~~Chemical props of Amines~~, ~~DR. S. K. JHA~~

lect = 5

Basic Strength can be checked by the value of electronegativity of the element:

$$\text{Basicity} \propto \frac{1}{\text{Electronegativity}}$$

means more is the electronegativity of the element lesser will be the Basic strength.

$CH_3-C\equiv N$, $CH_3-CH=NH$, $CH_3-CH_2-NH_2$

sp, sp^2, sp^3

s character: 50% 33% 25%

more is s-character $\propto$ electronegativity

So the order of Basic Strength will be as follows

$CH_3-CH_2-NH_2 > CH_3-CH=NH > CH_3-C\equiv N$.

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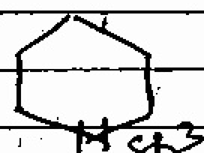

sp^2 (Pyridine) $s = 33\%$

sp^3 (Pi-pyridine) $s = 25\%$

$$s\text{-character} \propto \frac{1}{\text{Basic Strength}}$$

or $\text{No. of } \pi \text{ bond in molecule} \propto \frac{1}{\text{Basic Strength}}$

$CH_3-CH_2-CH_2-NH_2 > CH_3-CH=CH-NH_2 >$
I II

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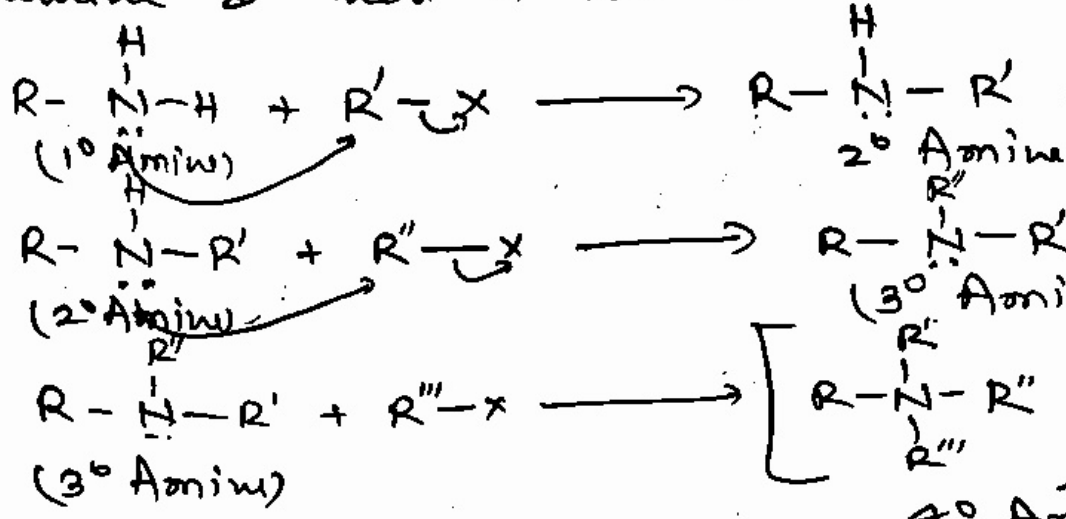
$HC\equiv C-CH=CH-NH_2$
III

2) Alkylation reaction of amines :→

When alkanamine(1°) react with alkyl halide it shows nucleophilic substitution reaction and gradually it form 2° Amine, then 3° amine & then 4° amine

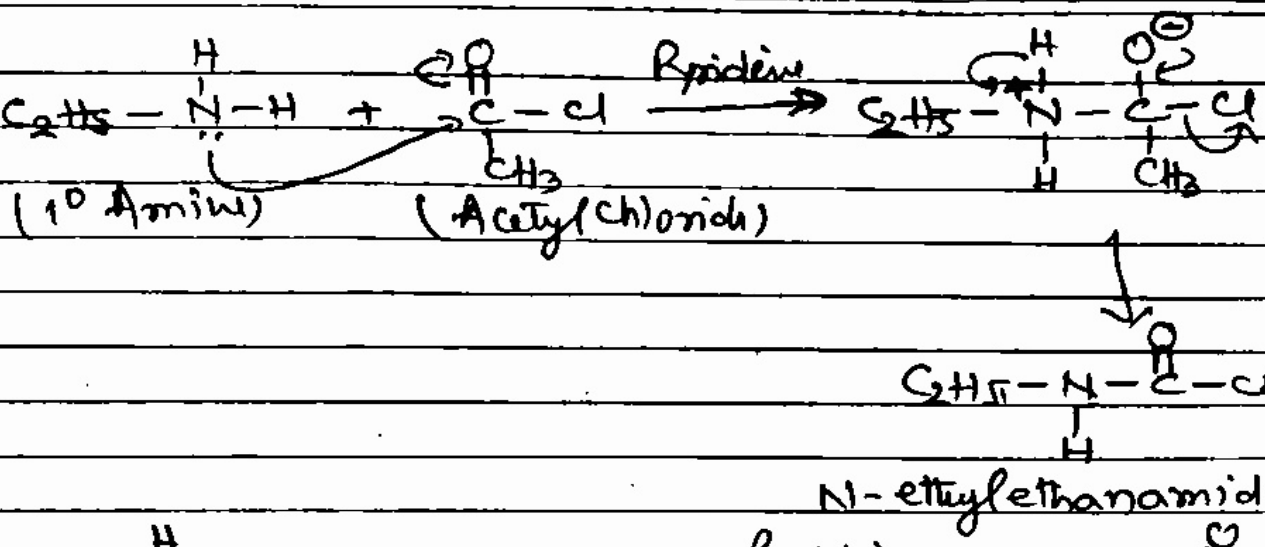


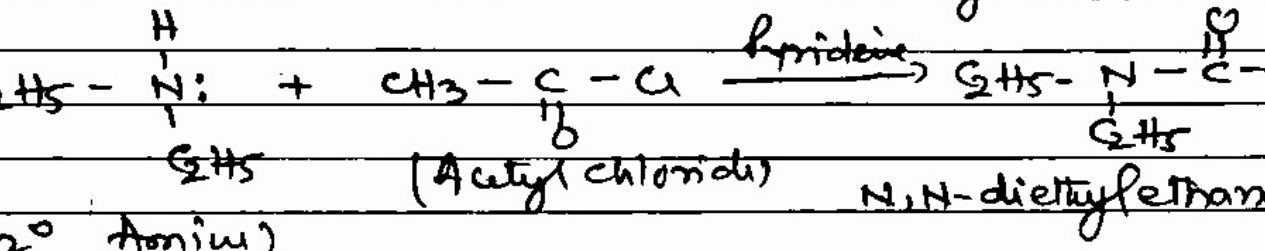
In the above reaction $\ddot{N}H_2$ act as nucleophile due to presence of lone pair of e on nitrogen atom.

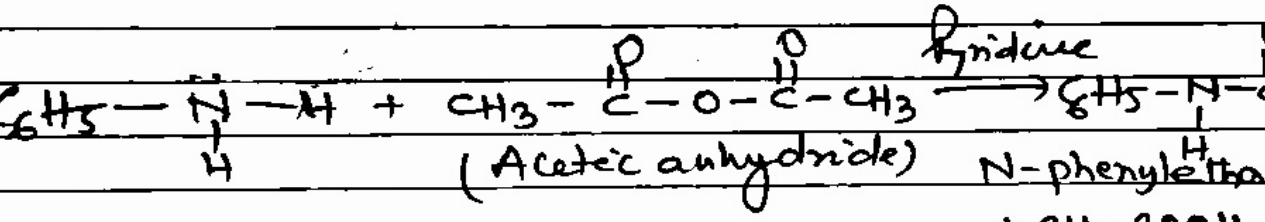
3) Acylation reaction :→ In this reaction 1° or 2° R/Ar. amine react with carboxylic acid derivative as acid chloride or esters or anhydride followed by nucleophilic substitution reaction. In this reaction one hydrogen atom is replaced from $-\ddot{N}H_2$ group or $-\ddot{N}-H$ group by acyl group in presence of a base stronger than amine ultimately it form amide, this reaction is called acylation reaction. In the form of base we use mainly pyridine.

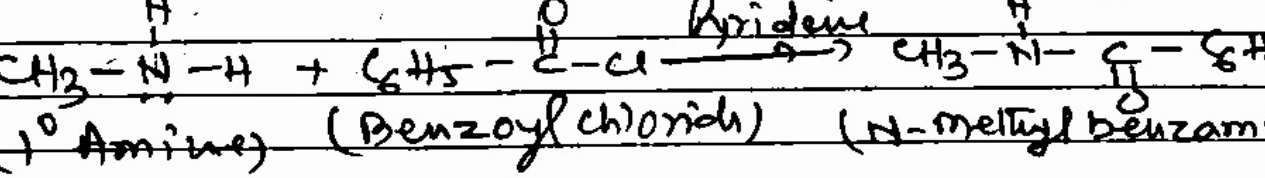
Note :1. -COR is called acyl group and COCH$_3$ is called acetyl group.

11- In reaction amine may be aliphatic or Aromatic 1° or 2°









Note: Whatever reaction is has shown by carboxylic acid derivative with amine 1° or 2° the same reaction can not be shown by carboxylic acid itself because it will form the salt.

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4) Carbileamine reaction: →

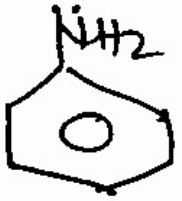
When aliphatic or aromatic primary (1°) amine is heated with ethanolic KOH or NaOH in presence of chloroform it form a very disgusting or foul smelling compound i.e isocyanide or carbile, thats why this reaction is called carbileamine reaction.

Note: This reaction is used to identify or to distinguish 1° amine.

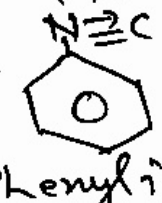
$$R-\underset{H}{\overset{|}{N}}-H + CHCl_3 + 3KOH \xrightarrow{\Delta} R-N\equiv C + 3KCl + 3H_2O$$

(Alkyl isocyanide)

Or



$$+ CHCl_3 + 3KOH \xrightarrow{\Delta}$$



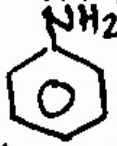
$$+ 3KCl + 3H_2O$$

(Phenylisocyanide)

5) Reaction with Nitrous acid: →

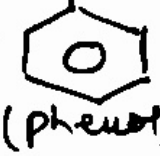
When primary or 1° amine either aliphatic or aromatic react with nitrous acid (it is formed due to combination of $NaNO_2 + HCl$) first it form diazonium salt which on further hydrolysis gives alcohol / phenol.

$$R-\underset{\text{1° Amine}}{\overset{|}{\ddot{N}}H_2} + HNO_2 \xrightarrow{NaNO_2 + HCl} \underset{\text{(Alkyl diazonium chloride)}}{R-\overset{+}{N}_2\bar{Cl}} \xrightarrow{H_2O} \underset{\text{(Alcohol)}}{R-OH} + N_2 + HCl.$$



$$+ HNO_2 \xrightarrow[273-278K]{NaNO_2 + HCl}$$

$$\xrightarrow{\text{warm the}}$$



$$+ N_2 + HCl$$

Aniline

Benzene diazonium chloride

(phenol)

1° amine.

Note: It is the test of 1° amine, 2° & 3° amine do not react in this way.