Padasalai's Telegram Groups!

(தலைப்பிற்கு கீழே உள்ள லிங்கை கிளிக் செய்து குழுவில் இணையவும்!)

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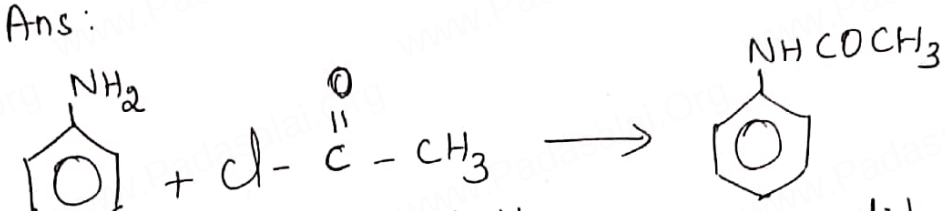
Unit - 13

Amines

1. Give reasons for the following:

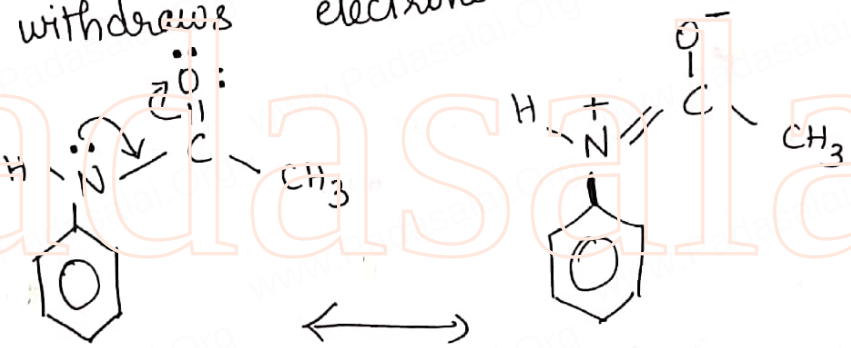
(a) Acetylation of aniline reduces its activation effect.

Ans:



Aniline Acetyl chloride Acetanilide

In acetanilide, the oxygen atom of the group withdraws electrons from $\ddot{N}H_2$ group as,



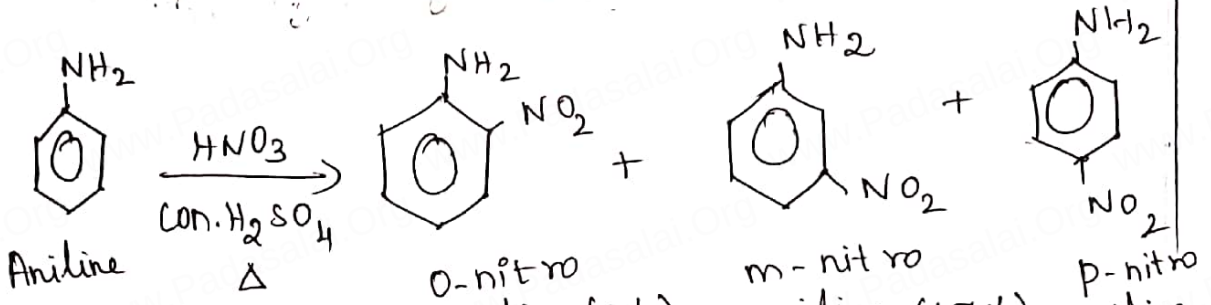
The electron pair on nitrogen gets displaced to the carboxyl group. Therefore the unshared pair of electron on nitrogen is less available for donation of the electron to aromatic ring.

(b) CH_3NH_2 is more basic than $C_6H_5NH_2$.

In aniline, lone pair of electron present on 'N' is in conjugation with the

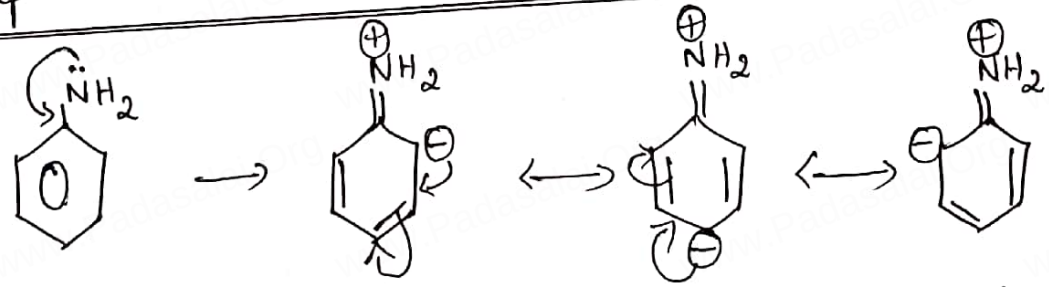
benzene ring and become less available for protonation because of resonance.

(c) Although $-NH_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.



The reason for the formation of large amount of m-nitroaniline is that under strongly acidic conditions, aniline gets protonated to anilinium ion ($-NH_3^+$ group). This is a deactivating group and is meta-directing, in nature.

(b)



This conjugation of lone pair of e^- is not present in case of methyl amine and lone pair of e^- of 'N' are fully available for protonation. That's why the basicity order of aniline and methyl amine is $CH_3NH_2 > C_6H_5NH_2$

2. Write the equations involved in Wolf Kishner reduction.

Ans:

$CH_3-\underset{\underset{H}{|}}{C}=O + NH_2-NH_2 \xrightarrow{-H_2O} CH_3-\underset{\underset{H}{|}}{C}=NNH_2$

Acetaldehyde — hydrazine — Hydrazone

Hydrazone $\xrightarrow[453-473K]{KOH,\ Glycol}$ $CH_3-CH_3 + N_2$

3 Q: Write the structure of compounds A, B and C.

$CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} A \xrightarrow{dil.\ NaOH} B \xrightarrow{\Delta} C$

Ans:

$CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} CH_3CHO$ (A) Acetaldehyde

$CH_3CHO \xrightarrow{dil.\ NaOH} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2CHO$

Aldol (B)

$\xrightarrow{\Delta}$

$CH_3-CH=CH-CHO$ (C)

4 Q: Write IUPAC name of the following compound:

(i) $CH_3NHCH(CH_3)_2$

Ans: N-methylpropan-2-amine.

(ii) $(CH_3)_2N-CH_2-CH_3$ Ans: N, N-dimethyl ethanamine

Q: Write the structure of A, B and C in the following:

$C_6H_5-CONH_2 \xrightarrow{aq.KOH} A \xrightarrow[0-5^\circ C]{NaNO_2+HCl} B \xrightarrow{KI} C$

Ans:

$C_6H_5-CONH_2 \xrightarrow{Br_2/aq.KOH} C_6H_5NH_2$ (A) Aniline $\xrightarrow[0-5^\circ C]{NaNO_2+HCl} C_6H_5N_2^+Cl^-$ (B) Benzene diazonium chloride $\xrightarrow{KI} C_6H_5I$ (C) Iodobenzene

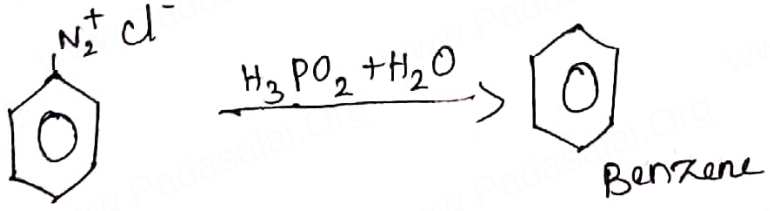
A - Aniline

B - Benzene diazonium chloride

C - Iodobenzene

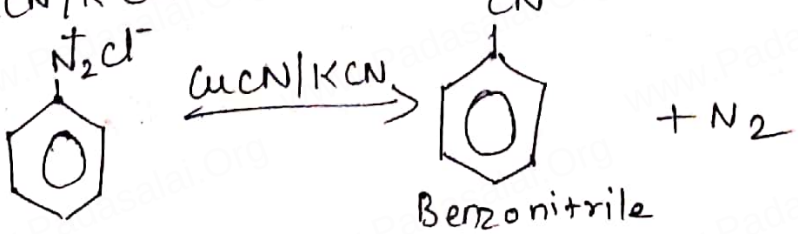
Q: Write the structures of main products when benzene diazonium chloride reacts with the following reagents:

(i) $H_3PO_2 + H_2O$



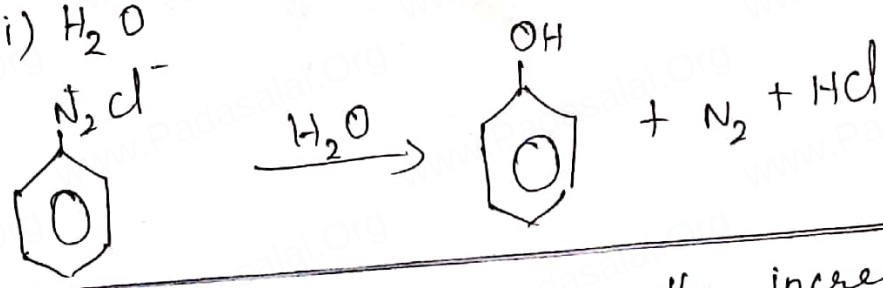
Benzene

(ii) $CuCN/KCN$



Benzonitrile

(iii) H_2O



7 Q: Arrange the following in the increasing order of their basic character in an aqueous solution:

Q: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$

Ans:

$$C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

+I effect of three C_2H_5 group increase the enormous availability of lone pair of nitrogen atom than +I effect of two ethyl groups. Thus the order of basicity is I < III < II.

8 Q: Give a simple chemical test to distinguish between the following pair of compounds:

$C_6H_5-NH_2$ and $C_6H_5-NH-CH_3$.

Ans:

$C_6H_5-NH_2$ (primary amine) and $C_6H_5-NH-CH_3$ (secondary amine) can be distinguished by Hinsberg's test. In this test amines are allowed to react with Hinsberg's reagent, benzene sulphonyl chloride ($C_6H_5SO_2Cl$). Primary amines reacts with this reagent to form N-alkyl benzene sulphonyl amide which is soluble in alkali but secondary amines gives sulphonamide which is insoluble in alkali.

9
Q: An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions.

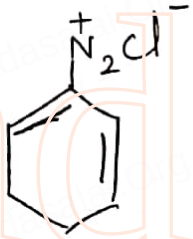
$(C_7H_7ON)\ A \xrightarrow{Br_2/KOH} C_6H_5NH_2 \xrightarrow[273\,K]{NaNO_2+HCl} B \xrightarrow{CH_3CH_2OH} C$

$C_6H_5NH_2 \xrightarrow{CHCl_3+NaOH} D$

$B \xrightarrow{KI} E$

Ans:

A  Benzamide

B  Benzene diazonium chloride

C  Benzene

D  Phenylisocyanide

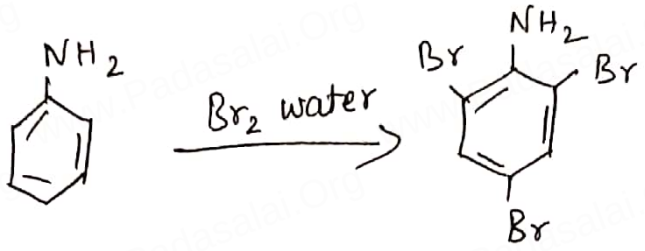
E  Iodobenzene

10
Q: Write the structures of main products when aniline reacts with the following reagents:

(i) Br_2 water (ii) HCl (iii) $(CH_3CO)_2O$ / Pyridine

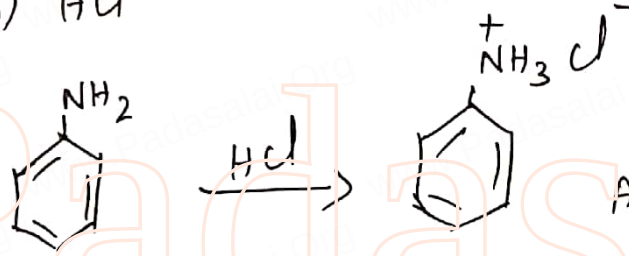
Ans:

(i)



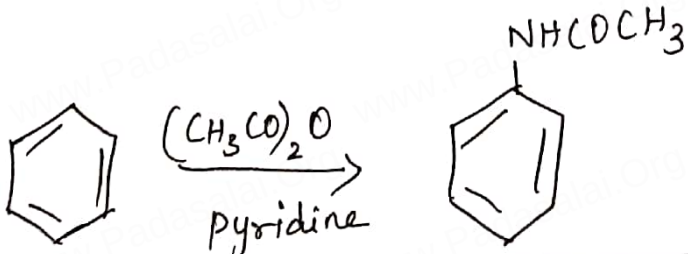
2,4,6-tribromo aniline

(ii) HCl



Anilinium chloride

(iii) $(CH_3CO)_2O$ / Pyridine



Acetanilide

11
Q: Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$.

Ans: Ethanol has high boiling point then ethylamine because oxygen, being

more electronegative forms strong extensive hydrogen bond as compared to that of nitrogen. In trimethylamine there is no hydrogen and hence has the lowest boiling point.

Increasing order of boiling point.

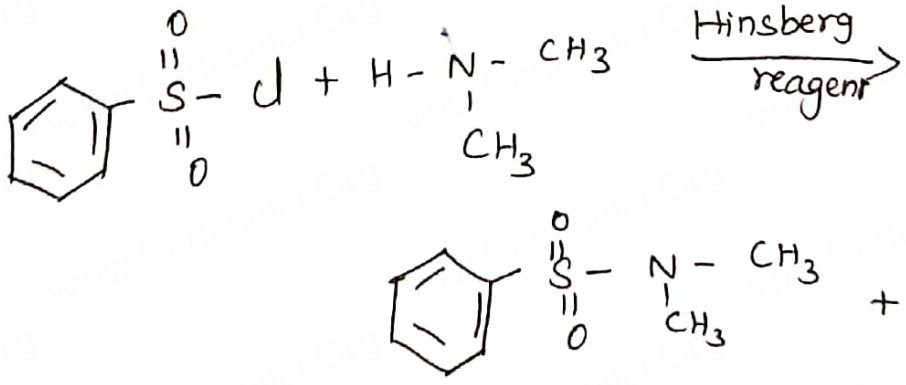
$(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$.

12 Q: Give a simple chemical test to distinguish between the following pair of compounds:

$(CH_3)_2NH$ and $(CH_3)_3N$.

Ans:

$(CH_3)_2NH$ reacts with benzene sulphonyl chloride (Hinsberg reagent) as follows:



N, N - Dimethyl benzene sulphonamide

$(CH_3)_3N$ does not react with benzene sulphonyl chloride.

13. Q: Account for the following:

(i) Primary amines ($R-NH_2$) have higher boiling point than tertiary amines (R_3N).

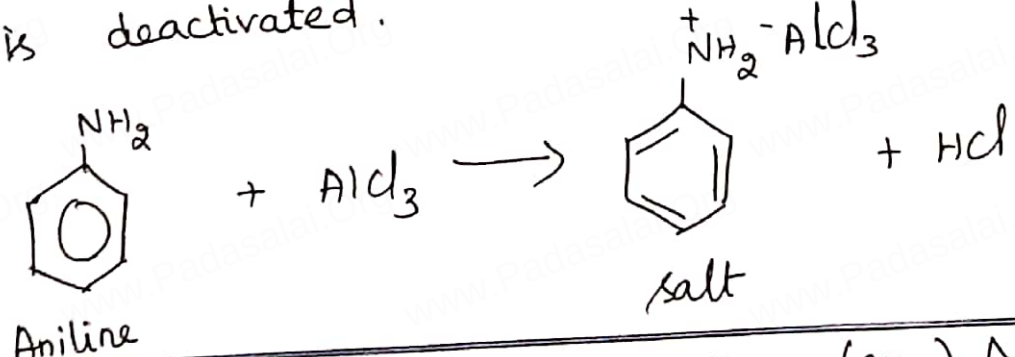
Ans:

Due to intermolecular hydrogen bonding in primary amines (presence of more number of H-atoms). They have high boiling point in comparison to tertiary amines.

Q (ii) Aniline does not undergo Friedel-Crafts reaction.

Ans:

Aniline does not undergo Friedel-Crafts reaction because Aniline is basic in nature and reacts with $AlCl_3$ to form a salt. The positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated.



Aniline

salt

(iii) Q: $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

Ans:

Due to steric hindrance and solvation effect in case of $(CH_3)_3N$, it is less basic than $(CH_3)_2NH$ in aqueous solution.

14 Q: Give the structures of A, B and C in the following reactions:

i) $C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow{NaNO_2+HCl} B \xrightarrow{H_2O} C$

Ans:

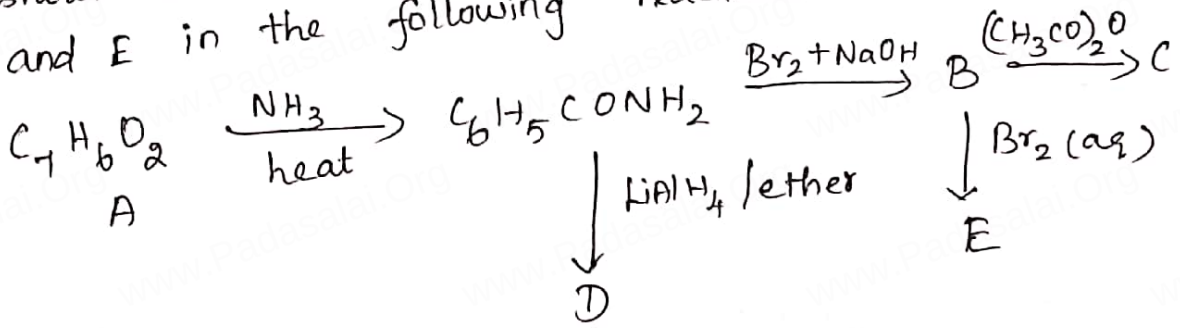
$C_6H_5NO_2 \xrightarrow{Sn+HCl} C_6H_5NH_2$ (A) Benzyl amine $\longrightarrow C_6H_5\overset{+}{N}_2Cl^-$ (B) Benzene diazonium chloride $\xrightarrow{H_2O} C_6H_5OH$ (C) Phenol

ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2+KOH} C$

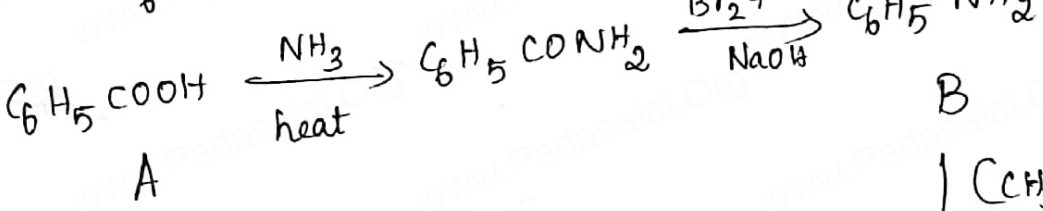
Ans:

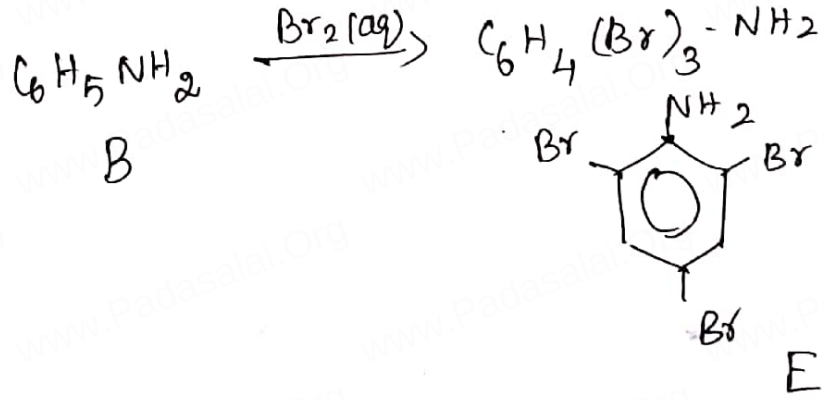
$CH_3CN \xrightarrow{H_2O/H^+} CH_3COOH$ (A) Acetic acid $\xrightarrow[\Delta]{NH_3} CH_3CONH_2$ Ethanamide (B) $\xrightarrow{Br_2+KOH} CH_3NH_2$ (C) Methanamine

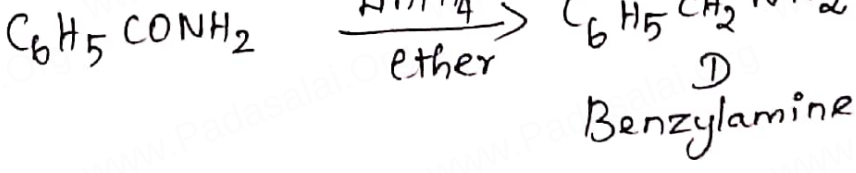
15. Q: An aromatic compound 'A' of molecular formula $C_7H_6O_2$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:

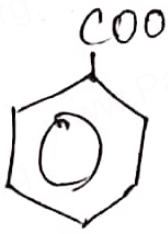


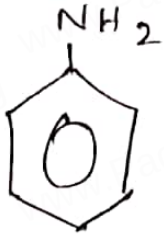
A ⇒ C_6H_5COOH B → Aniline



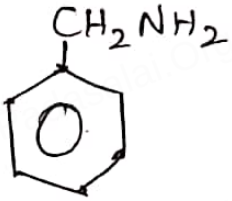


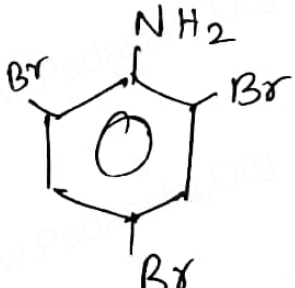


A C_6H_5COOH  Benzoic acid

B $C_6H_5NH_2$  Aniline

C $C_6H_5NHCOCH_3$  N-phenyl ethanamide

D $C_6H_5CH_2NH_2$  Benzylamine

E $C_6H_4(Br)_3NH_2$  2,4,6-tribromo aniline

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