Chapter 27

Amines

(A) AMINES

They are derivatives of ammonia and are obtained by replacement of one, two or all three H-atoms of NH_3 by alkyl or aryl groups.

For Ex: $CH_3NH_2, CH_3-NH-CH_3$, etc.

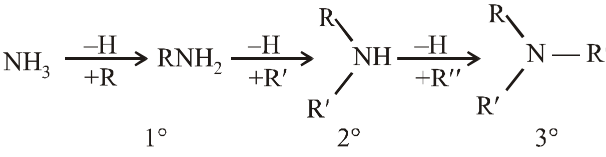
STRUCTURE OF AMINES

N in amines is sp^3 - hybridised and the geometry of amines is pyramidal.

The fourth orbital of N contains an unshared pair of e^-s, due to which the bond angle decreases from the tetraheral angle of 109.28′ to 107° in 1° and 2° amines. However in 3° amines bond angle increased upto 108° due to steric hindrance.

CLASSIFICATION OF AMINES

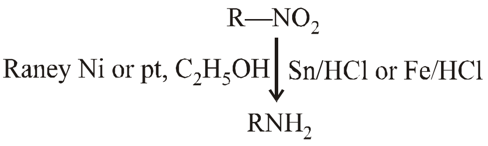
Amines are classified as 1°, 2° and 3° depending upon the number of H-atoms replaced by alkyl or aryl groups in NH_3.



Amines are said to be simple if all the alkyl or aryl groups are same and mixed if they are different.

PREPARATION OF AMINES

(i) Reduction of Nitro Compounds



$$\begin{array}{c} R—NO_2 \\ \text{Raney Ni or pt, } C_2H_5OH \Big\downarrow \text{Sn/HCl or Fe/HCl} \\ RNH_2 \end{array}$$

Note:

The yield can be increased to about 90% by using more powerful reductant like $LiAlH_4$ or $NaBH_4$.

(ii) By the Reduction of Nitriles: (Mendius reduction)

$$R/Ar-CN \xrightarrow[\text{or Na},C_2H_5OH]{\text{Raney Ni}/H_2 \text{ or } LiAlH_4} R/Ar-CH_2NH_2$$

$$R-N\equiv C \xrightarrow{\text{Raney Ni}/H_2} R-NH-CH_3$$

(iii) Ammonolysis of Alkyl Halides (Hofmann's Method) :

$$R–X + \underset{\text{(Excess)}}{H-NH_2} \xrightarrow[\text{Pressure}]{\Delta,\ 100°C} R–NH_2HX \xrightarrow[\text{Alkali}]{\Delta} R–NH_2$$

On taking the alkyl halides in excess, the primary amines gets further alkylated to form 2° & 3° amines and finally quaternary ammonium salt.

$$R–NH_2 \xrightarrow[\Delta]{RX} R_2NH \xrightarrow[\Delta]{RX} R_3N \xrightarrow{RX} R_4\overset{\oplus}{N}\overset{\ominus}{X}$$

Note:

(a) This reaction is an example of a nucleophilic substitution reaction in which ammonia molecule (NH_3) acts as a nucleophile.

(b) The order of reactivity of haloalkanes in ammonolysis reaction is $RI > RBr > RCl$.

(c) This method cannot be used for preparing aryl amines because simple aryl halides do not undergo nucleophilic substitution easily.

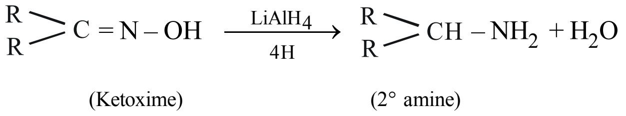
(iv) Reduction of amides

$$RCONH_2 \xrightarrow[\text{(ii)}H_2O]{\text{(i)}LiAlH_4/\text{ether}} RCH_2NH_2$$

(v) Hoffmann Bromamide Degradation

$$RCONH_2 + Br_2 + 4NaOH \rightarrow$$
$$R—NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(vi) By Oximes:

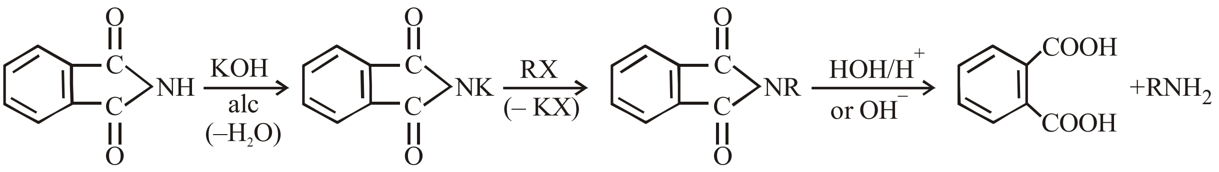


(vii) By Reductive Amination of carbonyl compounds :

$$R-CH=O+H_2NH \xrightarrow[-H_2O]{} \underset{\text{An aldimine}}{R-CH=NH} \xrightarrow[Ni]{H_2} R-CH_2-NH_2$$

$$R_2C=O+H_2NH \xrightarrow[-H_2O]{} \underset{\text{A ketimeine}}{R_2C=NH} \xrightarrow[Ni]{H_2} R_2CH_2-NH_2$$

(viii) Gabriel Phthalimide Synthesis



Phthalimide Pot. phthalimide N-alkyl phthalimide Phthalic acid 1° amine

(ix) Ammonolysis of Alkyl Halides (Hofmann's Method) :

$$R\text{–}X + \underset{(Excess)}{H-NH_2} \xrightarrow[\text{Pressure}]{\Delta,\,100°C} R\text{–}NH_2HX \xrightarrow[\text{Alkali}]{\Delta} R\text{–}NH_2$$

On taking the alkyl halides in excess, the primary amines gets further alkylated to form 2º & 3º amines and finally quaternary ammonium salt.

$$R\text{–}NH_2 \xrightarrow[\Delta]{RX} R_2NH \xrightarrow[\Delta]{RX} R_3N \xrightarrow{RX} R_4\overset{\oplus}{N}\overset{\ominus}{X}$$

This reaction is an example of a nucleophilic substitution reaction in which ammonia molecule (NH_3) acts as a nucleophile.The order of reactivity of haloalkanes in ammonolysis reaction is $RI > RBr > RCl$. This method cannot be used for preparing aryl amines because simple aryl halides do not undergo nucleophilic substitution easily.

Note:

(a) In reduction of nitro compounds, $Fe + HCl$ is preferred because $FeCl_2$ formed gets hydrolysed to release HCl during the reaction. Thus, only a small amount of HCl is required to initiate the reaction.

(b) Ammonolysis yields a mixture of 1°, 2°, 3° amines and quaternary ammonium salt. 1° amine is obtained as a major product by taking large excess of ammonia.

(c) Reduction of nitriles to amines results in ascent of amine series i.e. for preparation of amine with one carbon atom more than the starting amine.

(d) The amines formed by Hofmann bromamide degradation method contain one carbon atom less than the parent amide.

PHYSICAL PROPERTIES OF AMINES

(i) Pure amines are almost colourless but develop colour on keeping in air due to atmospheric oxidation.

(ii) Lower aliphatic amines are gases with fishy odour. 1° amines with 3 or more C-atoms are liquid and higher ones are solid.

(iii) Lower aliphatic amines are soluble in H_2O due to H–bonding. Solubility decreases with increase is size of hydrophobic alkyl part Alcohols are more soluble than amines in H_2O.

(iv) **Boiling point :** b.p. of alcohols & carboxylic acids > b.p. of amines > b.p. of alkanes and, b.p. of 1° amine > 2° amine > 3° amine

Explaination :

(a) Primary and secondary amines form inter molecular H-bonds, while tertiary amines do not form inter-molecular H-bonds. As a result, 1° & 2° amines show high B.P. than 3° amines.

(b) H-bonding in amines is through nitrogen atoms while in alcohols and carboxylic acids, it is through oxygen atoms and nitrogen is less electronegative than oxygen. So H-bonding in amines is weaker than that in carboxylic acids and alcohols.

CHEMICAL PROPERTIES OF AMINES

Amines are reactive due to (i) difference in electronegativity between N and H, (ii) presence of lone pair of e^{-1} s of N.

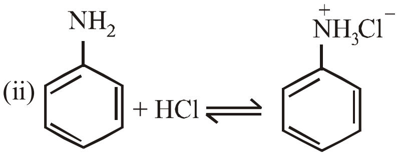
Chemical reactions are as follows:

Amines R/NH$_2$

Basic Character

(i) $RNH_2 + HX \rightleftharpoons R\overset{+}{N}H_3X^-$

(ii)



(iii) $R_3N + HNO_3 \longrightarrow R_3NH^+NO_3^-$

These amine salts are ionic compounds.

(iv) **Reaction with water :** Give alkaline solution in water.

$$R-NH_2 + H_2O \rightarrow RN\overset{\oplus}{H_3}\,\overset{\ominus}{O}H \rightleftharpoons RNH_3^{\oplus} + OH^{\ominus}$$

Aqueous solution of alkylamine precipitate hydroxides of heavy metals

$$3RNH_3^{\oplus}OH^{\ominus} + FeCl_3 \rightarrow Fe(OH)_3 + 3R\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

$$3RNH_3^{\oplus}OH^{\ominus} + AlCl_3 \rightarrow Al(OH)_3 + 3R\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

Reactions With Electrophiles

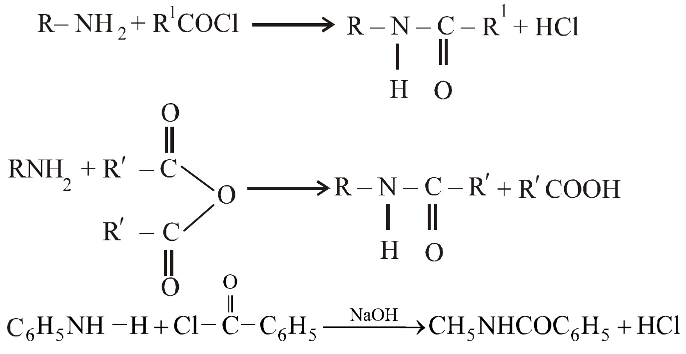
(i) **Alkylation:**

$$RNH_2 + RX \longrightarrow R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4\overset{+}{N}X^-$$

$$[R_4\overset{+}{N}]\overset{-}{X} + AgOH \longrightarrow [R_4\overset{+}{N}]\overset{-}{O}H + AgX$$

$$ArNH_2 + RX \longrightarrow ArNH(R) \xrightarrow{RX} ArNR_2$$

(ii) **Acylation:**



$$R-NH_2 + R^1COCl \longrightarrow R-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-R^1 + HCl$$

$$RNH_2 + (R'-\overset{O}{\overset{\|}{C}})_2O \longrightarrow R-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-R' + R'COOH$$

$$C_6H_5NH-H + Cl-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{NaOH} CH_5NHCOC_6H_5 + HCl$$

Benzanilide

(iii) **With aldehydes:**

$$\underset{}{R-NH_2} + \underset{\text{(Acetaldehyde)}}{CH_3-CH=O} \xrightarrow{\Delta} \underset{\text{(Schiff's base)}}{R-N=CH-CH_3} + H_2O$$

(iv) **Schotten- Baumann reaction**: Benzoylation of compounds containing an active hydrogen atom such as alcohols, phenols, and amines with benzoyl chloride in presence of dil. aq NaOH.

(v) **Carbylamine Reaction :**

$$RNH_2 + CHCl_3 + 3KOH\ (alc.)$$

$$\downarrow \Delta$$

$$RNC + 3KCl + 3H_2O$$

Miscellaneous Reactions

(i) **With HNO_2:**

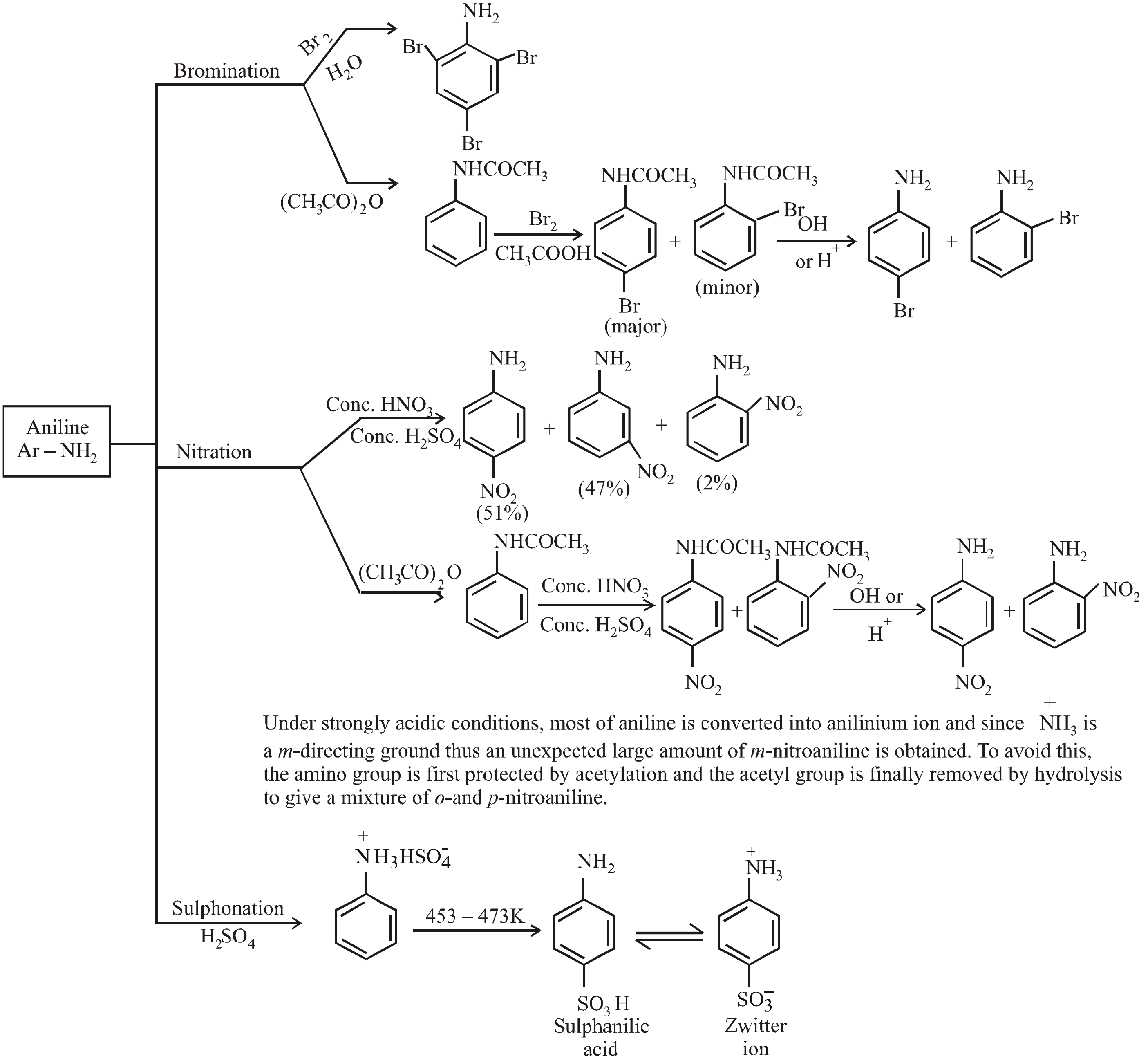
$$RNH_2 + HNO_2 \longrightarrow \underset{\text{unstable}}{\left[R-\overset{+}{N_2}\overset{-}{Cl}\right]} \xrightarrow{H_2O} ROH + N_2 + HCl$$

$$ArNH_2 \xrightarrow[273-278\text{ K}]{NaNO_2 + HCl} Ar\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$$

(ii) **Hinsberg's Reaction :** (See distinguish between 1°, 2° and 3° amines)

(iii) **With Grignard's reagant:**

$$R-NH-H + X-Mg-R' \longrightarrow \underset{\text{(Alkane)}}{R'-H} + R-NHMgX$$



Under strongly acidic conditions, most of aniline is converted into anilinium ion and since $-\overset{+}{N}H_3$ is a *m*-directing ground thus an unexpected large amount of *m*-nitroaniline is obtained. To avoid this, the amino group is first protected by acetylation and the acetyl group is finally removed by hydrolysis to give a mixture of *o*-and *p*-nitroaniline.

BASIC CHARACTER OF AMINES

(i) Amines have an unshared pair of e^{-1} s on nitrogen due to which they behave as Lewis base.

(ii) $$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3 + OH^-$$

$$K_{eq} = \frac{\left[R\overset{+}{N}H_3\right]\left[OH^-\right]}{[RNH_2][H_2O]} \Rightarrow K_{eq}[H_2O] = \frac{\left[R\overset{+}{N}H_3\right]\left[OH^-\right]}{[RNH_2]}$$

$$\Rightarrow K_b = \frac{\left[R\overset{+}{N}H_3\right]\left[OH^-\right]}{[RNH_2]} \quad (K_{eq}[H_2O] = K_b)$$

also, $pK_b = -\log K_b$.

Larger the value of K_b or smaller the value of pK_b, stronger is the base.

(iii) Aliphatic amines are stronger bases than NH_3 due to + I - effect of alkyl groups leading to high e^- – density on N – atom.

(iv) Aromatic amines are weaker bases than NH_3 due to e^- with - drawing nature of aryl group resulting is decreased e^- density on N.

(v) The order of basicity of amines in gaseous phase is:

3° amine > 2° amine > 1° amine

This is because with increase in the number of alkyl groups + I - effect increases and thus e^- – density on N - atom also increases.

(vi) In aqueous solution, besides I-effect, solvation and steric effects also play a role. Thus in aqueous medium, basic strength increases. Order for different alkyl groups is:

Alkyl group	**Relative strength**
$-CH_3$	$Me_2NH > MeNH_2 > Me_3N > NH_3$
$-C_2H_5$	$Et_2NH > EtNH_2 > NH_3 > Et_3N$
$-CH(CH_3)_2$	$Iso\,Pr.NH_2 > NH_3 > Iso\,Pr_2\,NH > Iso\,Pr_3\,N$
$-C(CH_3)_3$	$NH_3 > tert.Bu.NH_2 > tert.\ Bu_2NH > tert.\ Bu_3N$

(vii) An electron releasing group such as $-CH_3$, – OH, etc., present in the benzene ring at ortho and para positions increases the basic strength of aromatic amines. This is due to the stabilization of the ammonium cation formed after protonated of amine.

(viii) An electron withdrawing group such as $-NO_2$, –CN, $-SO_3H$, –X, etc. present in the benzene ring at ortho and para positions decreases the basic strength of aromatic amines. This due to the destabilization of the ammonium cation formed after protonation of amine.

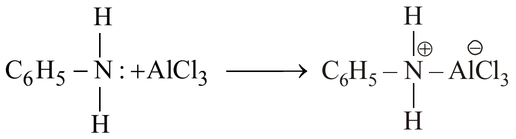
Note:

(a) Carbylamine reaction is used to distinguish between 1° (aliphatic and aromatic) and 2° / 3° amines.

(b) Reaction with HNO_2 is used to distinguish between 1° aliphatic and 1° aromatic amines.

(c) In aniline, $-NH_2$ is a strong activating group. Thus, it gives trisubstituted bromine derivative. To avoid this, the $-NH_2$ group is protected by acetylation and then carrying out the desired substitution. Electron attracting group (>C=O) present in acetanilide decreases availability of lone pair on nitrogen atom and hence decreases electron density on benzene ring of aniline.

(d) Aniline does not undergo Friedel - Crafts reaction due to salt formation with $AlCl_3$ (a Lewis acid) which is used as a catalyst.

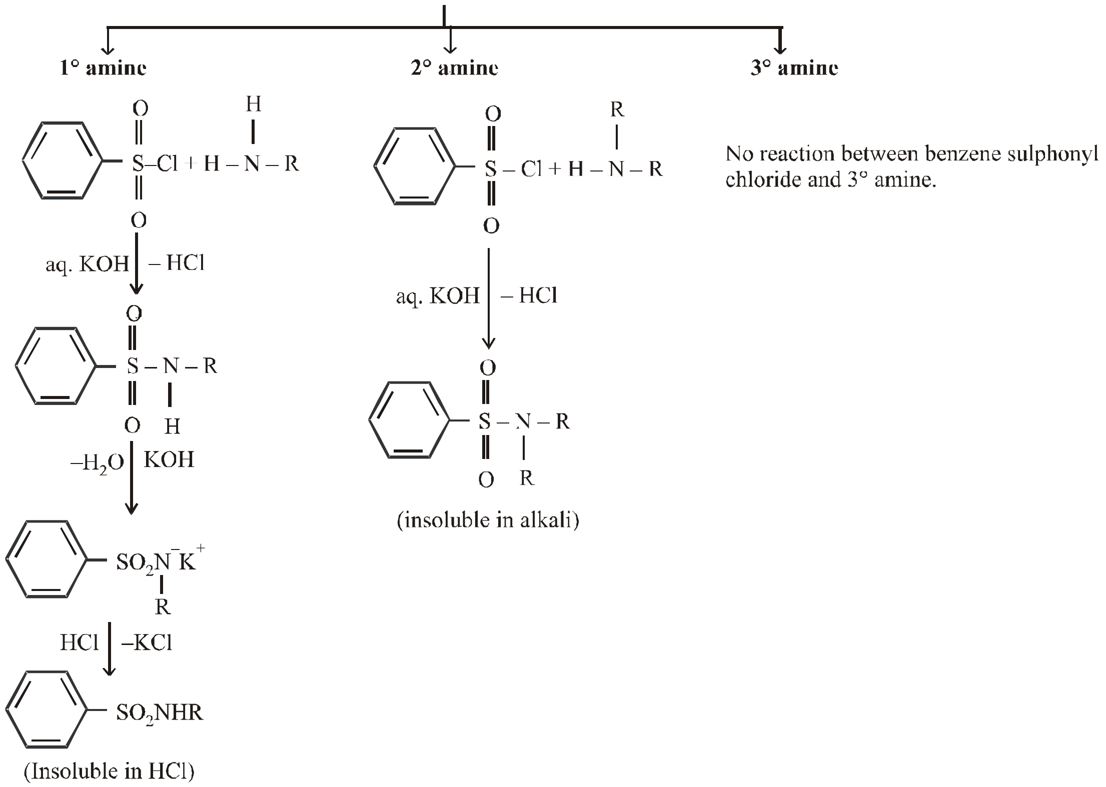


$$C_6H_5-\underset{H}{\overset{H}{N}}: + AlCl_3 \longrightarrow C_6H_5-\underset{H}{\overset{H}{\overset{\oplus}{N}}}-\overset{\ominus}{A}lCl_3$$

DISTINCTION BETWEEN 1°, 2° AND 3° AMINES

(i) Hinsberg's Test:

Hinsberg's reagent is benzene sulphonyl chloride ($C_6H_5SO_2Cl$).



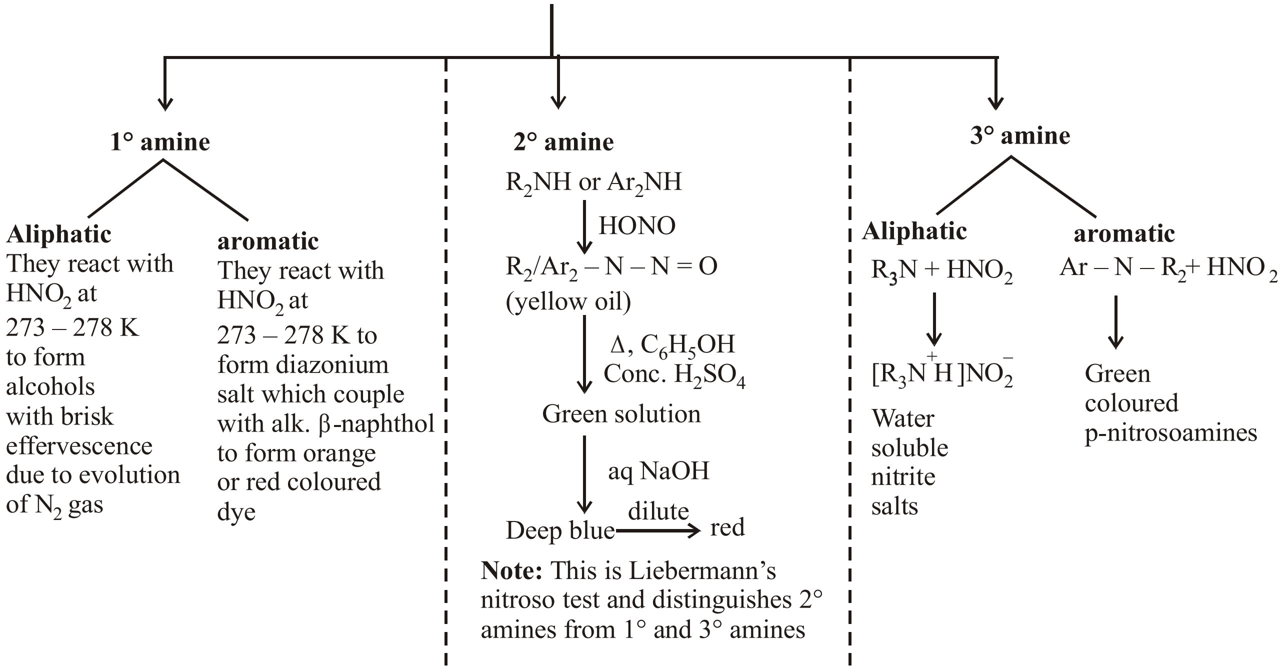
No reaction between benzene sulphonyl chloride and 3° amine.

(ii) Carbylamine or Isocyanide Test

$$R—NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R—NC + 3KCl + 3H_2O$$

Shown only by 1°, 2° and 3° amines do not show this reaction.

(iii) Nitrous Acid Test:



1° amine

Aliphatic
They react with HNO_2 at 273 – 278 K to form alcohols with brisk effervescence due to evolution of N_2 gas

aromatic
They react with HNO_2 at 273 – 278 K to form diazonium salt which couple with alk. β-naphthol to form orange or red coloured dye

2° amine

$$R_2NH \text{ or } Ar_2NH \xrightarrow{HONO} R_2/Ar_2-N-N=O \text{ (yellow oil)} \xrightarrow[\text{Conc. } H_2SO_4]{\Delta,\ C_6H_5OH} \text{Green solution} \xrightarrow{\text{aq NaOH}} \text{Deep blue} \xrightarrow{\text{dilute}} \text{red}$$

Note: This is Liebermann's nitroso test and distinguishes 2° amines from 1° and 3° amines

3° amine

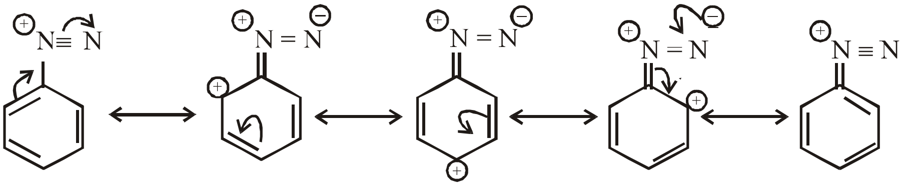
Aliphatic
$R_3N + HNO_2 \rightarrow [R_3\overset{+}{N}H]\overset{-}{NO_2}$
Water soluble nitrite salts

aromatic
$Ar-N-R_2 + HNO_2 \rightarrow$ Green coloured p-nitrosoamines

(B) DIAZONIUM SALTS

They have the general formula $RN_2^+X^-$ where R → aryl group $X^- \rightarrow Cl^-, Br^-, HSO_4^-, BF_4^-$

The stability of arenediazonium ion is explained on the basis of resonance:



PREPARATION OF DIAZONIUM SALT

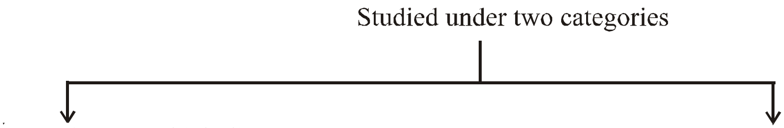
$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278\,K} C_6H_5N_2^+Cl^- + NaCl + 2\,H_2O$$

The process is called diazotisation. Due to its instability, diazonium salt is not stored and is used immediately after its preparation.

PHYSICAL PROPERTIES OF DIAZONIUM SALTS

(i) It is a colourless crystalline solid.
(ii) Soluble in water, stable in cold reacts with warm H_2O.
(iii) Decomposes in dry state.
(iv) Benzediazonium fluoroborate is water insoluble and stable at room temperature.

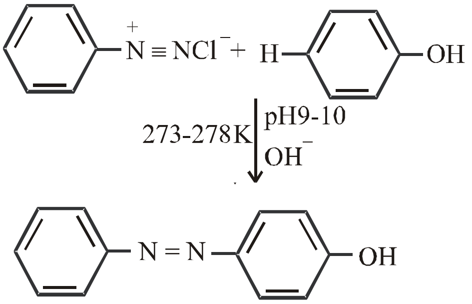
CHEMICAL PROPERTIES OF DIAZONIUM SALTS



Reactions in which diazo group is retained

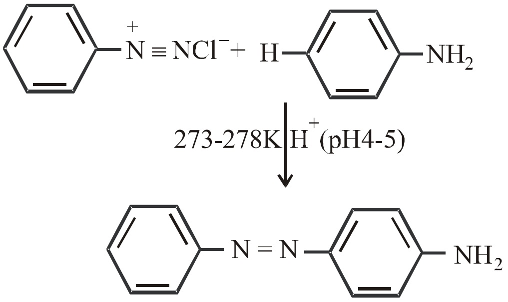
(i) Coupling reactions

(a)



p-Hydroxyazobenzene
(orange dye)

(b)

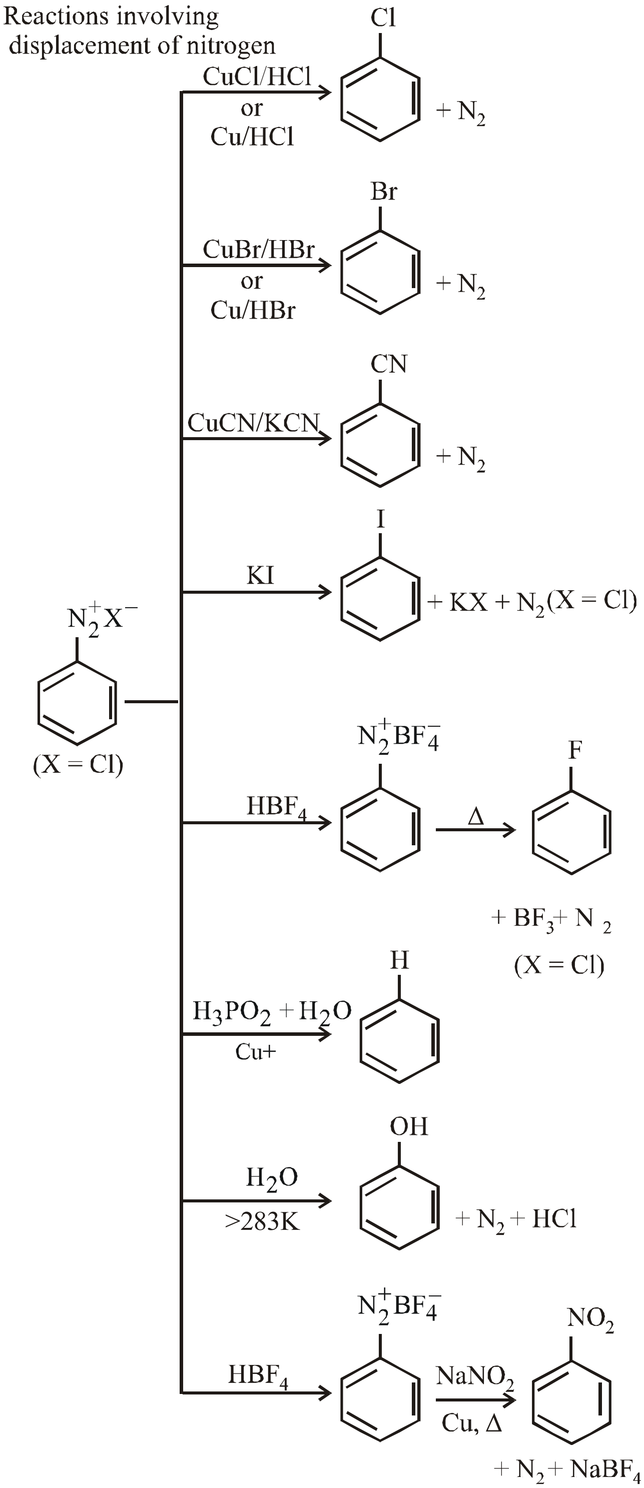


p-Aminoazobenzene
(Yellow dye)

(ii) Reduction to arylhydrazines:

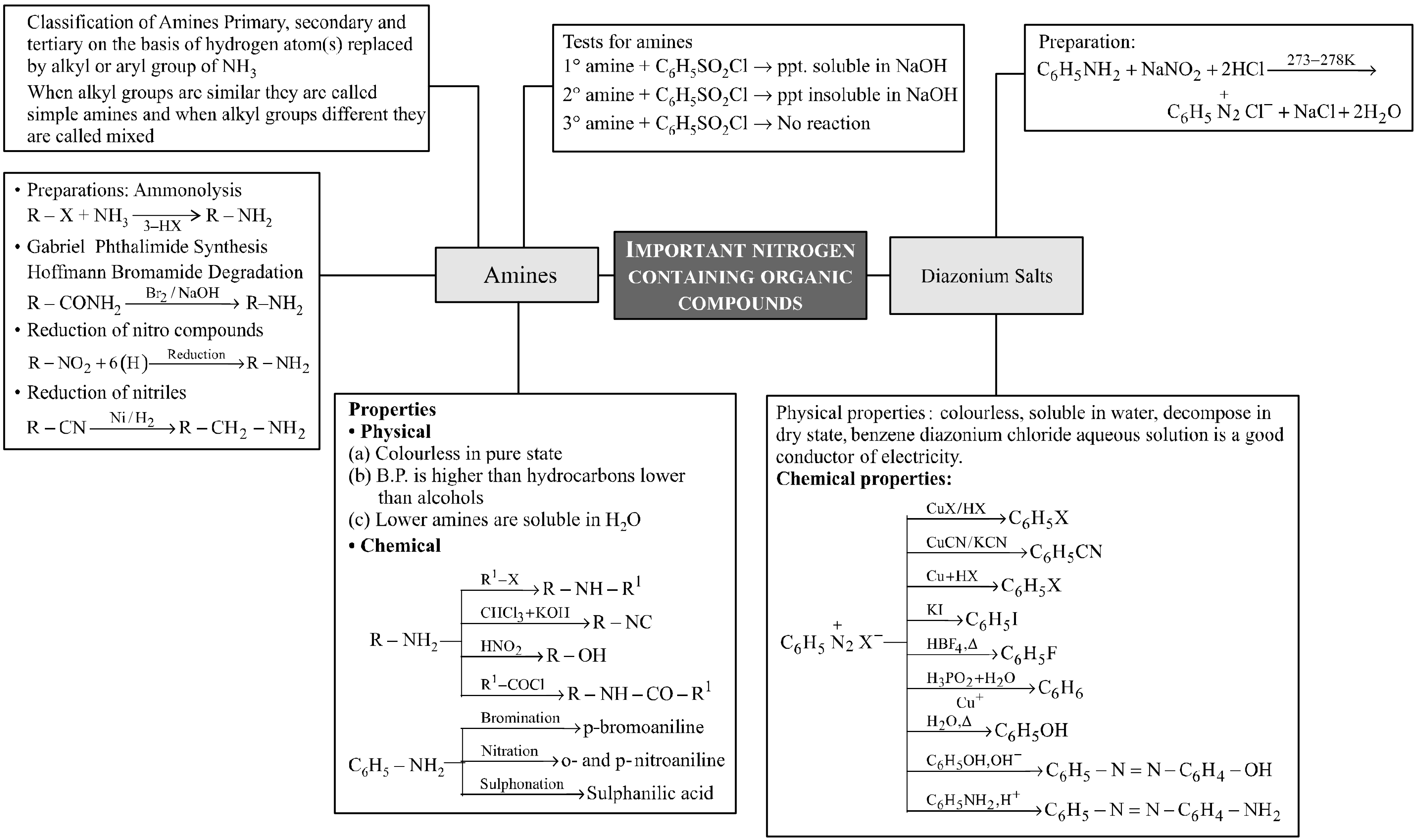
$$Ar-N_2^+X^- \xrightarrow[\text{or } Na_2SO_3]{SnCl_2/HCl} Ar-NH-NH_2$$

Note: Coupling usually occurs at p-position w.r.t. to –OH or – NH_2 group. If p-position is blocked, it occurs at o-position.



Note: Conversion of diazonium salt to haloarenes by suing CuX/HX is called sandmeyer reaction whereas if Cu/HX is used reaction is called Gattermann reaction.

CONCEPT MAP



IMPORTANT NITROGEN CONTAINING ORGANIC COMPOUNDS

Amines

Classification of Amines Primary, secondary and tertiary on the basis of hydrogen atom(s) replaced by alkyl or aryl group of NH_3

When alkyl groups are similar they are called simple amines and when alkyl groups different they are called mixed

- Preparations: Ammonolysis
  $R - X + NH_3 \xrightarrow[3-HX]{} R - NH_2$
- Gabriel Phthalimide Synthesis
  Hoffmann Bromamide Degradation
  $R - CONH_2 \xrightarrow{Br_2 / NaOH} R - NH_2$
- Reduction of nitro compounds
  $R - NO_2 + 6(H) \xrightarrow{\text{Reduction}} R - NH_2$
- Reduction of nitriles
  $R - CN \xrightarrow{Ni / H_2} R - CH_2 - NH_2$

Tests for amines

1° amine + $C_6H_5SO_2Cl \rightarrow$ ppt. soluble in NaOH

2° amine + $C_6H_5SO_2Cl \rightarrow$ ppt insoluble in NaOH

3° amine + $C_6H_5SO_2Cl \rightarrow$ No reaction

Properties

- **Physical**

(a) Colourless in pure state

(b) B.P. is higher than hydrocarbons lower than alcohols

(c) Lower amines are soluble in H_2O

- **Chemical**

$R - NH_2 \xrightarrow{R^1-X} R - NH - R^1$

$R - NH_2 \xrightarrow{CHCl_3 + KOH} R - NC$

$R - NH_2 \xrightarrow{HNO_2} R - OH$

$R - NH_2 \xrightarrow{R^1-COCl} R - NH - CO - R^1$

$C_6H_5 - NH_2 \xrightarrow{\text{Bromination}}$ p-bromoaniline

$C_6H_5 - NH_2 \xrightarrow{\text{Nitration}}$ o- and p-nitroaniline

$C_6H_5 - NH_2 \xrightarrow{\text{Sulphonation}}$ Sulphanilic acid

Diazonium Salts

Preparation:

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5\overset{+}{N_2}Cl^- + NaCl + 2H_2O$

Physical properties : colourless, soluble in water, decompose in dry state, benzene diazonium chloride aqueous solution is a good conductor of electricity.

Chemical properties:

$C_6H_5\overset{+}{N_2}X^- \xrightarrow{CuX/HX} C_6H_5X$

$C_6H_5\overset{+}{N_2}X^- \xrightarrow{CuCN/KCN} C_6H_5CN$

$C_6H_5\overset{+}{N_2}X^- \xrightarrow{Cu+HX} C_6H_5X$

$C_6H_5\overset{+}{N_2}X^- \xrightarrow{KI} C_6H_5I$

$C_6H_5\overset{+}{N_2}X^- \xrightarrow{HBF_4,\Delta} C_6H_5F$

$C_6H_5\overset{+}{N_2}X^- \xrightarrow[Cu^+]{H_3PO_2+H_2O} C_6H_6$

$C_6H_5\overset{+}{N_2}X^- \xrightarrow{H_2O,\Delta} C_6H_5OH$

$C_6H_5\overset{+}{N_2}X^- \xrightarrow{C_6H_5OH, OH^-} C_6H_5 - N = N - C_6H_4 - OH$

$C_6H_5\overset{+}{N_2}X^- \xrightarrow{C_6H_5NH_2, H^+} C_6H_5 - N = N - C_6H_4 - NH_2$

EXERCISE - 1
Conceptual Questions

1. Acetaldoxime reacts with P_2O_5 to produce
(a) ethyl cyanide (b) propyl cyanide
(c) methyl cyanide (d) none of these

2. Acetamide and ethylamine can be distinguished by reacting with
(a) aqueous HCl and heat
(b) aqueous NaOH and heat
(c) acidified $KMnO_4$
(d) bromine water.

3. The compound obtained by heating a mixture of a primary amine and chloroform with ethanolic potassium hydroxide (KOH) is
(a) an alkyl cyanide
(b) a nitro compound
(c) an alkyl isocyanide
(d) an amide

4. Which of the following reagents will convert *p*-methylbenzenediazonium chloride into *p*-cresol?
(a) Cu powder (b) H_2O
(c) H_3PO_2 (d) C_6H_5OH

5. C_3H_9N can not represent the following
(a) primary amine
(b) secondary amine
(c) tertiary amine
(d) quaternary ammonium salt

6. Which one of the following methods is neither meant for the synthesis nor for separation of amines?
(a) Curtius reaction (b) Wurtz reaction
(c) Hofmann method (d) Hinsberg method

7. Benzamide on reaction with $POCl_3$ gives
(a) aniline (b) chlorobenzene
(c) benzylamine (d) benzonitrile

8. Which of the following will produce isopropyl amine –

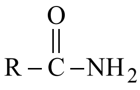
(I) $(CH_3)_2CO \xrightarrow{NH_2OH} X \xrightarrow{LiAlH_4}$

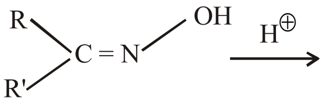
(II) $CH_3-CH_2-CHO \xrightarrow[heat]{NH_3} X \xrightarrow{LiAlH_4}$

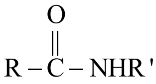
(III) $(CH_3)_2CH-OH + PCl_5 \longrightarrow X \xrightarrow{NH_3}$

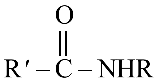
(IV) $CH_3-CH_2-CH_2-NH_2 \xrightarrow{heat}$

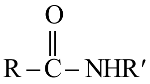
(a) I, II (b) II, III
(c) I, III (d) IV only

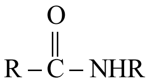
9. Reaction of  $R-\overset{O}{\overset{\|}{C}}-NH_2$ with a mixture of Br_2 and KOH produces RNH_2. During the reaction, which of the intermediate product is formed :
(a) $R-NH-Br$ (b) $H-CO-NBr_2$
(c) $R-N=C=O$ (d) all of these

10.  $\xrightarrow{H^{\oplus}}$ [X], the product and name of this reaction is –

(a)  $R-\overset{O}{\overset{\|}{C}}-NHR'$; Pinnacole rearrangement

(b)  $R'-\overset{O}{\overset{\|}{C}}-NHR$; Fries rearrangement

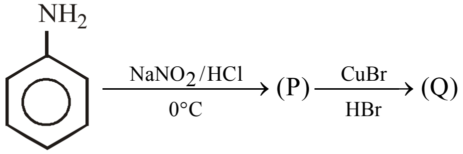
(c)  $R-\overset{O}{\overset{\|}{C}}-NHR'$; Beckmann's rearrangement

(d)  $R-\overset{O}{\overset{\|}{C}}-NHR'$, Allylic rearrangement

11. Which of the following reactions can produce aniline as main product?
(a) $C_6H_5NO_2 + Zn/KOH$
(b) $C_6H_5NO_2 + Zn/NH_4Cl$
(c) $C_6H_5NO_2 + LiAlH_4$
(d) $C_6H_5NO_2 + Zn/HCl$

12. $R-NH_2 + \underset{(excess)}{CH_3COCl} \longrightarrow A$.

The product (A) will be –
(a) $RNHCOCH_3$ (b) $RN(COCH_3)_2$
(c) $R\overset{+}{N}(COCH_3)_3Cl^-$ (d) $R-CONH_2$

13. 

The compound Q is –
(a) bromo benzene (b) chlorobenzene
(c) benzyl bromide (d) benzyl chloride

14. Identify Z in the following sequence of reactions –

$$CH_3-COONH_4 \xrightarrow{\Delta} X \xrightarrow{P_2O_5} Y \xrightarrow{H_2O/H^{\oplus}} Z$$

(a) $CH_3-CH_2-CO-NH_2$ (b) CH_3-CN
(c) $(CH_3CO)_2O$ (d) CH_3-COOH

15. Among the following which one does not act as an intermediate in Hofmann rearrangement ?
(a) *R*NCO (b) $RCO\ddot{N}$
(c) $RCO\ddot{N}HBr$ (d) *R*NC

16. Propionamide on Hofmann degradation gives –
(a) methyl amine (b) ethyl amine
(c) propyl amine (d) ethyl cyanide

17. The basicity of aniline is less than that of cyclohexylamine. This is due to
(a) + R effect of —NH_2 group
(b) – I effect of —NH_2 group
(c) – R effect of —NH_2 group
(d) hyperconjugation effect

18. When phenol and benzene diazonium chloride are coupled, the main product is :
(a) aniline (b) *p*-hydroxyazobenzene
(c) azobenzene (d) chlorobenzene

19. Ethylamine can be prepared by the action of bromine, caustic potash and :
(a) acetamide (b) propionamide
(c) formamide (d) methyl cyanide

20. The number of primary amines of formula $C_4H_{11}N$ is :
(a) 1 (b) 3 (c) 4 (d) 2

21. In the diazotization of arylamines with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to
(a) Supress the concentration of free aniline available for coupling
(b) Supress hydrolysis of phenol
(c) Ensure a stoichiometric amount of nitrous acid
(d) Neutralise the base liberated

22. *p*-Chloroaniline and anilinium hydrogen chloride can be distinguished by :
(a) Sandmeyer reaction (b) Carbylamine reaction
(c) Hinsberg's reaction (d) $AgNO_3$

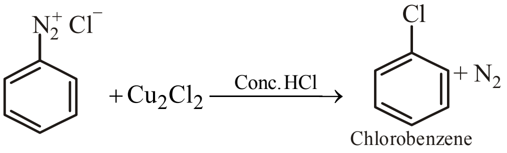
23. The conversion of acetophenone to acetanilide is best accomplished by using :
(a) Beckmann rearrangement
(b) Curtius rearrangement
(c) Lossen rearrangement
(d) Hofmann rearrangement

24. High basicity of Me_2NH relative to Me_3N is attributed to :
(a) effect of solvent (b) inductive effect of Me
(c) shape of Me_2NH (d) shape of Me_3N

25. In the reaction,

$$RNH_2 \xrightarrow{HNO_2} A + B + C\uparrow ; \text{C is}$$

(a) NH_3 (b) N_2 (c) O_2 (d) CO_2

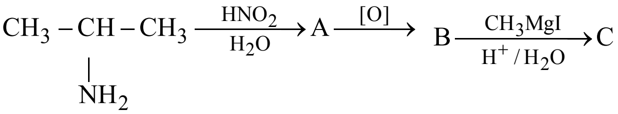
26.


Above reaction is known as:
(a) Strecker's reaction (b) Sandmeyer's reaction
(c) Wohl-Ziegler reaction (d) Stephen's reaction

27. Nitrobenzene and hydrogen in presence of zinc combines to form :
(a) azobenzene (b) benzene
(c) azoxybenzene (d) aniline

28. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitrosoamine. The compound is
(a) CH_3NH_2 (b) $CH_3CH_2NH_2$
(c) $CH_3CH_2NHCH_2CH_3$ (d) $(CH_3CH_2)_3N$

29. In the following sequence of reactions, the compound C formed would be



$$\underset{\underset{NH_2}{|}}{CH_3-CH-CH_3} \xrightarrow[H_2O]{HNO_2} A \xrightarrow{[O]} B \xrightarrow[H^+/H_2O]{CH_3MgI} C$$

(a) 1,1-dimethyl ethanol
(b) butanol-1
(c) butanol-2
(d) 2-methyl-propanol-1

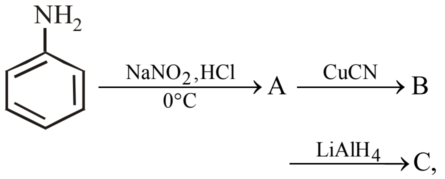
30. $CH_3COOH \xrightarrow[Heat]{NH_3} A \xrightarrow[(-H_2O)]{P_2O_5} B \xrightarrow[(-H_2O)]{P_2O_5} C$
The compound 'C' is :
(a) acetamide (b) ammonium acetate
(c) methyl cyanide (d) aniline

31. Azo dye is prepared by the coupling of phenol and
(a) diazonium chloride
(b) *o*-nitroaniline
(c) benzoic acid
(d) chlorobenzene

32. Nitrosoamines ($R_2N-N=O$) are soluble in water. On heating them with concentrated H_2SO_4, they give secondary amines. This reaction is called
(a) Perkin reaction
(b) Sandmeyer's reaction
(c) Fitting reaction
(d) Liebermann nitroso reaction

33. Primary amines react with benzaldehyde to form:
(a) diazonium salts (b) azo dyes
(c) anilides (d) schiff's base

34. In the reaction sequence



the product 'C' is:
(a) benzonitrile (b) benzaldehyde
(c) benzoic acid (d) benzylamine

35. The end product (Y) in the reaction sequence

$$CH_3CONH_2 \xrightarrow[\Delta]{P_2O_5} X \xrightarrow{Sn/HCl} Y \text{, is :}$$

(a) ethane nitrile (b) acetic acid
(c) ethanamine (d) chloroethane

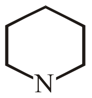
36. The structural formula of methyl aminomethane is
(a) $(CH_3)_2CHNH_2$ (b) $(CH_3)_3N$
(c) $(CH_3)_2NH$ (d) CH_3NH_2

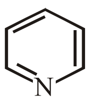
37. The end product of the reactions is

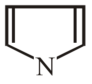
$$C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{H.NH_2} C$$

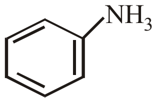
(a) ethyl cyanide (b) ethyl amine
(c) methyl amine (d) acetamide

38. Which of the following is strongest base :

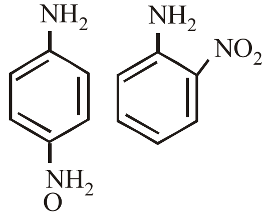
(a) 

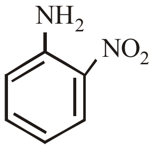
(b) 

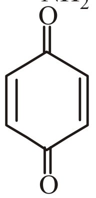
(c) 

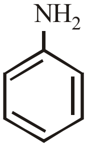
(d) 

39. Aniline when treated with conc. HNO_3 gives

(a) 

(b) 

(c) 

(d) 

40. If methyl is alkyl group, then which order of basicity is correct
(a) $R_2NH > RNH_2 > R_3N > NH_3$
(b) $R_2NH > R_3N > RNH_2 > NH_3$
(c) $RNH_2 > NH_3 > R_2NH > R_3N$
(d) $NH_3 > RNH_2 > R_3NH > R_3N$

41. Among the following, the strongest base is
(a) $C_6H_5NH_2$ (b) $p-NO_2C_6H_4NH_2$
(c) $m-NO_2C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$

42. A primary amine is formed an amide by the treatment of bromine and alkali. The primary amine has :
(a) 1 carbon atom less than amide
(b) 1 carbon atom more than amide
(c) 1 hydrogen atom less than amide
(d) 1 hydrogen atom more than amide

43. Benzene diazonium chloride reacts with hypophosphorous acid to produce:
(a) phenol
(b) benzene
(c) *p*-hydroxyazobenzene
(d) benzonitrile

44. Nitration of aniline also gives *m*-nitro aniline, in strong acidic medium because
(a) in electrophilic substitution reaction amino group is meta directing
(b) inspite of substituents nitro group always goes to m-position
(c) in strong acidic medium, nitration of aniline is a nucleophilic substitution reaction
(d) in strong acidic medium aniline present as anilinium ion

45. Which is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl?
(a) Acetic acid (b) Acetamide
(c) Methyl cyanide (d) Acetic anhydrides

46. $C_6H_5NH_2 + CS_2 \xrightarrow{HgCl_2} C_6H_5NCS + HgS + 2HCl$
the above reaction is:
(a) Libermann's nitroso reaction
(b) Carbylamine reaction
(c) Hinsberg's reaction
(d) Hoffmann mustard oil reaction

47. Consider the following sequence of reactions :

$$\text{Compound}[A] \xrightarrow{\text{Reduction}} [B] \xrightarrow{HNO_2} CH_3CH_2OH$$

The compound [A] is
(a) CH_3CH_2CN (b) CH_3NO_2
(c) CH_3NC (d) CH_3CN

48. Ethyl isocyanide on hydrolysis in acidic medium generates
(a) propanoic acid and ammonium salt
(b) ethanoic acid and ammonium salt
(c) methylamine salt and ethanoic acid
(d) ethylamine salt and methanoic acid

49. What will be the final product in the following reaction sequence –

$$CH_3CH_2CN \xrightarrow{H^+/H_2O} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{NaOBr} C$$

(a) $CH_3CH_2CONH_2$ (b) CH_3CH_2COBr
(c) $CH_3CH_2NH_2$ (d) $CH_3CH_2CH_2NH_2$

50. In the reaction :

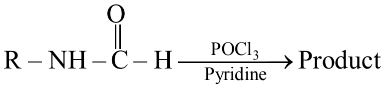
$$C_6H_5CHO + C_6H_5NH_2 \longrightarrow C_6H_5N = CHC_6H_5 + H_2O$$

The compound, $C_6H_5N = CHC_6H_5$ is known as
(a) aldol (b) Schiff's base
(c) Schiff's reagent (d) Benedict's reagent

51. Methyl cyanide is less basic than methylamine because:
(a) there is a triple bond between carbon and nitrogen atoms
(b) molecular weight is higher than methylamine
(c) the lone pair of electrons in nitriles belongs to *sp*-orbital and lone pair of electrons in amines belongs to sp^3 -orbital
(d) None of these

52. In the reaction : $R - C \equiv N + 4(H) \xrightarrow{X} RCH_2NH_2$
X can be :
(a) $LiAlH_4$ (b) H_2SO_4 (c) Ni (d) 2KBr

53. Aromatic nitriles (ArCN) are not prepared by reaction :
(a) $ArX + KCN$ (b) $ArN_2^+ + CuCN$
(c) $ArCONH_2 + P_2O_5$ (d) $ArCONH_2 + SOCl_2$

54. 

$$R - NH - \overset{\overset{\displaystyle O}{\|}}{C} - H \xrightarrow[\text{Pyridine}]{POCl_3} \text{Product}$$

In the given reaction what will be the product
(a) $R - N = C = O$ (b) $R - \overset{+}{N} \equiv C^-$
(c) $R - C \equiv N$ (d) None of these.

55. When primary amine is heated with CS_2 in presence of excess mercuric chloride, it gives isothiocyanate. This reaction is called
(a) Hoffmann bromide reaction
(b) Hoffmann mustured oil reaction
(c) Carbylamine reaction
(d) Perkin reaction

56. Hydrolysis of phenyl isocyanide forms
(a) Benzoic acid (b) Formic acid
(c) Acetic acid (d) None of these

57. Nitrobenzene on treatment with zinc dust and aqueous ammonium chloride gives:
(a) $C_6H_5N = NC_6H_5$ (b) $C_6H_5NH_2$
(c) C_6H_5NO (d) C_6H_5NHOH

58. *n*-Propylamine yields a volatile compound *X* on warming with alc. alkali and chloroform. *X* has an offensive odour. The structure of *X* is

(a) $CH_3CH_2CH_2CN$ (b) $(CH_3)_2CHCN$
(c) $CH_3CH_2CH_2NC$ (d) $(CH_3)_2CHNC$

59. $CH_3-CH_2C\equiv N \xrightarrow{X} CH_3CH_2CHO$. The compound *X* is

(a) $SnCl_2/HCl/H_2O$, boil (b) $H_2/Pd-BaSO_4$
(c) $LiAlH_4$ / ether (d) $NaBH_4$/ ether / H_3O^+

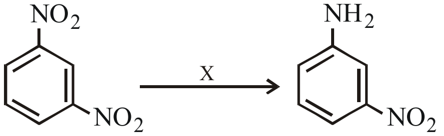
60. Benzamide and benzyl amine can be distinguished by

(a) cold dil. NaOH
(b) cold dil. HCl
(c) both a & b
(d) $NaNO_2$, HCl, 0ºC, then β-naphthol

61. Acetanilide on nitration followed by alkaline hydrolysis mainly gives –

(a) *o*-Nitroaniline (b) *p*-Nitroaniline
(c) *m*-Nitroaniline (d) 2, 4, 6-Trinitroaniline

62. In the reaction :



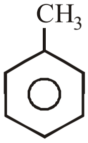
; X is

(a) SiC (b) H_2SO_4
(c) $KMnO_4$ (d) Fe + HCl

63. Amine that cannot be prepared by Gabriel phthalimide synthesis is

(a) aniline (b) benzylamine
(c) methylamine (d) *iso*-butylamine

64. Which of the following will be easily nitrated?

(a) 

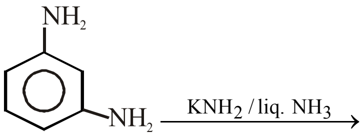
(b) 

(c) CH_3NO_2 (d) $C_6H_5NO_2$

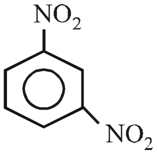
65. Nitrobenzene is reduced to azoxybenzene using

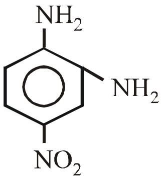
(a) Sn/HCl (b) Zn/NH_4Cl
(c) As_2O_3/NaOH (d) Zn/NaOH

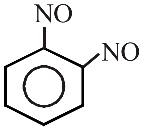
66. Product of the reaction

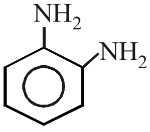


? is

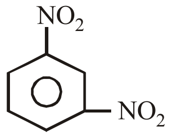
(a) 

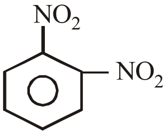
(b) 

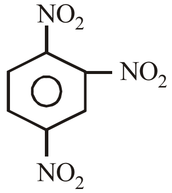
(c) 

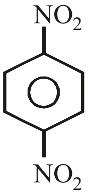
(d) 

67. Nitrobenzene, on reaction with fuming nitric acid at 90°C, gives

(a) 

(b) 

(c) 

(d) 

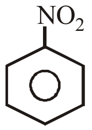
68. In the series of reaction

$C_6H_5NH_2 \xrightarrow[0-5°C]{NaNO_2/HCl} X \xrightarrow[H_2O]{HNO_2} Y + N_2 + HCl$ X and Y are respectively

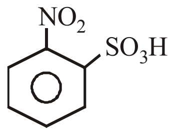
(a) $C_6H_5\ N=N\ C_6H_5, C_6H_5N_2^{\oplus}Cl^{\ominus}$
(b) $C_6H_5N_2^{\oplus}Cl^{-}, C_6H_5-N=N-C_6H_5$
(c) $C_6H_5N_2^{\oplus}Cl^{-}, C_6H_5NO_2$
(d) $C_6H_5NO_2, C_6H_6$

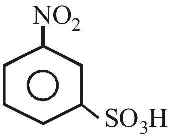
69. A primary amine that can be obtained both by the reduction of cyanides and amides is

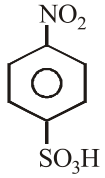
(a) methyl amine (b) benzyl amine
(c) aniline (d) *iso*-propyl amine

70. 

$\xrightarrow[\Delta]{\text{Conc. } H_2SO_4} A$ Product 'A' in above reaction is

(a) 

(b) 

(c) 

(d) None of these

71. Anilinium hydrogensulphate on heating with sulphuric acid at 453-473 K produces

(a) benzene sulphonic acid (b) anthranilic acid
(c) aniline (d) sulphanilic acid

72. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine?

(a) Methyl isocyanide (b) Acetamide
(c) Methyl cyanide (d) Nitroethane

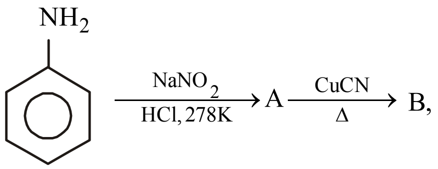
73. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 in the mixture, nitric acid acts as a/an :

(a) acid (b) base
(c) catalyst (d) reducing agent

74. Acetamide is treated with the following reagents separately. Which one of these would yield methylamine?

(a) $NaOH-Br_2$ (b) Sodalime
(c) Hot conc. H_2SO_4 (d) PCl_5

75. In the chemical reactions :



the compounds A and B respectively are :
(a) benzene diazonium chloride and benzonitrile
(b) nitrobenzene and chlorobenzene
(c) phenol and bromobenzene
(d) fluorobenzene and phenol

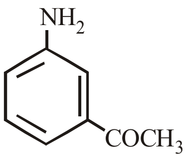
EXERCISE - 2
Applied Questions

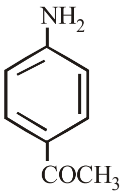
1. Aniline is treated with bromine water to give an organic compound 'X' which when treated with $NaNO_2$ and HCl at 0° C gives a water soluble compound 'Y'. Compound 'Y' on treatment with Cu_2Cl_2 and HCl gives compound 'Z'. Compound 'Z' is
(a) *o*-bromochlorobenzene
(b) *p*-bromochlorobenzene
(c) 2, 4, 6-tribromophenol
(d) 2, 4, 6-tribromochlorobenzene

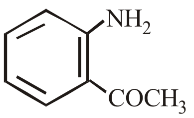
2. Which one of the following statements is not correct?
(a) pK_b of aniline is greater than that of methyl amine
(b) Aniline does not undergo Friedel-Crafts reaction
(c) Dimethyl amine is capable of forming intermolecular hydrogen bonding
(d) NH_3 is a stronger base than ethanamine

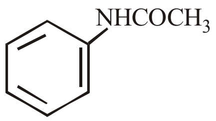
3. When aniline reacts with oil of bitter almonds (C_6H_5CHO) condensation takes place and benzal derivative is formed. This is known as
(a) Million's base (b) Schiff's reagent
(c) Schiff's base (d) Benedict's reagent

4. Aniline is an activated system for electrophilic substitution. The compound formed on heating aniline with acetic anhydride is

(a) 

(b) 

(c) 

(d) 

5. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated dry. The final product is
(a) 1,3, 5-tribromobenzene
(b) p-bromofluorobenzene
(c) p-bromoaniline
(d) 2,4, 6-tribromofluorobenzene

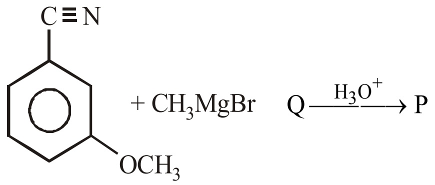
6. Choose the amide which on reduction with $LiAlH_4$ yields a secondary amine
(a) Ethanamide (b) N-Methylethanamide
(c) N,N-dimethylethanamide (d) Phenylmethanamide

7. $[A]\xrightarrow{\text{reduction}}[B]\xrightarrow{CHCl_3+KOH}$

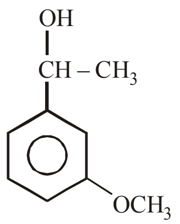
$[C]\xrightarrow{\text{reduction}}\text{N – Methylaniline, A is}$

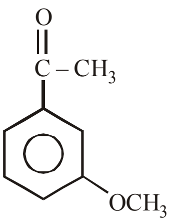
(a) Formaldehyde (b) Trichloromethane
(c) Nitrobenzene (d) Toluene

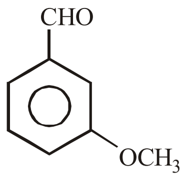
8. Intermediates formed during reaction of $R\underset{\underset{O}{\|}}{C}NH_2$ with Br_2 and KOH are
(a) RNHBr and RCONHBr
(b) RNHCOBr and RNCO
(c) RCONHBr and RNCO
(d) $RCONBr_2$

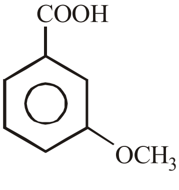
9. 

Product 'P' in the above reaction is

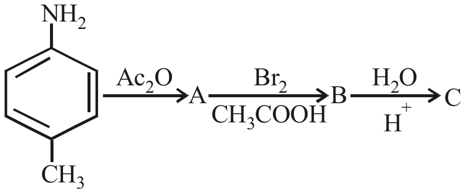
(a) 

(b) 

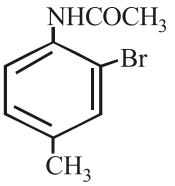
(c) 

(d) 

10. The final product C, obtained in this reaction



would be

(a)


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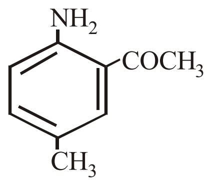

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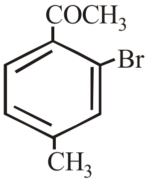
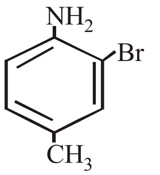


(d)


11. Choose the incorrect statement

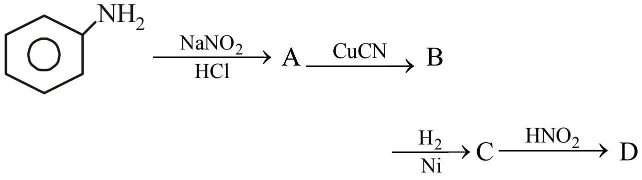
(a) Primary amines show intermolecular hydrogen bonds

(b) Tert-butylamine is a primary amine.

(c) Teritary amines do not show intermolecular hydrogen bonds.

(d) Isopropylamine is a secondary amine.

12. Aniline in a set of reactions yielded a product D.



The structure of the product D would be:

(a) C_6H_5NHOH (b) $C_6H_5NHCH_2CH_3$

(c) $C_6H_5CH_2NH_2$ (d) $C_6H_5CH_2OH$

13. Ethanoic acid on heating with ammonia forms compound A which on treatment with bromine and sodium hydroxide gives compound B. Compound B on treatment with $NaNO_2$/dil. HCl gives compound C. The compounds A, B and C respectively are

(a) ethanamide, methanamine, methanol

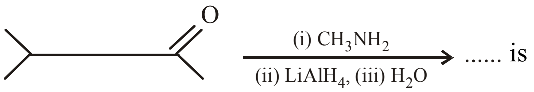
(b) propanamide, ethanamine, ethanol

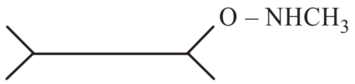
(c) N-ethylpropanamide, methaneisonitrile, methanamine

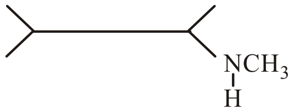
(d) ethanamine, bromoethane, ethanedia-zonium chloride

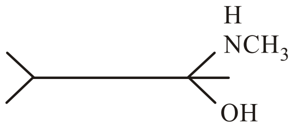
(e) methanamine, ethanamide, methanol

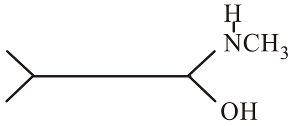
14. The major organic product formed from the following reaction:



(a)


(b)


(c)


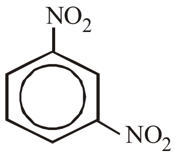
(d)


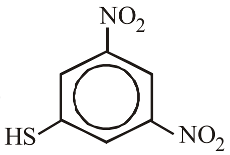
15. Among the following amines, which one has the highest pK_b value in aqueous solution?

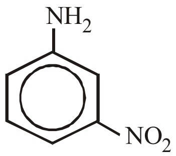
(a) Methanamine (b) N,N-Dimethylaniline

(c) Ethanamine (d) Benzenamine

16. The major product (70% to 80%) of the reaction between *m*-dinitrobenzene with NH_4HS is

(a)


(b)


(c)


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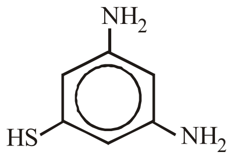
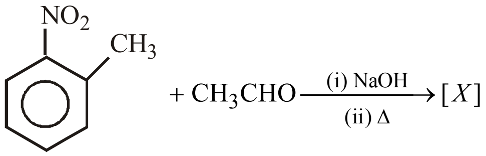
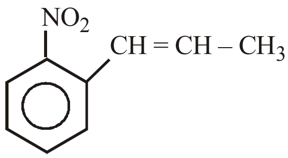
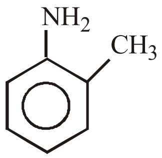
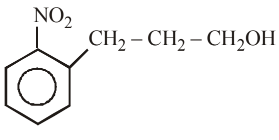


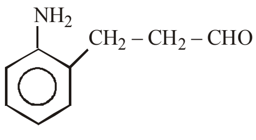
17.


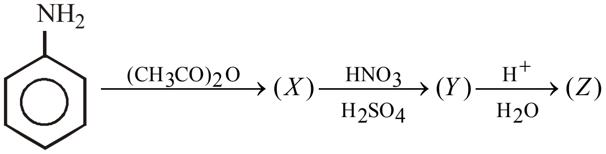
In this reaction [*X*] will be –

(a)


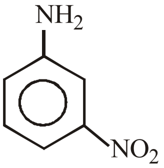
(b)


(c)


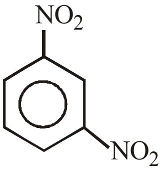
(d)


18. 

Product Z of the reaction

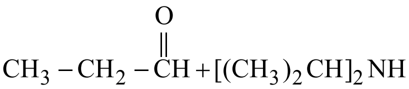
(a) 

(b) 

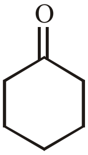
(c) 

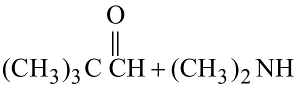
(d) 

19. In which of the following pairs of reactants is most effective in forming an enamine

(a) 

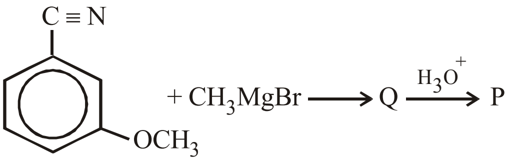
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}H+[(CH_3)_2CH]_2NH$

(b)  $+(CH)_3CNH_2$

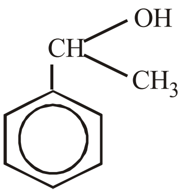
(c) 

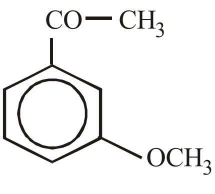
$(CH_3)_3C\,\overset{\overset{O}{\|}}{C}H+(CH_3)_2NH$

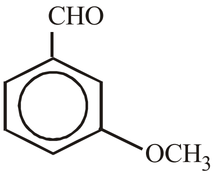
(d) None of these forms an enamine

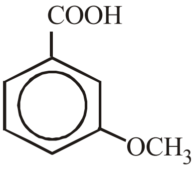
20. 

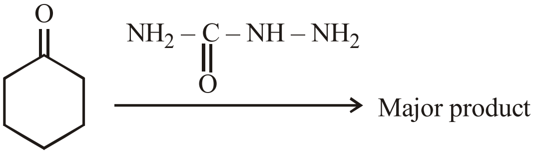
The product ‘P’ in the above reaction is

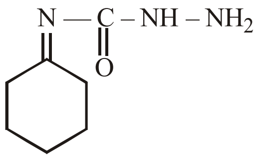
(a) 

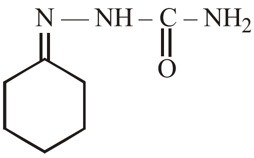
(b) 

(c) 

(d) 

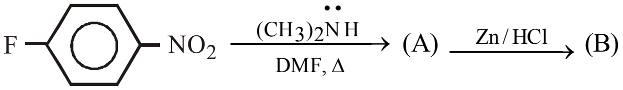
21. 

(a) 

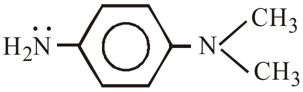
(b) 

(c) Both of these

(d) None of these

22. 

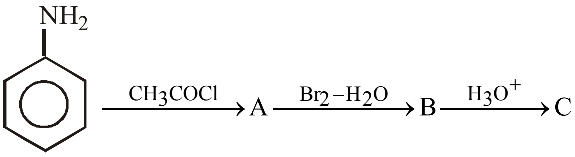
(B) is –

(a) 

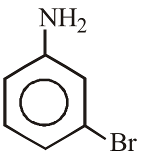
(b) 

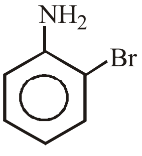
(c) 

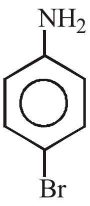
(d) 

23. 

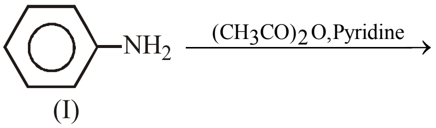
C (major product) is –

(a) 

(b) 

(c) 

(d) None of these

24. 

(I)

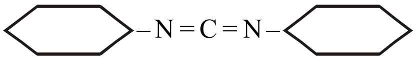
$$(II)\xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} III$$

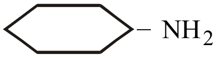
The basicity order of I, II and III is –

(a) III > I > II (b) I > II > III

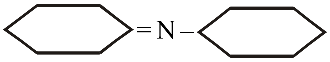
(c) III > II > I (d) II > III > I

25. Which of the following compounds is an enamine ?

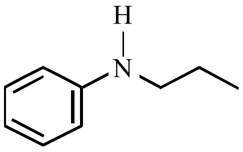
(a) 

(b) 

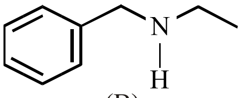
(c) 

(d) 

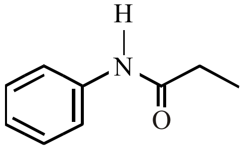
26. Which one of the following compound is most basic?



(A)



(B)



(C)

(a) (A) (b) (B)

(c) (C) (d) All are equally basic

27. The correct stability order of the following resonance structures is

$H_2C=\overset{+}{N}=\overset{-}{N}$ (I)

$H_2\overset{+}{C}-N=\overset{-}{N}$ (II)

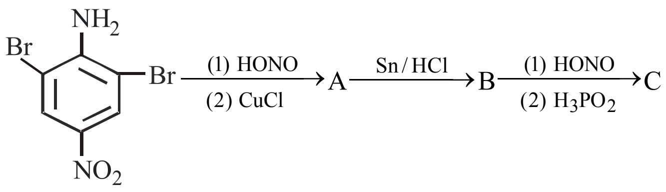
$H_2\overset{-}{C}-\overset{+}{N}\equiv N$ (III)

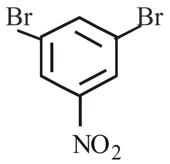
$H_2\overset{-}{C}-N=\overset{+}{N}$ (IV)

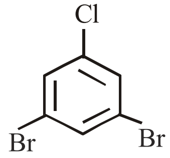
(a) (I) > (II) > (IV) > (III) (b) (I) > (III) > (II) > (IV)

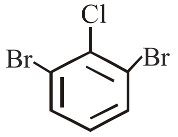
(c) (II) > (I) > (III) > (IV) (d) (III) > (I) > (IV) > (II)

28. The product – (C) obtained in the following sequence of reactions is



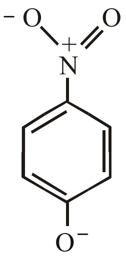
(a) 

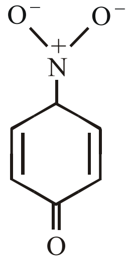
(b) 

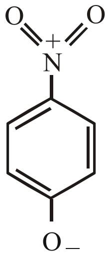
(c) 

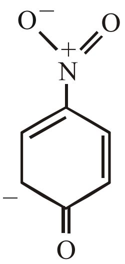
(d) None of these

29. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

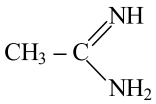
(a) 

(b) 

(c) 

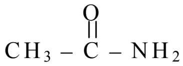
(d) 

30. The correct order of basicities of the following compounds is

1. 
$CH_3-C(=NH)NH_2$

2. $CH_3-CH_2-NH_2$

3. $(CH_3)_2NH$

4. 
$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4

(c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

31. An organic compound A containing nitrogen, on acid catalysed hydrolysis produces a water soluble organic compound B and a gaseous compound C. When methyl magnesium bromide is slowly added to A in 1 : 1 ratio and hydrolysed, it produces a compound which can be obtained by dry distillation of the calcium salt of B. The compound A is

(a) N-methylmethanamide

(b) N-ethylmethanamide

(c) acetonitrile

(d) N, N-dimethylmethanamide

32. Match the compounds given in List - I with their characteristic reactions given in List - II. Select the correct option.

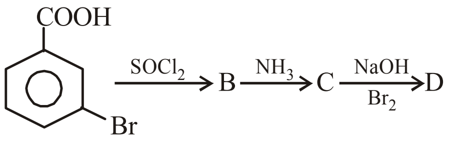
List - I **Compounds**	**List - II** **Reactions**
(1) $CH_3CH_2CH_2CH_2NH_2$	(i) alkaline hydrolysis

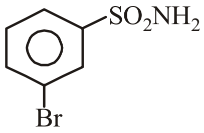
(2) $CH_3C \equiv CH$	(ii) with KOH (alcohol) and $CHCl_3$ produces bad smell
(3) $CH_3CH_2COOCH_3$	(iii) gives white ppt. with ammonical $AgNO_3$
(4) $CH_3CH(OH)CH_3$	(iv) with Lucas reagent cloudiness appears after 5 minutes

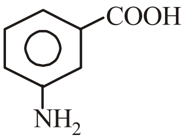
Options :

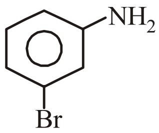
	(1)	(2)	(3)	(4)
(a)	(iv)	(ii)	(iii)	(i)
(b)	(ii)	(i)	(iv)	(iii)
(c)	(iii)	(ii)	(i)	(iv)
(d)	(ii)	(iii)	(i)	(iv)

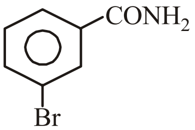
33. In a set of reactions *m*-bromobenzoic acid gave a product D. Identify the product D.



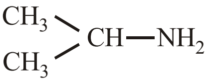
(a) 

(b) 

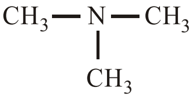
(c) 

(d) 

34. An organic compound (C_3H_9N) (A), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A).

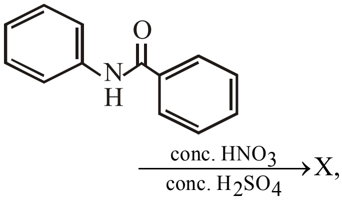
(a) 
$(CH_3)_2CH—NH_2$

(b) $CH_3CH_2—NH—CH_3$

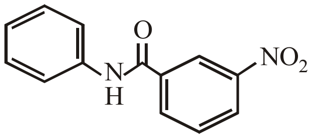
(c) 
$CH_3—N(CH_3)—CH_3$

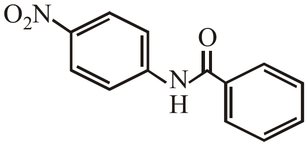
(d) $CH_3CH_2CH_2—NH_2$

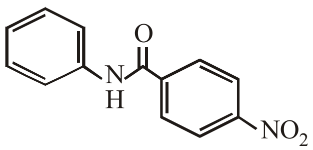
35. In the following reaction

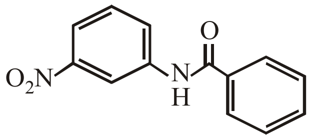


the structure of the major product ‘X’ is

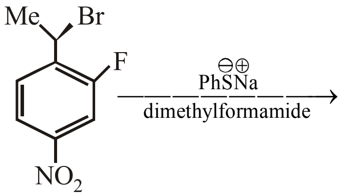
(a) 

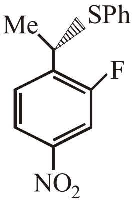
(b) 

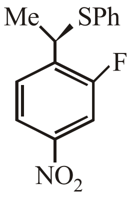
(c) 

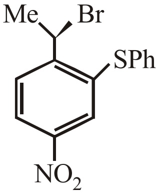
(d) 

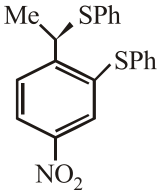
36. The major product of the following reaction is



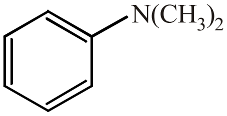
(a) 

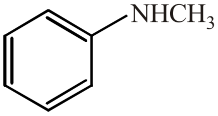
(b) 

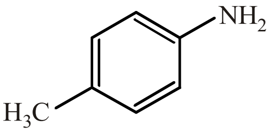
(c) 

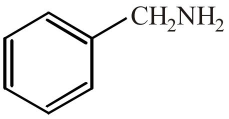
(d) 

37. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is

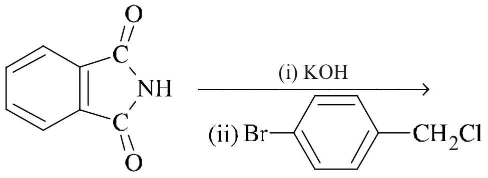
(a) 

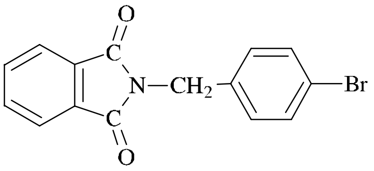
(b) 

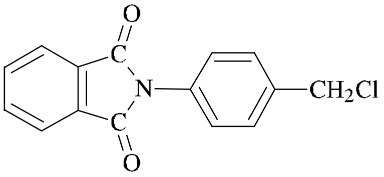
(c) 

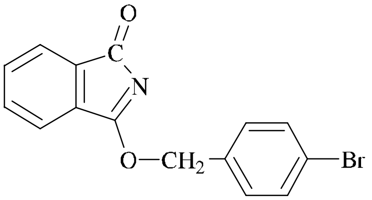
(d) 

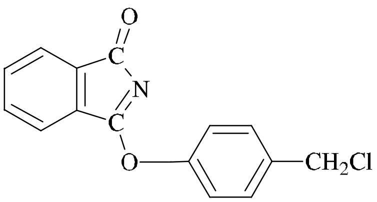
38. The major product of the following reaction is



(a) 

(b) 

(c) 

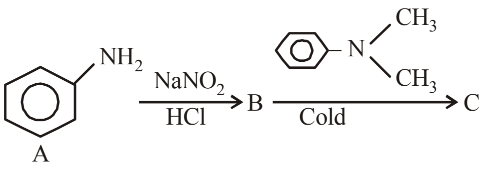
(d) 

39. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is :

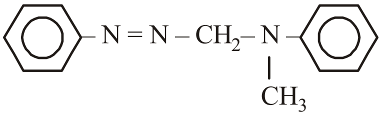
(a) 2 (b) 5

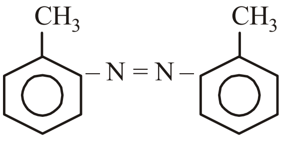
(c) 4 (d) 6

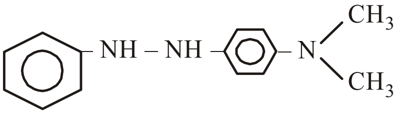
40. In a reaction of aniline a coloured product C was obtained.

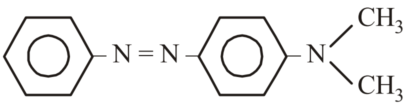


The structure of C would be :

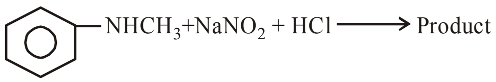
(a) 

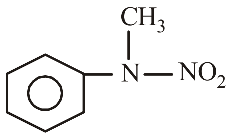
(b) 

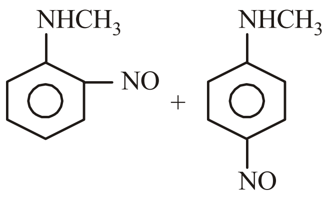
(c) 

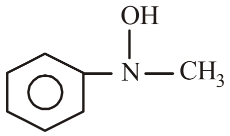
(d) 

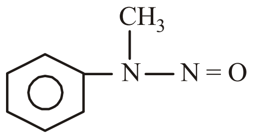
41. Predict the product:



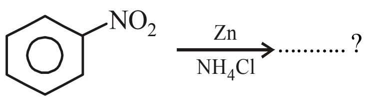
(a) 

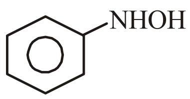
(b) 

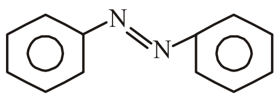
(c) 

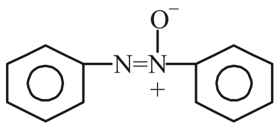
(d) 

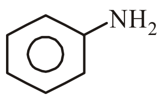
42. What is the product obtained in the following reaction :



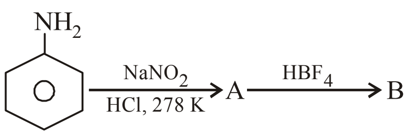
(a) 

(b) 

(c) 

(d) 

43. In the chemical reactions,



the compounds 'A' and 'B' respectively are

(a) nitrobenzene and fluorobenzene

(b) phenol and benzene

(c) benzene diazonium chloride and fluorobenzene

(d) nitrobenzene and chlorobenzene

44. Which one of the following is the strongest base in aqueous solution ?

(a) Methylamine (b) Trimethylamine

(c) Aniline (d) Dimethylamine

45. Which of the following statements about primary amines is **'False'** ?

(a) Alkyl amines are stronger bases than aryl amines

(b) Alkyl amines react with nitrous acid to produce alcohols

(c) Aryl amines react with nitrous acid to produce phenols

(d) Alkyl amines are stronger bases than ammonia

46. Ortho-Nitrophenol is less soluble in water than *p*- and *m*-Nitrophenols because :

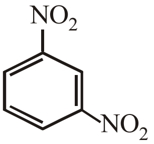
(a) *o*-Nitrophenol is more volatile than those of *m*- and *p*-isomers.

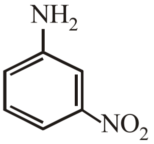
(b) *o*-Nitrophenol shows intramolecular H-bonding

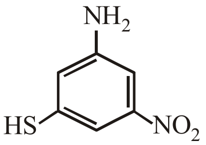
(c) *o*-Nitrophenol shows intermolecular H-bonding

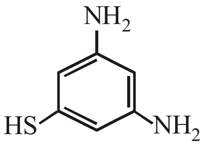
(d) Melting point of *o*-Nitrophenol is lower than those of *m*- and *p*-isomers.

47. The major product (70% to 80%) of the reaction between m-dinitrobenzene with NH_4HS is

(a)


(b)


(c)


(d)


DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

(a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement -1

(b) Statement -1 is true, Statement-2 is true ; Statement-2 is NOT a correct explanation for Statement - 1

(c) Statement - 1 is true, Statement-2 is false

(d) Statement -1 is false, Statement-2 is true

48. **Statement-1 :** Amines are basic in nature.

Statement-2 : Presence of lone pair of electron on nitrogen atom.

49. **Statement-1 :** Nitrating mixture used for carrying out nitration of benzene consists of conc. HNO_3 + conc. H_2SO_4.

Statement-2 : In presence of H_2SO_4, HNO_3 acts as a base and produces NO_2^+ ions.

50. **Statement-1 :** CN^- ion is an ambident nucleophile.

Statement-2 : Nucleophiles are electron rich species.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Which of the following is a 3° amine?

(a) 1-methylcyclohexylamine

(b) Triethylamine

(c) tert-butylamine

(d) N-methylaniline

2. The correct IUPAC name for $CH_2=CHCH_2NHCH_3$ is

(a) allyl methylamine

(b) 2-amino-4-pentene

(c) 4-aminopent-1ene

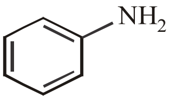
(d) N-methylprop-2-en-1-amine

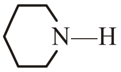
3. Amongst the following, the strongest base in aqueous medium is ....

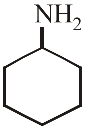
(a) CH_3NH_2 (b) $NCCH_2NH_2$

(c) $(CH_3)_2NH$ (d) $C_6H_5NHCH_3$

4. Which of the following is the weakest Bronsted base?

(a)


(b)


(c)


(d) CH_3NH_2

5. Benzylamine may by alkylated as shown in the following equation?

$$C_6H_5CH_2NH_2 + R—X \longrightarrow C_6H_5CH_2NHR$$

Which of the following alkyl halides is best suited for this reaction through S_N1 mechanism?

(a) CH_3Br (b) C_6H_5Br

(c) $C_6H_5CH_2Br$ (d) C_2H_5Br

6. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

(a) H_2(excess) / Pt (b) $LiAlH_4$ in ether

(c) Fe and HCl (d) Sn and HCl

7. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as a source of nitrogen is ....

(a) sodium amide, $NaNH_2$

(b) sodium azide, NaN_3

(c) potassium cyanide, KCN

(d) potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

8. The source of nitrogen in Gabriel synthesis of amines is ....

(a) sodium azide, NaN_3

(b) sodium nitrite, $NaNO_2$

(c) potassium cyanide, KCN

(d) potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

9. Amongst the given set of reactants, the most appropriate for preparing 2° amine is ....

(a) $2°\ R-Br + NH_3$

(b) $2°\ R-Br + NaCN$ followed by H_2/Pt

(c) $1°\ R-NH_2 + RCHO$ followed by H_2/Pt

(d) $1°\ R-Br(2\ mol)$ + potassium phthalimide followed by H_3O^+/heat

10. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is ....

(a) excess H_2

(b) Br_2 in aqueous NaOH

(c) iodine in the presence of red phosphorus

(d) $LiAlH_4$ in ether

11. The best reagent for converting 2-phenylpropanamide into 1-phenylethanamine is ....

(a) excess H_2 / Pt (b) NaOH / Br_2

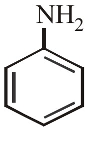
(c) $NaBH_4$ / methanol (d) $LiAlH_4$ / ether

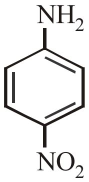
12. Hoffmann bromamide degradation reaction is shown by ....

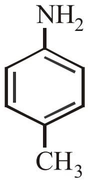
(a) $ArNH_2$ (b) $ArCONH_2$

(c) $ArNO_2$ (d) $ArCH_2NH_2$

13. The correct increasing order of basic strength for the following compounds is ....


(I)


(II)


(III)

(a) II < III < I (b) III < I < II

(c) III < II < I (d) II < I < III

14. Methylamine reacts with HNO_2 to form ....

(a) $CH_3-O-N=O$ (b) CH_3-O-CH_3

(c) CH_3OH (d) CH_3CHO

15. The gas evolved when methylamine reacts with nitrous acid is ....

(a) NH_3 (b) N_2

(c) H_2 (d) C_2H_6

16. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiates the reaction is ....

(a) NO_2 (b) NO^+

(c) NO_2^+ (d) NO_2^-

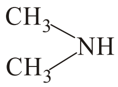
17. Reduction of aromatic nitro compounds using Fe and HCl gives ....

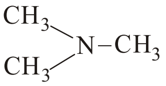
(a) aromatic oxime (b) aromatic hydrocarbon

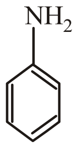
(c) aromatic primary amine (d) aromatic amide

18. The most reactive amine towards dilute hydrochloric acid is ....

(a) CH_3-NH_2

(b) 

(c) 

(d) 

19. Acid anhydrides on reaction with primary amines give ....

(a) amide (b) imide

(c) secondary amine (d) imine

20. The reaction $Ar\overset{+}{N}_2Cl^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuCl$ is named as ....

(a) Sandmeyer reaction (b) Gattermann reaction

(c) Claisen reaction (d) Carbylamine reaction

21. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is

(a) Hoffmann bromamide reaction

(b) Gabriel phthalimide synthesis

(c) Sandmeyer reaction

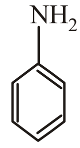
(d) reaction with NH_3

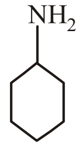
22. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride?

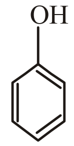
(a) Aniline (b) Phenol

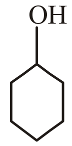
(c) Anisole (d) Nitrobenzene

23. Which of the following compounds is the weakest Bronsted base?

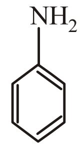
(a) 

(b) 

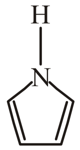
(c) 

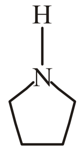
(d) 

24. Among the following amines, the strongest Bronsted base is ....

(a) 

(b) NH_3

(c) 

(d) 

25. The correct decreasing order of basic strength of the following species is .... H_2O, NH_3, OH^-, NH_2^-

(a) $NH_2^- > OH^- > NH_3 > H_2O$

(b) $OH^- > NH_2^- > H_2O > NH_3$

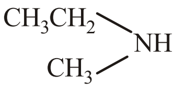
(c) $NH_3 > H_2O > NH_2^- > OH^-$

(d) $H_2O > NH_3 > OH^- > NH_2^-$

26. Which of the following should be most volatile?

I. $CH_3CH_2CH_2NH_2$

II. $(CH_3)_3N$

III. 
$CH_3CH_2NHCH_3$

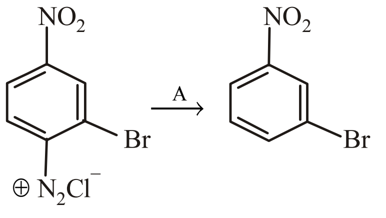
IV. $CH_3CH_2CH_3$

(a) II (b) IV

(c) I (d) III

NEET/AIPMT (2013-2017) Questions

27. In the reaction



A is : ***[2013]***

(a) Cu_2Cl_2 (b) H_3PO_2 and H_2O

(c) H^+/H_2O (d) $HgSO_4/H_2SO_4$

28. Nitrobenzene on reaction with conc. HNO_3/H_2SO_4 at 80 -100°C forms which one of the following products ?

(a) 1, 3 - Dinitrobenzene ***[2013]***

(b) 1, 4 - Dinitrobenzene

(c) 1, 2, 4 - Trinitrobenzene

(d) 1, 2 - Dinitrobenzene

29. On hydrolysis of a "compound", two compounds are obtained. One of which on treatment with sodium nitrite and hydrochloric acid gives a product which does not respond to iodoform test. The second one reduces Tollen's reagent and Fehling's solution. The "compound" is

(a) $CH_3\,CH_2\,CH_2\,CON(CH_3)_2$ ***[NEET Kar. 2013]***

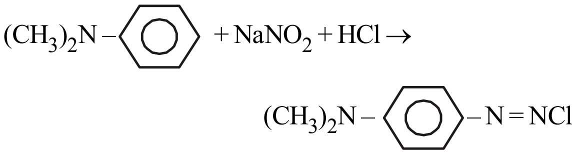
(b) $CH_3\,CH_2\,CH_2\,NC$

(c) $CH_3\,CH_2\,CH_2\,CN$

(d) $CH_3\,CH_2\,CH_2\,ON=O$

30. Some reactions of amines are given. Which one is not correct ? ***[NEET Kar. 2013]***

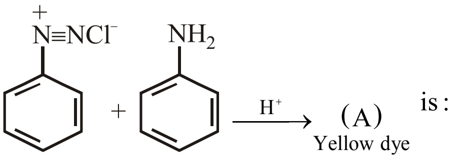
(a) $(CH_3)_2NH + NaNO_2 + HCl \rightarrow (CH_3)_2N-N=O$

(b) 

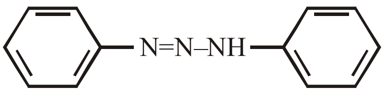
(c) $CH_3CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2OH + N_2$

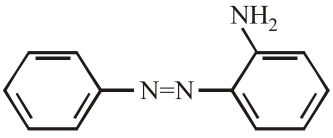
(d) $CH_3NH_2 + C_6H_5SO_2Cl \rightarrow CH_3NHSO_2C_6H_5.$

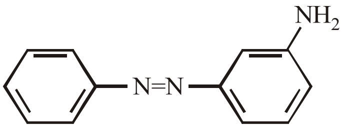
31. In the following reaction, the product (A) ***[2014]***

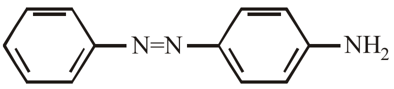


is :

(a) 

(b) 

(c) 

(d) 

32. Which of the following will be most stable diazonium salt $RN_2^+X^-$? ***[2014]***

(a) $CH_3\,N_2^+X^-$ (b) $C_6H_5N_2^+X^-$

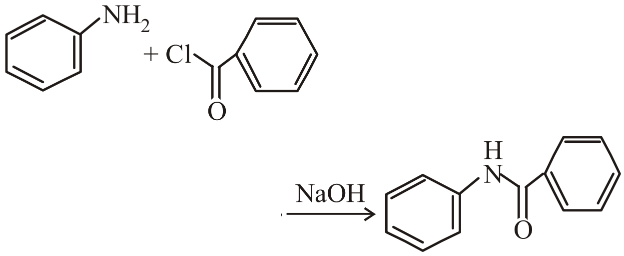
(c) $CH_3CH_2N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$

33. The electrolytic reduction of nitrobenzene in strongly acidic medium produces : ***[2015]***

(a) Azoxybenzene (b) Azobenzene

(c) Aniline (d) p-Aminophenol

34. The following reaction



is known by the name : ***[2015 RS]***

(a) Friedel-Craft's reaction

(b) Perkin's reaction

(c) Acetylation reaction

(d) Schotten-Baumen reaction

35. The number of structural isomers possible from the molecular formula C_3H_9N is: ***[2015 RS]***

(a) 4 (b) 5

(c) 2 (d) 3

36. Method by which Aniline cannot be prepared is: ***[2015 RS]***

(a) hydrolysis of phenylisocyanide with acidic solution

(b) degradation of benzamide with bromine in alkaline solution

(c) reduction of nitrobenzene with H_2/Pd in ethanol

(d) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

37. The correct statement regarding the basicity of arylamines is ***[2016]***

(a) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring π electron system.

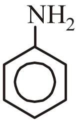
(b) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic ring π electron system.

(c) Arylamines are generally more basic than alkylamines because of aryl group.

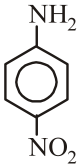
(d) Arylamines are generally more basic than alkylamines, because the nitrongen atom in arylamines is *sp*-hybridized.

38. The correct increasing order of basic strength for the following compounds is: ***[2017]***

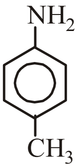
(I)



(II)



(III)



(a) III < I < II (b) III < II < I

(c) II < I < III (d) II < III < I

39. Which of the following reactions is appropriate for converting acetamide to methanamine ? ***[2017]***

(a) Hoffmann hypobromamide reaction

(b) Stephens reaction

(c) Gabriel phthalimide synthesis

(d) Carbylamine reaction

Hints & Solutions

EXERCISE - 1

1. (c) $\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Hydroxylamine}}{H_2NOH} \rightarrow \underset{\text{Acetaldoxime}}{CH_3CH = N - OH}$

$$\begin{tikzcd} CH_3CHO + H_2NOH \arrow[r] & CH_3CH = N - OH \arrow[d, "P_2O_5 \text{ (dehydrating agent)}", "-H_2O"'] \\ & \underset{\text{Methyl cyanide}}{CH_3 - CN} \end{tikzcd}$$

2. (b) Acetamide and ethylamine can be distinguished by heating with NaOH solution. Acetamide evolves NH_3 but ethylamine does not.

$$CH_3CONH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3$$

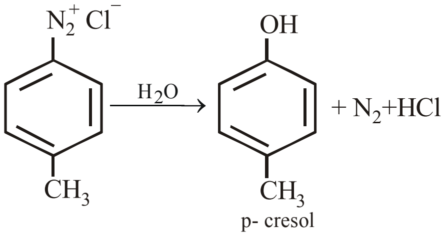
$$CH_3CH_2NH_2 + NaOH \longrightarrow \text{No reaction.}$$

3. (c) We know that

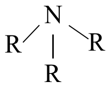
$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3CH_2NC + 3KCl + 3H_2O$$

In this reaction, bad smelling compound ethyl isocyanide (CH_3CH_2NC) is produced. This equation is known as **carbylamine reaction**.

4. (b)



5. (d)

1° amine	RNH_2
2° amine	RNHR
3° amine	

quaternary ammonium salt is R_4N^+.

6. (b) Wurtz reaction is for the preparation of hydrocarbons from alkyl halide

$$RX + 2Na + XR \longrightarrow R - R + 2NaX$$

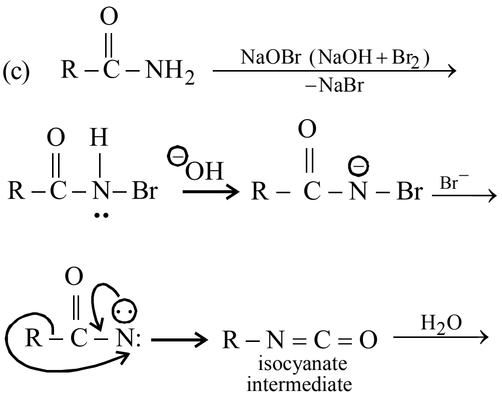
7. (d) $POCl_3$ is a dehydrating agent. Hence

$$C_6H_5CONH_2 \xrightarrow{POCl_3} C_6H_5CN + H_2O$$

8. (c) $$(CH_3)_2CO \xrightarrow{NH_2OH} (CH_3)_2CH = N - OH \xrightarrow{LiAlH_4} (CH_3)_2CHNH_2$$

$$(CH_3)_2CHOH \xrightarrow{PCl_5} (CH_3)_2CHCl \xrightarrow{NH_3} (CH_3)_2CHNH_2$$

9. (c)



$$RNH_2 + CO_2$$

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

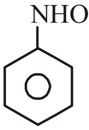
Overall reaction

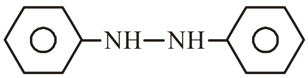
$$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + 2NaBr + Na_2CO_3 + H_2O$$

10. (c) Backmann rearrangement is used to form N-alkyl amide.

11. (d) Various products are formed when nitroarenes are reduced. These are given below for $C_6H_5NO_2$.

Medium	**Main product**
In acidic medium	Aniline $(C_6H_5NH_2)$ (metal/HCl)
In neutral medium	Phenyl hydroxylamine, (Zn/NH_4Cl)

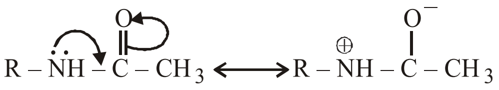


In alkaline medium 

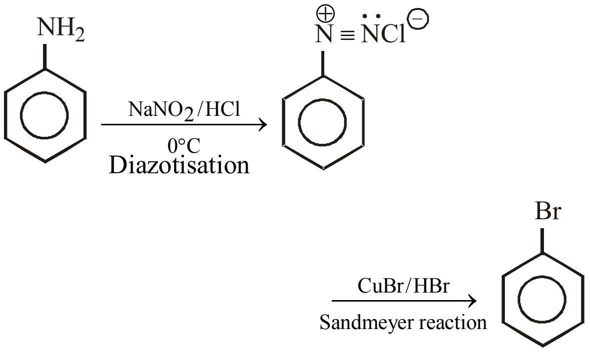
Hydrazobenzene

Thus, Aniline will be main product in case of (d).

12. (a) Acylation occurs in one step only because lone pair of nitrogen is delocalized with acyl group.



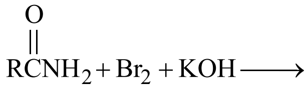
13. (a)



14. (d) $$CH_3-COONH_4 \xrightarrow{\Delta} \underset{(X)}{CH_3-CONH_2}$$

$$\xrightarrow{\Delta/P_2O_5} \underset{(Y)}{CH_3-CN} \xrightarrow{H_3O^{\oplus}} \underset{(Z)}{CH_3-COOH}$$

15. (d) (i)



$$R\overset{\overset{O}{\|}}{C}NH_2+Br_2+KOH \longrightarrow$$

$$RCONHBr+KBr+H_2O$$

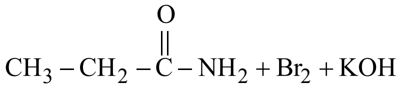
(ii) $RCONHBr+KOH \rightarrow RNCO+KBr+H_2O$

(iii) $RNCO+2KOH \rightarrow RNH_2+K_2CO_3$

$RCONH_2+Br_2+4KOH \rightarrow$

$RNH_2+2KBr+K_2CO_3+2H_2O$

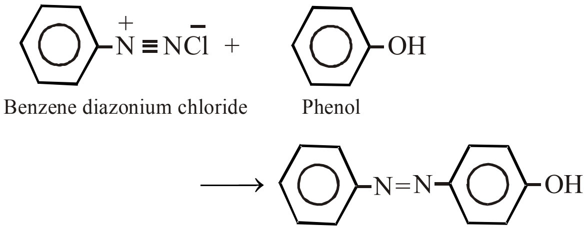
16. (b)



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2+Br_2+KOH$$

$$\xrightarrow{\Delta} CH_3-CH_2-\ddot{N}H_2$$

17. (b)



Benzene diazonium chloride

Phenol

p-Hydroxyazobenzene
(orange dye)

18. (a) The reason for the lesser basicity of aniline as compared to that of cyclohexylamine is +R effect of $-NH_2$ group (*i.e.*, electron releasing resonance effect of $-NH_2$ group).

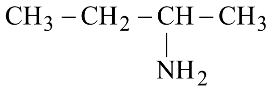
19. (b) $\underset{\text{Propanamide}}{CH_3CH_2CONH_2}+Br_2+4KOH \longrightarrow$

$\underset{\text{Ethylamine}}{CH_3CH_2NH_2}+2KBr+K_2CO_3+2H_2O$

This is Hofmann bromamide reaction in which amide is converted into amine having one carbon atom less than amide.

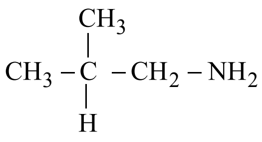
20. (c) 1° amines have $-NH_2$ group in their structure. 4 primary amines are possible by $C_4H_{11}N$.

$CH_3-CH_2-CH_2-CH_2NH_2$
(i)



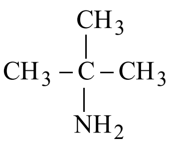
$$CH_3-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

(ii)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-NH_2$$

(iii)



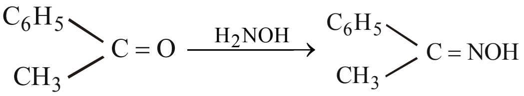
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{NH_2}{|}}{C}}-CH_3$$

(iv)

21. (a) Excess of HCl is used to convert free aniline to aniline hydrochloride otherwise free aniline would undergo coupling reaction with benzenediazonium chloride.

22. (d) *p*-Chloroaniline and anilinium hydrogen chloride can be distinguished by $AgNO_3$. Anilinium hydrogen chloride will give white ppt of AgCl on reaction with $AgNO_3$ but *p*-chloronoaniline will not react with it because Cl is directly attached to benzene nucleus.

23. (a)



Oxime

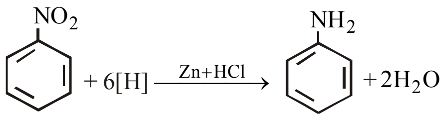
$$\xrightarrow[\text{(Beckmann rearrangement)}]{PCl_5} \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3}$$

24. (a) Secondary amines are more basic than tertiary amines due to stabilisation of 2° amine by hydrogen bonding with solvent molecule.

25. (b) $RNH_2 \xrightarrow{HNO_2} \underset{(A)}{ROH}+\underset{(B)}{H_2O}+\underset{(C)}{N_2}\uparrow$

26. (b) The given reaction is known as Sandmeyer's reaction.

27. (d) Aniline is formed

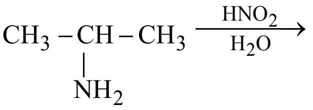


Aniline

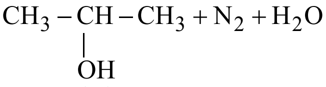
This is reduction in acidic medium.

28. (c) Since the organic amino compound on reaction with nitrous acid at low temperature produces an oily nitrosoamine so the organic amino compound is a secondary aliphatic amines.

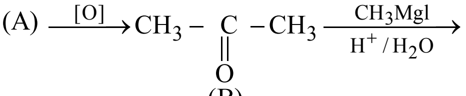
29. (a)



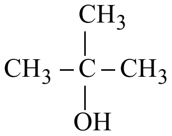
$$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3 \xrightarrow[H_2O]{HNO_2}$$



$$\underset{(A)}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}+N_2+H_2O$$



$$(A) \xrightarrow{[O]} \underset{(B)}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} \xrightarrow[H^+/H_2O]{CH_3MgI}$$



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

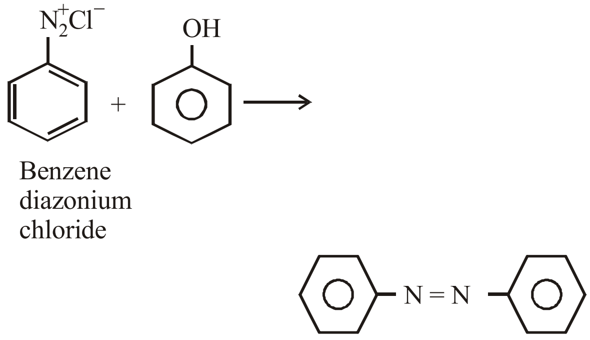
(C)
1,1-dimethyl
ethanol

30. (c) $CH_3COOH \xrightarrow[\text{Heat}]{NH_3} CH_3COONH_4$

$\xrightarrow[-H_2O]{P_2O_5} CH_3CONH_2 \xrightarrow[-H_2O]{P_2O_5} CH_3CN$

(Methyl cynide)

31. (a) Azo dye is prepared by diazo coupling reaction of phenol with diazonium salt.



p–hydroxyazobenzene

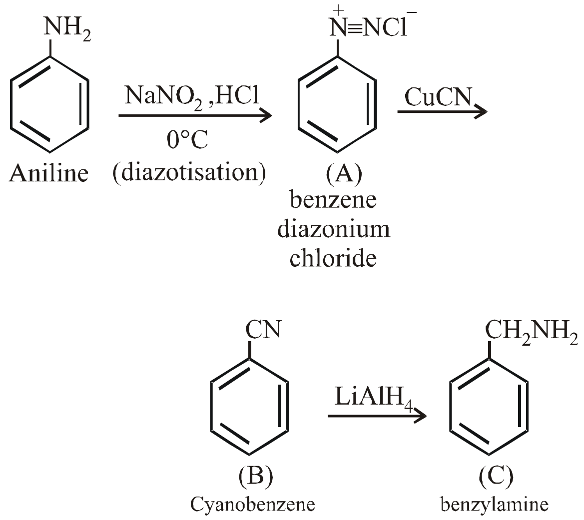
(– N = N –) group is called azo – group.

32. (d) The given reaction is known as Liebermann Nitroso reaction.

33. (d) Primary amines react with benzaldehyde in presence of a trace of an acid as catalyst to form Schiff's base or Anil

$$\underset{1°\text{amine}}{R-NH_2}+\underset{\text{benzaldehyde}}{O=CHC_6H_5}\xrightarrow{H^+}\underset{\text{Schiff's base or Anil}}{RN=CHC_6H_5}+H_3\overset{+}{O}$$

34. (d)



35. (c) Completing the given reaction we get

$$CH_3CONH_2\xrightarrow[\Delta]{P_2O_5}$$

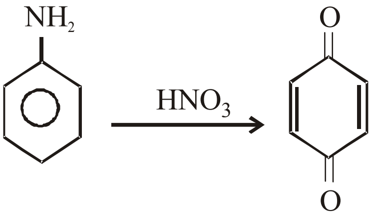
$$CH_3C\equiv N\xrightarrow{Sn/HCl}\underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

36. (c)

37. (b) $\underset{\text{Ethyl amine}}{C_2H_5NH_2}\xrightarrow{HNO_2}\underset{\text{Ethyl alcohol}}{C_2H_5OH}\xrightarrow{PCl_5}C_2H_5Cl\xrightarrow{NH_3}\underset{\text{Ethyl amine}}{C_2H_5NH_2}$

38. (a) In (b), (c) and (d) lone pair of nitrogen is linked with sp^2 hybridised carbon which is acidic in nature therefore it attracts the electron pair towards itself. In (a) lone pair of nitrogen is free because it is attached with carbon which is sp^3 hybridised. So it is most basic.

39. (c)



p-Benzoquinone

40. (a) $R_2NH > RNH_2 > R_3N > NH_3$.

41. (d)

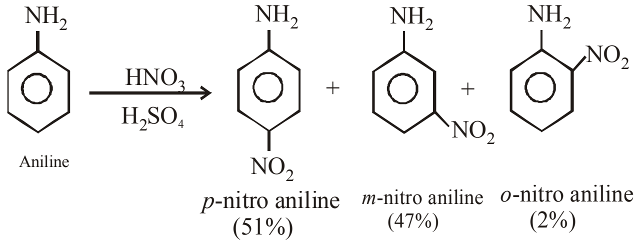
42. (a) The reaction is Hoffmann bromamide reaction

$$R-\overset{\overset{O}{\|}}{C}-NH_2+Br_2+4NaOH\longrightarrow R-NH_2+2NaBr+Na_2CO_3+2H_2O$$

$R-NH_2$ contains one carbon less than $R-\overset{\overset{O}{\|}}{C}-NH_2$

43. (b) $C_6H_5N_2Cl+H_3PO_2+H_2O\longrightarrow C_6H_6+N_2+HCl+H_3PO_3$

44. (d)



The reason for this is that, in acidic condition protonation of $-NH_2$ group gives anilinium ion ($\overset{+}{N}H_3$), which is of deactivating nature and of *m*-directing nature.

45. (b) Methyl cyanide on treatment with conc. HCl give acetamide.

$$\underset{\text{Acetonitrile}}{CH_3C\equiv N}\xrightarrow{\text{Conc.HCl}}\underset{\text{Acetamide}}{CH_3CONH_2}.$$

46. (d) The reaction is known as Hoffmann's mustard oil reaction.

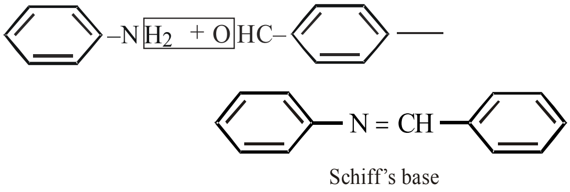
47. (d) $CH_3CN\xrightarrow{\text{Reduction}}CH_3-CH_2-NH_2\xrightarrow{HONO}CH_3-CH_2-OH+N_2+HO_2$

48. (d) Ethyl isocyanide on hydrolysis form primary amines.

$$CH_3CH_2N\overset{\rightarrow}{=}C+H_2O\xrightarrow{H^+}CH_3CH_2NH_2+HCOOH$$

49. (c) $$CH_3CH_2CN \xrightarrow{H^+/H_2O} CH_3CH_2COOH \xrightarrow[\Delta]{NH_3}$$
$$CH_3CH_2CONH_2 \xrightarrow[NaOBr]{\text{Hoffman bromide reaction}} CH_3CH_2NH_2$$

50. (b) Primary amines react with aldehydes or ketones to form compound known as Schiff's base



51. (c) $$\underset{sp}{CH_3—C\equiv N};\quad \underset{sp^3}{CH_3—\ddot{N}H_2}$$

52. (a) Among the given reagents, only $LiAlH_4$ is the reducing agent.

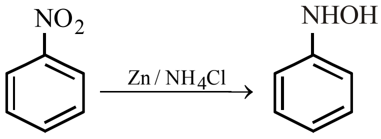
53. (a) Aryl halide (ArX) does not undergo nucleophilic substitution because they have strong C—X bond due to resonance.

54. (b) N-alkyl formamides when dehydrated with $POCl_3$ in presence of pyridine give isocyanides.

55. (b)

56. (b) Hydrolysis of phenyl isocyanide forms formic acid.

57. (d)



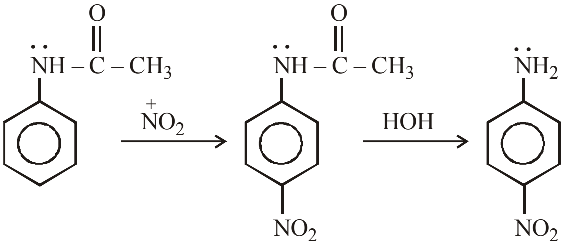
58. (c)

59. (a) It is Stephen's reaction.

$$CH_3CH_2C\equiv N \xrightarrow{SnCl_2/HCl} CH_3CH_2CH=NH.HCl$$
$$\xrightarrow{H_2O} CH_3CH_2CHO+NH_4Cl$$

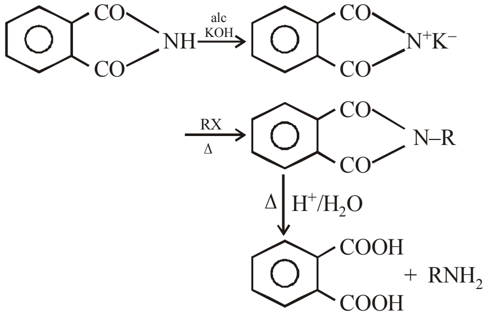
60. (b) Cold dil. NaOH does not attack to either of the compound, while cold dil. HCl reacts only with benzyl amine $C_6H_5CH_2NH_2$.

61. (b)



62. (d) The reaction involves the conversion of $–NO_2$ to $–NH_2$ group (reduction) which occurs in presence of Fe/HCl.

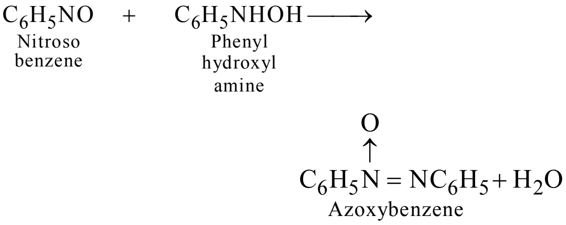
63. (a) Aniline cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with potassium phthalimide under ordinary conditions to give N-phenyl phthalimide (i.e., cleavage of C–X bond in haloarenes is quite difficult).



64. (a) Of the given compounds toluene which contains an electron donating group in the ring will be nitrated easily.

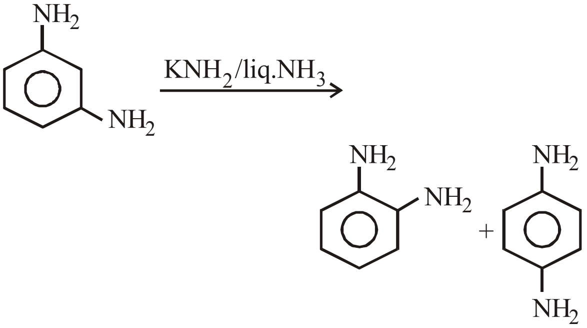
65. (c) When nitrobenzene is reduced in alkaline medium like Na_3AsO_3 / NaOH or glucose / NaOH, azoxybenzene is formed as the reduction product.

$$C_6H_5NO_2 \xrightarrow[-H_2O]{2H} C_6H_5NO \xrightarrow{2H} C_6H_5NHOH$$



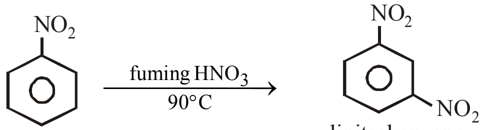
$$\underset{\text{Nitroso benzene}}{C_6H_5NO} + \underset{\text{Phenyl hydroxyl amine}}{C_6H_5NHOH} \longrightarrow \underset{\text{Azoxybenzene}}{C_6H_5\overset{\overset{O}{\uparrow}}{N}=NC_6H_5}+H_2O$$

66. (d)



It is an example of nucleophilic aromatic substitution. It procceds via the formation of an intermediate benzyne.

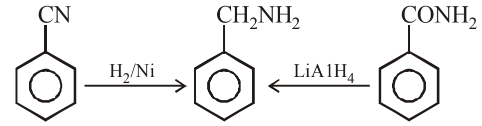
67. (a)



nitrobenzene *m*-dinitrobenzene

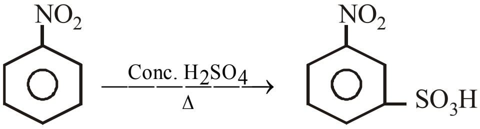
68. (c) $$C_6H_5NH_2 \xrightarrow[0^\circ C–5^\circ C]{NaNO_2/HCl} \underset{(X)}{C_6H_5N_2^+Cl^-} \xrightarrow[H_2O]{HNO_2} \underset{(Y)}{C_6H_5NO_2}+N_2+HCl$$

69. (b) Out of the given options, only benzyl amine can be obtained by both the methods.

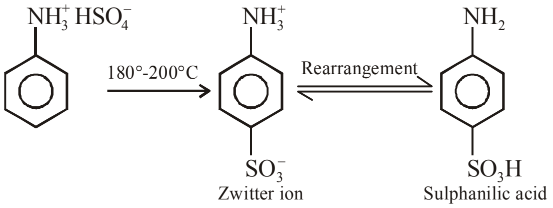


Benzene nitrile Benzyl amine Benzamide

70. (b)



71. (d)



72. (a) Reduction of alkyl isocyanides in presence of $LiAlH_4$ yields secondary amines containing methyl as one of the alkyl group.

$$R-N\equiv C+4[H]\xrightarrow{LiAlH_4}\underset{2°\text{amine}}{R-NH-CH_3}$$

e.g., $CH_3-N\equiv C+4[H]\xrightarrow{LiAlH_4}\underset{\text{dimethyl amine}}{CH_3-NH-CH_3}$

whereas, alkyl cyanides give 1° amine on reduction.

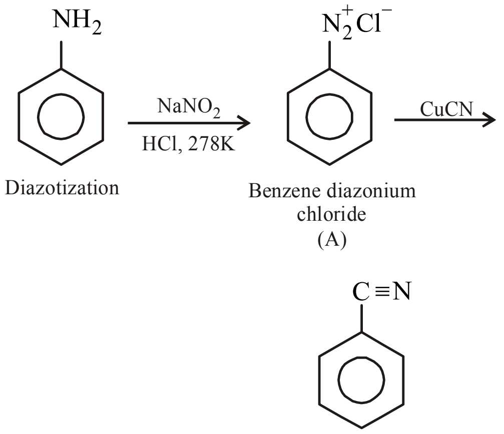
73. (b) $HONO_2+H_2SO_4\longrightarrow NO_2^++H_2O+HSO_4^-$

Nitric acid acts as a base by accepting a proton.

74. (a) $CH_3CONH_2\xrightarrow[Br_2]{NaOH}CH_3NH_2$

(Hofmann bromamide reaction)

75. (a)



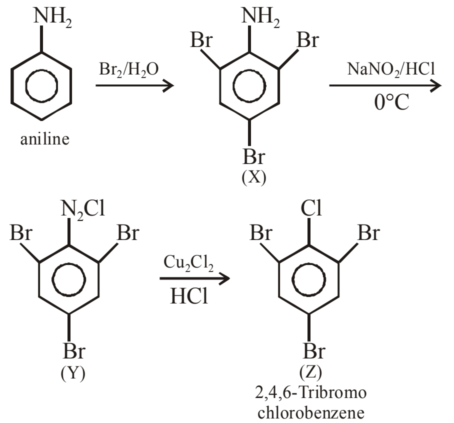
Diazotization

Benzene diazonium chloride
(A)

Benzonitrile
(B)
Sandmeyer reaction

EXERCISE - 2

1. (d)



2. (d) NH_3 is a weaker base than ethanamine.

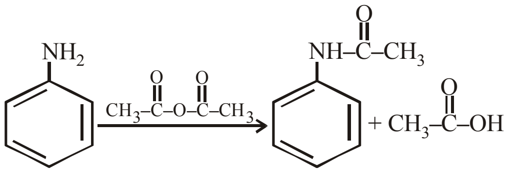
3. (c) Benzaldehyde reacts with primary aromatic amine to form schiff's base

$$\underset{\text{Benzaldehyde}}{C_6H_5CH=O}+\underset{\text{Aniline}}{C_6H_5NH_2}\longrightarrow$$

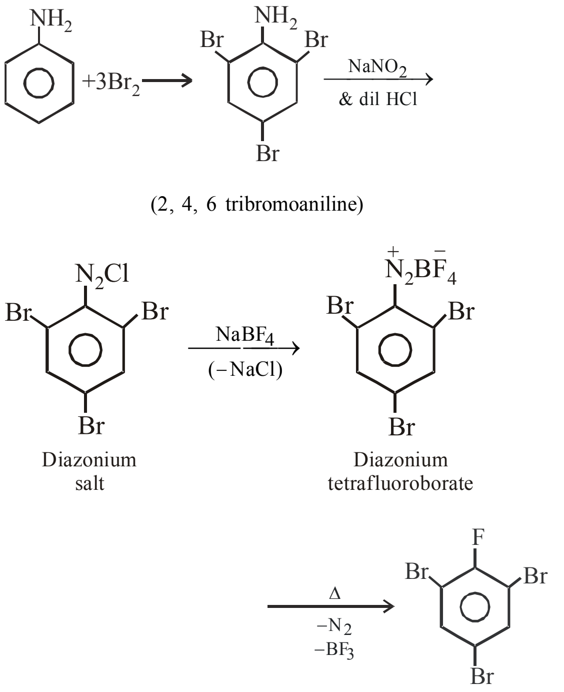
$$\underset{\text{Benzylidene aniline}}{C_6H_5CH=NC_6H_5}+H_2O$$

This is know as Schiff's base reaction.

4. (d) Aniline when treated with acetic anhydride forms acetanilide.



5. (d)



2,4,6 tribromofluorobenzene

6. (b) Reduction reactions of given amines are following

$$\underset{\text{Ethanamide}}{CH_3CONH_2}\xrightarrow{LiAlH_4}\underset{\text{ethanamine (1° amine)}}{CH_3CH_2NH_2}$$

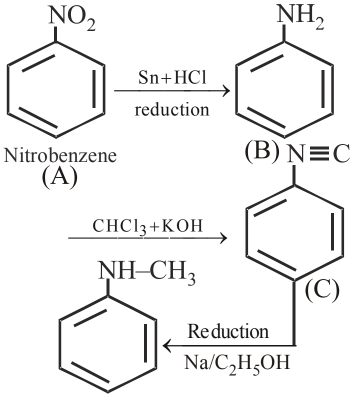
$$\underset{\text{N,N−dimethyl ethanamide}}{CH_3CON(CH_3)_2}\xrightarrow{LiAlH_4}\underset{\substack{\text{N,N−dimethylethanamine}\\ \text{(3°amine)}}}{CH_3CH_2N(CH_3)_2}$$

$$\underset{\text{Phenylmethanamide}}{C_6H_5CONH_2}\xrightarrow{LiAlH_4}\underset{\text{phenylmethanamine (1° amine)}}{C_6H_5CH_2NH_2}$$

$$\underset{\text{N−methylethanamide}}{CH_3CONH-CH_3}\xrightarrow{LiAlH_4}\underset{\text{N−methylethanamine (2° amine)}}{CH_3CH_2NHCH_3}$$

Thus N-methyl ethanamide gives 2° amine on reduction.

7. (c)



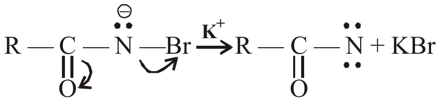
N-methylaniline

8. (c) The mecahnism of Hoffmann bromide reaction is

(i) $RCONH_2 + Br_2 \rightarrow RCONHBr + HBr$

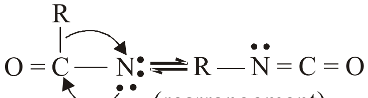
(ii) $RCONHBr + HBr \xrightarrow{OH^-} R-CO\overset{\ominus}{\ddot{N}}Br + H_2O$

(iii)



$$R-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{\ddot{N}}-Br \xrightarrow{K^+} R-\underset{\underset{O}{\|}}{C}-\ddot{N} + KBr$$

(iv)

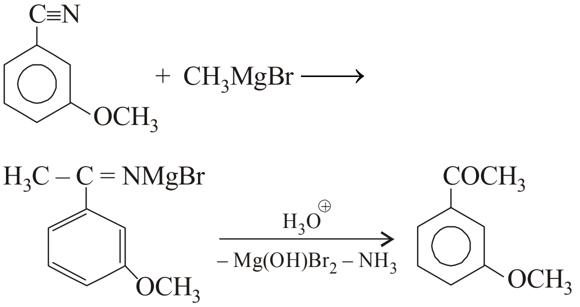


$$O=\overset{\overset{R}{|}}{C}-\ddot{N}: \rightleftharpoons R-\ddot{N}=C=O$$

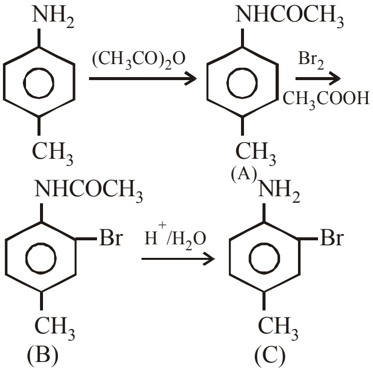
(rearrangement)

(v) $R-\ddot{N}=C=O + 2KOH \rightarrow RNH_2 + K_2CO_3$

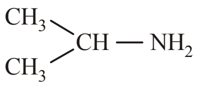
9. (b)



10. (d)

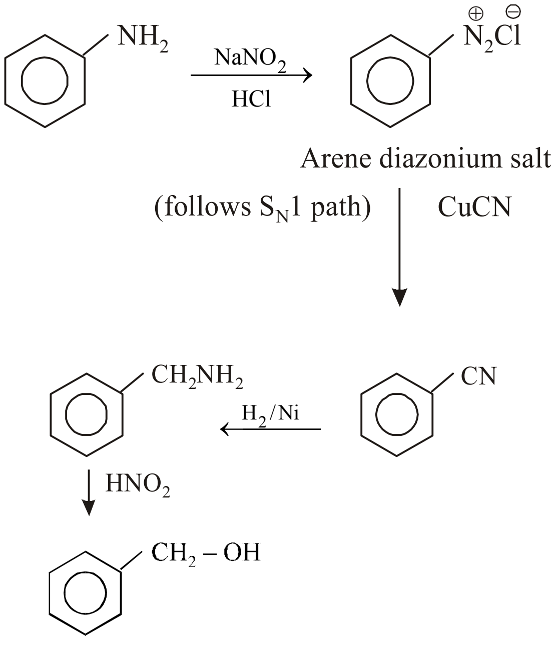


11. (d) Isopropylamine is a primary amine.



1°amine

12. (d)

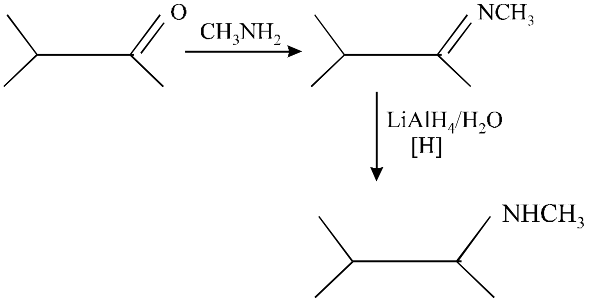


Benzyl alcohol

13. (a) $\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Ethanamide}}{\underset{(A)}{CH_3CONH_2}}$

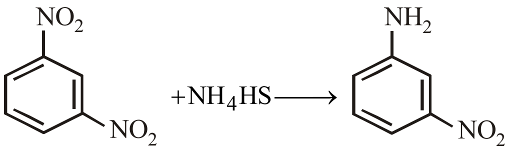
$$\xrightarrow{Br_2/NaOH} \underset{\text{Methanamine}}{\underset{(B)}{CH_3NH_2}} \xrightarrow{NaNO_2/dil.HCl} \underset{\text{Methanol}}{\underset{(C)}{CH_3OH}}$$

14. (b)

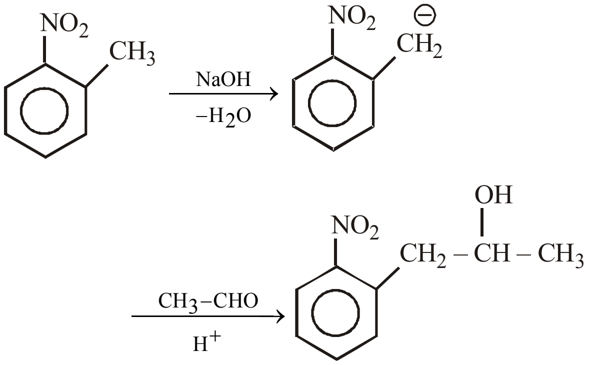


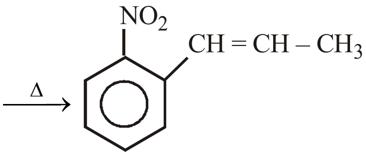
15. (d) Weak base has high pk_b value. Benzenamine (aniline) is the weakest base among the given amines. Therefore it has highest pk_b value.

16. (c)

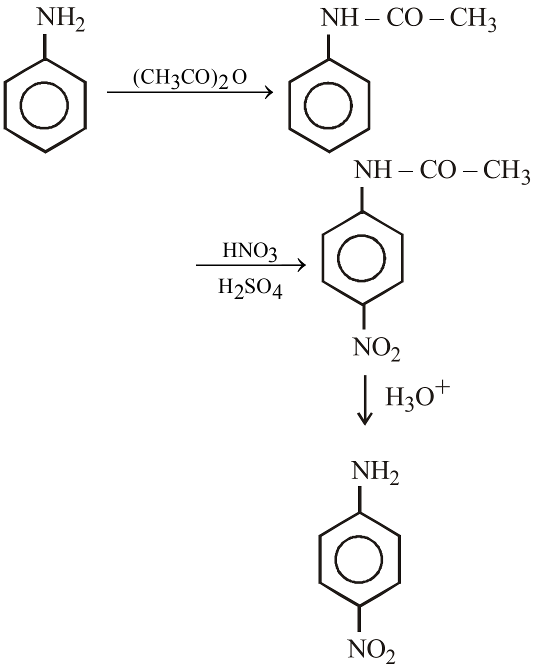


17. (a)

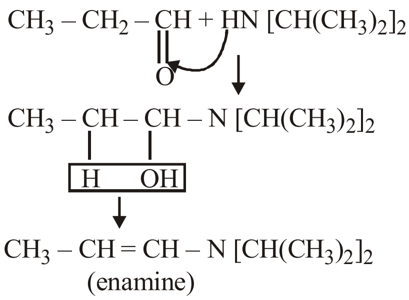




18. (b)

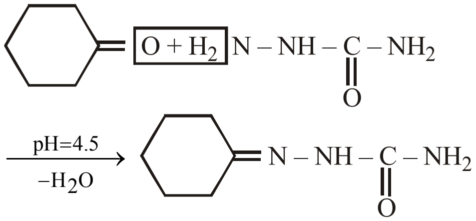


19. (a)

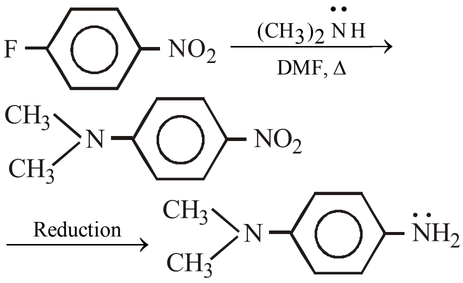


20. (b)

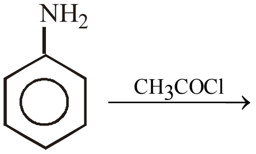
21. (b)

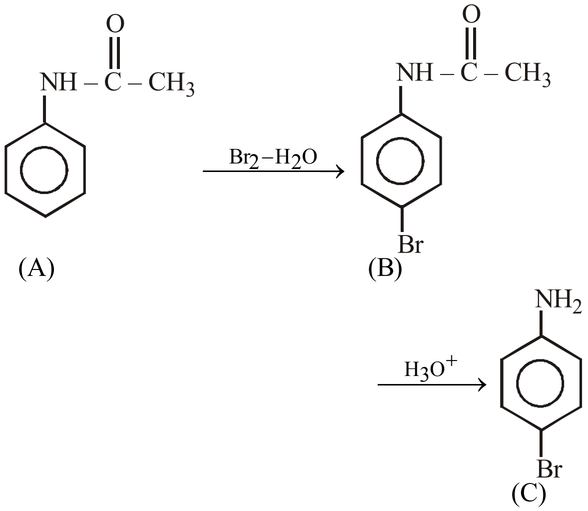


22. (a)

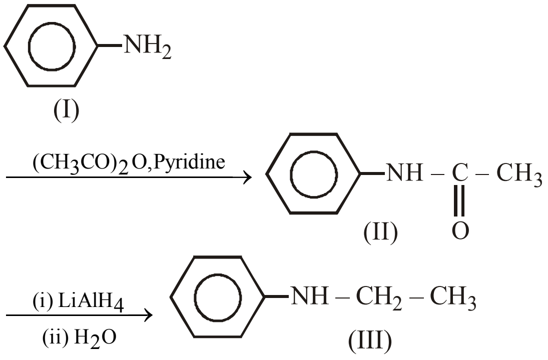


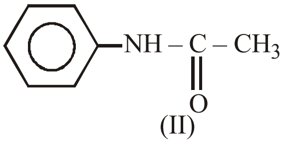
23. (c)

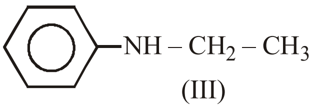




24. (a)



Product (II) is  and (III) is



∴ III > I > II, As + I effect increases the basic strength and – R, – I effect shown by $-COCH_3$ reduces the basic strength.

25. (c) Enamine (ene for carbon-carbon double bond and amine for amine group). $>C=C-N<$

26. (b) In (b) the lone pair of electrons on N is not in conjugation with benzene ring, hence it is not involved in resonance causing the compound to be most basic.

27. (b) $H_2C = N^+ = N^- \; > \; H_2C^- - N^+ \equiv N$

I
Octet complete,
6 covalent bond,
–ve charge on N

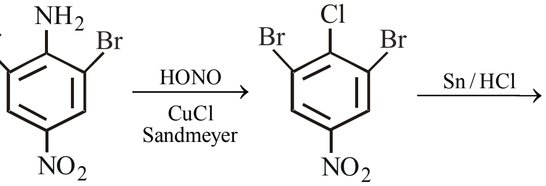
III
Octet complete,
6 covalent bond,
–ve charge on C

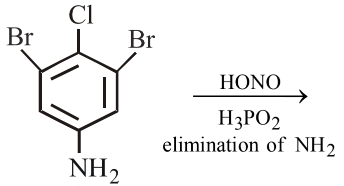
$> H_2C^+ - N = N^- > H_2C^- - N = N^+$

II
Octet incomplete,
5 covalent bond,
–ve charge on N

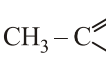
IV
Octet incomplete,
5 covalent bond,
–ve charge on C

28. (c)

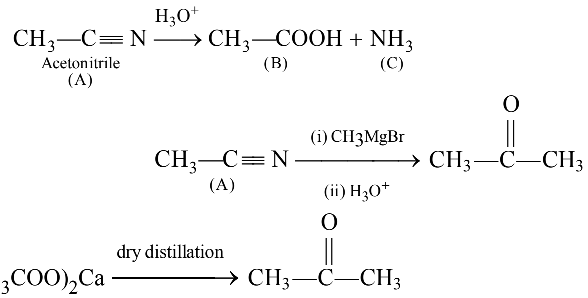




29. (c) N can't have more than 8 electrons in its valence shell as it does not have any *d* orbital. In (c), N has 10 electrons.

30. (d)  $CH_3-C\overset{NH}{\underset{NH_2}{\lessgtr}}$ is most basic

$(CH_3)_2NH$ is less basic than $CH_3CH_2NH_2$ due to steric hindrance because of two bulky $-CH_3$ groups on nitrogen atom.

31. (c) 

$$\underset{\substack{\text{Acetonitrile}\\(A)}}{CH_3-C\equiv N} \xrightarrow{H_3O^+} \underset{(B)}{CH_3-COOH} + \underset{(C)}{NH_3}$$

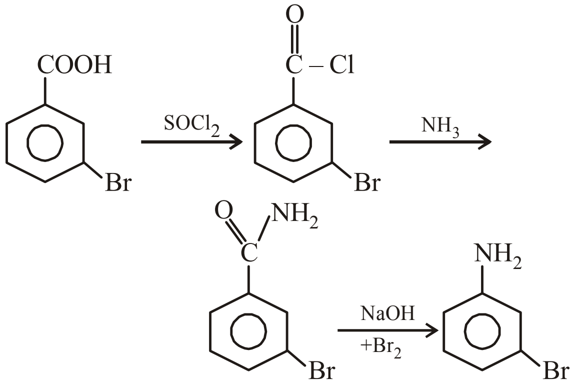
$$\underset{(A)}{CH_3-C\equiv N} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

$$(CH_3COO)_2Ca \xrightarrow{\text{dry distillation}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

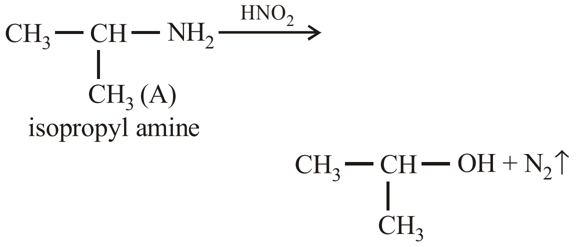
From above reaction sequence, Acetonitrile is the given organic compounds.

32. (d) (1) $CH_3\,CH_2-CH_2-CH_2-NH_2$
   (ii) with KOH (alcohol) and $CHCl_3$ produces bad smell
(2) $CH_3C\equiv CH$
   (ii) gives white ppt with ammonical $AgNO_3$
(3) $CH_3\,CH_2\,COOCH_3$
   (i) alkaline hydrolysis
(4) $CH_3\,CHOH-CH_3$
   (iv) with Lucas reagent cloudiness appears after 5 minutes

33. (c)



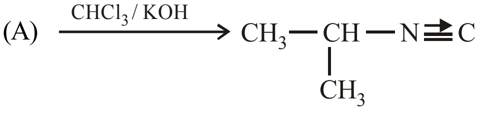
34. (a)



$$\underset{\underset{CH_3\ (A)}{|}}{CH_3-CH}-NH_2 \xrightarrow{HNO_2} \underset{\underset{CH_3}{|}}{CH_3-CH}-OH + N_2\uparrow$$

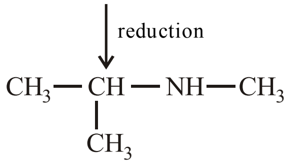
isopropyl amine

isopropyl alcohol



$$(A) \xrightarrow{CHCl_3/KOH} \underset{\underset{CH_3}{|}}{CH_3-CH}-N\equiv C$$

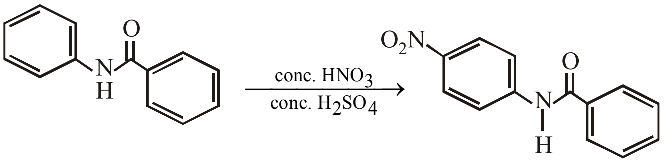
isopropyl isocyanide



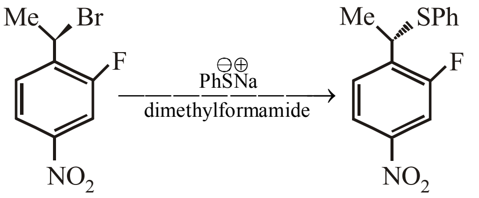
$$\xrightarrow{\text{reduction}} \underset{\underset{CH_3}{|}}{CH_3-CH}-NH-CH_3$$

Isopropyl methyl amine

35. (b) The benzene ring which is directly attached with nitrogen atom of acidamide group is more activated than the other, so nitration will take place at para position of this activated ring.



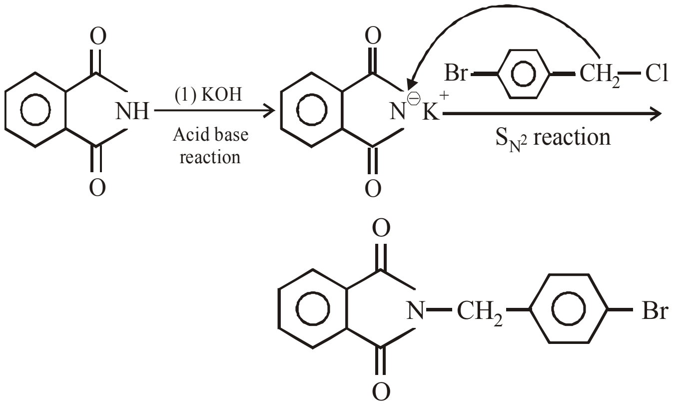
36. (a)



S_N2 Mechanism ∴ Inversion takes place

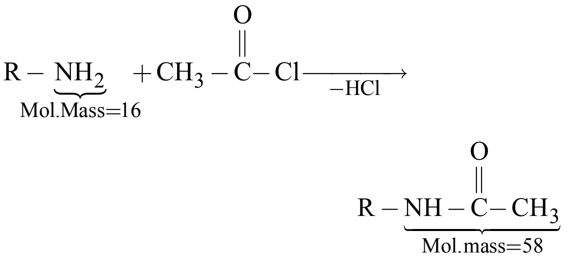
37. (c) Only primary aromatic amines undergo diazotisation followed by coupling.

38. (a)



Due to resonance C – Br bond shows partial double bond character. Therefore nucleophile does not replace Br in above reaction.

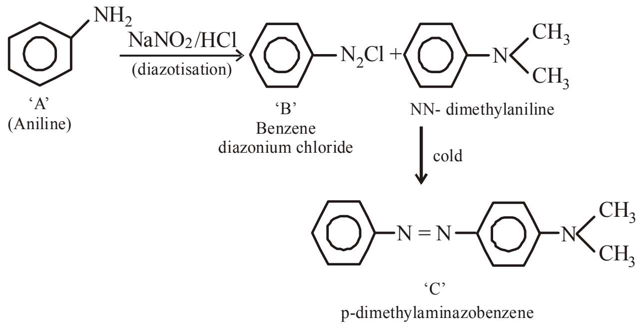
39. (b)



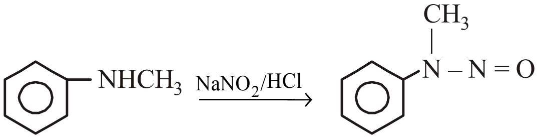
$$R-\underbrace{NH_2}_{\text{Mol.Mass}=16} + CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[-HCl]{} \underbrace{R-NH-\overset{\overset{O}{\|}}{C}-CH_3}_{\text{Mol.mass}=58}$$

Now since the molecular mass increases by 42 unit as a result of the reaction of one mole of CH_3COCl with one-NH_2 group and the given increase in mass is 210. Hence the number of $-NH_2$ groups is $= 210/42 = 5$.

40. (d) The reaction can be completed as follows:



41. (d) Secondary amine with ($NaNO_2$ + HCl) gives a nitroso product



N– Nitroso – N– methylaniline

42. (a) When nitro compound is reduced with a neutral reducing agent (Zn dust + NH_4Cl) the corresponding hydroxyl amine is formed

$$\underset{}{C_6H_5NO_2 + 4[H]} \xrightarrow{\text{Zn dust}+NH_4Cl} \underset{\text{Phenyl hydroxylamine}}{C_6H_5NHOH}$$

43. (c) Primary aromatic amines react with nitrous acid to yield arene diazonium salts.

$$\underset{1^\circ\text{ Aromatic amine}}{ArNH_2} + NaNO_2 + 2HX \xrightarrow{\text{cold}} \underset{\text{Arene diazonium salt}}{Ar{-}N{=}N^+X^-} + NaX + 2H_2O$$

The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF_4). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as Balz-Schiemann reaction.

$$Ar{-}N_2^+X^- \xrightarrow{HBF_4} Ar{-}N_2^+BF_4^-\downarrow \xrightarrow{\text{heat}} Ar{-}F + BF_3 + N_2$$

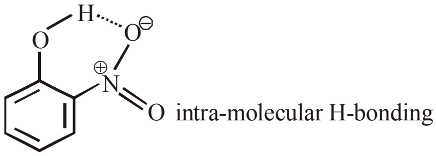
44. (d) Aromatic amines are less basic than aliphatic amines. Among aliphatic amines the order of basicity is 2° > 1° > 3°. The electron density is decreased in 3° amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases. Further Phenyl group show – I effect, thus decreases the electron density on nitrogen atom and hence the basicity.

∴ dimethylamine (2° aliphatic amine) is strongest base among given choices.

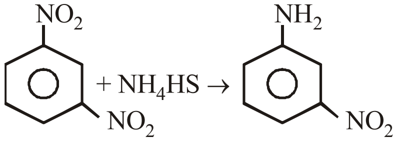
∴ The correct order of basic strength is Dimethylamine > Methyl amine > Trimethyl amine > Aniline.

45. (c) Aryl amines do not produce phenol on treatment with nitrous acid

46. (b) *o*-nitrophenol shows intramolecular H-bonding and forms chelate. Compounds involved in chelation become non-polar. Consequently such compounds are soluble in non-polar solvents like ether, benzene etc. and are only sparingly soluble in water whereas meta and para isomers are more soluble in water & less soluble in non-polar solvents.



47. (b)



48. (a) Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.

49. (a) $HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3O^+$

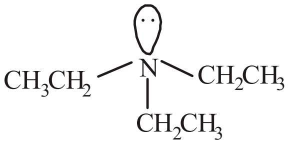
50. (b) Nucleophilic species which have more than one site of reaction are called ambident nucleophiles.

$$:\bar{C} = N: \leftrightarrow :C = \bar{N}:$$

EXERCISE - 3

Exemplar Questions

1. (b) 3° amine is the amine in which nitrogen is attached to three alkyl groups whether they are same or different.

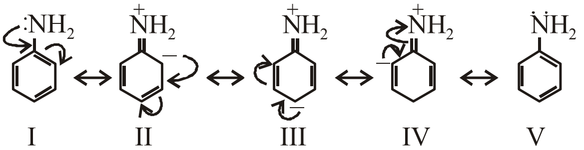


Triethylamine
(3° amine)

2. (d) IUPAC name of $\overset{3}{C}H_2 = \overset{2}{C}H\overset{1}{C}H_2NHCH_3$ is N-methylprop-2-en-1-amine.

3. (c) More the hydrogen bonding more will be the basicity in gaseous phase but in aqueous solution solvation effect also play the role. By combining both the effects order of basicity in aqueous medium is 2° > 3° > 1° > NH_3. The inductive effect comes to play when order of amines is same as in case of (c) & (d) where both the amines are secondary. +I group increase the basicity and –I group will decrease the basicity of amines.

4. (a) In aniline, lone pair of nitrogen is not available for donation to the acid as it is involved in the resonance. Thus, it will act as the weakest Bronsted base amongst the given compounds.

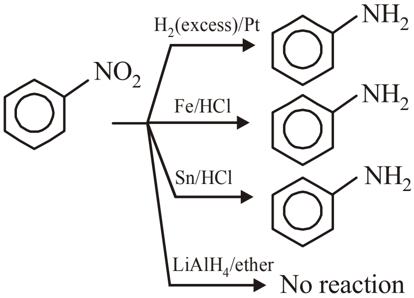


5. (c) S_N1 reaction involves the formation of carbocation, so, more stable carbocation will have higher reactivity towards S_N1 mechanism.

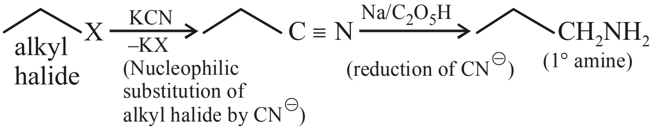
$$C_6H_5CH_2Br \longrightarrow C_6H_5-\overset{\oplus}{C}H_2 + Br^{\ominus}$$

As $C_6H_5\overset{\oplus}{C}H_2$ is the most stabilised carbocation due to resonance, hence it will be most reactive towards S_N1 mechanism.

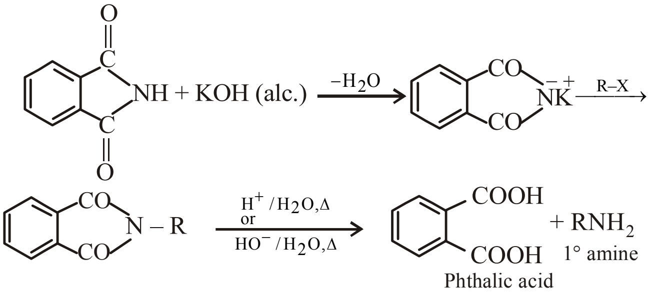
6. (b)



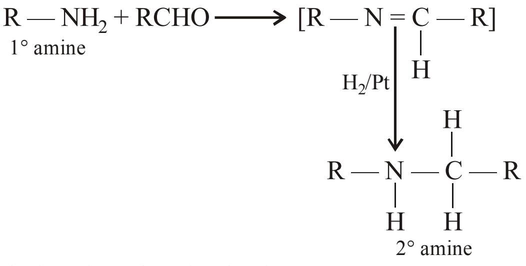
7. (c) 1° amine with increased $-CH_2$ group can be achieved by following the given steps:



8. (d) Potassium phthalimide is the source of nitrogen in Gabriel phthalimide synthesis.

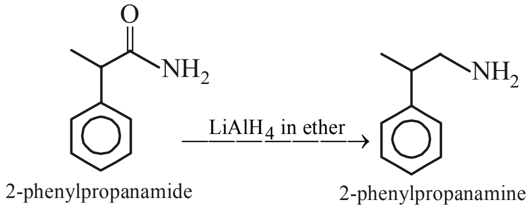


9. (c) Reaction can be represented as

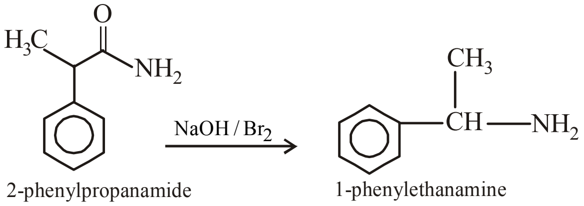


$$\underset{1^\circ\text{ amine}}{R-NH_2} + RCHO \longrightarrow [R-N=\underset{H}{\underset{|}{C}}-R] \xrightarrow{H_2/Pt} \underset{2^\circ\text{ amine}}{R-\underset{H}{\underset{|}{N}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-R}$$

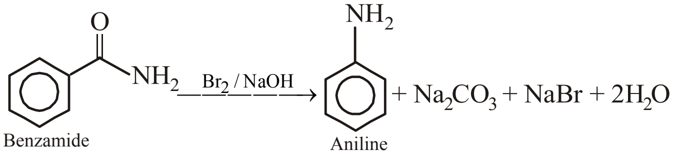
10. (d) $LiAlH_4$ in ether is the best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine because $LiAlH_4$ will reduce carbonyl group but does not reduce benzene ring.



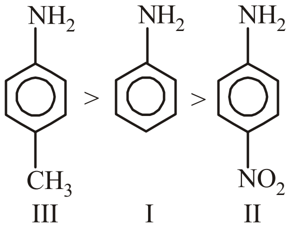
11. (b) Hoffmann bromamide reaction.



12. (b) Hoffmann bromamide degradation reaction:

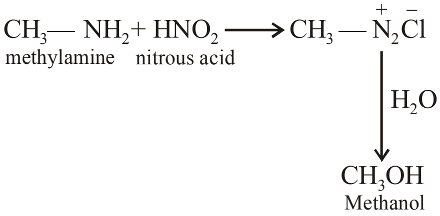


13. (d)



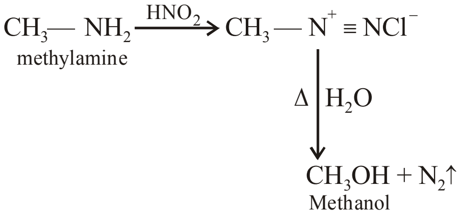
Higher the electron density towards ring, higher will be its basic strength. Electron donating group increases the basic strength while electron withdrawing group decreases the basic strength.

14. (c)



$$\underset{\text{methylamine}}{CH_3-NH_2} + \underset{\text{nitrous acid}}{HNO_2} \longrightarrow CH_3-\overset{+}{N}_2\overset{-}{Cl} \xrightarrow{H_2O} \underset{\text{Methanol}}{CH_3OH}$$

15. (b)

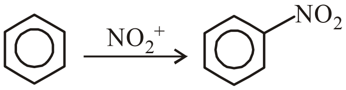


$$\underset{\text{methylamine}}{CH_3-NH_2} \xrightarrow{HNO_2} CH_3-\overset{+}{N} \equiv NCl^- \xrightarrow[\Delta]{H_2O} \underset{\text{Methanol}}{CH_3OH + N_2\uparrow}$$

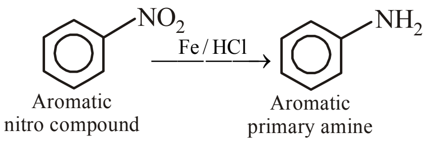
16. (c) For the nitration of benzene, $NO_2^{\oplus}$ acts as an electrophile (electrophilic substitution reaction).

Step 1: $H_2SO_4 \longrightarrow H^+ + HSO_4^-$

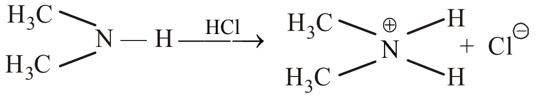
Step 2: $H^+ + H-\ddot{O}-NO_2 \rightleftharpoons H_2O + \underset{\text{nitronium ion}}{\overset{+}{N}O_2}$



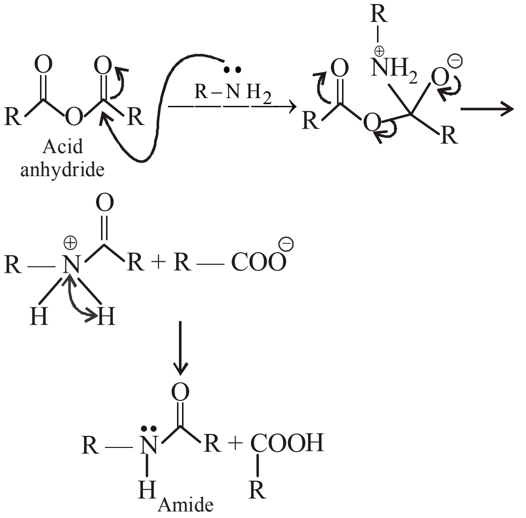
17. (c) Reduction of aromatic nitro compounds gives aromatic 1° amine.



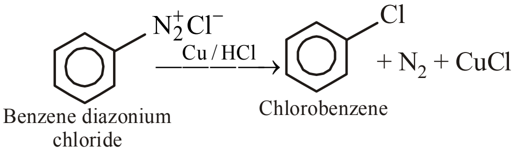
18. (b) Reactivity of a base towards dilute HCl is directly proportional to the strength of the base.
Thus, as $(CH_3)_2NH$ has the highest basic strength, so it will have highest reactivity.



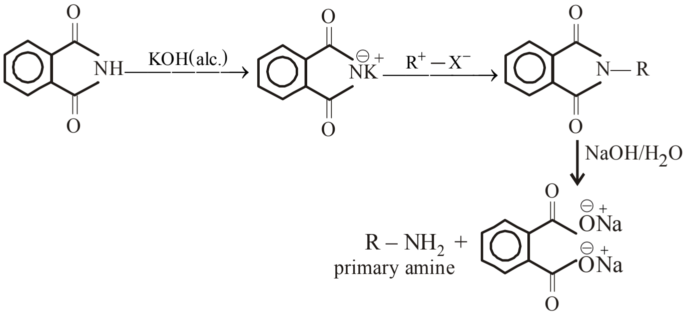
19. (a)



20. (b) Gattermann reaction:



21. (b) Gabriel phthalimide synthesis is the best method of preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain.

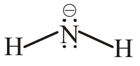


22. (d) Diazonium cation is a weak E^+ so it will not react with compound containing electron withdrawing group. Also, NO_2 group is an electron withdrawing group thus, nitrobenzene will not undergo azo coupling reaction with benzene diazonium chloride.

23. (c) Phenol has the least tendency to accept a proton and also exhibit acidic character due to polar O – H bond hence, it is a weak Bronsted base.

24. (d) Pyrrolidine will be the strongest base as the lone pair on nitrogen are not involved in resonance and are easily available for the donation. So, basic strength becomes high.

25. (a)



Most basic

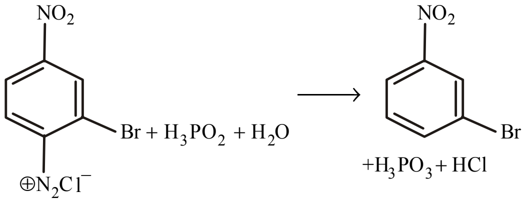
Amide ion is the most basic among the given species due to the presence of negative charge and two lone pairs of electron on nitrogen atom. The species which are having lone pair of electrons are more basic than neutral species. So, NH_3 and H_2O are less basic than NH_2^- and OH^-. Also, nitrogen is less electronegative than oxygen hence it can easily donate e^-s.

∴ The correct order of basic strength will be:
$NH_2^- > OH^- > NH_3 > H_2O$

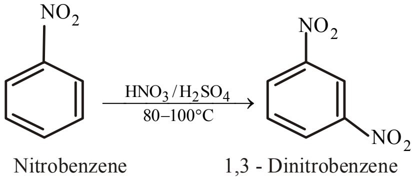
26. (b) On comparison to amines, hydrocarbons have lower boiling point, hence they are more volatile whereas amines are having higher boiling point due to H-bonding.

NEET/AIPMT (2013-2017) Questions

27. (b)



28. (a)

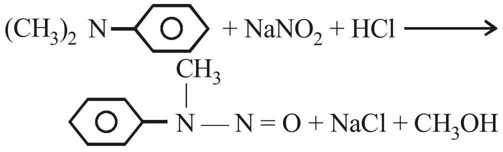


29. (b) Hydrolysis of propyl isocyanide $(CH_3CH_2CH_2NH_2)$ gives $CH_3CH_2CH_2NH_2 + HCOOH$.
On treatment with $NaNO_2$ and HCl I gives $CH_3CH_2CH_2OH$ which does not give iodoform test. II (HCOOH) reduces Tollen's reagent and Fehling's solution.

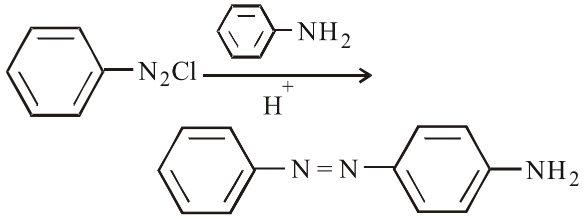
$$\underset{\text{Propyl isocyanide}}{CH_3CH_2CH_2NC} \xrightarrow{H_2O}$$

$$CH_3CH_2CH_2NH_2 + \underset{\text{II}}{HCOOH}$$

30. (b) Secondary amine react with nitrous acid to give N-Nitrosoamines.

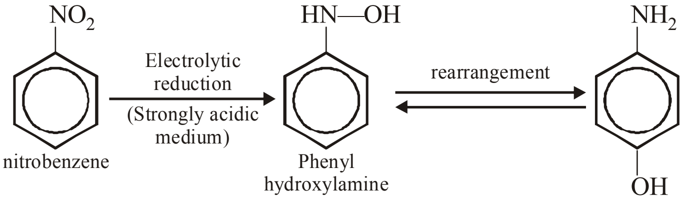


31. (d)

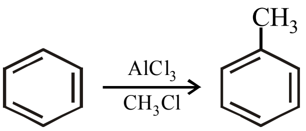


32. (b) Arene diazonium salts are most stable among the given options because of the dispersal of +ve charge on the benzene ring due to resonance.

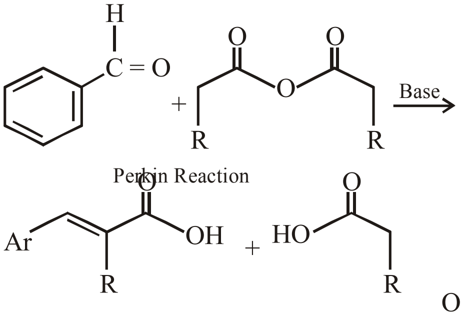
33. (d)



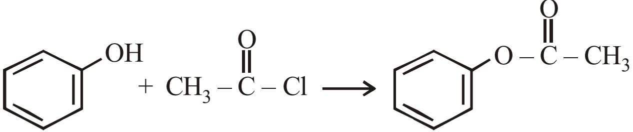
34. (d)



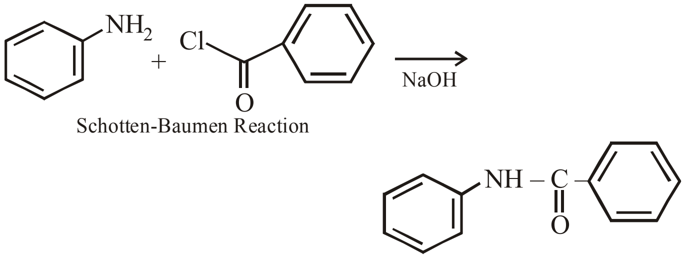
(Friedel Craft's Reaction)



Perkin Reaction



Acetylation Reaction

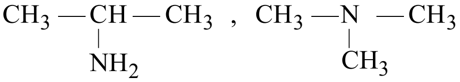


Schotten-Baumen Reaction

35. (a) C_3H_9N

$CH_3—CH_2—CH_2—NH_2$

$CH_3 – NH – CH_2 – CH_3$.



$$\underset{\displaystyle NH_2}{CH_3 — \overset{}{CH} — CH_3}\ ,\quad CH_3 — \underset{\displaystyle CH_3}{N} — CH_3$$

36. (d) Because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide easily.

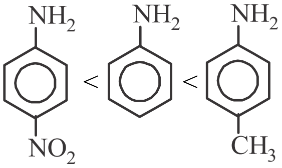
37. (a) Arylamines are generally less basic than alkylamines due to following factors

(a) Due to resonance in aromatic amines.

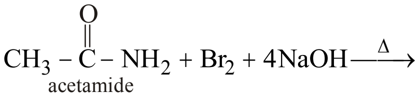
(b) Lower stability of anilinium ion

38. (c) – NO_2 group has strong – R effect and –CH_3 shows +R effect.

∴ Order of basic strength is



39. (a)



$$\underset{\text{acetamide}}{CH_3 – \overset{\displaystyle O}{\overset{\|}{C}} – NH_2} + Br_2 + 4NaOH \xrightarrow{\Delta}$$

$$\underset{\text{methanamine}}{CH_3 – NH_2} + 2NaBr + Na_2CO_3 + 3H_2O$$

It is called Hoffmann Bromamide reaction.