

Expt. No. ....

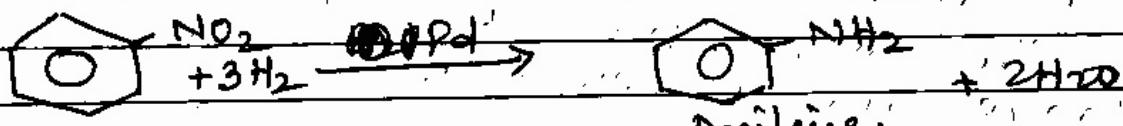
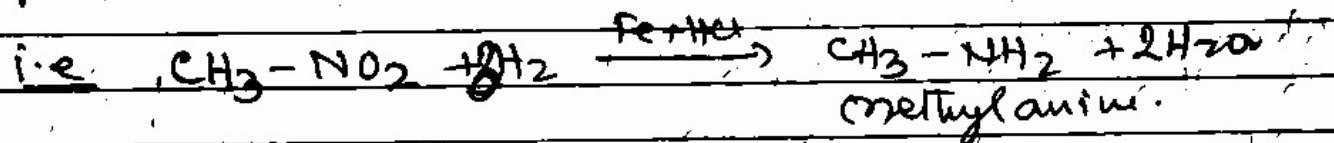
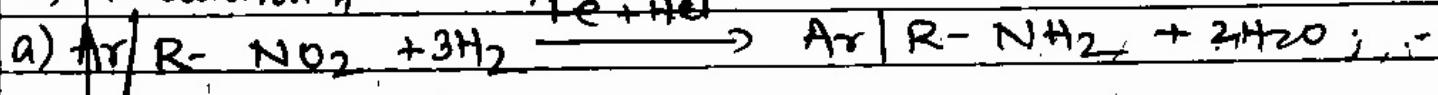
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DI(H) & S, XII, Part II, Group B: Preparation of Amine  
Lec-II DR. S. K. JHA

## Preparation of Amines: →

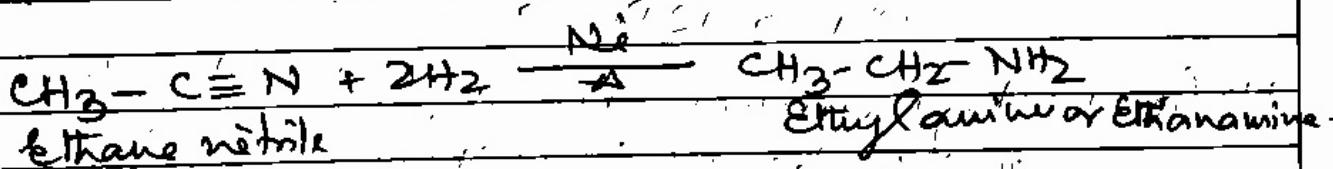
1. By reduction of nitro Compounds, nitriles and amides and oximes by LiAlH<sub>4</sub>, H<sub>2</sub>/Pt Ref/H<sub>2</sub>O or H<sub>2</sub>/Pd or H<sub>2</sub>/Ni, amines can be formed easily. During reduction reaction amine is formed and there is no change in carbon atom from reactant to product.

A) Reduction of nitro Comp:  $\rightarrow$

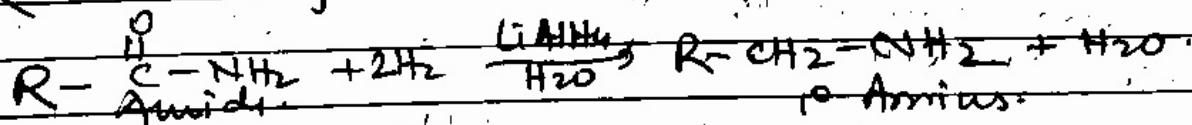


b) Reduction of Quinone  $\rightarrow$  Ni

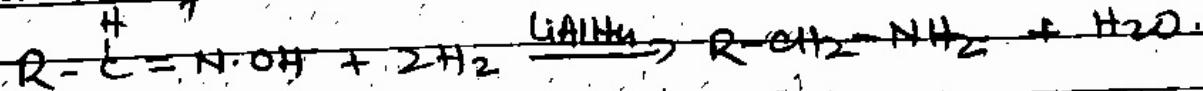
$$\text{R}-\text{C}\equiv\text{N} + 2\text{H}_2 \rightarrow \dots$$



c) Reduction of amide  $\rightarrow$



d) Reduction of Adenosines →



Note: we can use  $H_2/Pt$  in all above reactions to reduce nitro, anilid, Cyano & oxime to form amines.

(6)

## 2. Ammonolysis of alkyl halides. →

In alkyl halide due to high electronegativity of halogen the bond becomes polar and easily it can be broken by nucleophiles. When alkyl halide is treated with alcoholic or ethanolic ammonia then it shows nucleophilic substitution reaction in which halogen atom is replaced by  $\text{NH}_2$  group, the process in which  $\text{C}-\text{X}$  bond is broken by ammonia is called ammonolysis. This reaction is carried out at  $373^\circ\text{K}$  in a ~~hot~~ sealed tube.

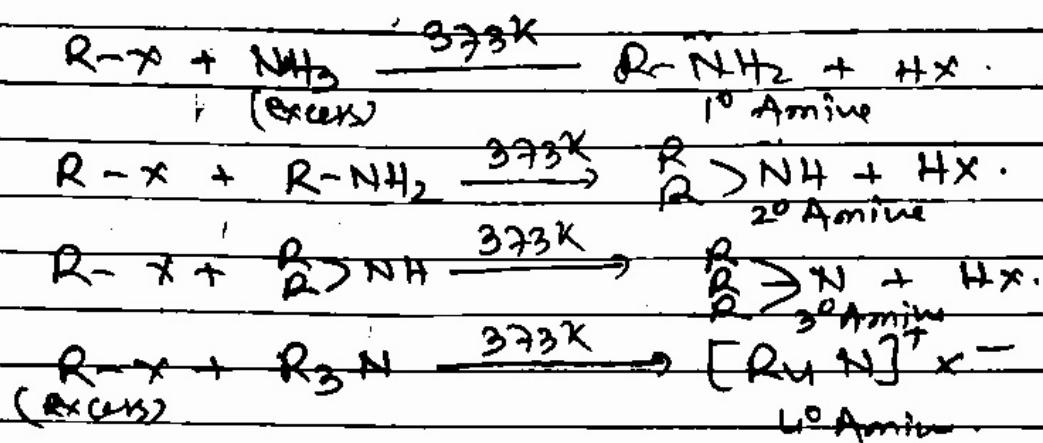
- When alkyl halide is in excess quaternary salt is the final product.
- If ammonia is in excess, primary amine is the major product or it is formed in large amount with respect to other amines.
- The reactivity of ~~alkyl~~ Alkyl halide is as follows  
 $\text{R}\text{I} > \text{RBr} > \text{R-Cl}$ .

Note 1. Aryl amines can not be prepared by this method because aryl halides are less reactive towards nucleophilic substitution reaction hence  $\text{C}_6\text{H}_5\text{NH}_2$  can not be prepared.

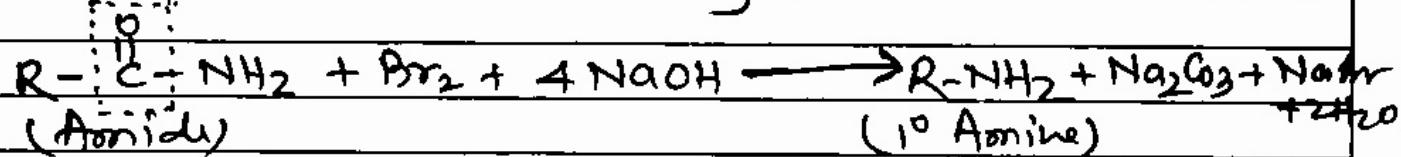
This method is not so applicable in laboratory because it form  $^0$ ,  $^1$ ,  $^2$ ,  $^3$  &  $^4$  amines, as product & separation of these are difficult.

but it is industrial process.

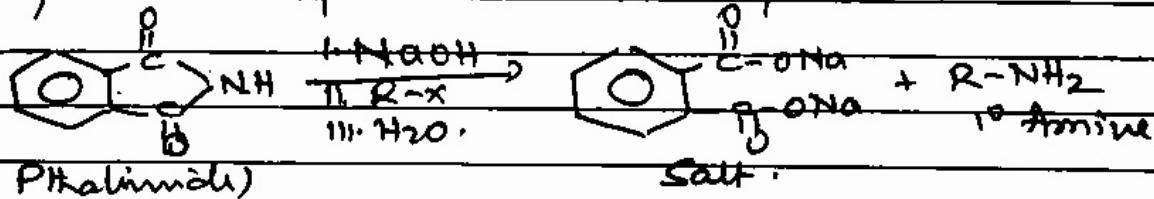




Ques 3. Hoffmann bromamide degradation method:-  
 When amide is treated with  $Br_2$  and aqueous or ethanolic strong base  $NaOH$  or  $KOH$  it form primary amines. In this reaction  $\text{C=O}$  group disappear from amide to form  $1^{\circ}$  Amine So one carbon atom decreases from reactant to product hence it is also called degradation reaction.



4. Gabriel phthalimide Synthesis : →



When phthalimide is treated with ethanolic Sodium hydroxide form sodium salt of phthalimide which on heating with alkyl halide shows SN reaction to form N-(alkyl)phthalimide which on further alkaline hydrolysis give primary amine.

Teacher's Signature : \_\_\_\_\_

N.B. Primary aromatic amines can not be prepared by Gabriel phthalimide process because it do not show nucleophilic substitution reaction, or sodium or potassium salt of phthalimide do not shows substitution reaction with aryl halide, so further product will not form.

