AMINES AND DIAZO COMPOUNDS

CHEMISTRY

Give the structure of A B C in the following

$$CH_2Br \xrightarrow{KCN} A \xrightarrow{LiALHY} B \xrightarrow{HNO_2} C$$

- 1) CH_3CN , CH_3CH_2OH , $CH_3CH_2 NH_2$
- 2) $CH_3 CH_2 NH_2$, CH_3CH_2OH , CH_3CN
- 3) CH_3CN , $CH_3CH_2 NH_2$, $CH_3CH_2 OH$
- 4) $CH_3CH_2 NH_2$, CH_3CN , $CH_3CH_2 OH$
- $CH_3COOH \xrightarrow{NH_3} A \xrightarrow{Br_2+KoH} B \xrightarrow{CHCl_3NaOH}$ 2.
 - 1) CH_3CONH_2 , CH_3NH_2 , CH_3NC 2) CH_3NH_2 , CH_3CONH_2 , CH_3NC
 - 3) CH_3CN , CH_3NH_2 , CH_3CONH_2 4) CH_3NH_2 , CH_3NC , CH_3CONH_2
- Write the main products of the following reaction $CH_3CH_2NH_2 \xrightarrow{HNO_2} 0^0C$ 3.

 - 1) $CH_3 OH$ 2) $CH_3 CH_2 OH$
- 3) $CH_3 \overset{CH_3}{C} OH$ 4) $CH_3 \overset{CH_3}{C} OH$

- $C_6H_5So_2Cl So_2Cl + C_2H_5NH_2 \rightarrow$ 4.
 - 1) $C_6H_5So_2N(C_2H_5)_2$
 - 3) $C_6H_5(SO_2)_2 C_6H_5$

- 2) $C_6H_5(So_2)_2 NH_{C_2H_2}$
- 4) $C_6H_5So_2 NH_{CH_2}$

- $CH_2 CO NH_2 \xrightarrow{Br_2 + NaOH} \rightarrow$ 5.
 - 1) $CH_3 CH_2 OH$
 - 3) $CH_3 NH_2$

- 2) $CH_3 CH_2 NH_2$
- 4) $CH_2 OH$
- Compare the boiling points among isomeric amines 6.
 - 1) Primary amine > Secondary amine > Tertiary amines
 - 2) Primary amines < Secondary amines < Tertiary amines
 - 3) Secondary amines > Tertiary amines > Primary
 - 4) Secondary amines < tertiary amines < Primary amines $60^{0} c$

 $Aniline \xrightarrow{Con HSo_4} \rightarrow$ 7.

8.

9.

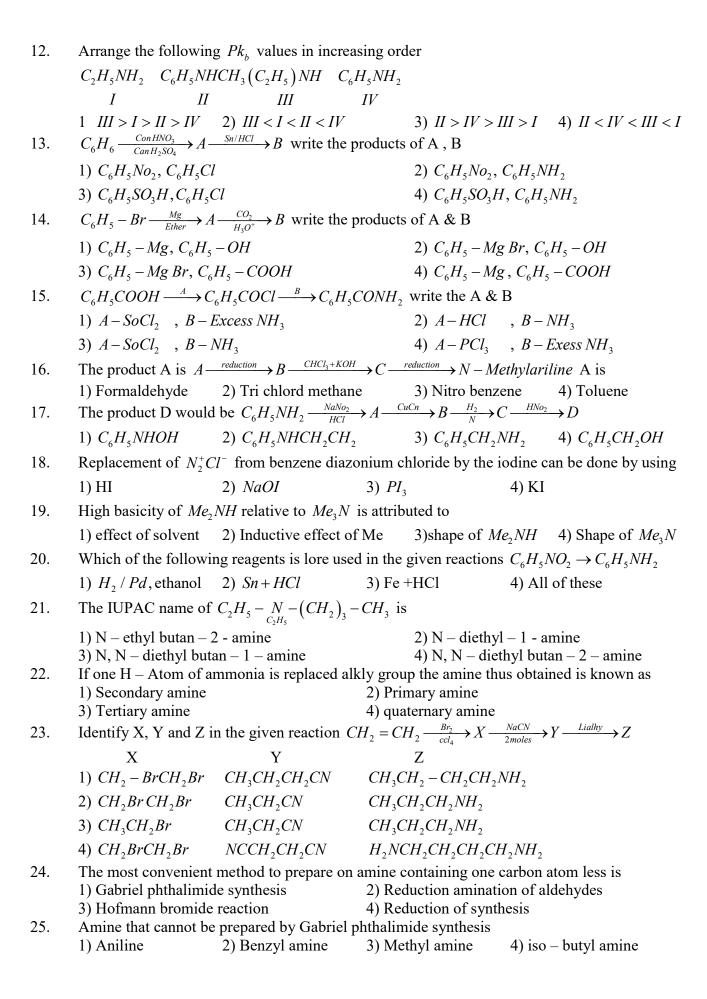
- 1) meta amino benzene sulphenic acid
- 3) ortho amino benzene sulphonic acid
- O Nitro acetomide on hydrolysis gives
 - 1) O Nitro Iso cyanide
 - 3) O Nitro aniline
 - $C_6H_5NH_2 + CHCl_3 \xrightarrow{alc\ KoH} \rightarrow$
 - 1) C_6H_5CN
- 2) C_6H_5COOH

- 2) Para amino benzene sulphenic acid
- 4) Both 2 & 3
- 2) O Nitro cyanide
- 4) O Nitro carboxylic acid
- 3) C_6H_5NC
- 4) Both 1 & 3

- $C_6H_5N_2^+Cl^- + H_3Po_3 \xrightarrow{H_2O}$ 10.
 - 1) C_6H_6
- 2) $H_3 Po_3$ 3) $C_6 H_5 NH_2$ 4) Both 1 & 2

- $C_6H_5NO_2 \xrightarrow{Fe/HCl} \rightarrow$ 11.
 - 1) C_6H_5NC 2) C_6H_5CN

- 3) $C_6H_5N_2^+Cl^-$ 4) $C_6H_5NH_2$



- 26. Identify the reagents X, Y and Z for the following Products
 - i) Benzenedi azonium chloride \xrightarrow{X} Phenol
 - ii) Benzenedi diazunium chloride $\xrightarrow{\gamma}$ iodo benzene
 - iii) Benzenedi azonium chloride \xrightarrow{Z} Cyno Benzene

- 27. The best reagent for converting 2 phenyl propagandize in to 1 phenyl Ethen amide is
 - 1) Excess H_2/Pt

2) *NaOH / Br*₂

3) NaBH₄ / methanol

- 4) LiAlH₄ / ether
- 28. Which of the following is an aromatic amine
 - 1) Aniline

2) N – methyl aniline

3) 2 – Phenyl Ethan amine

- 4) None of the above
- 29. Which of the following reaction will not give a primary amine
 - 1) $CH_3CONH_2 \xrightarrow{Br_2/KOH}$

2) $CH_3CN \xrightarrow{LiAlHy}$

3) $CH_3NC \xrightarrow{LiAlHy}$

- 4) $CH_3CONH_2 \xrightarrow{LiAlHy}$
- 30. Aliphatic amines are basic than NH_3 but aromatic amines are basic than NH_3
 - 1) More, Less
- 2) Less, More
- 3) Both (1) and (2)
- 4) None of these

KEY

1-10	3	1	2	2	3	1	3	3	3	2
11-20	4	2	2	3	1	3	4	4	1	4
21-30	3	2	4	3	1	3	2	1	3	1

SOLUTIONS

1
$$CH_3Br \xrightarrow{KCN} CH_3CN$$
 $CH_3CN \xrightarrow{LiAlHY} CH_3CH_2NH_2$
 $CH_3CN \xrightarrow{Reduction} CH_3CH_2NH_2$
 $CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH$
2. $CH_3COOH \xrightarrow{NH_3} CH_3 - CO - NH_2$
 $CH_3CO - NH_2 \xrightarrow{H-NH_2} CH_2OH$
 $CH_3CO - NH_2 \xrightarrow{Br_2+KOH} CH_3 - NH_2$
 $CH_3 - NH_2 \xrightarrow{CHCl_3+NaOH} CH_3NC$
 $CH_3 - NH_2 \xrightarrow{CHCl_3+NaOH} CH_3NC$
 $CH_3 - NH_2 \xrightarrow{CHCl_3+NaOH} CH_3NC$
 $COrmsiso cynaides$

3.
$$CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2 - OH$$

 $C_6H_5SO_2Cl + C_2H_5NH_2 \xrightarrow{-HCl} C_6H_5So_2 - NH - C_2H_5$ 4. Hins burg reagent Hear coupling reaction is involved

 $CH_3CONH_2 \xrightarrow{Br_2+NaOH} CH_3NH_2$ 5.

Hear Hoffmann's Bromide rexⁿ involved gives primary amines

- 6. Due to intermolecular hydrogen bonding present in primary & Secondary amines at have more boiling point in tertiary amines absence of inter molecular hydrogen bonding less boiling point
- $C_6H_5NH_2 \xrightarrow{ConH_2SO_4} \text{O-amino benzene sulphonic acid}$ $C_6H_5NH_2 \xrightarrow{ConH_2SO_4} C_6H_5NH_3^+HSO_4^- \xrightarrow{-H_2O} C_6H_5NHSO_3H \text{ O-amino benzene sulphonic acid}$ 7.
- 8. O – Nitro acetamide under hydrolyses

O – Nitro acetamide $\xrightarrow{H_3O^+}$ O – Nitro aniline and acetic acid

 $C_6H_5NH_2 + CHCl_3 \xrightarrow{alcKOH} C_6H_5NC$ 9. Hear carbylamines reaction is involved

 $C_6H_5N_2^+ + H_3Po_2 \xrightarrow{H_2O} C_6H_6 + H_3Po_3 + N_2 + HCl$ 10.

 $C_6H_5NO_2 \xrightarrow{Fc/HCl} C_6H_5NH_2$ 11.

Hear Reduction takes place addition of 'H' atoms and removal of hydrogen's

12. More no of alkyl groups present +I effect will increases + I effect α basicity (Kb)

Then +I effect $\alpha = \frac{1}{P^{K_b}}$

More no of alkyl groups increases then P^{K_b} values decreases

- Benzene under nitration gives nitro benzene $C_6H_6 \xrightarrow{HNo_3 \atop H_3SO_4} C_6H_5NO_2$ 13. Nitrobenzene under reduction snl/Hcl give aniline $C_6H_5NO_2 \xrightarrow{snHCl} C_6H_5NH_2$
- $C_6H_5Br \xrightarrow{Mg} C_6H_5MgBr \rightarrow Grignard reagent$ 14. $C_6H_5MgBr \xrightarrow{CO_2} C_6H_5COOH \rightarrow \text{hydrolysis}$
- $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl + SO_2 + HCl$ 15.
- $C_6H_5No_2 \xrightarrow{reduction} C_6H_5NH_2 \xrightarrow{CH_3Cl+KOH} C_6H_5NC$ 16. $C_6H_5NC \xrightarrow{reduction} N \text{ methy/amiline}$
- $C_6H_5NH_2 \xrightarrow{NaNo_2} C_6H_5N_2^+ \xrightarrow{CuCN} C_6H_5CN$ 17. Sandmayer reaction mvolves an above re x^n

 $C_6H_5CN \xrightarrow{H_2/Ni} C_6H_5CH_2OH$

- Replacement by iodide ion iodine is not easily introduced into the benzene ring directly but when the 18. diazonium salt solution is treated with potassium iodide iodobentene is formed $C_6H_5N_2^+ + KI \rightarrow C_6H_5I + KCl + N_2$
- Secondary amines are more basic than tertiary amines due to stabilization of 2⁰ amine by hydrogen 19. bending with solvent molecule
- $C_6H_5NO_2 \xrightarrow{Under\ reduction} C_6H_5NH_2$ 20.

Nitro benzene under reduction gives aniline hear H_2/Pd ethanol, Sn+HCl, Fe+HCl all are reducing agents

 $C_2H_5 - N_1 - CH_2 - CH_2 - CH_2 - CH_3$ 21.

N, N di ethyl but am 1 – amine

 $NH_3 \xrightarrow{CH_3} CH_3 - NH_2$ Primary amine 22.

$$CH_2 - CH_2 \xrightarrow{Br_2 \ CCl_4} CH_2 - CH_2$$

23.

$$\begin{array}{ccc} CH_2 - CH_2 & \xrightarrow{2NaCN} & CH_2 - CH_2 & \text{(Nuclei ophilze sub station re } x^n \text{)} \\ CH_2 - CH_2 & \xrightarrow{Liality} & NH_2CH_2CH_2CH_2NH_2 & \text{(Nuclei ophilze sub station re } x^n \text{)} \end{array}$$

24. Hoffmann bromide reaction is best method

25.

In Gabriel phthalamide synthesis only aliphatic amines are prepared does not prepare aromatic amines aniline is aromatic amine

26. i)
$$C_6H_5N_2^+Cl^- \xrightarrow{H_2O} C_6H_5 - OH$$

ii) $C_6H_5N_2^+Cl^- \xrightarrow{KI} C_6H_5 - I$ (Sand Mayer)

ii)
$$C_6H_5N_2^+Cl^- \xrightarrow{warm} C_6H_5$$
 OII

ii) $C_6H_5N_2^+Cl^- \xrightarrow{KI} C_6H_5 - I$ (Sand Mayer rex^n)

27. $CH_3 - CH - CONH_3 \xrightarrow{Br_2 \ NaOH} CH_3 - CH - NH_2 + Na_2CO_3 + NaBr + H_2O_3$

28. A rematic spring many the NH group attaches to growths ring.

- Aromatic amine means the NH_2 group attaches to aromatic ring 28.
- 29. $CH_3NC \xrightarrow{Laalhy} CH_3NHCH_3$ Remaining all gives primary amines
- Aliphatic amines are stronger base than ammonia due to +I effect of alkyl groups leading to high 30. electron density on the nitrogen atom their Pk_6 values lie in the range of 3 to 4.22 on the other hand aromatic amines are weaker base than ammonia due to the electron withdrawing nature of the aryl group