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# XII UNIT 13

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Organic Compounds Containing Nitrogen

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DECEMBER 18, 2020

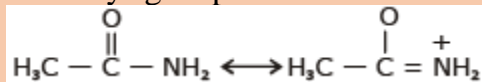
CHEMISTRY MANTRA

105 Dilbagh Nagar Extension Jalandhar

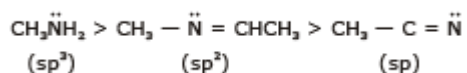
## Basic Character and Preparation of Amines (All Methods)

### 1. BASIC NATURE OF AMINES

1. Aniline is less basic than ammonia. The phenyl group exerts- I (inductive effect, i.e., it withdraw electrons. This results in the lower availability of electrons on nitrogen for protonation.
2. Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalized by resonance with the carbonyl group which makes it less available for protonation.



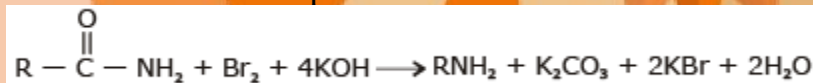
3. The compound with least 's' character ( $\text{sp}^3$  hybridized) is most basic and with more 's' character ( $\text{sp}$ -hybridized) is least basic. Examples in decreasing order of basicity are :



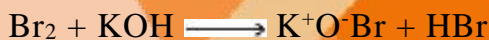
- (i)
  - (ii)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 > \text{H}_2\text{C} = \text{CHCH}_2\text{NH}_2 > \text{HC} \equiv \text{CCH}_2\text{NH}_2$
  - (iii)  $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$
- Electron withdrawing ( $\text{C}_6\text{H}_5-$ ) groups cause decrease in electron density on nitrogen atom and there by decreasing basicity.
- (v)  $\text{CH}_3\text{CH}_2\text{NH}_2 > \text{C}_6\text{H}_5\text{CONH}_2 > \text{CH}_3\text{CONH}_2$

### 2. METHODS OF PREPARATION

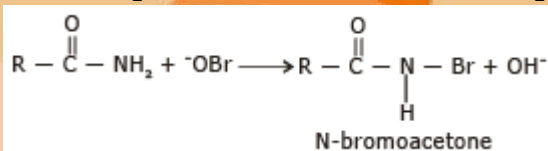
**1. Hoffmann's bromamide reaction :** Amines (only primary) can also be prepared by Hoffmann degradation. In this method the amine will have one carbon atom less than the amide. The reaction proceeds via formation of nitrene.



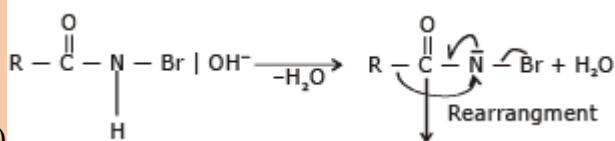
**Mechanism of above reaction has been proposed as given below :**



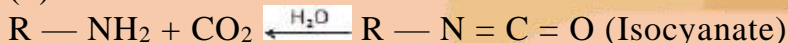
Mechanism



(a)



(b)



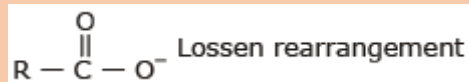
**2. Curtius, Schmidt and Lossen Rearrangement :** These reaction are basically rearrangement reactions in which carbon migrates from carbon to nitrogen with the formation of an



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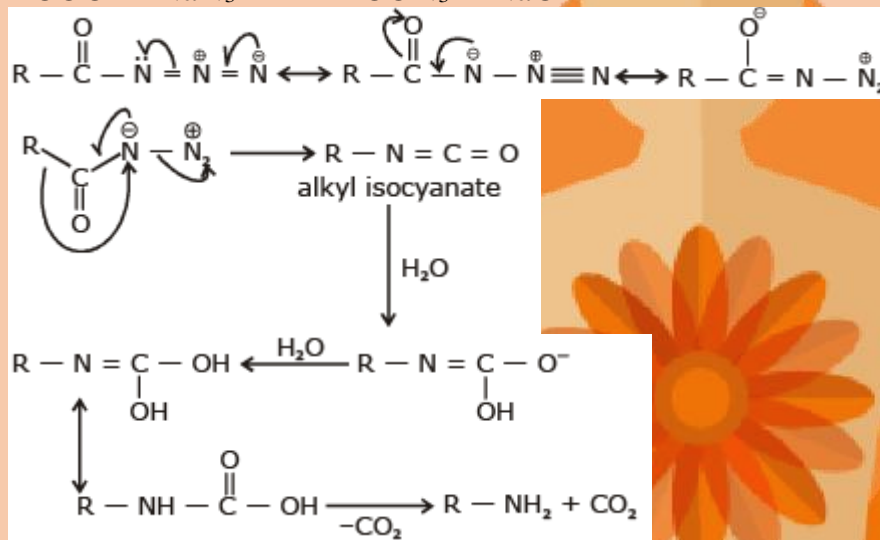
isocyanate. In these migration i.e., 1, 2 shift, migrating group is an alkyl or aryl group and leaving group may be

- Br in Hoffmann rearrangement.
- N<sub>2</sub> in Curtius and Schmidt rearrangement.

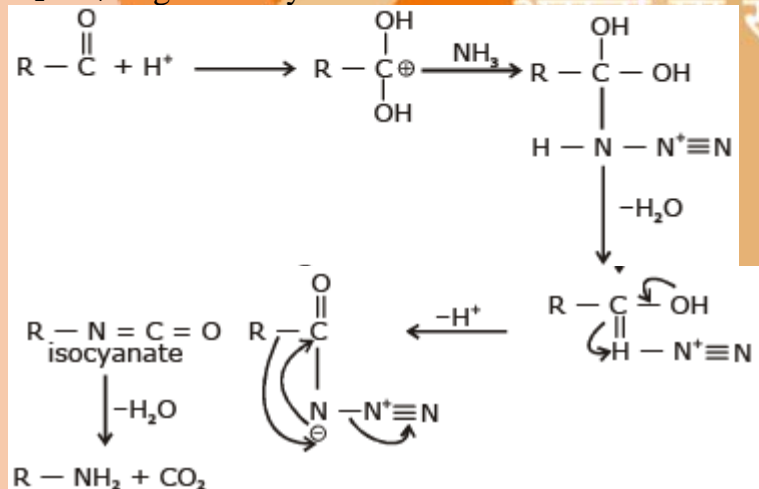


The isocyanate formed on hydrolysis gives amine.

(a) Curtius Reaction : Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates on hydrolysis gives corresponding amines.

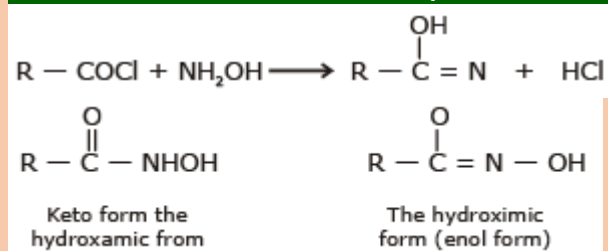


(b) **Schmidt Reaction** : Carboxylic acid reacts with hydrazoic acid in presence of concentrated H<sub>2</sub>SO<sub>4</sub> to give isocyanates.

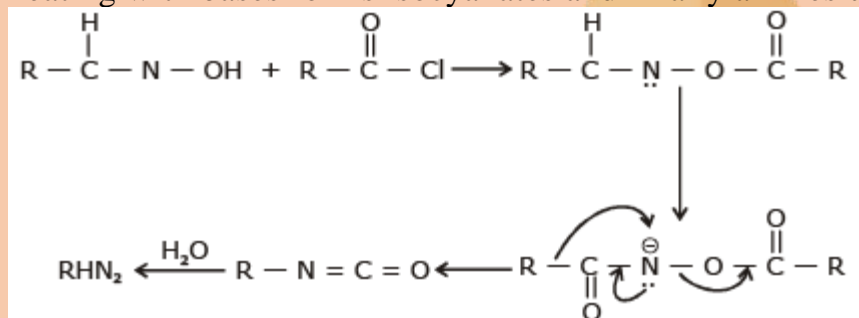


(c) **Lossen Reaction** : Hydroxylamine on treatment with acid chloride gives acyl derivatives of hydroxyl amine the acyl derivatives exist in two tautomeric form keto form called hydroxamic form and enol form called hydroximic acid.





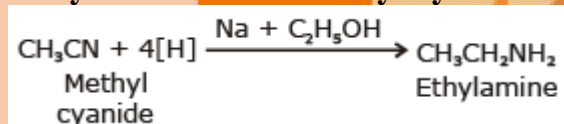
The hydroxamic form (keto form) forms o-acyl derivatives of hydroxamic form which on heating with bases forms isocyanates and finally amines upon hydrolysis.



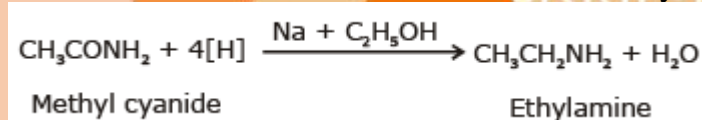
### 3. By reduction of nitroethane :



#### 4. By reduction of methyl cyanide :



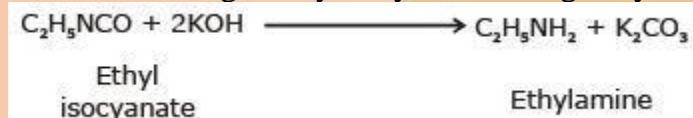
**5. By reduction of acetamide :** Ethylamine is obtained by reduction of acetamide with sodium and absolute alcohol or  $\text{LiAlH}_4$  in ether or hydrogen in presence of nickel catalyst.



**6. By reduction of aldoxime :** Aldoxime on reduction with hydrogen and nickel catalyst or sodium and absolute alcohol or  $\text{LiAlH}_4$  in ether yields ethylamine.



**7. By the hydrolysis of ethyl isocyanate :** Ethyl isocyanate on heating with caustic potash solution undergoes hydrolysis forming ethylamine.

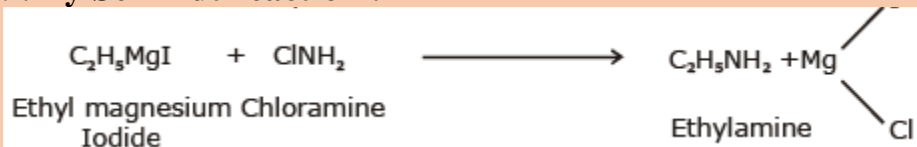


**8. By the acid hydrolysis of ethyl isocyanide :** Ethyl isocyanide undergoes hydrolysis with a mineral acid and forms ethylamine.

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### 9. By Schmidt reaction :

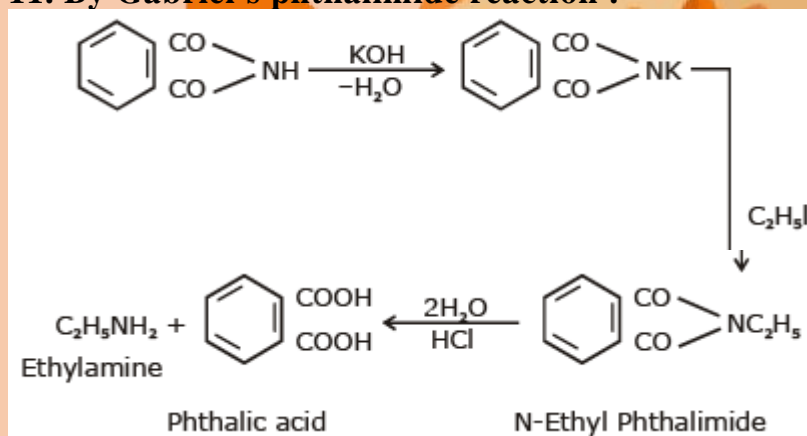


In this reaction the acyl azide  $(\text{RCO})_2\text{N}_2$  and alkyl isocyanate  $(\text{R}-\text{NCO})$  are formed as an intermediate.

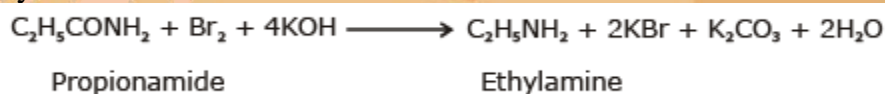
**10. By the action of chloramine on Grignard reagent :** When chloramine reacts with ethyl magnesium iodide, the formation of ethylamine occurs.



### 11. By Gabriel's phthalimide reaction :



**12. Laboratory preparation of ethylamine :** Ethylamine is prepared in the laboratory by Hoffmann's bromide reaction. Propionamides are heated with bromine and potassium hydroxide solution.



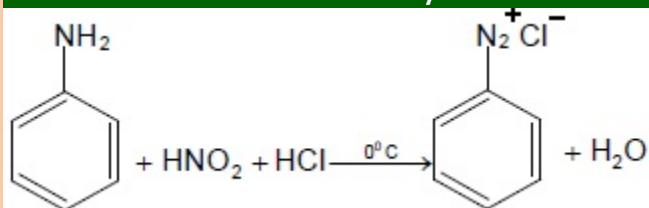
## Diazonium Salt and Diazotisation

### Diazonium Salt:

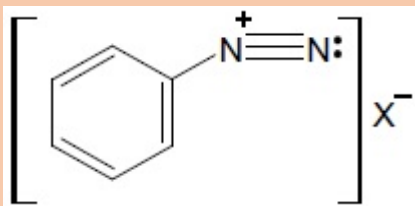
When primary aromatic amine is treated with nitrous acid in a cool solution, product is unstable compound, known as diazonium salt.



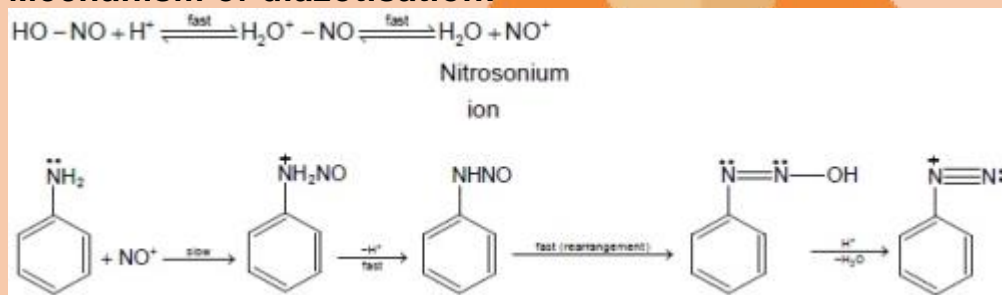




This reaction is known as diazotisation. Diazonium salts have the structure



### Mechanism of diazotisation:



### Illustration:

**Why ice cold condition have to be maintained in the diazotisation reaction of aniline?**

**Ans:** Because benzene diazonium chloride is unstable and decomposes to give phenol above 278k.

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