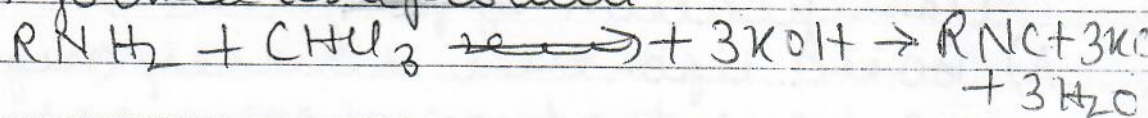
cyanides are is formed as a product.



(3) From diazonium salt \rightarrow when diazonium salt is treated with $CuCN$ aromatic cyanide is formed as a product.

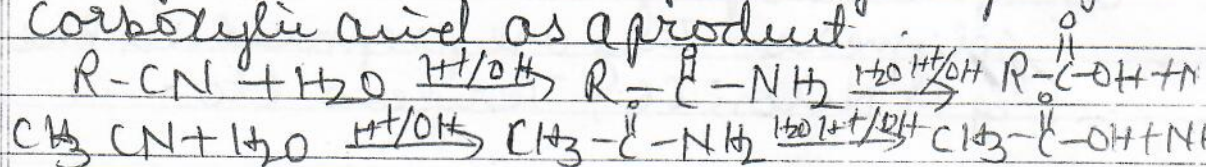


(4) From carbyl amine rxn \rightarrow This rxn is used to prepare iso cyanide when 1° amine react with chloroform in presence of alcoholic KOH iso cyanide is formed as a product.

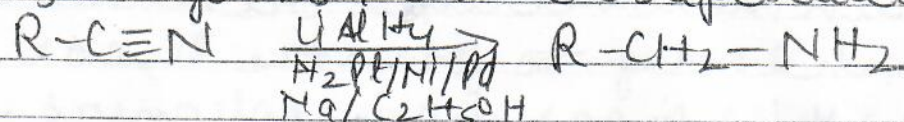


Properties \rightarrow

(1) Hydrolysis \rightarrow cyanides on partial hydrolysis in presence of an acid or a base forms an amide as a product & on complete hydrolysis gives carboxylic acid as a product.



(2) Reduction \rightarrow Cyanides on reduction with diff. reducing agents such as $LiAlH_4$, H_2 , $Ni/Pt/Pd$, Na/C_2H_5OH forms 1° amine as a product.



iso cyanides on reduction gives 2° amines as a product.

