CHAPTER -22

NITROGEN COMPOUNDS

SYNOPSIS

1. Cyanides & isocyanides

They are salts of hydrocyanic acid which exist in two tautomeric forms

$H-C\equiv N$ (I) $\qquad$ $H-N\overset{\rightarrow}{\equiv}C$ (II)

Preparation

$RX + KCN \rightarrow RCN + KX$ (cyanides)

$RX + AgCN \rightarrow RNC + AgX$ (isocyanides)

$RCONH_2 \xrightarrow{P_2O_5} RCN + H_2O$ (cyanide)

$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$

Properties

1. Reduction $\qquad RCN + 2H_2 \xrightarrow{Ni/Pt} RCH_2NH_2$

$RNC + 2H_2 \rightarrow RNH\,CH_3$

2. Hydrolysis $\qquad RCN \xrightarrow{H_2O/H^+} RCOOH + NH_4^+$

$RNC \xrightarrow{H_2O/H^+} RNH_2 + HCOOH$

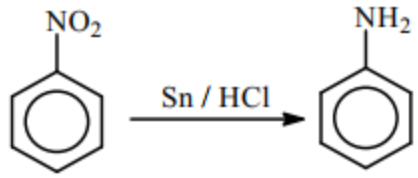
1. Nitrocompounds

Organic compounds containing nitro groups ($-NO_2$) as functional group are called nitrocompounds.

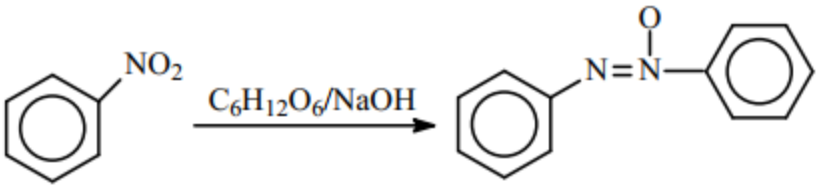
They are prepared by nitrating the compound using nitrating mixture

Properties of nitrobenzene : Reduction

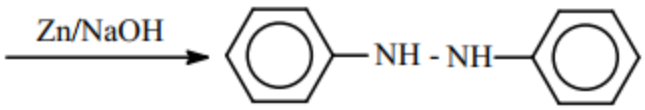
a) in acidic medium



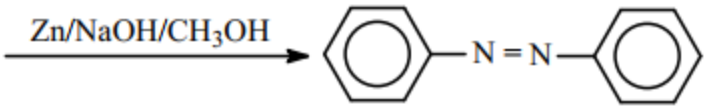
2. Reduction in alkaline medium



azoxybenzene

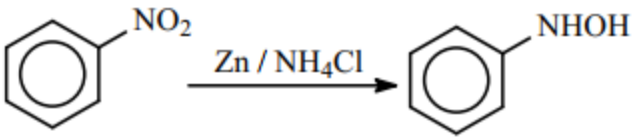


hydrazobenzene



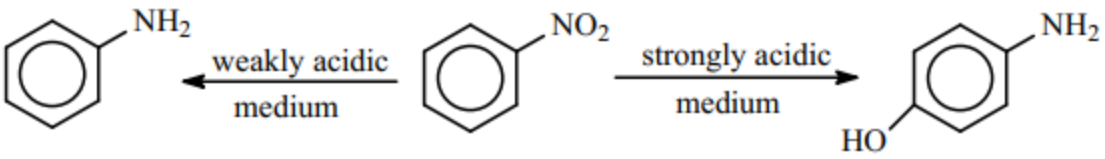
azobenzene

3. **Neutral medium**



phenyl hydroxyl amine

Electrolytic reduction



aniline

p-aminophenol

Amines

Amines are derivatives of ammonia in which the H-atom are replaced by alkyl or aryl group. They are classified as 1° amine (RNH_2), 2° amine (R_2NH) and 3° amine (R_3N).

Preparation

1. Reduction of nitrocompounds, $RNO_2 \xrightarrow{H} RNH_2$

2. Reduction of cyanide or isocyanide, $RCN \xrightarrow{H} RCH_2NH_2$ (1° amine)

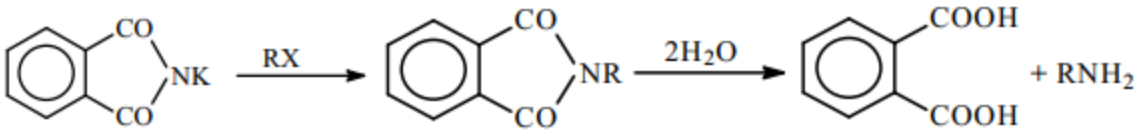
   $RNC \rightarrow RNHCH_3$ (2° amine)

3. Reduction of oximes, $RCH = N.OH \xrightarrow{H} RCH_2NH_2 + H_2O$

4. Hofmann's bromamide reaction

   $RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$

5. Gabriel phthalimide reaction



Properties : (a) Basic character

All the amines are basic in nature since they contain a lone pair of electrons on the nitrogen atom. Aliphatic amines are more basic than ammonia. In aqueous solution, the basicity order is 2° > 1° > 3°. In non-aqueous solution, the order of basicity is 3° > 2° > 1°.

All aromatic amines are weaker bases than ammonia.

Chemical properties

1. Alkylation; $RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$

2. Acylation; $RNH_2 + R'COCl \rightarrow RNHCOR'$

3. Carbyl amine reaction; $RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$

   This is answered only by primary amines

4. With nitrous acid

   Aliphatic 1° amines with HNO_2 gives alcohol with the evolution of N_2 gas

   Aromatic 1° amine with HNO_2 at 0°C gives diazonium salts

   Aliphatic and aromatic 2° amines react with HNO_2 to give N-nitrosoamines

   Aliphatic 3° amines with HNO_2 gives soluble nitrites.

   Atomatic 3° amines with HNO_2 gives p-nitroso amines

5. With benzenesulphonyl chloride - (Hinsberg's reagent)

   1° amine with Hinsberg's reagent give N-alkyl benzene sulphonamide which is soluble in alkali

   2° amine gives N,N-dialkylbenzene sulphonamide which is insoluble in alkali

   3° amine has no reaction

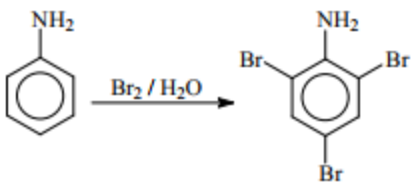
6. Both aliphatic and aromatic 1° amine with CS_2 in presence of $HgCl_2$ gives isothiocyanate(Mustard oil reaction)

   $RNH_2 + S = C = S \xrightarrow{HgCl_2} RNCS + HgS + 2HCl$

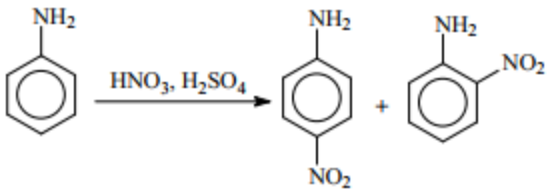
Electrophilic Substitution Reactions in aniline

–NH_2 group is O, P directing and activate the benzene ring

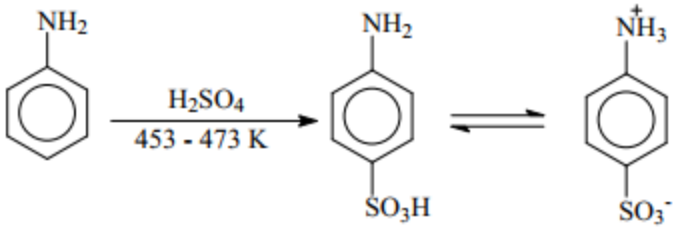
1. Bromination



2. Nitration



3. Sulphonation



sulphanilic acid zwitter ion

4. Do not answer Friedel - Crafts reaction

Diazonium Salts

Preparation

$$RNH_2 + NaNO_2 + 2HCl \xrightarrow{0^\circ C} RN_2Cl + NaCl + 2H_2O$$

This process is called diazotisation.

Only aromatic diazonium salts are stable.

General formula : R – N = N – X where R - aryl group and X^-, Cl^-, Br^-, HSO_4^- etc.

Properties

(1) Substitution reactions : In these reactions N_2 is eliminated

$$C_6H_5 - N = N - Cl \xrightarrow{H_2O} C_6H_5OH + N_2 + HCl$$

$$\xrightarrow[HCl]{CuCl} C_6H_5Cl + N_2$$

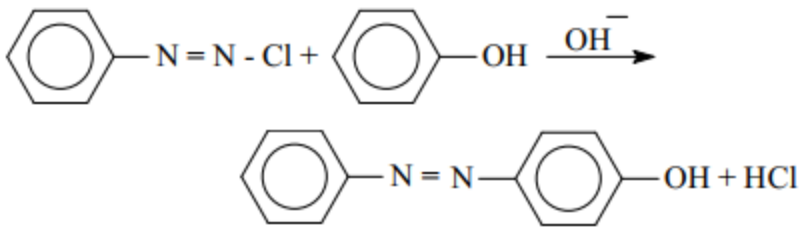
$$\xrightarrow[HBr]{CuBr} C_6H_5Br + N_2$$

$$\xrightarrow[\Delta]{KI} C_6H_5I + N_2$$

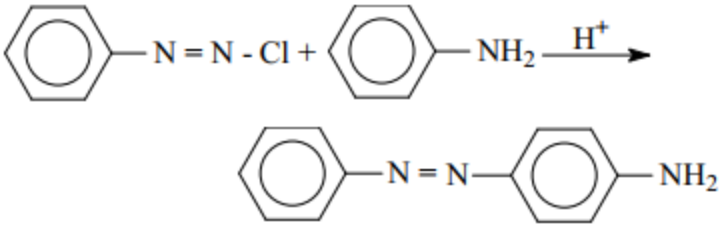
$$\xrightarrow[\Delta]{HBF_4} C_6H_5F + N_2 + BF_3$$

$$\xrightarrow{C_6H_5/NaOH} C_6H_5 - C_6H_5 + N_2$$

2) Coupling reactions : In these reactions N_2 gas is not eliminated



P-hydroxyazobenzene



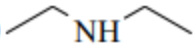
P-amino azobenzene

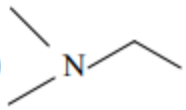
PART-I (JEE MAIN)

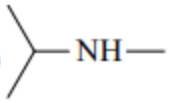
SECTION-I- Straight objective type questions

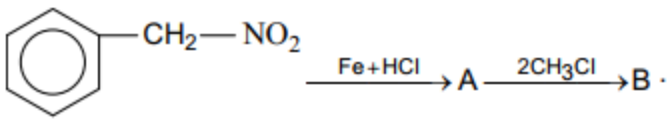
1. Among the following isomeric amines, the one having lowest boiling point is

1) 

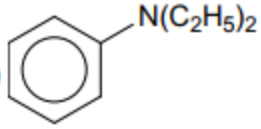
2) 

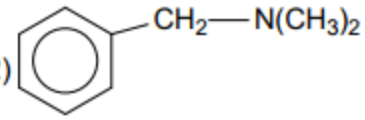
3) 

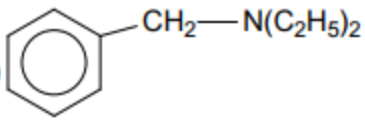
4) 

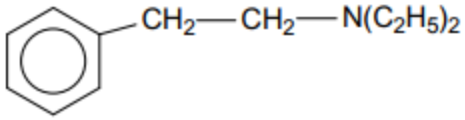
2. 

The final product B in the above reaction scheme is

1) 

2) 

3) 

4) 

3. **Assertion (A)** : In order to convert R – Cl to pure R – NH_2, Gabriel phthalimide synthesis can be used

Reason (R) : With proper choice of alkyl halides, phthalimide synthesis can be used to prepare 1^0, 2^0 or 3^0 amines

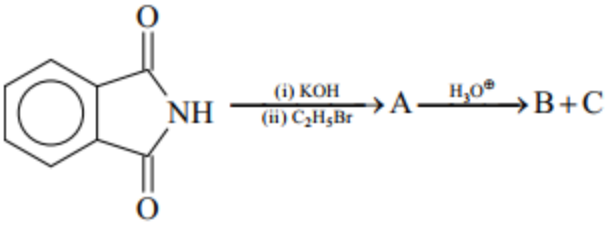
Choose the correct option

1) Both A and R are true and R is the correct explanation of A

2) Both A and R are true, but R is not the correct explanation of A

3) A is true and R is false

4) Both A and R are false

4. 

B and C in the above reaction sequence are respectively

1) Benzoic acid and aniline

2) Phthalic acid and ethylamine

3) Phthalic acid and aniline

4) Benzoic acid and ethylamine

5. The end-product in the following reaction sequence would be :

$$\text{Ethylamine} \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{NH_3}$$

1) Ethyl isocyanide 2) Ethylamine 3) Methylamine 4) Acetamide

6. The correct set of products obtained in the following reactions are

$$RCN \xrightarrow{LiAlH_4} (A);\ RCN \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} (B);\ RNC \xrightarrow{LiAlH_4} (C);\ RNH_2 \xrightarrow{HNO_2} (D)$$

	A	B	C	D
1)	2º amine	Ethyl ketone	1º Amine	Alcohol
2)	1º amine	Methyl ketone	2º Amine	Alcohol
3)	2º amine	Methyl ketone	1º Amine	Amine
4)	1º amine	Ethyl ketone	2º Amine	Alcohol

7. Method by which aniline cannot be prepared is :

1) Reduction of nitrobenzene with H_2/Pd in ethanol

2) Potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

3) Hydrolysis of phenylisocyanide with acidic solution

4) Treatment of benzamide with bromine in alkaline solution

8. Which of the following amines gives a characteristic offensive odour when heated with chloroform and caustic soda?

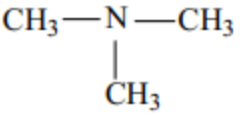
1) $C_6H_5NH_2$ 2) $(C_6H_5)_2NH$ 3) $(CH_3)_2NH$ 4) $(CH_3)_3N$

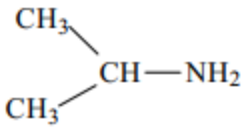
9. An amine on reaction with Hinsberg reagent gives a white precipitate, which is insoluble in alkaline solution. This amine can be prepared by ammonolysis of ethyl chloride. The correct structure of amine is

1) $(CH_3CH_2)_2NH$ 2) $CH_3CH_2NH_2$

3) $(CH_3CH_2)_3N$ 4) $CH_3CH_2CH_2NH_2$

10. An organic compound C_3H_9N (A), when treated with nitrous acid, gave an alcohol and N_2 gas. (A) on warming with $CHCl_3$ and caustic potash gave (C) which is also obtained from the reaction of isopropyl chloride with AgCN. Predict the structure of (A) :

1)  2) $CH_3CH_2CH_2-NH_2$

3)  4) $CH_3CH_2-NH-CH_3$

11. **Assertion (A)** : Mononitration of aniline can be conveniently done by protecting the amino group by acetylation

Reason (R) : Acetylation increases the electron density in the benzene ring

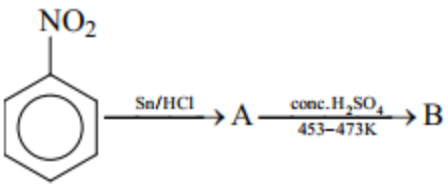
Choose the correct option

1) Both A and R are true and R is the correct explanation of A

2) Both A and R are true, but R is not the correct explanation of A

3) A is true and R is false

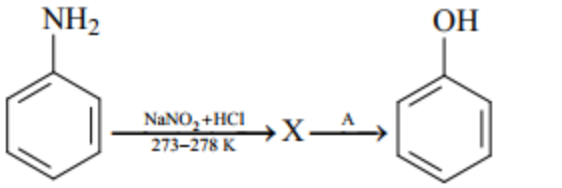
4) Both A and R are false

12. 

Identify product B

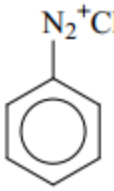
1) Anilinium hydrogen sulphate 2) Benzenesulphonamide

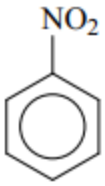
3) Sulphanilic acid 4) Benzanilide

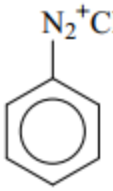
13. 

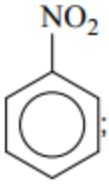
Major product

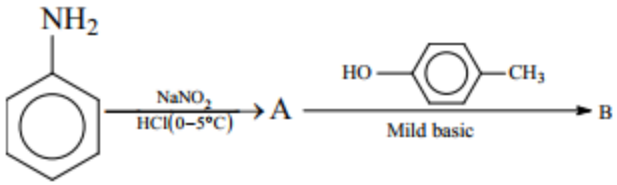
In the above chemical reaction, intermediate 'X' and reagent "A' are

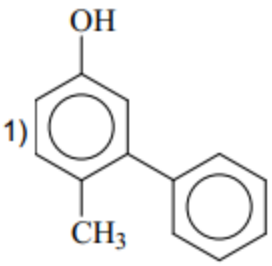
1) X =  ; A = H_3PO_2

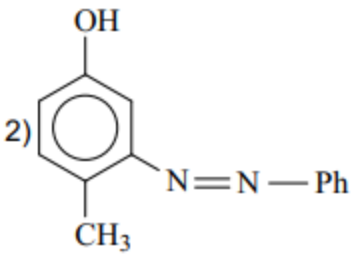
2) X =  ; A = H_2O / warm

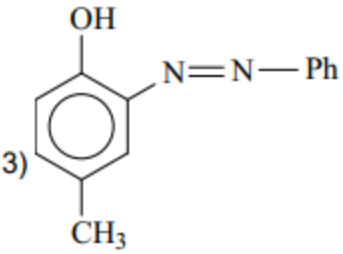
3) X =  ; A=H_2O/warm

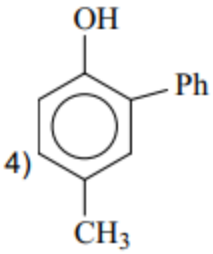
4) X =  ; A = H_3PO_2

14. Product B in the below reaction is 

1) 

2) 

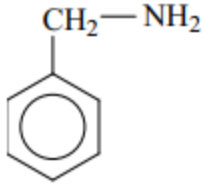
3) 

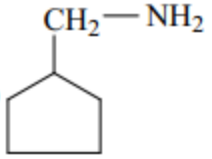
4) 

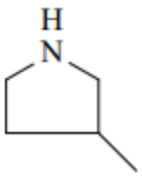
SECTION-II - Numerical Type Questions

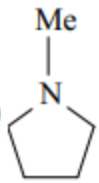
15. How many of the following could be prepared by Gabriel phthalimide synthesis?

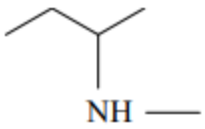
a) 

b) 

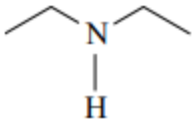
c) 

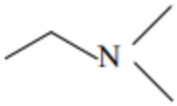
d) 

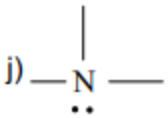
e) 

f) 

g) 

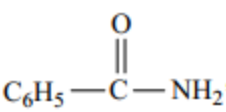
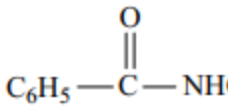
h) 

i) 

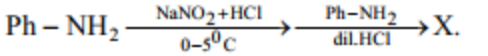
j) 

16. How many moles of NaOH will be consumed in the conversion of one mole of ethanamide into methylamine during Hoffmann bromamide reaction?

17. Amongst the following, the total number of amides which can undergo Hoffmann bromamide reaction is .....

 ,  , $C_6H_5CON(CH_3)_2$, CH_3CONH_2, $CH_3CONHCH_3$, $CH_3CON(CH_3)_2$, $(CH_3)_2CHCONH_2$, $(CH_3)_2CHCONHCH_3$

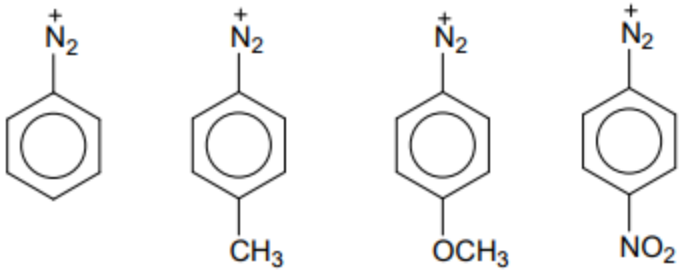
18. In the reaction shown below, the total number of carbon and nitrogen atoms present in the final product X is ———



PART-II (JEE ADVANCED)

Section-III - Only one option correct type

19. The reactivity order of the following diazonium cations in coupling reaction is



I II III IV

A) I > II > III > IV B) IV > III > II > I C) III > II > I > IV D) IV > I > II > III

20. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is

A) Methylamine B) Ethylamine C) Diethylamine D) Triethylamine

21. Which of the following statements is not correct?

A) Replacement of halogen by NH_2 in alkyl halide is a nucleophilic substituion reaction

B) Aryl halides show more reactivity as compared to alkyl halides in the replacement of halogen by the NH_2 group

C) During the replacement of halogen by - NH_2 group, ammonia is taken in large excess so as to avoid formation of 2^0 and 3^0 amines

D) Tertiary alkyl halide generally produces alkene instead of the replacement of halogen by NH_2 group

22. Ethyl isocyanide on hydrolysis in acidic medium generates

A) propanoic acid and ammounium salt B) ethanoic acid and ammonium salt

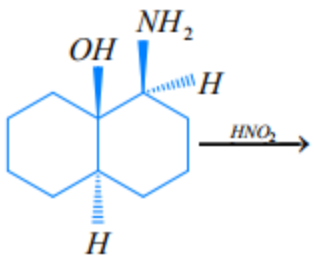
C) methylamine salt and ethanoic acid D) ethylamine salt and methanoic acid

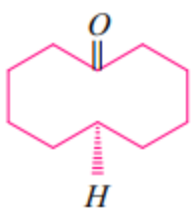
23. In the chemical reaction $CH_3CH_2NH_2 + CHCl_3 + KOH \rightarrow (A) + (B) + H_2O$, the compounds (A) and (B) are

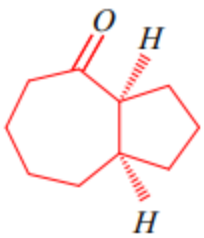
A) C_2H_5CN and KCl B) $CH_3CH_2CONH_2$ and K_2CO_3

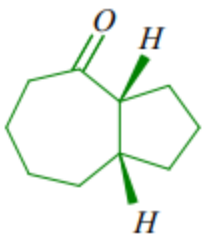
C) CH_3CH_2NC and K_2CO_3 D) CH_3CH_2NC and KCl

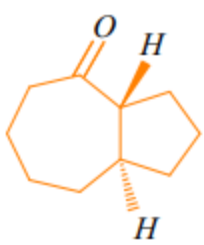
24. Predict the product for the following reaction



A) 

B) 

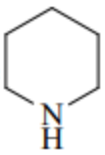
C) 

D) 

Section IV - One or more option correct type

25. Identify the correct option(s) for the following reaction series

$$C_2H_5I \xrightarrow{\text{alc.KOH}} (X) \xrightarrow[CCl_4]{Br_2} (Y) \xrightarrow[\text{Excess}]{KCN} (Z) \xrightarrow{LiAlH_4} A$$

A) A= 

B) Z = $CH_2(COOH)-CH_2(COOH)$

C) Z = $CH_2(CN)-CH_2(CN)$

D) A = $CH_2(CH_2NH_2)-CH_2(CH_2NH_2)$

26. Correct option(s) for the following sequence of reaction is/are

$$PhCH_3 \xrightarrow[2.\ H_3O^+]{1.KMnO_4-KOH,\ Heat} T \xrightarrow[2.\ Heat]{1.\ NH_3} U \xrightarrow{W} R \xrightarrow[KOH]{CHCl_3} \text{Foul smelling compound}$$

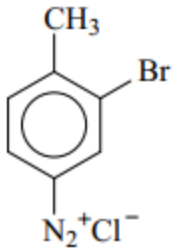
A) $W = LiAlH_4;\ R = Ph-\overset{\overset{O}{\|}}{C}-NH_2$

B) $U = Ph-\overset{\overset{O}{\|}}{C}-NH_2;\ W = LiAlH_4$

C) W = Br_2/NaOH; R = Ph–NH_2

D) $T = Ph-COOH;\ U = Ph-CH_2-NH_2$

27. Consider the reaction sequence shown below

$$P \xrightarrow[Fe]{Br_2} Q \xrightarrow{Sn+HCl} R \xrightarrow[0°-5°C]{NaNO_2+HCl} \text{  } \xrightarrow[H_2O]{H_3PO_2} S.$$

Choose the correct option(s)

A) P is o-Nitrotoluene

B) S is o-Bromotoluene

C) R is p-toluidine

D) Q is m-Bromonitrobenzene

28. Activating effect of NH_2 group in aniline can be reduced by treating with

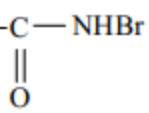
A) Pyridine

B) Acetone

C) Acetic anhydride

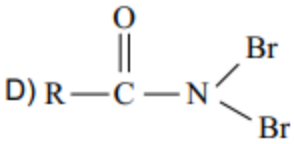
D) Acetyl chloride

29. Reaction of R–CO–NH_2 with a mixture of Br_2 and KOH gives R–NH_2 as the main product. The intermediate(s) involved in the reaction is/are

A) 

B) R–NHBr

C)

D) 

30. The conversion, $CH_3CN \rightarrow CH_3CH_2NH_2$ can be effected by using

A) H_3O^+ (at low temperature)

B) $LiAlH_4$

C) Na(Hg), C_2H_5OH

D) H_2, Pd

31. Benzylamine can be prepared by

A) $C_6H_5CONH_2 \xrightarrow{LiAlH_4/ether}$

B) $C_6H_5CN \xrightarrow{LiAlH_4/ether}$

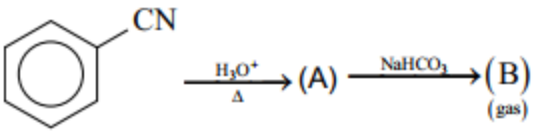
C) Phthalimide $\xrightarrow[(iii)\,Aq.NaOH,\Delta]{(i)\,KOH \;(ii)\,C_6H_5CH_2Br}$

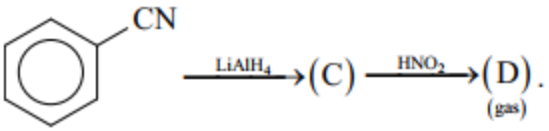
D) $C_6H_5CH_2CONH_2 \xrightarrow{NaOBr}$

Section V - Numerical type questions

32. The deamination of n-butylamine with sodium nitrite and hydrochloric acid gives 'x' isomeric butenes. The value of x is .....

33. Consider the following reactions





Total number of atoms present in the molecule of B and D is .....

34. How many of the following can undergo diazotisation reaction more faster than aniline.

p-Toluidine, p-Methoxyaniline, p-Nitroaniline, p-Cyanoaniline, p-Hydroxyaniline, m-Nitroaniline, Sulphanilic acid

Section-VI - Matrix match type

35. Match the following:

Column-I (Compound)	Column-II (Preparation/Chemical property)
I) Anilline	P) Can be made by Gabriel phthalimide reaction
II) N-Methylaniline	Q) Undergoes electrophilic substitution reaction with HNO_2
III) N,N-Dimethylaniline	R) Forms yellow oily product with HNO_2
IV) Benzylamine	S) Gives azo dye test

A) $I \rightarrow S;\ II \rightarrow R;\ III \rightarrow Q;\ IV \rightarrow P$

B) $I \rightarrow PS;\ II \rightarrow RS;\ III \rightarrow Q;\ IV \rightarrow PS$

C) $I \rightarrow S;\ II \rightarrow R;\ III \rightarrow Q;\ IV \rightarrow PS$

D) $I \rightarrow PS;\ II \rightarrow R;\ III \rightarrow Q;\ IV \rightarrow P$