13

Amines

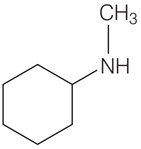
Multiple Choice Questions (MCQs)

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

(a) 1-methylcyclohexylamine
(b) Triethylamine
(c) *tert*-butylamine
(d) N-methylaniline

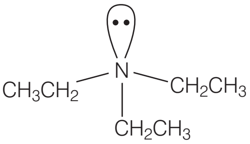
Ans. ***(b)*** The structure of given amines are as follows

(a)



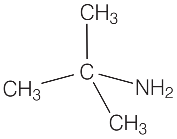
1-methyl cyclohexylamine
(2° amine)

(b)



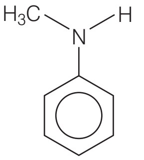
Ttriethylamine
(3° amine)

(c)



tert butylamine
(1° amine)

(d)



N- methyl aniline

Hence, triethylamine is tertiary amine. The correct choice is (b).

Q. 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

Ans. ***(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
Hence, option (d) is correct.

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

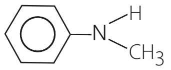
(a) CH_3NH_2 (b) $NCCH_2NH_2$

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

Thinking Process

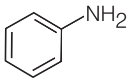
This problem is based on concept of basic strength of various types of amine depending upon inductive effect, resonance and solvation.

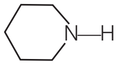
Ans. *(c)*

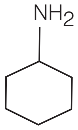
	Compound	Factors responsible for basic character are
(a)	$CH_3 - NH_2$	Inductive effect (+ I)
(b)	$NC - CH_2 - NH_2$	Inductive effect (– I)
(c)	$(CH_3)_2NH$	Inductive effect (+ I) and Solvation
(d)		– I effect and resonance

Since, + I effect and solvation increases basic character while –I effect and resonance decreases basic character. Hence, correct choice is (c).

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

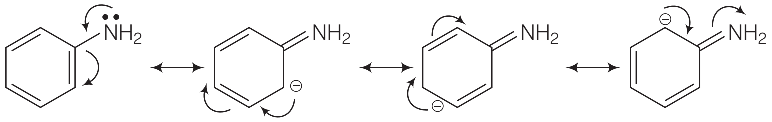
(a) 

(b) 

(c) 

(d) CH_3NH_2

Ans. *(a)* Aniline is weakest Bronsted base among the given four compounds due to resonance present in case of aniline.



Resonating structure of aniline

Hence, lone pair of nitrogen are less available for donation to the acid.

Q. 5 Benzylamine may be 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

Ans. *(c)* S_N1 reaction proceeds through formation of carbocation. Hence, more stable be the carbocation more reactivity towards S_N1 mechanism.

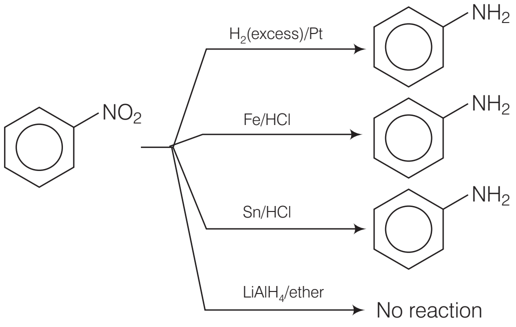
	Alkyl halides		**Intermediate**
(a)	CH_3Br	$\longrightarrow$	$CH_3^{\oplus}$
(b)	C_6H_5Br	$\longrightarrow$	$C_6H_5^{\oplus}$
(c)	$C_6H_5CH_2Br$	$\longrightarrow$	$C_6H_5 — CH_2^{\oplus}$ (more stable)
(d)	C_2H_5Br	$\longrightarrow$	$C_2H_5^{\oplus}$

Hence, the reaction will proceed through S_N1 mechanism when, $C_6H_5CH_2Br$ is the substrate. because on ionisation it gives a resonance stabilised carbocation ($C_6 H_5 CH_2$).

Q. 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

Ans. *(b)* Aryl nitro compound can't be converted into amine using $LiAlH_4$ in ether.

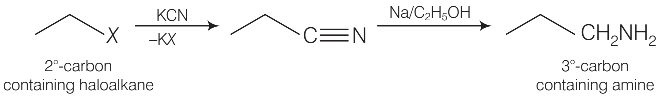


Hence, option (b) is the correct choice.

Q. 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 source of nitrogen is ....

(a) sodium amide, $NaNH_2$
(b) sodium azide, NaN_3
(c) potassium cyanide, KCN
(d) potassium phthalimide $C_6H_4(CO)_2N^-K^+$

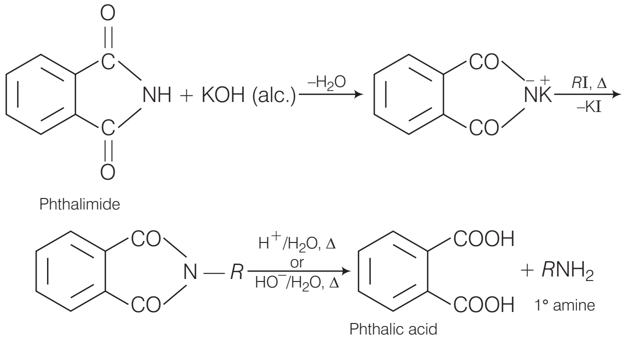
Ans. *(c)* In order to prepare 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain. The reagent used as a source of nitrogen is KCN. Chemical transformation can be shown as



Q. 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 $C_6H_4(CO_2)N^-K^+$

Ans. *(d)* Source of nitrogen in Gabriel phthalimide synthesis is potassium phthalimide.



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

(a) $2^\circ R-\text{Br} + NH_3$

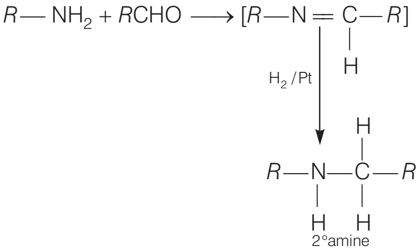
(b) $2^\circ R-\text{Br} + \text{NaCN}$ followed by H_2/Pt

(c) $1^\circ R-NH_2 + R\text{CHO}$ followed by H_2/Pt

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

Ans. *(c)*

Chemical transformation can be shown as



$$R-NH_2 + R\text{CHO} \longrightarrow [R-N=\underset{\substack{|\\H}}{C}-R] \xrightarrow{H_2/\text{Pt}} R-\underset{\substack{|\\H}}{N}-\overset{\substack{H\\|}}{\underset{\substack{|\\H}}{C}}-R$$

While other given set of reactants give primary amine only.

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

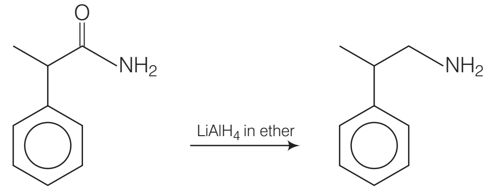
(a) excess H_2

(b) Br_2 in aqueous NaOH

(c) iodine in the presence of red phosphorus

(d) $LiAlH_4$ in ether

Ans. *(d)* The best reagent tor converting 2-phenylpropanamide into 2- phenylpropanamine is $LiAlH_4$ in ether. Reaction is as given below



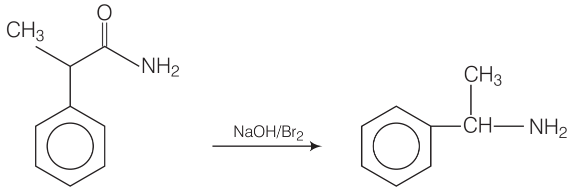
2- phenyl propanamide 2- phenyl propanamine

Q. 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

Ans. *(b)* The best reagent for converting 2-phenylpropanamide into 1-phenylethanamine is by NaOH / Br_2 and chemical transformation can be done as



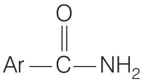
2-phenyl propapanide 1-phenyl ethanamine

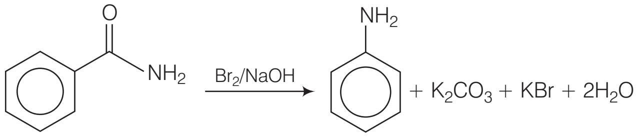
This occurs due to intramolecular migration of alkyl group. It is an example of Hofmann bromamide reaction.

Q. 12 Hofmann bromamide degradation reaction is shown by ....

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

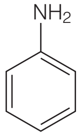
(c) $ArNO_2$ (d) $ArCH_2NH_2$

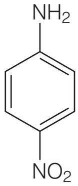
Ans. *(b)* Hofmann bromamide degradation is shown by  $Ar-\overset{\overset{\large O}{\|}}{C}-NH_2$ by which amide is converted into amine *via* undergoing intramolecular migration of phenyl group.

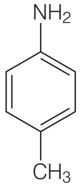


Benzamide Aniline

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

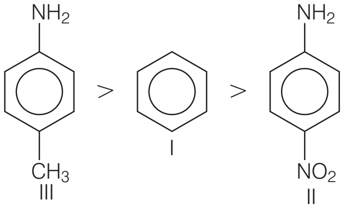

(I)


(II)


(III)

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

Ans. ***(d)*** The correct increasing order of basic strength is as follows



Greater the electron density towards ring, greater will be its basic strength.

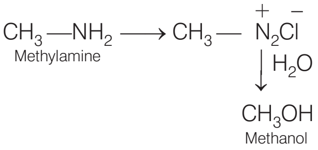
Electron withdrawing group decreases basic strength while electron donating group increases basic strength.

Q. 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

Ans. ***(c)*** Methylamine reacts with HNO_2 (nitrous acid) to form methanol.



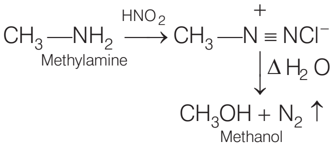
$$\underset{\text{Methylamine}}{CH_3-NH_2} \longrightarrow CH_3-\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{H_2O} \underset{\text{Methanol}}{CH_3OH}$$

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

(a) NH_3 (b) N_2

(c) H_2 (d) C_2H_6

Ans. ***(b)*** Chemical reaction takes place during reaction of methylamine with nitrous acid is as follows



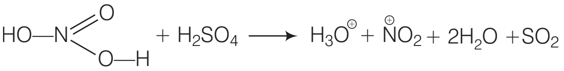
$$\underset{\text{Methylamine}}{CH_3-NH_2} \xrightarrow{HNO_2} CH_3-\overset{+}{N}\equiv NCl^- \xrightarrow{\Delta\ H_2O} \underset{\text{Methanol}}{CH_3OH} + N_2\uparrow$$

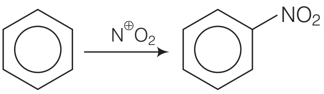
Q. 16 In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiates the reaction is ....

(a) NO_2 (b) NO^+

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

Ans. ***(c)*** Nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3 proceeds as





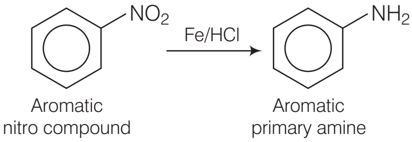
This reaction is known as electrophilic substitution reaction.

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

(a) aromatic oxime (b) aromatic hydrocarbon

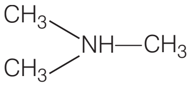
(c) aromatic primary amine (d) aromatic amide

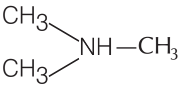
Ans. ***(c)*** Aromatic nitro compound on reaction with Fe and HCl gives aromatic primary amine as shown below

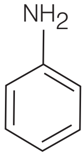


Q. 18 The most reactive amine towards dilute hydrochloric acid is ....

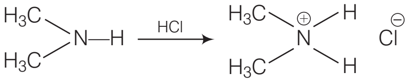
(a) CH_3-NH_2

(b)


(c)


(d)


Ans. ***(b)*** Greater will be the strength of base, greater will be its reactivity towards dilute HCl. Hence, $(CH_3)_2NH$ has highest basic strength as it has highest reactivity.

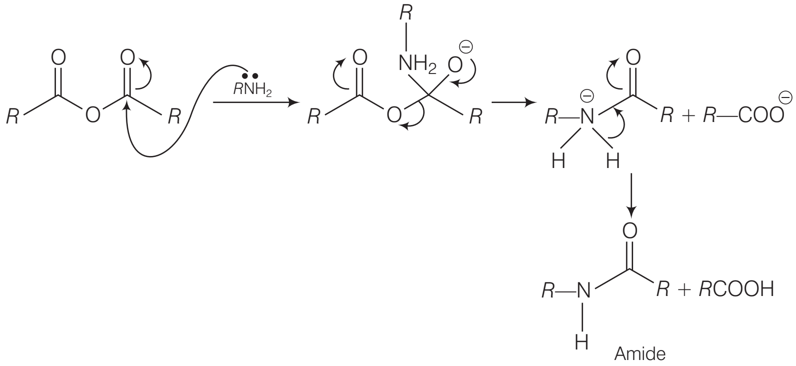


Q. 19 Acid anhydrides on reaction with primary amines give ....

(a) amide (b) imide

(c) secondary amine (d) imine

Ans. ***(a)*** Acid anhydride on reaction with primary amine produces amide as

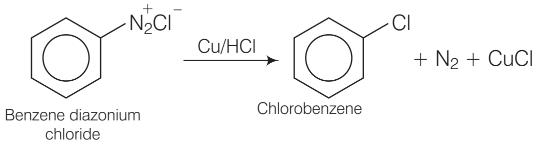


Q. 20 The reaction $Ar\overset{+}{N_2}Cl^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuCl$ is named as ....

(a) Sandmeyer reaction (b) Gattermann reaction

(c) Claisen reaction (d) Carbylamine reaction

Ans. ***(b)***



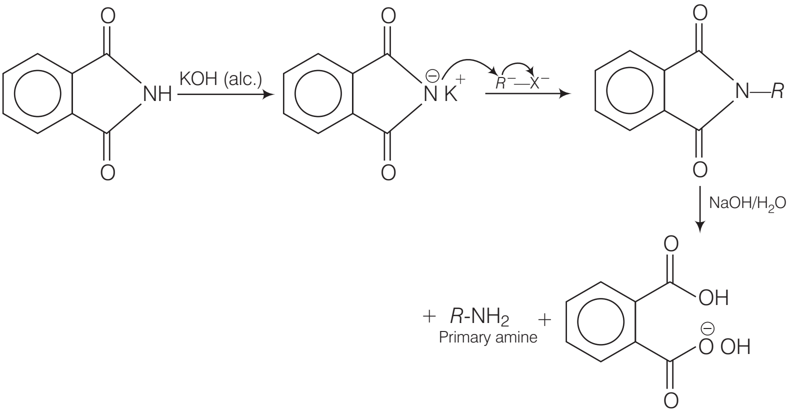
This reaction is called Gattermann reaction. In this reaction, Cl, Br and CN can be introduced into the benzene ring by simply treating diazonium salts with HCl, HBr, KCN, respectively in presence of copper powder instead of using Cu (I) salts.

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

(a) Hofmann bromamide reaction (b) Gabriel phthalimide synthesis

(c) Sandmeyer reaction (d) reaction with NH_3

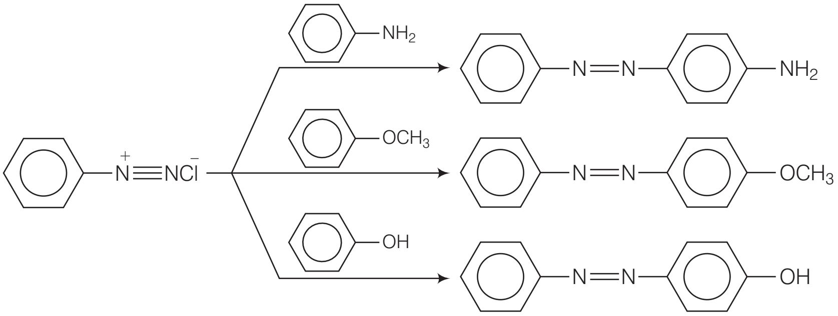
Ans. ***(b)*** Best method of preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is Gabriel phthalimide synthesis



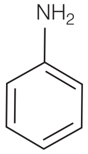
Q. 22 Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride?

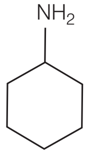
(a) Aniline (b) Phenol (c) Anisole (d) Nitrobenzene

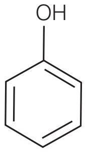
Ans. *(d)* Nitrobenzene will not undergo azo coupling reaction with benzene diazonium chloride while other three undergo diazo coupling reaction very easily. Diazonium cation is a weak E^+ and hence reacts with electron rich compounds cotaining electron donating group *i.e.,* —OH_1 —NH_2 and —OCH_3 groups and not with compounds containing electron withdrawing group, *i.e.,* NO_2 etc.

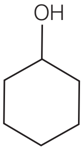


Q. 23 Which of the following compounds is the weakest Bronsted base?

(a)


(b)


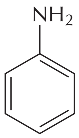
(c)


(d)


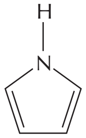
Ans. *(c)* Phenol is weakest Bronsted base as phenol after loosing H^+ produces least stable conjugate acid among the compounds.

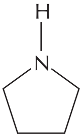
Oxygen has more electronegative than N. So, O—H bond is more polar and it has highest value of acidic character. Since, phenol is more acidic that alcohol, therefore, phenol has the least tendency to accept a proton and hence it is weak Bronsted base. Hence, phenol is least basic among given four choices.

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

(a)


(b) NH_3

(c)


(d)


Ans. *(d)* Aniline is a weaker base than NH_3 due to delocalization of lone pair of electrons of the N-atom over the benzene ring. pyrrole is not more basic because the lone pair of electrons on the N-atom is donated towards aromatic sextet formation.

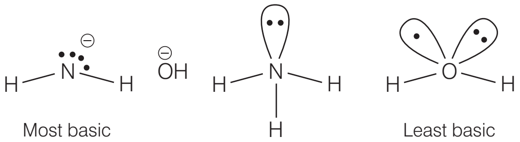
Therefore, pyrrolidine is strongest base as lone pair of nitrogen does not involved in resonance and also due to presence of two alkyl ring residue, basic strength becomes high among given four compounds.

Q. 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) $H_2O > NH_3 > OH^- > NH_2^-$

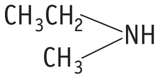
Ans. *(a)*



Basic strength of the above species can be explained on the basis of electronegativity of central atom and its proton accepting tendency. Here, amide ion is most basic among given compounds due to presence of negative charge and two pair of electrons on nitrogen atom.

Q. 26 Which of the following should be most volatile?

I. $CH_3CH_2CH_2NH_2$ II. $(CH_3)_3N$

III. 

$(CH_3CH_2)(CH_3)NH$

IV. $CH_3CH_2CH_3$

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

Ans. *(b)* 1° and 2° amines have higher boiling points due to intermolecular H-bonding but less votatile than 3° amines and hydrocarbons of comparable molecular mass. Further, because of polar C-N bonds, 3° amines are more polar than hydrocorbons which are almost non-polar. Hence, due to weak dipole-dipole interactions, 3° amines have higher boiling point (*i.e.,* less volatile) than hydrocarbons.

In other words, hydrocarbons are more volatile among given compounds as amine are less volatile than hydrocarbon.

Q. 27 Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?

(a) Reaction of nitrite with $LiAlH_4$

(b) Reaction of amide with $LiAlH_4$ followed by treatment with water

(c) Heating alkylhalide with potassium salt of phthalimide followed by hydrolysis

(d) Treatment of amide with bromine in aqueous solution of sodium hydroxide.

Ans. *(a, b, c)*

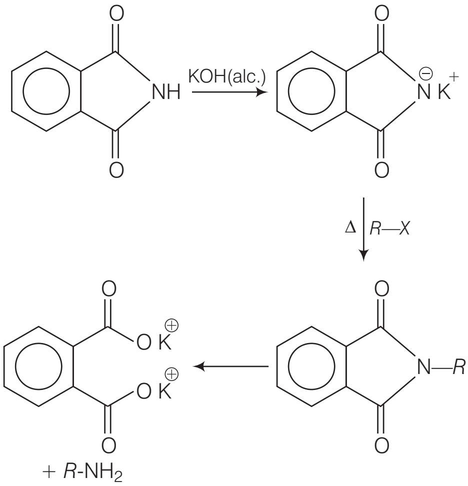
Aliphatic and arylalkyl primary amines can be easily prepared by the reduction of the corrsponding nitriles with $LiAlH_4$.

$$\underset{\text{Alkynitrile}}{R-C\equiv N} \text{ or } \underset{\text{Arynitrile}}{Ar-C\equiv N} \rightarrow LiAlH_4 \; \underset{\text{1° amine}}{RCH_2NH_2 \text{ or } ArCH_2NH_2}$$

Heating alkyl halide with Primary, secondary and tertiary amine can be prepared by reduction of $LiAlH_4$ followed by treatment with water.

$$\underset{\text{1°amide}}{R-CONH_2} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4 \text{ / ether}} R-CH_2-NH_2$$

Heating alkyl halide with potassium salt of phthalimide followed by hydrolysis produces primary amine. This process is known as Gabriel phthalimide reaction. The number of carbon atoms in the chain of amines of product is same as reactant.



Multiple Choice Questions (More Than One Options)

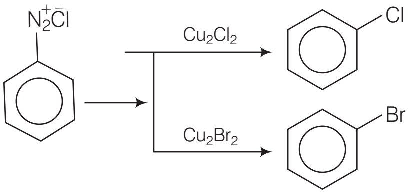
Q. 28 Which of the following cannot be prepared by Sandmeyer's reaction?

(a) Chlorobenzene (b) Bromobenzene

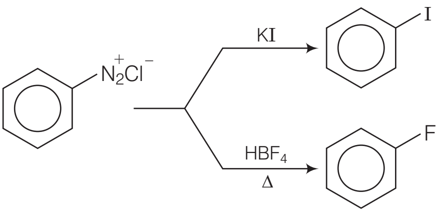
(c) Iodobenzene (d) Fluorobenzene

Ans. *(c, d)*

Sandmeyer's reaction is used for preparation of chlorobenzene and bromobenzene.



Iodobenzene and fluorobenzene can be prepared by direct reaction of diazonium salt with KI and HBF_4/Δ.

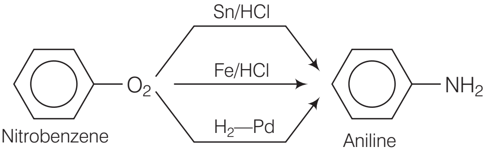


Q. 29 Reduction of nitrobenzene by which of the following reagent gives aniline?

(a) Sn/HCl (b) Fe/HCl (c) H_2 – Pd (d) Sn / NH_4OH

Ans. *(a, b, c)*

Reduction of nitrobenzene by Sn/HCl, Fe/HCl and H_2- Pd gives aniline as follows



Q. 30 Which of the following species are involved in the carbylamine test?

(a) *R*—NC (b) $CHCl_3$ (c) $COCl_2$ (d) $NaNO_2$ + HCl

Ans. *(a, b)*

Carbylamine reaction Amine on reaction with a mixture of $CHuCl_3$ and KOH produces alkyl isocyanate. $R\text{-}NH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

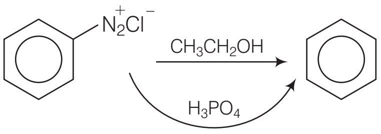
Only *R*NC and $CHCl_3$ are involved in carbylamine reaction. Hence, (a) and (b) are correct.

Q. 31 The reagents that can be used to convert benzenediazonium chloride to benzene are ....

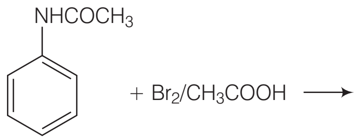
(a) $SnCl_2$ / HCl (b) CH_3CH_2OH (c) H_3PO_2 (d) $LiAlH_4$

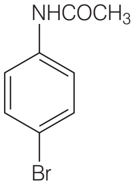
Ans. *(b, c)*

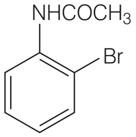
Benzene diazonium chloride can be converted into benzene using protic acid as follows

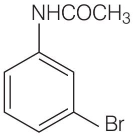


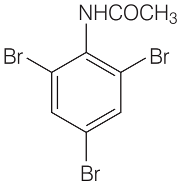
Q. 32 The product of the following reaction is ....



(a)


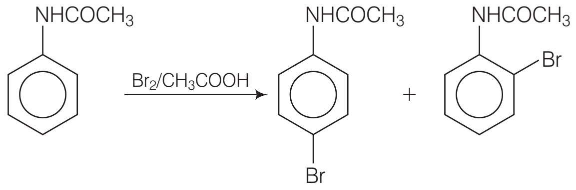
(b)


(c)


(d)


Ans. ***(a, b)***

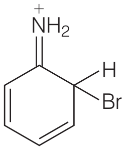
N-acetylaniline on reaction with Br_2 in presence of acetic acid produces *p*-bromo N-acetyl aniline (major) and *o*-bromo-N acetyl aniline (minor) as follows

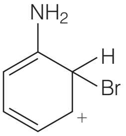


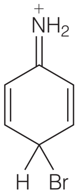
The N-acetyl group is a *ortho*, *para* directing group.

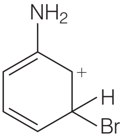
Hence, (a) and (b) are correct.

Q. 33 Arenium ion involved in the bromination of aniline is ....

(a)


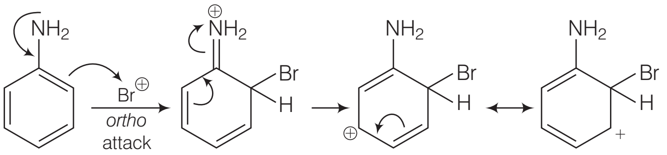
(b)


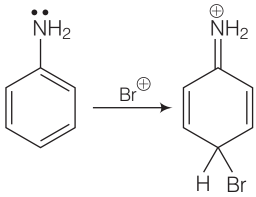
(c)


(d)


Ans. ***(a, b, c)***

Arenium ion involved in the bromination of aniline are as follows

(i)


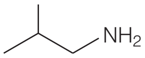
(ii)


Q. 34 Which of the following amines can be prepared by Gabriel synthesis?

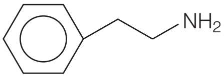
(a) Isobutyl amine
(b) 2-phenylethylamine
(c) N-methylbenzylamine
(d) Aniline

Ans. ***(a, b)***

Isobutylamine and 2-phenylethyl amine are primary amine can be prepared easily by Gabriel phthalimide reaction.



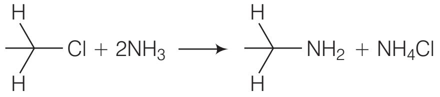
isobutyl amine

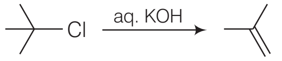


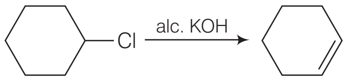
2 Phenyl ethyl amine

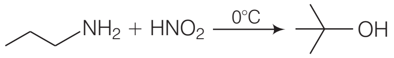
Refer to answer of question 8.

Q. 35 Which of the following reactions are correct?

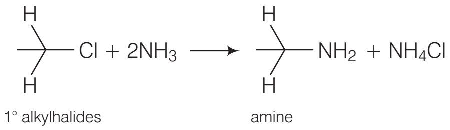
(a)


(b)


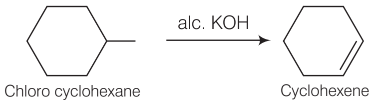
(c)


(d)


Ans. *(a, c)*

(a)


This is an example of nucleophilic substitution reaction.

(c)


This is an example of elimination reaction.

Q. 36 Under which of the following reaction conditions, aniline gives p-nitro derivative as the major product?

(a) Acetyl chloride/pyridine followed by reaction with conc. $H_2SO_4 +$ conc. HNO_3

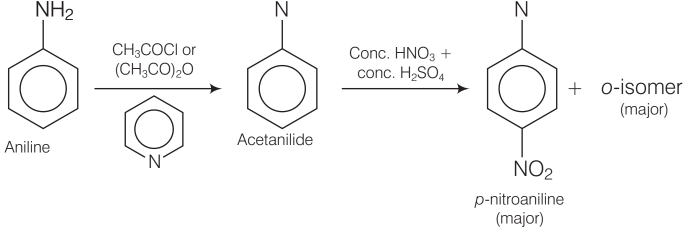
(b) Acetic anhydride/pyridine followed by conc. $H_2SO_4 +$ conc. HNO_3

(c) Dil. HCl followed by reaction with conc. $H_2SO_4 +$ conc. HNO_3

(d) Reaction with conc. $HNO_3 +$ conc. H_2SO_4

Ans. *(a, b)*

Aniline or reaction with acetyl chloride or acetic anhydride in the presence of pyridine produces N-acetyl aniline which is a *ortho*, *para* directing group which on further reaction with nitrating mixture (conc. $HNO_3 +$ conc. H_2SO_4) produces *p*-nitroaniline preferentially as shown below.



Q. 37 Which of the following reactions belong to electrophilic aromatic substitution?

(a) Bromination of acetanilide

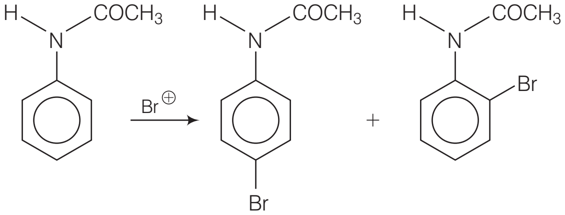
(b) Coupling reaction of aryldiazonium salts

(c) Diazotisation of aniline

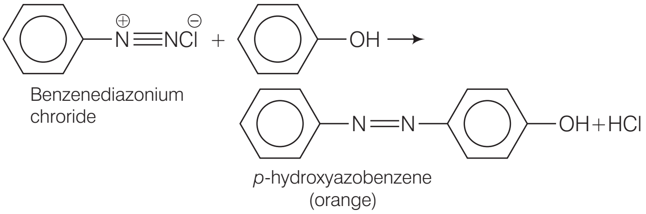
(d) Acylation of aniline

Ans. *(a, b)*

Bromination of acetanilide and coupling reaction of aryldiazonium salts is an example of electrophilic aromatic substitution reaction.



Coupling reaction of aryldiazonium salts

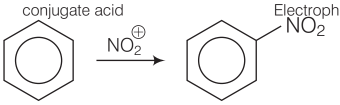


Short Answer Type Questions

Q. 38 What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

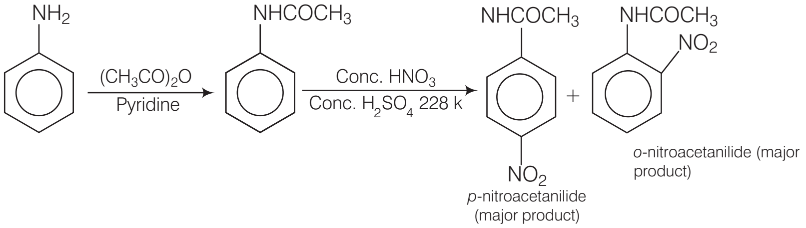
Ans. HNO_3 acts as a base in the nitrating mixture and provide the electrophile, NO_2^+ on reaction with H_2SO_4 as follows

$$\underset{\text{Base}}{HNO_3} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow \underset{\text{conjugate acid}}{H_2NO_3^+} + HSO_4^- \longrightarrow \underset{\text{Electrophile}}{NO_2^+} + HSO_4^- + H_2O$$



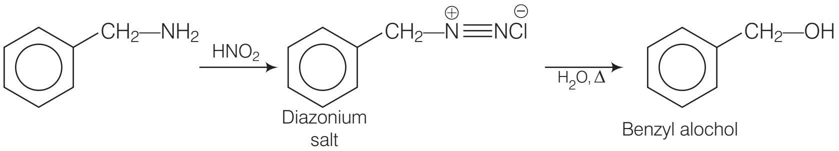
Q. 39 **Why is NH_2 group of aniline acetylated before carrying out nitration?**

Ans. In order to check the activation of benzene ring by amino group, first it is acetylated with acetic anhydride or acetyl chloride in presence of pyridine to form acetanilide which can be further nitrated easily by nitrating mixture.



Q. 40 **What is the product when $C_6H_5CH_2NH_2$ reacts with HNO_2?**

Ans. $C_6H_5CH_2NH_2$ on reaction with HNO_2 produces $C_6H_5CH_2N_2^+Cl^-$ as follows

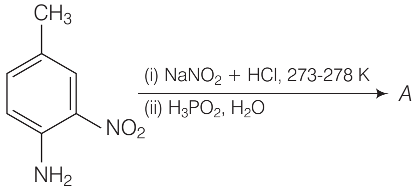


Q. 41 **What is the best reagent to convert nitrile to primary amine?**

Ans. Best reagent to convert nitrile to aniline is sodium/alcohol or $LiAlH_4$.

$$\underset{\text{Methylnitrile}}{CH_3—C\equiv N} \xrightarrow[\text{Na/alcohol}]{LiAlH_4} \underset{\text{Ethylamine}}{CH_3—CH_2—NH_2}$$

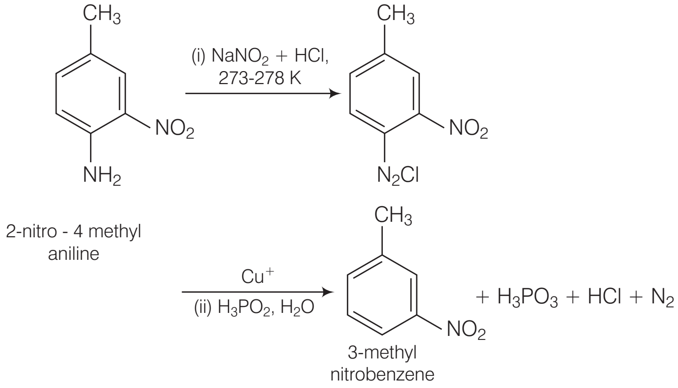
Q. 42 **Give the structure of 'A' in the following reaction.**



Thinking Process

This problem is based on the concept of preparation of diazonium salt and its chemical properties.

Ans. Complete conversion can be shown as



Q. 43 What is Hinsberg reagent?

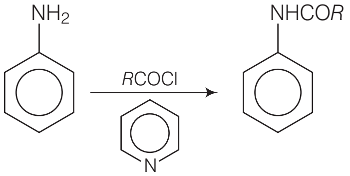
Ans. Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) is known as Hinsberg reagent. It is used to distinguish between primary, secondary and tertiary amine.

Q. 44 Why is benzene diazonium chloride not stored and is used immediately after its preparation?

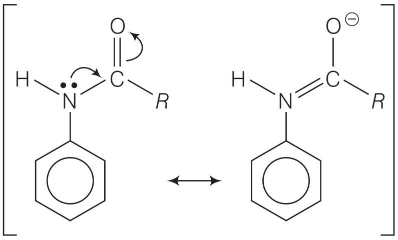
Ans. Benzene diazonium chloride are highly unstable and stable for a very short time span in solution at low temperature. Due to its instability, it is used immediately after its preparation.

Q. 45 Why does acylation of —NH_2 group of aniline reduces its activating effect?

Ans. Acylation of —NH_2 group of aniline reduces its activity due to resonance of lone pair of nitrogen towards the carbonyl group hence *o*–, *p*⁻ directive influence of amino group get disturbed.



The resonating structure are

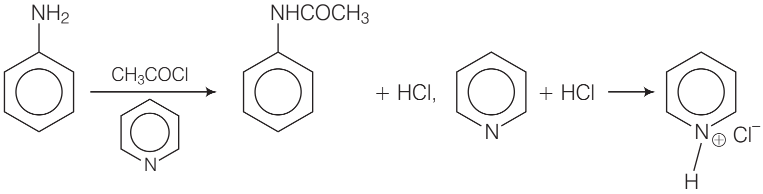


Q. 46 Explain why $MeNH_2$ is stronger base than MeOH?

Ans. Basicity of $MeNH_2$ and MeOH can be explained on the basis of electronegativity of N and O atom. $MeNH_2$ is stronger base than MeOH because of low electronegativity value of N, it is easy for nitrogen to loose its lone pair readily than compared to MeOH.

Q. 47 What is the role of pyridine in the acylation reaction of amines?

Ans. Pyridine being a base, is used to remove the side product *i.e.,* HCl from reaction mixture.



Q. 48 Under what reaction condition (acidic, basic) the coupling reaction of aryl diazonium chloride with aniline is carried out?

Ans. In strongly basic conditions, benzenediazonium chloride is converted into diazohydroxide and diazoate as both of which are not electrophilic and do not couple with aniline.

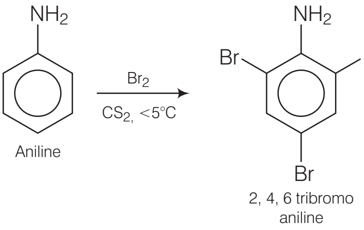
$$C_6H_5\overset{+}{N} \equiv NC\overset{-}{l} + OH\ SO_2\,\underset{\text{Diazohydroxide}}{CH_5 - N = N - OH} \xrightleftharpoons{NaOH} \underset{\text{Sodium diazoate}}{C_6H_5 - N = N - \overset{-}{O}Na^+}$$

Similarly, in highly acidic conditions, aniline gets converted into anilinium ion. From this, result aniline is no longer nucleophilic acid and hence will not couple with diazonium chloride. Hence, the reaction is carried out under mild conditions, *i.e.*, pH' –4 – 5

$$\underset{\text{Aniline}}{C_6H_5NH_2} + H^+ \rightarrow \underset{\substack{\text{Anilinium ion}\\\text{(coupling do not occur)}}}{C_6H_5 - \overset{+}{N}H_3}$$

Q. 49 Predict the product of reaction of aniline with bromine in non-polar solvent such as CS_2.

Ans. Aniline on reaction with Br_2 in non-polar solvent CS_2 produces 2, 4, 6 tribromo aniline.



Aniline has high reactivity towards bromine as it gives the triply substituted product.

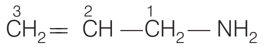
Q. 50 Arrange the following compounds in increasing order of dipole moment.

$$CH_3CH_2CH_3,\ CH_3CH_2NH_2,\ CH_3CH_2OH$$

Ans. Dipole moment of amine, alcohol and hydrocarbon can be explained on the basis of bond polarity of C—H, N—H and O—H bond. As the bond polarity increase, dipole moment increases $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$

Q. 51 What is the structure and IUPAC name of the compound, allyl amine?

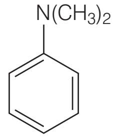
Ans. Structural formula of allyl amine is as follows



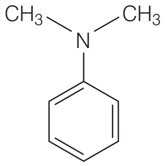
$$\overset{3}{C}H_2 = \overset{2}{C}H - \overset{1}{C}H_2 - NH_2$$

Prop-2-ene-1-amine (IUPAC name)

Q. 52 Write down the IUPAC name of



Ans.



N, N-dimthyl benzenamine

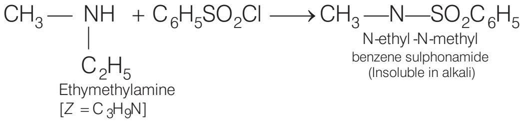
During naming of N-substituted amine, substituted group present at N are added as suffix on N-alkyl in IUPAC nomenclature.

Q. 53 A compound Z with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify Z.

Thinking Process

This process is based on concept of Hinsberg test. Only amine containing replaceable H gives Hinsberg test.

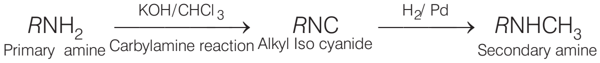
Ans. $Z(C_3H_9N)$ is an aliphatic amine. On reaction with $C_6H_5SO_2Cl$ (Hinsberg's reagent), it gives a product insoluble in alkali. It means that the product does not have a replaceable H-atom attached to the N- atom. So, compound Z is a secondary amine (ethyl methyl amine).



$$\underset{\substack{\text{Ethymethylamine}\\ [Z = C_3H_9N]}}{CH_3 - \underset{C_2H_5}{\underset{|}{NH}}} + C_6H_5SO_2Cl \longrightarrow \underset{\substack{\text{N-ethyl -N-methyl}\\ \text{benzene sulphonamide}\\ \text{(Insoluble in alkali)}}}{CH_3 - N - SO_2C_6H_5}$$

Q. 54 A primary amine, RNH_2 can be reacted with CH_3—X to get secondary amine, R—$NHCH_3$ but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where RNH_2 forms only 2° amine?

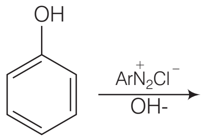
Ans.



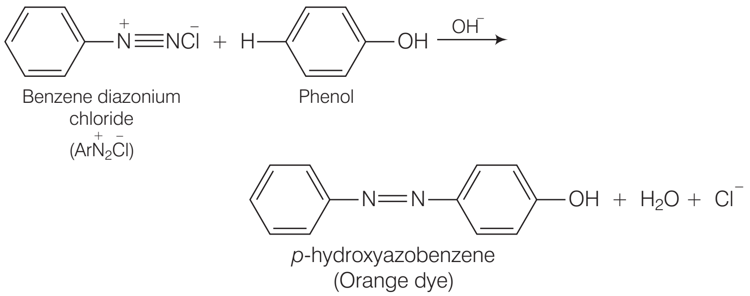
$$\underset{\text{Primary amine}}{RNH_2} \xrightarrow[\text{Carbylamine reaction}]{KOH/CHCl_3} \underset{\text{Alkyl Iso cyanide}}{RNC} \xrightarrow{H_2/\,Pd} \underset{\text{Secondary amine}}{RNHCH_3}$$

Primary amines show carbylamine reaction in which two H-atoms attached to N-atoms of NH_2 are replaced by one C-atom. On catalytic reduction, isocyanide (formed) produces secondary amine and not tertiary or quaternary salts.

Q. 55 Complete the following reaction.

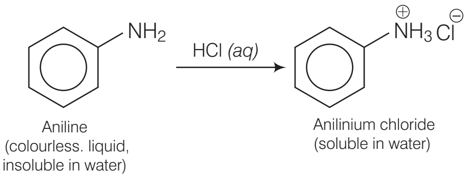


Ans. The reaction exhibits azo-coupling reaction of phenols. Benzene diazonium chloride reacts with phenol in such a manner that the *para* position of phenol is coupled with diazonium salt to form *p*-hydroxy azobenzene.

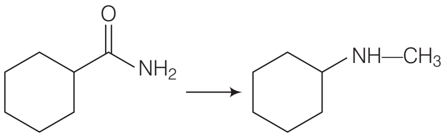


Q. 56 Why is aniline soluble in aqueous HCl?

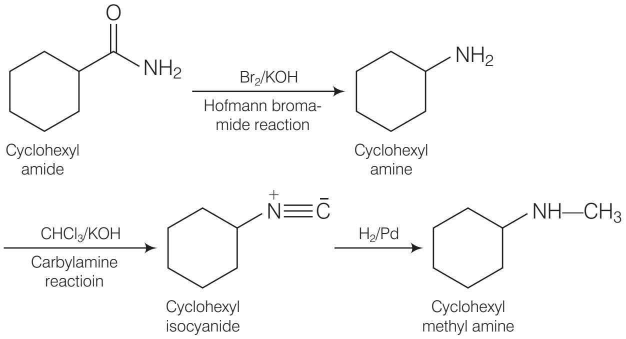
Ans. Aniline is soluble in aqueous HCl due to formation of ionic anilinium chloride.



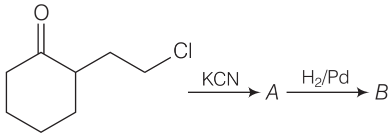
Q. 57 Suggest a route by which the following conversion can be accomplished.



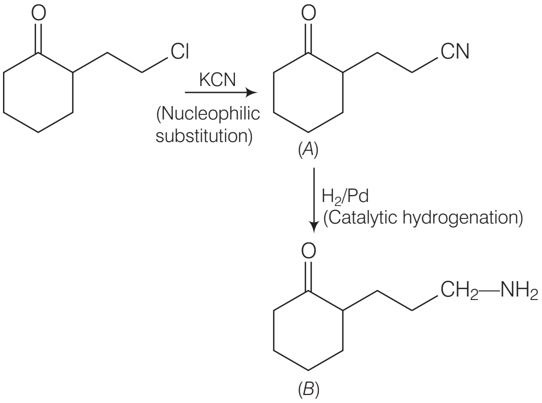
Ans. Complete conversion can be performed as



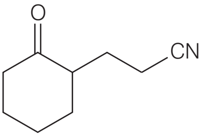
Q. 58 Identify A and B in the following reaction.



Ans. Complete conversion can be performed as

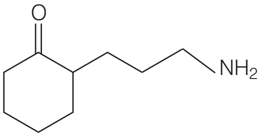


Hence, A =



3-(2-oxocyclohexyl propanenitrile)

B =



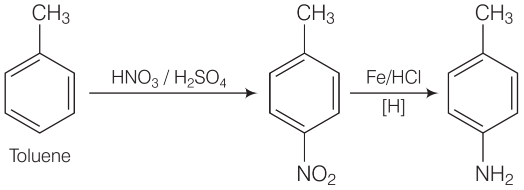
2-(3-aminopropyl) -cyclohex-1-one

Q. 59 How will you carry out the following conversions?

(i) Toluene ⟶ p-toluidine

(ii) p-toluidine diazonium chloride ⟶ p-toluic acid

Ans. **(i)** Conversion of toluene to *p*-toluidine can be done as

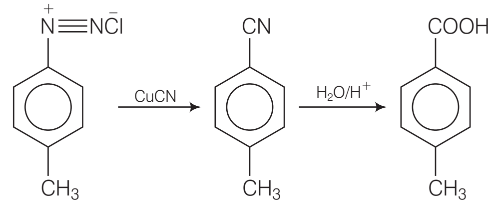


Toluene

4-methyl nitrobenzene

p-toluidine

(ii) Conversion of *p*-toluidine diazonium chloride to *p*-toluic acid can be done as



p-toluidine diazonium chloride

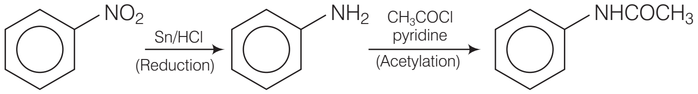
p-tolulic acid

Q. 60 Write following conversions

(i) Nitrobenzene $\longrightarrow$ Acetanilide

(ii) Acetanilide $\longrightarrow$ p-nitroaniline

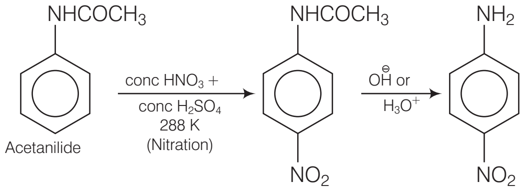
Ans. **(i)** Nitrobenzene can be converted into acetanilide as follows



Nitrobenzene

acetanilide

(ii) Acetanilide can be converted into *p* - nitroaniline as follows



p-Nitroacetanilide

p-Nitroacetaniline (major product)

Q. 61 A solution contains 1 g mol. each of p-toluene diazonium chloride and p-nitrophenyl diazonium chloride. To this 1 g mol. of alkaline solution of phenol is added. Predict the major product. Explain your answer.

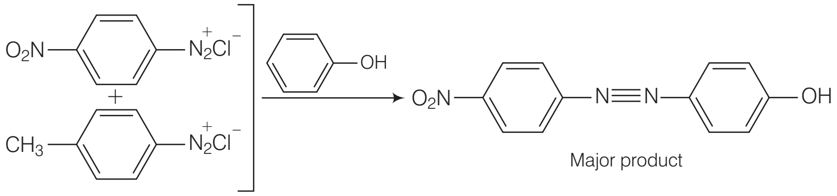
Thinking Process

This problem is based upon conceptual mixing of electrophilicity of ring system and diazo-coupling reaction.

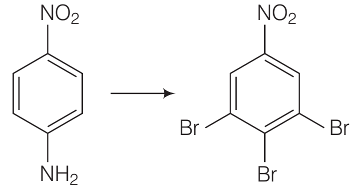
Ans. The above stated reaction is an example of electrophilic aromatic substitution. In alkaline medium, phenol generates phenoxide ion which is more electron rich than phenol and more reactive for electrophilic attack.

The electrophile in this reaction is aryldiazonium cation. As we know, stronger the electrophile faster is the reaction. *p*-nitrophenyldiazonium cation is a stronger electrophile than *p*-toluene diazonium cation.

So, nitrophenyl diazonium chloride couples preferentially with phenol.



Q. 62 How will you bring out the following conversion?

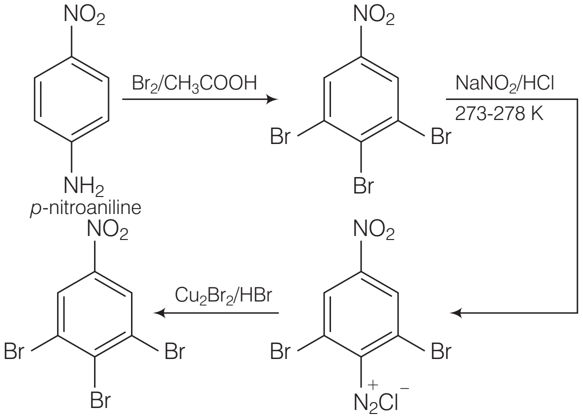


p-nitroanlline 3, 4, 5-tribromonitrobenzene

Thinking Process

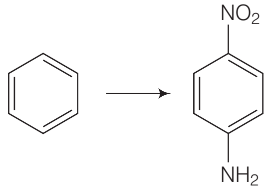
This problem includes conceptual mixing of bromination, nitration and Sandmeyer's reaction. Follow the steps to approach towards given product.
Bromination of p-nitroaniline followed by diazotisation and Sandmeyer's reaction

Ans. Complete conversion of above reaction can be shown as

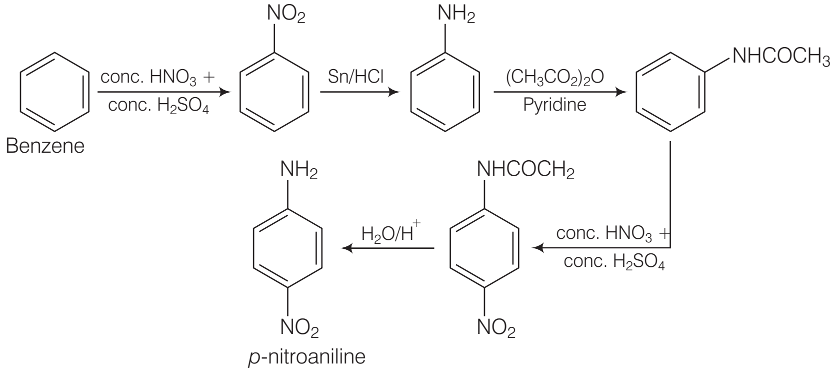


3, 4, 5-tribromonitrobenzene

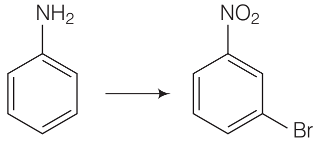
Q. 63 How will you carry out the following conversion?



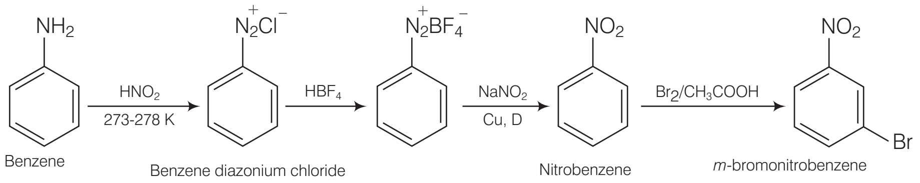
Ans. Conversion of benzene to *p*-nitroaniline can be done as



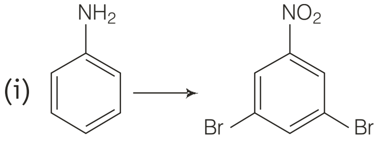
Q. 64 How will you carry out the following conversion?

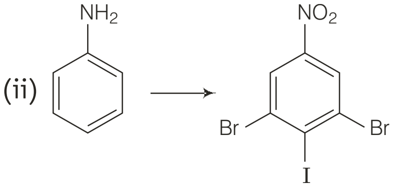


Ans. Conversion of aniline to *m*-bromo nitrobenzene can be completed as

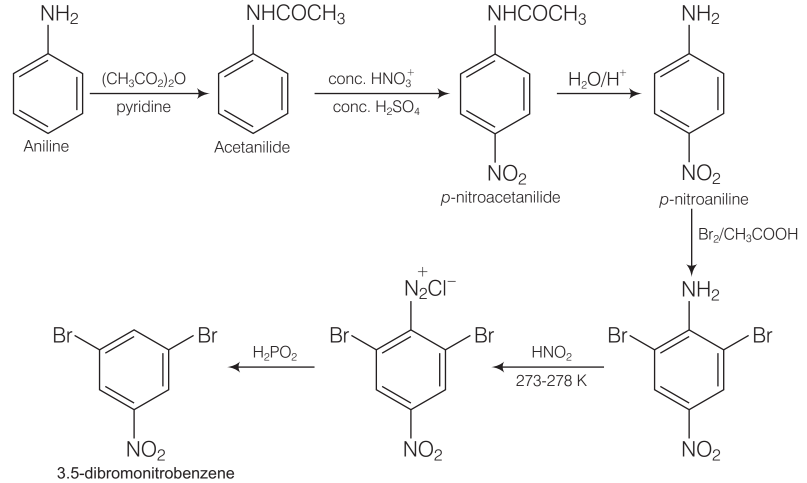


Q. 65 How will you carry out the following conversions?



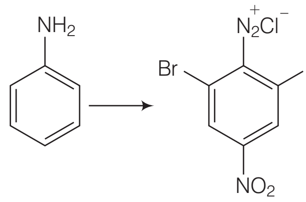


Ans. (i) Conversion of aniline to 3, 5-dibromonitrobenzene can be completed as

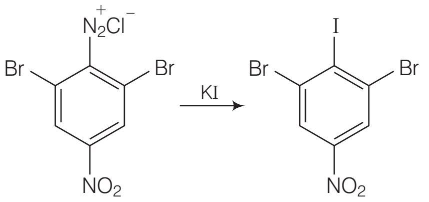


(ii) Conversion (*A*) given below is same as in part (i) given above after that reaction (*B*) can be carried out.

(A)



(B)

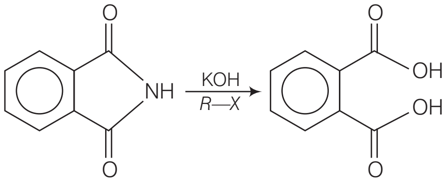


Matching The Columns

Q. 66 Match the reactions given in Column I with the statements given in Column II.

	Column I		Column II
A.	Ammonolysis	1.	Amine with lesser number of carbon atoms
B.	Gabriel phthalimide synthesis	2.	Detection test for primary amines.
C.	Hofmann bromamide reaction	3.	Reaction of phthalimide with KOH and *R*—*X*
D.	Carbylamine reaction	4.	Reaction of alkylhalides with NH_3

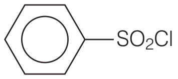
Ans. **A.** → (4) **B.** → (3) **C.** → (1) **D.** → (2)

	Reaction	Statements
A.	Ammonolysis	Reaction of alkylhalide with NH_3 $R - X \longrightarrow RNH_2 + HCl\cdot$
B.	Gabriel phthalimide synthesis	Reaction of phthalimide with KOH and R—X. 
C.	Hofmann bromamide reaction	Amine with lesser number of carbon atoms. $RCONH_2 \xrightarrow{NaOX} RNH_2$
D.	Carbylamine reaction	Detection test of primary amines.

Q. 67 Match the compounds given in Column I with the items given in Column II.

	Column I		Column II
A.	Benzene sulphonyl chloride	1.	Zwitter ion
B.	Sulphanilic acid	2.	Hinsberg reagent
C.	Alkyl diazonium salts	3.	Dyes
D.	Aryl diazonium salts	4.	Conversion to alcohols

Ans. A. → (2) B. → (1) C. → (4) D. → (3)

	Compounds	Items
A.	Benzene sulphonyl chloride	Hinsberg reagent 
B.	Sulphanilic acid	Zwitter ion (dipolar ion) 
C.	Alkyl diazonium salts	Conversion to alcohols $R - N_2^+X^- \xrightarrow{H_2O} ROH$
D.	Aryl diazonium salts	Dyes

Assertion and Reason

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

(a) Both assertion and reason are wrong.

(b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Both assertion and reason are correct statements and reason is correct explanation of assertion.

(e) Assertion is wrong statement but reason is correct statement.

Q. 68 Assertion (A) Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

Reason (R) Acyl group sterically hinders the approach of further acyl groups.

Ans. *(c)* Assertion is correct statement but reason is wrong statement.

Acylation of amine gives a monosubstituted product whereas alkylation of amine gives polysubstituted product because acylation in amine takes place at N-atom and alkylation takes place at *o* and *p* position.

Q. 69 Assertion (A) Hofmann's bromamide reaction is given by primary amines.

Reason (R) Primary amines one more basic than secondary amines.

Ans. *(a)* Both assertion and reason are wrong.

Correct Assertion Hofmanns bromamide reaction is given by amide.

Correct Reason Amide on reaction with NaOX produces amine having one carbon less than amide.

Q. 70 Assertion (A) N-ethylbenzene sulphonamide is soluble in alkali.

Reason (R) Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

Ans. *(d)* Both assertion and reason are correct and reason is the correct explanation of assertion.

N-ethylbenzene is soluble in alkali because hydrogen attached to nitrogen in sulphonamide is strongly acidic and forms a salt during reaction between these two.

Q. 71 Assertion (A) N, N-diethylbenzene sulphonamide is insoluble in alkali.

Reason (R) Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

Ans. *(d)* Both assertion and reason are correct and reason is not the correct explanation of assertion.

N, N-diethylbenzene sulphonamide is insoluble in alkali due to absence of acidic H attached to nitrogen.

Q. 72 Assertion (A) Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.

Reason (R) $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

Ans. *(d)* Assertion and reason both are correct and reason is the correct explanation of assertion.

Only small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam because $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

Q. 73 Assertion (A) Aromatic 1° amines can be prepared by Gabriel phthalimide synthesis.

Reason (R) Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.

Ans. *(a)* Both assertion and reason are wrong. Aryl 1° amine can't be prepared by Gabriel phthalimide reaction because aryl halide don't undergo nucleophilic substitution with anion formed by phthalimide.

Q. 74 Assertion (A) Acetanilide is less basic aniline.

Reason (R) Acetylation of aniline results in decrease of electron density on nitrogen.

Ans. *(d)* Assertion and reason both are correct and reason is the correct explanation of assertion.

Acetanilide is less basic than aniline because acetylation of aniline results in decrease of electron density on nitrogen.

Long Answer Type Questions

Q. 75 A hydrocarbon 'A' (C_4H_8) on reaction with HCl gives a compound 'B,' (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound 'C,' ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 mols of acetaldehyde. Identify compounds 'A' to 'D'. Explain the reactions involved.

Thinking Process

This problem includes conceptual mixing of ozonolysis, optical activity, ammonolysis and diazotisation. Follow the steps to solve the problem

Analyse the overall reaction once then sequentially predict a molecule for each A,B,C and D on the basis of information provided in the question.

Fit every molecule in a flow chart made by using information provided in the question and reach to the correct compounds.

Ans. (i) Addition of HCl to compound '*A*' shows that compound '*A*' is alkene. Compound '*B*' is C_4H_9Cl.

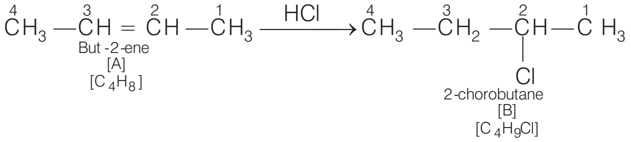
(ii) Compound '*B*' reacts with NH_2, it forms amine '*C*'.

$$\underset{[A]}{C_4H_8} \xrightarrow{HCl} \underset{[B]}{C_4H_9Cl} \xrightarrow{NH_3} \underset{[C]}{C_4H_{11}N} \text{ or } C_4H_9NH_2$$

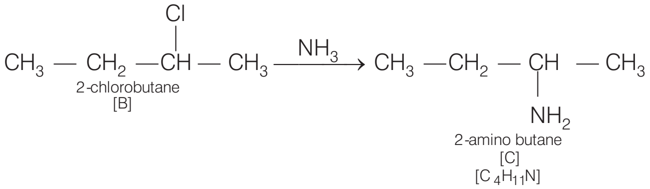
(iii) '*C*' gives diazonium salt with $NaNO_2$ / HCl, which yields an optically active alcohol. So, '*C*' is aliphatic amine.

(iv) '*A*' on ozonolysis produces 2 moles of CH_3CHO. So, '*A*' is $CH_3-CH=CH-CH_3$ (But-2-ene).

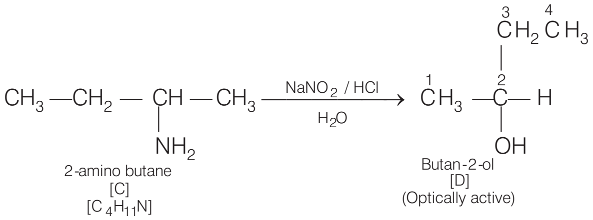
Reactions

(i) 

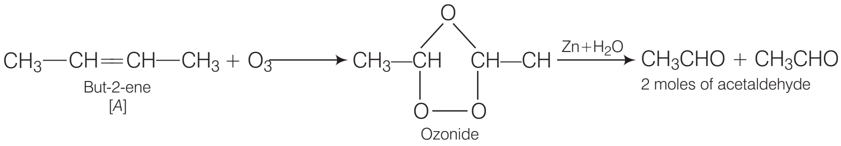
$$\underset{\substack{\text{But -2-ene}\\ [A]\\ [C_4H_8]}}{\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3} \xrightarrow{HCl} \underset{\substack{\text{2-chorobutane}\\ [B]\\ [C_4H_9Cl]}}{\overset{4}{C}H_3-\overset{3}{C}H_2-\underset{Cl}{\overset{2}{C}H}-\overset{1}{C}H_3}$$

(ii) 

$$\underset{\substack{\text{2-chlorobutane}\\ [B]}}{CH_3-CH_2-\overset{Cl}{CH}-CH_3} \xrightarrow{NH_3} \underset{\substack{\text{2-amino butane}\\ [C]\\ [C_4H_{11}N]}}{CH_3-CH_2-\underset{NH_2}{CH}-CH_3}$$

(iii) 

$$\underset{\substack{\text{2-amino butane}\\ [C]\\ [C_4H_{11}N]}}{CH_3-CH_2-\underset{NH_2}{CH}-CH_3} \xrightarrow[H_2O]{NaNO_2\ /\ HCl} \underset{\substack{\text{Butan-2-ol}\\ [D]\\ \text{(Optically active)}}}{\overset{1}{C}H_3-\underset{OH}{\overset{\overset{3}{C}H_2\overset{4}{C}H_3}{\overset{2}{C}}}-H}$$

(iv) 

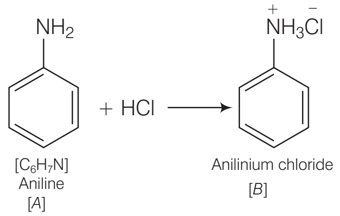
Q. 76 A colourless substance 'A' (C_6H_7N) is sparingly soluble in water and gives a water soluble compound 'B' on treating with mineral acid. On reacting with $CHCl_3$ and alcoholic potash 'A' produces an obnoxious smell due to the formation of compound 'C'. Reaction of 'A' with benzenesulphonyl chloride gives compound 'D' which is soluble in alkali. With $NaNO_2$ and HCl, 'A' forms compound 'E' which reacts with phenol in alkaline medium to give an orange dye 'F'. Identify compounds 'A' to 'F'.

Thinking Process

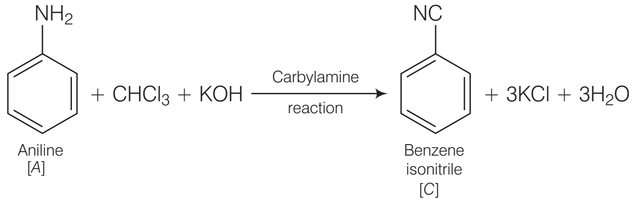
This problem is based on chemical properties of aniline and property and solubility of their derivatives.

Ans.

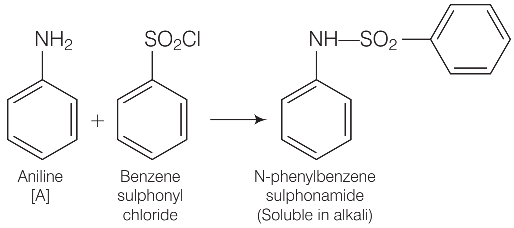
(i)



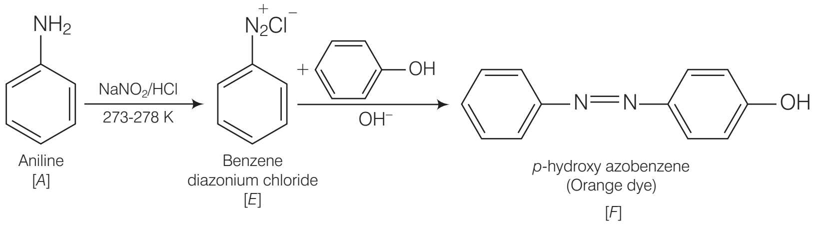
(ii)



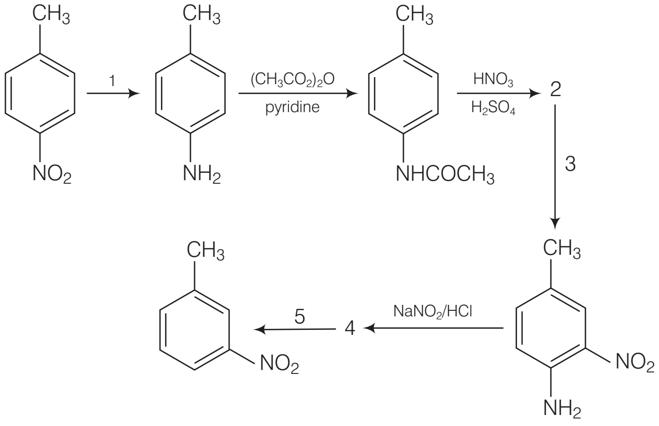
(iii)



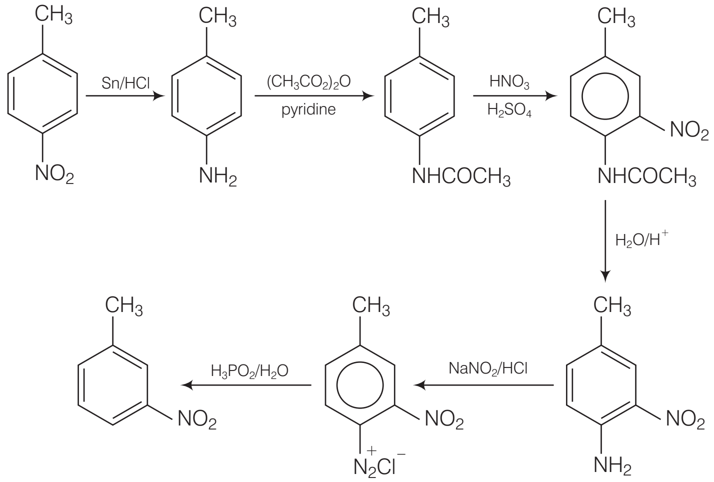
(iv)



Q. 77 Predict the reagent or the product in the following reaction sequence.



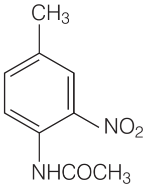
Ans. Correct sequence can be represented as follows including all reagents.



Hence,

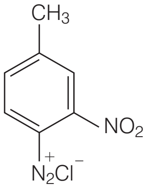
(i) 1 = Sn/HCl

(ii) 2 =



(iii) 3 = H_2O/H^+

(iv) 4 =



(v) 5 = H_3PO_2/H_2O