# **UNIT** - 13

## ORGANIC NITROGEN COMPOUNDS

# 1. Write down the possible isomers of the C<sub>4</sub>H<sub>9</sub>NO<sub>2</sub> give their IUPAC names

i) 
$$CH_3$$
- $CH_2$ - $CH_2$ - $CH_2$ - $NO_2$ 

iii) 
$$CH_3$$
-  $CH$  -  $CH_2$  -  $CH_3$   $NO_2$ 

$$^{\rm V)}_{\rm CH_3}\text{-}_{\rm CH}\text{-}_{\rm CH_2}\text{-}_{\rm NO_2}$$
 
$$_{\rm CH_3}^{\rm V}$$

vii) 
$$\begin{array}{c} \operatorname{CH_3} \\ \operatorname{CH_3^-} \operatorname{C-NO_2} \\ \operatorname{CH_3} \end{array}$$

ii) 
$$CH_3$$
- $CH_2$ - $CH_2$ - $CH_2$ -O - N = O

iv) 
$$CH_3$$
-  $CH$  -  $CH_2$  -  $CH_3$   
O -  $N$  =  $O$ 

vi) 
$$CH_3$$
-  $CH$ -  $CH_2$ -  $O$ -N=O  $CH_3$ 

$$\begin{array}{c} \text{CH}_3\\ \text{Viii)} \quad \text{CH}_3\text{-} \overset{\text{C}}{\text{C}}\text{-}\text{O-N=O}\\ \text{CH}_3\end{array}$$

i) 1- nitro butane

iii) 2 - nitro butane

v) 2- methyl - 1- nitro propane

vii) 2- methy-2-nitro propane

ii) 1-nitrosooxybutane

iv) 2- nitroso oxy butane

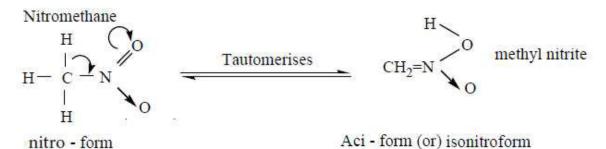
vi) 2 - methyl -1-nitroso oxy propane

viii ) 2-methyl-2-nitroso oxy propane

#### 2. There are two isomers with the formula CH<sub>3</sub>NO<sub>2</sub> How will you distinguish between them?

#### Tautomerism:

Primary and secondary nitroalkanes, having  $\alpha\text{-H}$  , also show an equilibrium mixture of two tautomers namely nitro and aci- form



#### Distinguish between two form

S.No.	Nitro form	Aci – form	
1.	Less acidic	More acidic and also called pseudoacids	
		(or) nitronic acids	
2.	Dissolves in NaOH slowly	Dissolves in NaOH instantly	
3.	Decolourises FeCl <sub>3</sub> solution	With FeCl <sub>3</sub> gives reddish brown colour	
4.	Electrical conductivity is low	Electrical conductivity is high	

#### 3. What happends when

- i. 2 Nitropropane boiled with HCI
- ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.
- iii. Oxidation of tert butylamine with KMnO<sub>4</sub>
- iv. Oxidation of acetoneoxime with trifluoroperoxy acetic acid.
- i. 2 Nitropropane boiled with HCI

$$\begin{array}{c} \text{CH}_3\text{-}\text{CH} \text{-}\text{NO}_2 \\ \text{CH}_3 \end{array} \xrightarrow{\begin{array}{c} \textbf{boiling HCl} \\ \text{CH}_3 \end{array}} \begin{array}{c} \text{CH}_3\text{-}\text{C=O} \\ \text{CH}_3 \end{array} + \text{N}_2\text{O} + \text{H}_2\text{O} \\ \text{Acetone} \end{array}$$

ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.

ii) Oxidation of tert - butylamine with KMnO<sub>4</sub>

iv. Oxidation of acetoneoxime with trifluoro peroxy acetic acid.

Oxidation of acetoneoxime with trifluoroperoxy acetic acid gives 2 - nitropropane (20) respectively.

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3}\text{- C = N -OH + (O)} & \xrightarrow{\text{CF}_{3}\text{-COOOH}} & \text{CH}_{3}\text{- CH-NO}_{2} + \text{H}_{2}\text{O} \\ \text{acetoneoxime} & \text{CH}_{3} \\ & \text{2 - nitropropane (2^{0})} \end{array}$$

#### 4. How will you convert nitrobenzene into

i. 1,3,5 - trinitrobenzene

ii. o and p- nitrophenol

iii. m - nitro aniline

iv. azoxybenzene

v. hydrozobenzene

vi. N - phenylhydroxylamine

vii. aniline

i) Conversion of nitrobenzene into 1,3,5 - trinitrobenzene

#### Ji Conversion of nitrobenzene into o and p- nitrophenol

#### iii) Conversion of nitrobenzene into m - nitro aniline

NO<sub>2</sub>
Nitration 373K
$$+$$
 3 (NH<sub>4</sub>)<sub>2</sub> S<sub>x</sub>
 $\longrightarrow$ 
NO<sub>2</sub>
 $+$  6NH<sub>3</sub> + 2H<sub>2</sub>O + 3S<sub>x</sub>
 $\longrightarrow$ 
 $\longrightarrow$ 
NO<sub>2</sub>
 $\longrightarrow$ 
NO<sub>2</sub>
 $\longrightarrow$ 
NH<sub>2</sub>
 $\longrightarrow$ 
m-nitroaniline

#### iv) Conversion of nitrobenzene into azoxybenzene hydrozobenzene

4 
$$+ 3As_2O_3 + 18NaOH \rightarrow 2$$
  $+ 6Na_3AsO_4 + 9H_2O$ 

#### iv) Conversion of nitrobenzene into hydrozobenzene

$$C_6H_5-NO_2 \xrightarrow{\textbf{Zn / NaOH}} [C_6H_5-N=N-C_6H_5] \xrightarrow{\textbf{2[H]}} C_6H_5-NH=NH-C_6H_5$$

#### iv) Conversion of nitrobenzene into N - phenylhydroxylamineaniline

$$C_6H_5-NO_2 + 2[H] \xrightarrow{\mathbb{Z}n / NH_4Cl} C_6H_5-NH-OH + ZnO$$
Neutral medium

#### iv) Conversion of nitrobenzene into aniline

$$C_6H_5$$
-NO $_2$  + 6[H]  $\xrightarrow{Sn/HCll}$   $C_6H_5$ -NH $_2$  Acid medium

Identify compounds A,B and C in the following sequence of reactions. 5.

i) 
$$C_6H_5-NO_2 \xrightarrow{Fe/HCI} A \xrightarrow{HNO_2/273K} B \xrightarrow{C_6H_5OH} C$$

Ans:  $C_6H_5-NO_2 \xrightarrow{Fe/HCI} C_6H_5-NO_2 \xrightarrow{HNO_2/273K} C_6H_5-N_2CI$ 

$$\xrightarrow{C_6H_5OH}$$

$$\begin{array}{c}
C_6H_5OH \\
\text{Coupling reaction}
\end{array}$$

$$\begin{array}{c}
N = N - \\
\end{array}$$
OH

p- hydroxy azobenzene

A- Aniline

B - Benzene diazonium chloride

C - p - hydroxy azobenzene

ii) 
$$C_6H_5-N_2CI \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$$

A- Cyanobenzene

B - Benzoic acid

C - Benzamide

iii) 
$$CH_3$$
- $CH_2$ I  $\xrightarrow{NaCN}$   $A \xrightarrow{OH^-}$   $B \xrightarrow{NaOH + Br_2}$   $C$  partial hydrolysis

Ans: 
$$CH_3$$
- $CH_2$ I  $\xrightarrow{NaCN}$   $CH_3$ - $CH_2$ CN  $\xrightarrow{OH^-}$   $CH_3$ - $CH_2$ CONH $_2$   $\xrightarrow{NaOH + Br_2}$   $CH_3$ - $NH_2$  partial hydrolysis

A- Ethyl cyanide

B - Acetamide

C - Methyl amine

reaction

iv) 
$$CH_3$$
- $NH_2$   $\xrightarrow{CH_3Br}$   $A$   $\xrightarrow{CH_3COCl}$   $B$   $\xrightarrow{B_2H_6}$   $C$ 

Ans:

$$\begin{array}{c} \mathsf{CH_3}\text{-}\mathsf{NH_2} & \xrightarrow{\mathsf{CH_3Br}} (\mathsf{CH_3})_2 \mathsf{NH} & \xrightarrow{\mathsf{CH_3COCl}} (\mathsf{CH_3})_2 \mathsf{N-CO-CH_3} \\ \\ & \xrightarrow{\mathsf{B_2H_6}} (\mathsf{CH_3})_2 \mathsf{N-CH(OH)-CH_3} \end{array}$$

A- N,N dimethyl amine

**B** - N,N-dimethyl acetamide

C - N,N-dimethyl 2- hydroxy ethan amine

v) 
$$C_6H_5$$
-NH<sub>2</sub> (CH<sub>3</sub>CO)<sub>2</sub>O/pyridine  $A$  HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>  $B$  H<sub>2</sub>O/H<sup>+</sup>  $C$ 

Ans:

A - Acetanilide

B - p- nitroacetanilide

C- p- nitro aniline

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vi)
$$\begin{array}{c} & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

A- p-N,N - dimethyl amino azobenzene

B - 2 - phenylazo - 4 -Methyl phenol

C - p - amino azobenzene (Yellow dye)

vii ) 
$$CH_3$$
- $CH_2$ - $NC \xrightarrow{HgO} A \xrightarrow{H_2O} B \xrightarrow{i)NaNO_2/HCl} C$ 
ii)  $H_2O$ 

$$\textbf{Ans}: \mathsf{CH_3\text{-}CH_2\text{-}NC} \xrightarrow{\quad \mathbf{HgO} \quad } \mathsf{CH_3\text{-}CH_2\text{-}N} = \mathsf{C} = \mathsf{O} \xrightarrow{\quad \mathbf{H_2O} \quad } \mathsf{CH_3\text{-}CH_2\text{-}NH_2}$$

$$\frac{i)\text{NaNO}_2 \text{/HCI}}{\text{unstable}} [\text{C}_2\text{H}_5\text{N}_2\text{CI}] \xrightarrow{ii) \text{H}_2\text{O}} \text{CH}_3\text{-CH}_2\text{OH} + \text{N}_2$$

A- Ethyl iso cyanate

B-Ethyl amine

**C-Ethanol** 

#### 6. Write short notes on the following

- i. Hofmann's bromide reaction
- ii. Ammonolysis
- iii. Gabriel phthalimide synthesis
- iv. Schotten Baumann reaction
- v. Carbylamine reaction
- vi. Mustard oil reaction
- vii. Coupling reaction
- viii. Diazotisation
- ix. Gomberg reaction

#### Hofmann's bromide reaction

When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

$$CH_3$$
- $CONH_2 \xrightarrow{Br_2/KOH} CH_3$ - $NH_2 + K_2CO_3 + KBr + H_2O$ 

#### ii. **Ammonolysis**

When Alkyl halides (or) benzylhalides are heated with alcoholic ammonia in a sealed tube, mixtures of 1<sup>0</sup>, 2<sup>0</sup> and 3<sup>0</sup> amines and quaternary ammonium salts are obtained

#### iii. Gabriel phthalimide synthesis

Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline cannot be prepared by this method because the arylhalides do not undergo nucleophilic substitution with the anion formed by phthalimide

#### iv. Schotten - Baumann reaction

Aniline reacts with benzoylchloride ( $C_6H_5COCI$ ) in the presence of NaOH to give N-phenyl benzamide. This reaction is known as Schotten - Baumann reaction

$$C_6H_5-NH_2+C_6H_5-C-C1$$

Pyridine
 $C_6H_5-NH-C-C_6H_5+C$ 

Aniline

Pyridine
 $C_6H_5-NH-C-C_6H_5+C$ 

N-phenyl benzamide

#### v. Carbylamine reaction

Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell. This reaction is known as carbylamines test. This test used to identify the primary amines

#### vi. Mustard oil reaction

i) When primary amines are treated with carbon disulphide (CS<sub>2</sub>), N - alkyldithio carbonic acid is formed which on subsequent treatment with HgCl<sub>2</sub>, give an alkyl isothiocyanate.

#### vii. Coupling reaction

Benzene diazonium chloride reacts with electron rich aromatic compounds like phenol, aniline to form brightly coloured azo compounds.

Phenol

Phenol

$$P = N = N - OH$$

Phenol

Phenol

Phenol

Phenol

Phydroxy azobenzene (orange dye)

#### viii. Diazotisation

Aniline reacts with nitrous acid at low temperature (273 - 278 K) to give benzene diazonium chloride which is stable for a short time and slowly decomposes seven at low temperatures. This reaction is known as **diazotization**.

$$NH_2$$
  
+ NaNO<sub>2</sub> + 2HCl  $\longrightarrow$   $N_2$  Cl  $\longrightarrow$  + NaCl + 2H<sub>2</sub>O  
Aniline Benzenediazonium chloride

#### ix. Gomberg reaction

Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction in known as the Gomberg reaction.

$$\begin{array}{c|c}
 & + & - \\
 & N_2CI + H - \\
\hline
 & Benzene
\end{array}$$
NaOH

Biphenyl

Biphenyl

#### 7. How will you distinguish between primary secondary and tertiary alphatic amines.

Reagents	Primary amine	Secondary amine	Tertiary amine
With HNO <sub>2</sub>	forms forms alcohol	N-nitroso amine	forms salt.
With CHCl <sub>3</sub> /KOH	forms carbylamine	No reaction.	No reaction
With CS <sub>2</sub> and HgCl <sub>2</sub>	alkyl isothiocyanate is formed	No reaction	No reaction
With Diethyl oxalate	dialkyl oxamide, a solid at room temperature is formed.	Forms N,N-dialkyl oxamic ester, a liquid.	No reaction
With acetyl chloride	forms N-alkyl acetamide.	form N,N-dialkyl acetamide	No reaction

#### i. Aniline does not undergo Friedel . Crafts reaction

ACFaiteslebaction is carried out in the presence of AlCl 3. But AlCl 3 is acidic in nature, while aniline is a strong base. Thus, aniline reacts with AlCl 3 to form a salt.

Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

#### ii. Diazonium salts of aromatic amines are more stable than those of aliphatic amines

In diazonium salt, the structure goes under resonance due to which the dispersal of positive charge is more and we know that higher is the resonance higher is the stability. Therefore diazonium salt of aromatic amines is more stable than those of aliphatic amines.

#### iii. pKb of aniline is more than that of methylamine

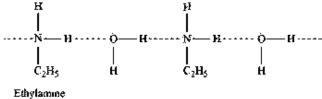
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate. On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, pK<sub>b</sub> of aniline is more than that of methylamine.

#### iv. Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

#### v. Ethylamine is soluble in water whereas aniline is not

Ethylamine when added to water forms intermolecular H-bonds with water. And therefore it is soluble in water. But aniline does not form H-bond with water to a very large extent due to the presence of a large hydrophobic -C6H5group. Hence, aniline is insoluble in water.



#### vi. Amines are more basic than amides

The lone pair of electrons on the amine are more available to accept a proton and act as a base. This is because in amides, the carbonyl (C=O) group is highly electronegative, so has a greater power to draw electrons towards it, making the lone pair of the amide nitrogen less available to accept a proton.

# vii. Although amino group is o - and p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m- nitroaniline

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

#### 9. Arrange the following

#### i. In increasing order of solubility in water, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>,(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH,C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>

The more extensive the H-bonding, the higher is the solubility. Thus,  $C_2H_5NH_2$  undergoes more extensive H-bonding than  $(C_2H_5)_2NH$ . Hence, the solubility in water of  $C_2H_5NH_2$  is more than that of  $(C_2H_5)_2NH$ .

$$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$$

#### ii. In increasing order of basic strength

#### a) aniline, p-toludine and p-nitroaniline

#### p-nitroaniline < aniline < p-toludine

In p-toluidine, the presence of electron-donating -CH<sub>3</sub> group increases the electron density on the N-atom. Thus, p-toluidine is more basic than aniline. -NO<sub>2</sub> group decreases the electron density over the N-atom in p-nitroaniline. Thus, p-nitroaniline is less basic than aniline.

# b) In increasing order of basic strength $C_6H_5NH_2$ , $C_6H_5NHCH_3$ , p-CI- $C_6H_4NH_2$ ,

i) Chlorine atom has both - I effect and + R effect so para chloro aniline is less basic than aniline

CH<sub>3</sub>- group is electron donating group in so increases electron density in N - atom so, N - Methyl aniline is more basic than aniline

$$p-CI-C_6H_4NH_2 < C_6H_5NH_2 < C_6H_5NHCH_3$$

#### iii. In decreasing order of basic strength in gas phase

$$C_2H_5NH_2$$
,  $(C_2H_5)_2NH$ ,  $(C_2H_5)_3N$  and  $NH_3$ 

In gas phase there is no hydrogen bonding , therefore stabalisation due to hydrogen bonding is not there. Therfore the only effect to determine the strength is the inductive effect. The +I effect increases with increase in the alkyl group. Therefore the basic strength will be the highest in  $(C_2H_5)_3N$  and least in  $NH_3$ . Therefore the decreasing order of basic strength in gas phase will be

$$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$$

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### iv. In increasing order of boiling point $C_6H_5OH$ , $(CH_3)_2NH$ , $C_2H_5NH_2$

The elcetronegativity of O is more than N. Therefore  $C_6H_5OH$  forms hydrogen bonding and because of the hydrogen bonding the alcohols will have higher boiling point than the amines with comparable molecular mass. Now between  $(CH_3)_2NH$  and  $C_2H_5NH_2$ ,  $C_2H_5NH_2$  has more hydrogen atom attached the Nitrogen. Therfore the extent of hydrogen bonding will be more in primary amines i.e  $C_2H_5NH_2$  as compared to sec or ter amines. Therfore  $C_2H_5NH_2$  will have higher boiling point as compared to  $(CH_3)_2NH$ . Therefore the increasing order of boiling point will be as given below.

Ans: 
$$(CH_3)_2NH < C_2H_5NH_2 < C_6H_5OH$$

#### v. In decreasing order of the pKb values C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH and CH<sub>3</sub>NH<sub>2</sub>

Larger the value of Kb or smaller the value of pKb, stronger is the base.

- (i) In  $C_2H_5$  NH $_2$ , only one  $-C_2H_5$  group is present while in  $(C_2H_5)_2$ NH, two  $-C_2H_5$  groups are present. Thus, the +I effect is more in  $(C_2H_5)_2$ NH than in  $C_2H_5$  NH $_2$ . Therefore, the electron density over the N-atom is more in  $C_2H_5)_2$ NH than in  $C_2H_5$  NH $_2$ . Hence,  $(C_2H_5)_2$ NH is more basic than  $C_2H_5$  NH $_2$ .
- ii) In  $C_6H_5NHCH_3$  is less basic than  $((C_2H_5)_2NH)$  and  $C_2H_5NH_2$  due to the delocalization of the lone pair in the former two. Further, among  $C_6H_5NHCH_3$  the former will be more basic due to the +I effect of -CH $_3$  group. Hence, the order of increasing basicity of the given compounds is as follows:

$$C_6H_5NHCH_3 < CH_3NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH_3$$

We know that the higher the basic strength, the lower is the pKb values.

$$C_6H_5NHCH_3 > CH_3NH_2 > C_2H_5NH_2 > (C_2H_5)_2NH$$

# vi. Increasing order of basic strength $C_6H_5NH_2$ , $C_6H_5N(CH_3)_2$ , $(C_2H_5)_2NH$ and $CH_3NH_2$

 ${
m C_6H_5N(CH_3)_2}$  is more basic than  ${
m C_6H_5NH_2}$  due to the presence of the + I effect of two -  ${
m CH_3}$  group in  ${
m C_6H_5N(CH_3)_2}$  Further  ${
m CH_3NH_2}$  contains one -  ${
m CH_3}$  group while  ${
m (C_2H_5)_2NH}$  contains two -  ${
m C_2H_5}$  group. Thus,  ${
m (C_2H_5)_2NH}$  is more basic than  ${
m CH_3NH_2}$ 

Now  $C_6H_5N(CH_3)_2$  is less basic than  $CH_3NH_2$  because of the - R effect of -  $C_6H_5$  group. Hence, the increasing order of the basic strength of the given compounds is as follows

$${\rm C_6H_5NH_2}{<{\rm C_6H_5N(CH_3)_2}{<{\rm CH_3NH_2}{<{\rm (C_2H_5)_2NH}}}$$

#### vii. In decreasing order of basic strength

$$CH_3CH_2NH_2$$
  $O_2N$   $NH_2$ ,  $NH_2$ ,  $NH_2$ ,  $CH_3$   $NH_2$ 

Aliphatic amines are more basic than aromatic amines.so  $\mathrm{CH_3CH_2NH_2}$  and  $\mathrm{CH_3}$  -  $\mathrm{NH_2}$  are more basic .  $\mathrm{CH_3CH_2NH_2}$  is more +I effect than  $\mathrm{CH_3}$  -  $\mathrm{NH_2}$  , so  $\mathrm{CH_3CH_2NH_2}$  more basic than  $\mathrm{CH_3}$  -  $\mathrm{NH_2}$  In case of substituted aniline, electron withdrawing group like -  $\mathrm{NO_2}$ , they have both - R effect as well as - I effect . as result all nitro amines are weaker bases than aniline .

$$CH_3CH_2NH_2 > CH_3 - NH_2 > NH_2 > O_2N - NH_2$$

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#### How will you prepare propan -1- amine from butane nitrile 10.

i) butane nitrile

ii) propanamide

ii) 1- nitropropane

#### i) Butane nitrile converted into propan -1- amine

$$CH_3$$
-  $CH_2$ - $CH_2$   $CN$   $\xrightarrow{H^+/Hydrolysis}$   $CH_3$ -  $CH_2$ - $CH_2$   $CONH_2$   $\xrightarrow{Br_2/KOH}$   $CH_3$ -  $CH_2$ - $CH_2$   $NH_2$  ii) propanamide converted into propan -1- amine Hoffmann's degradation

$$\mathsf{CH_3}\text{-}\,\mathsf{CH_2}\text{-}\mathsf{CONH_2} \xrightarrow{\quad \mathbf{LiAlH_4/H_2O} \quad } \mathsf{CH_3}\text{-}\,\mathsf{CH_2}\text{-}\mathsf{CH_2}\,\mathsf{NH_2}$$

iii) 1- nitropropane converted into propan -1- amine

$$\mathsf{CH_3}\text{-}\,\mathsf{CH_2}\text{-}\mathsf{CH_2}\mathsf{NO_2} \xrightarrow{\quad \mathbf{Sn/HCl} \quad} \mathsf{CH_3}\text{-}\,\mathsf{CH_2}\text{-}\mathsf{CH_2}\,\mathsf{NH_2} + 2\mathsf{H_2O}$$

#### 11. Identify A,B,C and D

$$\begin{array}{c} \text{CH}_3\text{-}\text{NO}_2 \xrightarrow{\quad \textbf{LiAlH}_4 \quad \text{CH}_3 \text{NH}_2 \quad } \text{CH}_3 \text{NH}_2 \rightarrow \quad \begin{array}{c} \textbf{H} \, \textbf{N} \, \textbf{O} \\ \textbf{2} \end{array} \rightarrow \\ \text{(CH}_3\text{-} \, \text{CH}_2)_2 \, \textbf{N-CH}_3 \xrightarrow{\quad \textbf{H}_2 \text{SO}_4 \quad } \\ \text{[(CH}_3\text{-} \, \text{CH}_2)_2 \, \textbf{NH}^+\text{-CH}_3 \, ] \, \text{HSO}_4 \end{array} \rightarrow \\ \end{array}$$

A - Methyl amine

B - N -Metyl ethan-1- amine

C - N,N-diethylmethylamine

D - Quarternary ammonium hydrogen sulphate

#### 12. How will you convert diethylamine into

i) N,N-diethylacetamide

ii) N- nitrosodiethylamine

#### i) Conversion of diethylamine into N,N-diethylacetamide

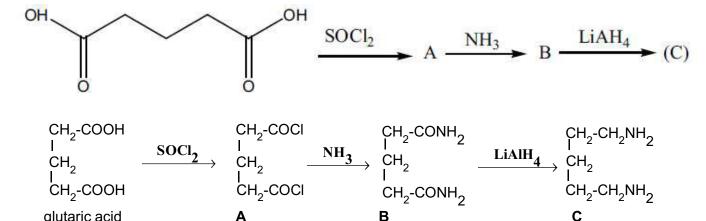
$$(CH_3 - CH_2)_2 N - H + CH_3 COCI \xrightarrow{pyridine} (CH_3 - CH_2)_2 N - CO - CH_3 + HCI$$

ii) Conversion of diethylamine into N- nitrosodiethylamine

$$(CH_3 - CH_2)_2 N - H \xrightarrow{HNO_2} (CH_3 - CH_2)_2 N - N = O (N-nitrosodiethylamine)$$

#### 13. Indentify A,B and C

glutaric acid



A- Glutaryl chloride

**B**-Pentanediamide (Glutaramide)

C-1,5 - diaminopentane

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#### 14. Indentify A,B,C and D

aniline + benzaldehyde  $\rightarrow$  A Conc HNO $_3$ /B C and D

$$\begin{array}{c|c}
O & H & NH_2 &$$

#### 15. Complete the following reaction

N-benzyl cyclo hexane imine

#### 16. Predict A,B,C and D for the following reaction

$$0 \xrightarrow{NH_3/\Delta} A \xrightarrow{i) \text{ KOH}} C \xrightarrow{H_2O/H^+} D + H_2N - CH - CH_3$$

$$CH_3$$

Ans:

A- phthalimide

**B** - 2 - Chloropropane

**C- N-** isopropyl phthalimide

D- phthalic acid

#### webStrake

17. Alibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of CO<sub>2</sub>. (B) on heating with liquid ammoniafollowed by treating with Br<sub>2</sub> /KOH gives (c) which on treating with NaNO<sub>2</sub> and HCl at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74.Identify A to D.

$$\stackrel{\text{i)} \ \text{CH}_3\text{-}\ \text{CH}_2\text{-}\text{CH-CH}_2\text{-Br} \xrightarrow{\quad \textbf{KCN} \quad \text{CH}_3\text{-}\ \text{CH}_2\text{-}\text{CH-CH}_2\text{-CN} \quad \xrightarrow{\quad \textbf{i)} \ \textbf{H}^+/\textbf{H}_2\textbf{O} \quad } \\ \stackrel{\text{ii)} \ \textbf{Heat} \quad \quad \text{CH}_3\text{-}\ \textbf{CH}_2\text{-}\text{CH}_2\text{-}\text{COOH} + \textbf{CO}_2 \\ \text{CN}$$

ii) 
$$\text{CH}_3\text{-}\text{CH}_2\text{-}\text{COOH} + \text{NH}_3$$
  $\text{(lig)} \xrightarrow{\text{Heat}} \text{CH}_3\text{-}\text{CH}_2\text{-}\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{KOH}} \text{CH}_3\text{-}\text{CH}_2\text{-}\text{CONH}_2$ 

$$\begin{array}{ccc} \text{iii) } \text{CH}_3\text{-} \text{CH}_2\text{-} \text{CH}_2\text{-} \text{CONH}_2 & & \underline{ & \text{NaNO_2/HCl} \\ & \text{Low T} & & \text{CH}_3\text{-} \text{ CH}_2\text{-} \text{CH}_2\text{-} \text{OH} & \underline{ & \text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+ \\ & \text{2(O)} & & \\ \end{array}} \text{CH}_3\text{-} \text{ CH}_2\text{-} \text{COOH}$$

A - 1,2 - diamino butane

B-1,2 dicyano butane

C-1 - amino prpane

D - Propanoic acid

Molecular mass of propanoic acid - 74

18. Indentify A to E in the following frequency of reactions.

$$\begin{array}{c|c} & CH_3Cl \\ \hline AlCl_3 & A & HNO_3/H_2SO_4 & B & Sn/HCl \\ \hline & (Major product) & O^{\circ}C & D & \hline \end{array}$$

Ans:

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{D - 60°C} \\ \end{array} \\ \begin{array}{c} \text{CH}_3 \\ \text{NaNO}_2/\text{HCl} \\ \text{NaNO}_2/\text{HCl} \\ \text{NaNO}_2/\text{HCl} \\ \text{273-278 K} \\ \end{array} \\ \begin{array}{c} \text{NaNO}_2/\text{HCl} \\ \text{NaNO}_2/\text{HCl} \\ \text{273-278 K} \\ \end{array} \\ \begin{array}{c} \text{NaNO}_2/\text{HCl} \\ \text{NaNO}_2/\text{HCl} \\ \text{NaNO}_2/\text{HCl} \\ \text{273-278 K} \\ \end{array} \\ \begin{array}{c} \text{NaNO}_2/\text{HCl} \\ \text{Nano}_2/\text{HCl} \\ \text{273-278 K} \\ \end{array} \\ \begin{array}{c} \text{Nano}_2/\text{HCl} \\ \text{Nano}_2/\text{HCl} \\$$

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