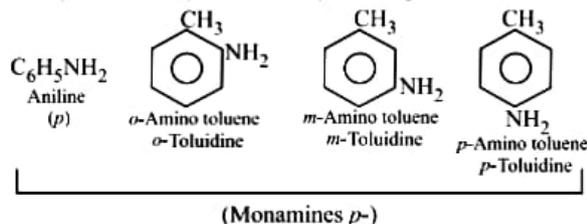


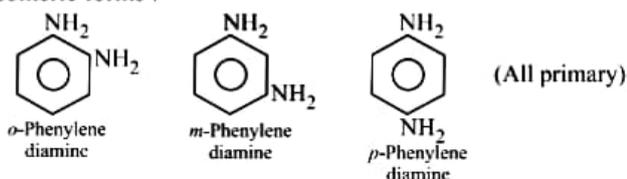
### B : Aromatic Amines

The amino derivatives of ammonia are called amines. These are of two types namely nuclear and side chain amines.

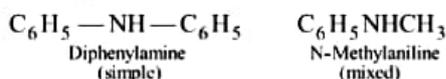
**A. Nuclear amines:** When  $\text{—NH}_2$  is directly bonded with ring carbon it is called nuclear (aromatic) amine. These are of three types, namely  $\text{—primary}$ , secondary and tertiary. The secondary and tertiary amines may be simple or mixed.



The diamino derivatives of benzene exists in three isomeric forms :



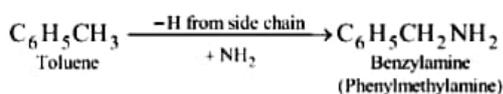
#### Secondary amines:



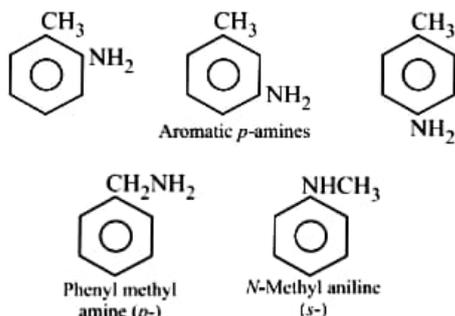
#### Tertiary amines :



**B. Side chain amines (aryl substituted aliphatic amines):** When  $\text{—NH}_2$  group is present in the side chain they are called side chain amines.

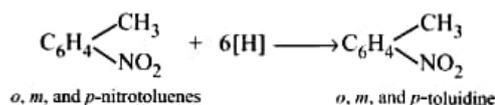
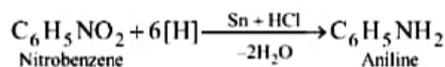


#### Isomers of formula $\text{C}_7\text{H}_9\text{N}$

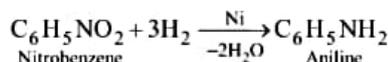


### Preparation of Primary Aromatic Amines

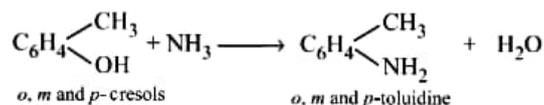
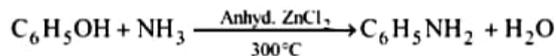
**1. By the reduction of nitro compounds:** When reduced  $\text{Sn + HCl}$ ,  $\text{Zn + HCl}$  or  $\text{Fe + HCl}$  nitro compounds give amines.



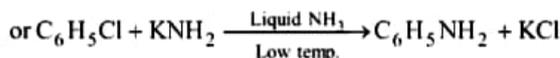
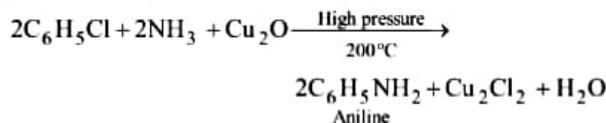
Catalytic reduction of nitro compounds also gives amines.



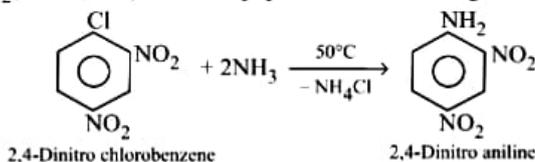
#### 2. Ammonolysis of phenols :



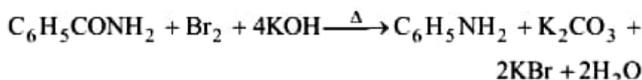
#### 3. Ammonolysis of aryl halides :



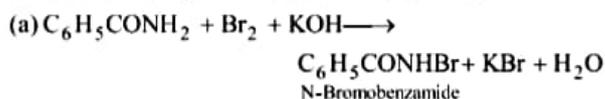
The halogen atom can be easily replaced when the compound contains electron-withdrawing groups ( $\text{—NO}_2$ ,  $\text{—CN}$ , etc.) in *o*- and *p*-position to the halogen atom.

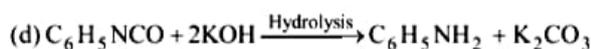
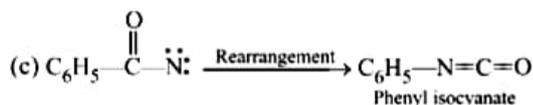
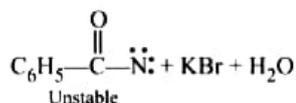


**4. By Hofmann bromamide reaction (Hofmann rearrangement or hypobromite reaction):** When benzamide or any other amide is heated with bromine (chlorine) and KOH (NaOH) solution, a primary amine containing one carbon atom less than amide is produced.

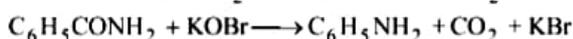


The reaction may also be expressed as follows:

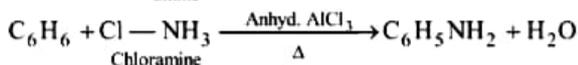
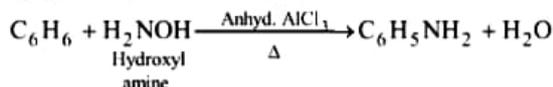




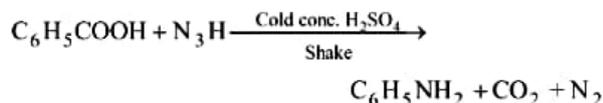
The reaction may also be expressed as follows :



### 5. By Friedel-Crafts reaction:

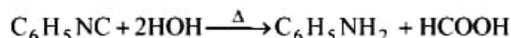


**6. By Schmidt reaction:** A mixture of benzoic acid and hydrozoic acid on shaking with colour conc.  $H_2SO_4$  gives aniline.

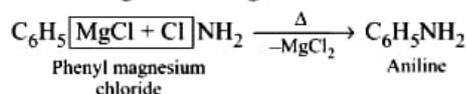


This reaction is known as Schmidt reaction.

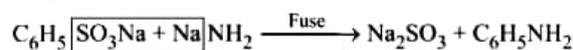
### 7. Hydrolysis of phenyl isocyanide and phenyl isocyanate:



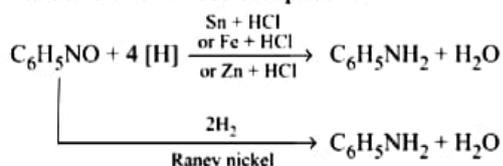
### 8. From Grignard's reagent:



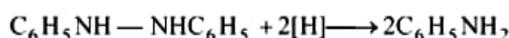
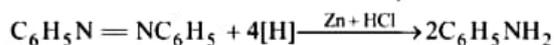
### 9. By the fusion of sodium benzene sulphonate with sodamide:



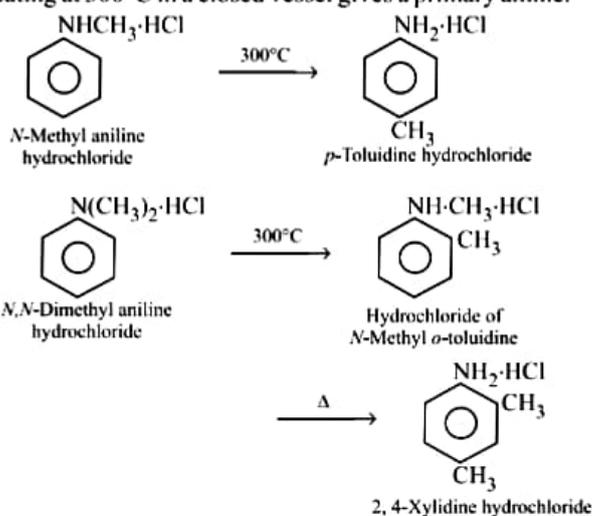
### 10. Reduction of nitroso compounds:



### 11. Reduction of azobenzene and hydrazobenzene:



**12. By Hofmann-Martius rearrangement:** The isomerisation of alkyl anilines to primary amino compounds is known as Hofmann-Martius rearrangement. In it the hydrochloride of a mixed type of secondary or tertiary amine on heating at  $300^\circ C$  in a closed vessel gives a primary amine.



In this rearrangement, the alkyl group migrates from the side chain to the nucleus (ring).

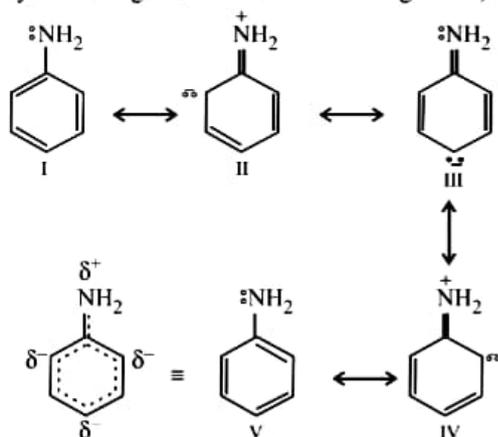
### Physical Properties

Aromatic primary monamines are colourless liquids or solids having peculiar unpleasant odour. They turn brown on exposure to light and air due to oxidation (the presence of  $-NH_2$  group greatly increases the electron density of ring hence they are highly susceptible to atmospheric oxygen). Since they are polar compounds ( $\mu D$  of aniline = 1.52 D) and capable of forming intermolecular hydrogen bonds hence boil at much higher temperatures than aliphatic amines of similar molecular weight. **Due to greater intermolecular attraction, they have higher boiling points than the corresponding non-polar compounds of similar molecular weights.** They are sparingly soluble in water but dissolves in benzene and other organic solvents. They are steam volatile and therefore can be purified by steam distillation. They are very toxic and even some of them are carcinogenic.

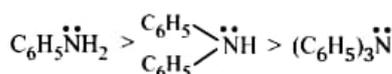
**Aniline:** Freshly prepared aniline is a colourless oily liquid (b. pt.  $184^\circ C$ ) with an unpleasant odour and is poisonous in nature. On exposure to light and air it turns red or brown due to oxidation. It is practically insoluble in water but readily soluble in organic solvents. It is steam volatile.

## Chemical Properties

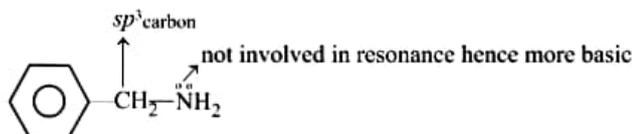
**Basic character of amines:** Basicity of a compound is its ability to donate a lone pair to a proton ( $H^+$ ). The greater the ease to donate this electron pair to proton, the greater will be its basic character. In case of aniline, the lone pair of electrons of nitrogen is delocalized into the benzene ring by resonance (the lone pair is in bonding interaction with  $\pi$ -electrons of ring there by increasing the number of resonating forms).



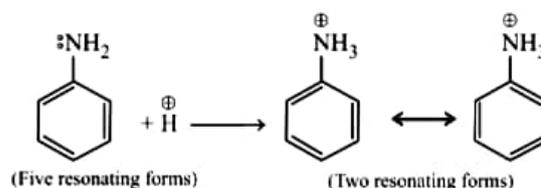
As a result of resonance the lone pair is less available for protonation. Therefore, aniline and other aromatic amines are less basic than aliphatic and aryl alkyl amine because there is no resonance in the later cases. In case of aniline the nitrogen atom develops positive charge II, III, IV which repels the proton of acid. The introduction of second and third aromatic ring on the nitrogen of aniline decreases the basicity still further.



Benzyl amine is more basic than aniline, it is because the nitrogen atom carrying lone pair of electrons is separated from ring carbon through one  $sp^3$  hybridised carbon atom. Thus, the lone pair on nitrogen atom cannot interact with  $\pi$ -electrons of ring *i.e.*, the lone pair cannot conjugated with double bond of benzene.



Aniline can interact with a proton to form anilinium ion (cation) which has only two resonating forms as compared to five resonating forms of aniline (I to V). Aniline is thus resonance stabilized to a greater extent than anilinium ion.



## Effect of Nuclear Substituents

(i) Electron-releasing groups (those which activate the ring towards electrophilic substitution) tend to increase the basic character of aniline, while electron-withdrawing groups (those which deactivate ring towards electrophilic substitution) like  $-NO_2$ ,  $-CN$ ,  $-CHO$ ,  $-SO_3H$ ,  $-Cl$ ,  $Br$ ,  $I$  etc., tend to decrease the basic character of aniline.

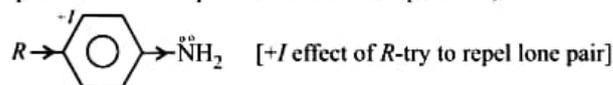
(ii) Activating (*o*, *p*) or deactivating (*m*-) group present in the *ortho* position of  $-NH_2$  group, always decreases the basic character of aniline. This is believed to be due to the **ortho effect** (steric effect).

(iii) The base-weakening effect of *m*-directing groups is greatest when they are present at the *o*- and *p*-position than at *m*-position.

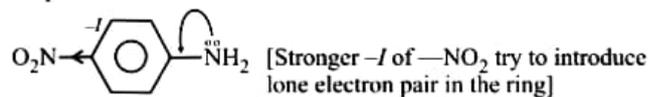
(iv) The presence of activating or deactivating group in *m*-position does not affect the basic character of aniline.

The effect of groups on the basic character of aniline may be explained on the basis of following points.

**(A) Inductive effect:** The presence of *+I* groups ( $-CH_3$ ,  $-NH_2$ ,  $-OCH_3$ , etc.) would push the electrons towards nitrogen atom of  $-NH_2$  group with the result that electron density on  $-NH_2$  group would increase and therefore the lone pair of electrons on nitrogen atom of  $-NH_2$  would be more available for protonation (observe the exception when *+I* is present in the *ortho* position).

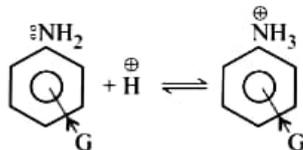


On the other hand electron withdrawing groups ( $-NO_2$ ,  $-COOH$ ,  $Cl$ ,  $-SO_3H$ ,  $-CN$ ,  $-NR_3$  etc.) would pull the electrons away from nitrogen of  $-NH_2$  group and thus make the lone pair of electrons on  $-NH_2$  less available for protonation.



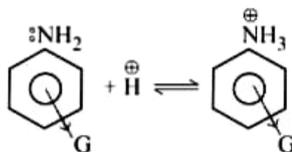
**(B) Stability of substituted anilinium ion:** The basic character of any compounds depends upon its ability to accommodate a positive charge, thus, more the possibility for the accommodation (dispersal) of the positive charge of  $C_6H_5NH_3^+$  ion, greater will be its basic character. The electron releasing groups (*+I* groups) tend to disperse the

positive charge of the anilinium ion, they stabilize the ion relative to aniline and hence increases the basic character.



(Group G releases (repels) electrons, disperses the positive charge, stabilizes the cation and hence increases the basic character.)

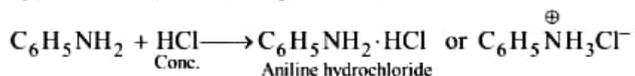
However, the electron-withdrawing group ( $-I$ ) tends to increase the positive charge of the  $C_6H_5NH_3^+$  ion, hence their presence destabilizes the cation relative to aniline and therefore decreases the basic character of aniline.



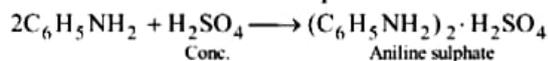
[G withdraws electrons, increases (concentrate) the positive charge and hence decreases the basic character]

## Reactions of $-NH_2$ Group of Aniline

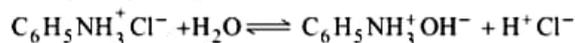
**1. Salt formation:** Although it is a weak mono acid base due to delocalization of lone electrons by resonance but it form crystalline salts with strong mineral acids.



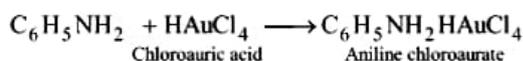
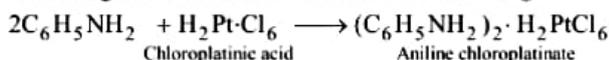
An aqueous solution of aniline hydrochloride gives a white ppt. on addition of  $AgNO_3$  solution hence presence of chloride ion in the side chain is proved.



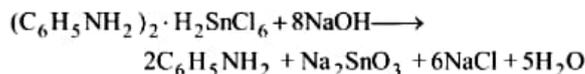
Aqueous solution of aniline sulphate reacts with  $BaCl_2$  solution to give a white ppt. of  $BaSO_4$ . These salts are hydrolysed (the salts of aliphatic amines and benzylamine are not hydrolysed).



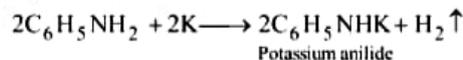
aniline gives double salts with metallic acids, e.g.,



Aniline chlorostannate is decomposed by caustic soda solution to regenerate aniline.

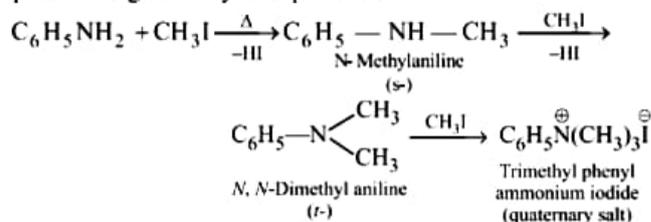


### 2. Action of active metals:



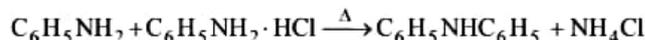
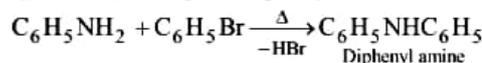
This reaction proves acidic nature of  $-NH_2$  group.

**3. Alkylation:** On heating with alkyl halides under pressure it gives alkylated products.

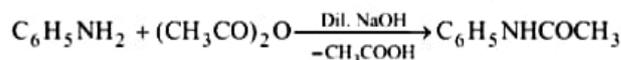
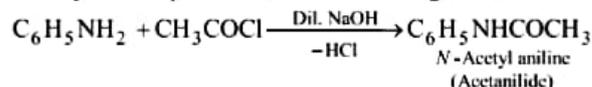


Due to ionisation in aqueous solution quaternary ammonium salt conducts electricity.

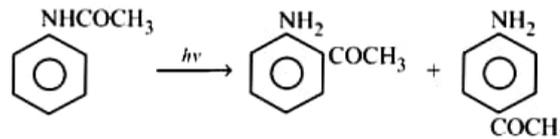
**4. Arylation:** On heating with halobenzene as well as aniline hydrochloride it gives diphenyl amine.



**5. Acetylation:** Aniline reacts with acetyl chloride or acetic anhydride in presence of dil. NaOH to give acetanilide.

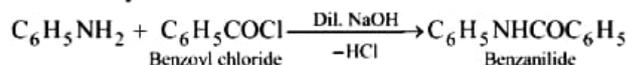


Acetanilide on heating gives a mixture of *o*- and *p*-anilines.



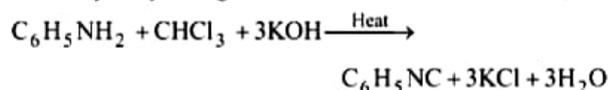
Acetylation reaction is used for the protection of  $-NH_2$  group.

### 6. Benzoylation:



It is known as **Schotten-Baumann reaction**.

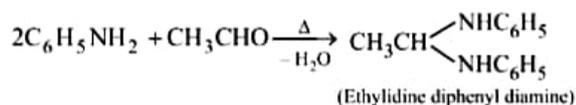
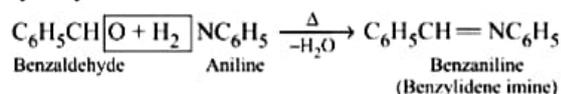
**7. Carbylamine reaction:** Aniline on heating with chloroform and alcoholic KOH yields pungent (suffocating or offensive or foul smelling) vapours of **phenyl isocyanide** (which on hydrolysis regenerates aniline and formic acid).



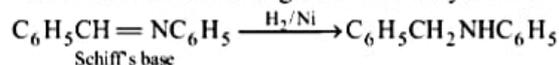
**8. Action of Grignard's reagent:**



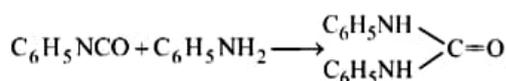
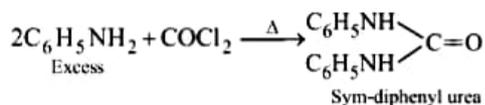
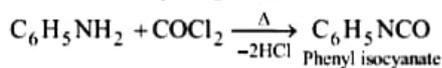
**9. Condensation with aldehydes:** On heating with aldehydes yields **Anils** or **Schiff's bases**.



Schiff's base on reduction gives a secondary amine.



**10. Reaction with phosgene:**



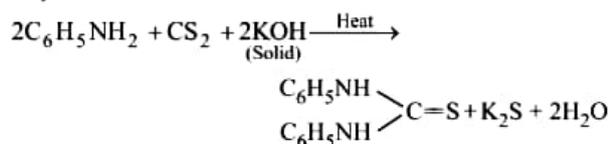
**11. Reaction with carbon disulphide:**

(a) On heating with  $\text{CS}_2$  and  $\text{HgCl}_2$  it gives phenyl isothiocyanate.

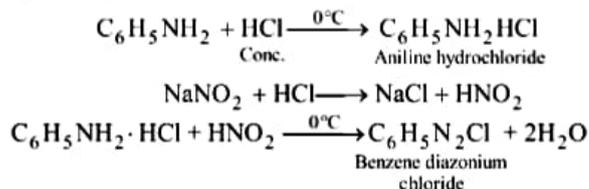


Since smell of phenyl isothiocyanate is similar to mustard oil hence it is known as **Hofmann Mustard oil** reaction.

(b) Aniline on heating with  $\text{CS}_2$  and solid KOH gives sym. diphenyl thiourea.



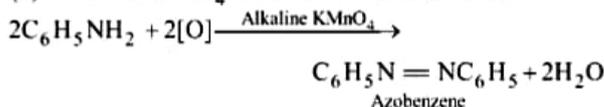
**12. Action of nitrous acid:** On reaction with nitrous acid ( $\text{NaNO}_2 + \text{HCl}$ ) in presence of mineral acid at  $0^\circ\text{C}$  it gives a diazonium salt.



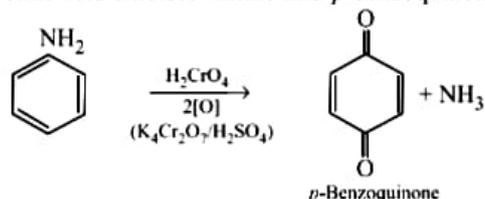
This is known as **diazo reaction** and the process as **diazotization**. **Aliphatic amine and benzyl amine do not form diazonium salts but give alcohols on reaction with nitrous acid.**

**13. Oxidation:** Aniline is readily oxidised because it is highly susceptible to atmospheric oxidation. The nature of oxidation product depends on the oxidising agent and the experimental conditions.

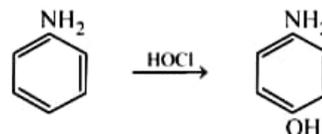
(a) Alkaline  $\text{KMnO}_4$  oxidises it to azobenzene.



(b) Chromic acid oxidises aniline into *p*-benzoquinone.



(c) Hypochlorous acid converts aniline into *p*-amino phenol.



(d) Pertrifluoro acetic acid oxidises aniline into nitrobenzene.



(e)  $\text{H}_2\text{O}_2$  also oxidises aniline into nitrobenzene.

(f) Per-acids oxidise it to nitrobenzene and azoxybenzene.

(g) Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  and acidified  $\text{KMnO}_4$  oxidises aniline into **aniline black**.

(h) Aniline on reaction with bleaching powder gives a violet colour.

(i) On treatment with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4$  aniline gives a blue colour.

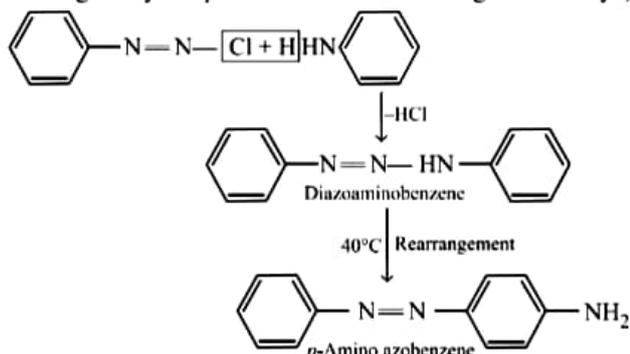
(j) Aniline reacts with dilute  $\text{H}_2\text{SO}_4$  in the presence of  $\text{CuSO}_4$  to give a black colour.

## Reactions of Nucleus

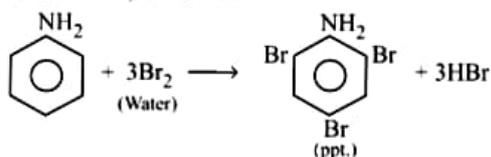
$-\text{NH}_2$  group due to  $+T$  effect, i.e.,  $+E$  and  $+M$ , is *ortho* and *para* directing.  $-\text{NH}_2$  group also have permanent

$-I$  effect (since nitrogen is more electronegative than carbon), but  $+T$  is greater than  $-I$  hence  $o$ ,  $p$ -substitution occurs frequently.

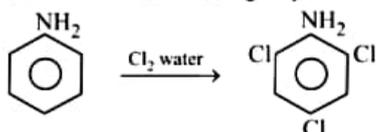
**1. Coupling with diazonium salts:** At room temp. aniline reacts with benzene diazonium chloride to give diazoaminobenzene (yellow dye which on heating at  $40^\circ\text{C}$  rearranges to yield  $p$ -amino azobenzene orange red azo dye).



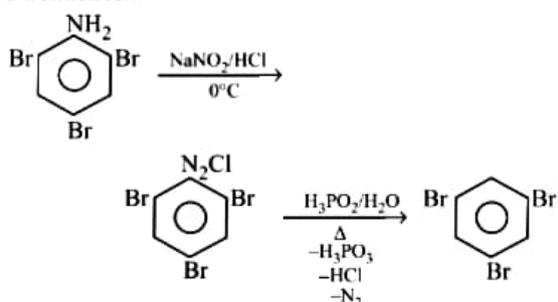
**2. Halogenation:** It is so highly activated that even on addition of  $\text{Br}_2$  water a precipitate of 2, 4, 6-tribromoaniline (sym. tribromoaniline) is formed.



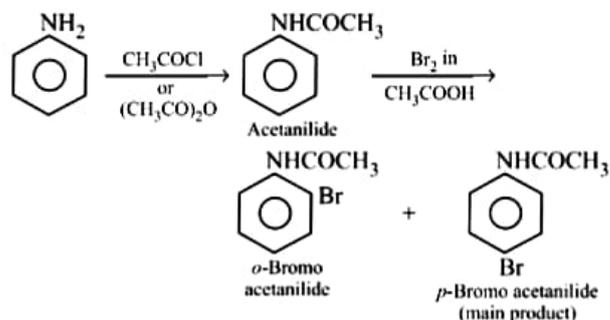
Similarly with chlorine water we get sym. trichloro aniline



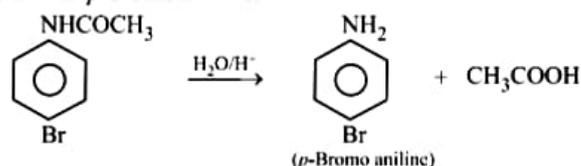
The above sym. tribromo and trichloro anilines on diazotization followed by reduction the diazonium salts with hypophosphorous acid yields sym. tribromo and trichloro benzenes.



Only one halogen atom in  $ortho/para$  position can be obtained from acetanilide, i.e., the amino group is first protected by acetylation process.

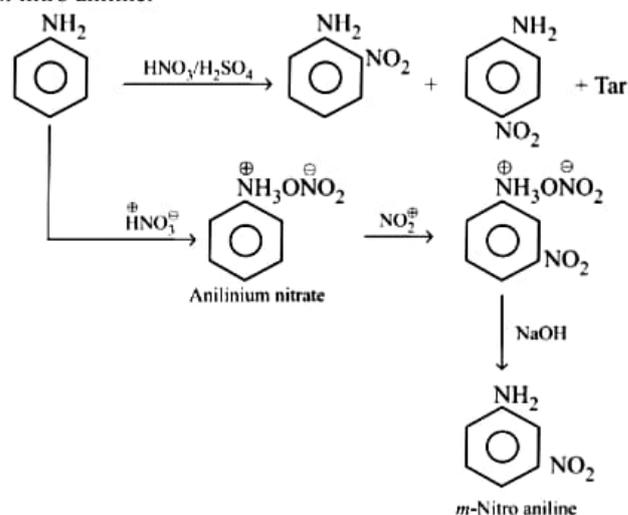


These  $ortho$  and  $para$  bromo acetanilides on hydrolysis yield  $o$ - and  $p$ -bromo anilines.

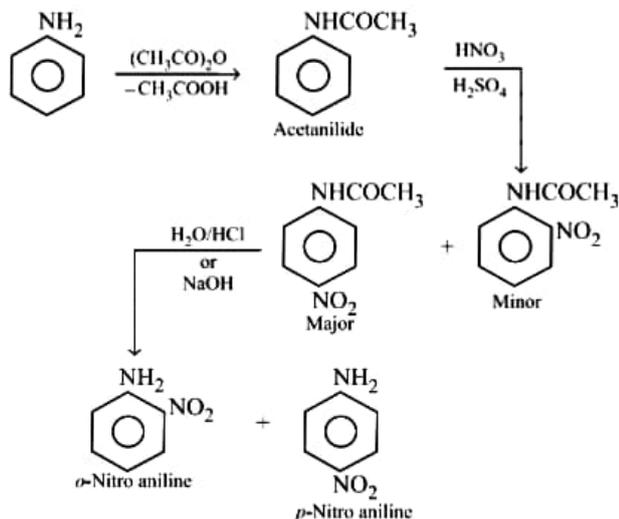


**Halogenation of aniline is faster in polar solvents but slower in non-polar solvents. An alkyl group cannot be used as an effective protecting group because it is electron releasing.**

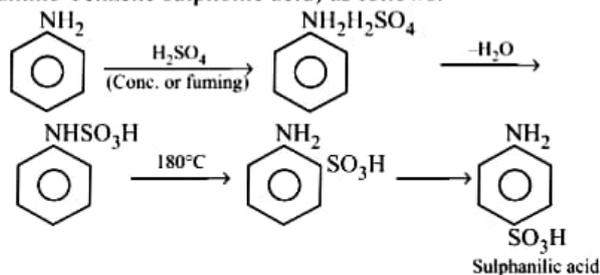
**3. Nitration:** Direct nitration of aniline is not possible due to two facts: (a) Being highly sensitive towards oxidation, direct nitration results in the production of tarry products along with only a little nitrated product. (b) Protonation of aniline yields anilinium ion which being  $m$ -directing gives  $m$ -nitro aniline.



In order to prevent the formation of above product,  $-\text{NH}_2$  group is first protected by acetylation to give acetanilide which is nitrated to a mixture of  $o$ - and  $p$ -acetanilides. These nitro acetanilides are then hydrolysed to get  $o$ - and  $p$ -nitro anilines.

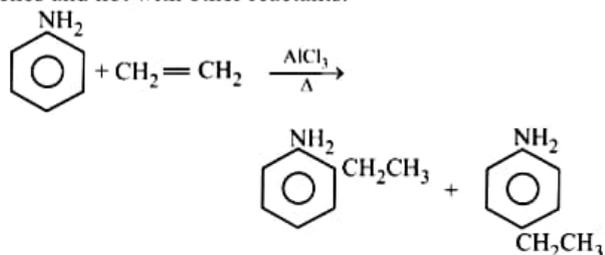


**4. Sulphonation:** Aniline on heating with excess of conc.  $\text{H}_2\text{SO}_4$  or fuming  $\text{H}_2\text{SO}_4$  at  $180^\circ\text{C}$  gives sulphanilic acid (*p*-amino-benzene sulphonic acid) as follows:

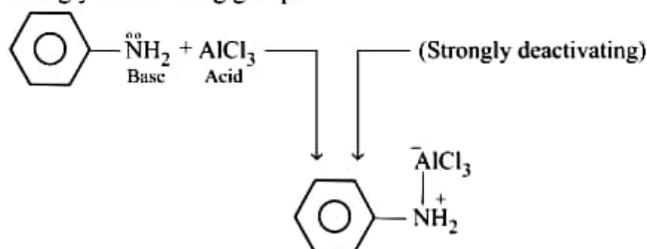


The above process is known as **Baking**.

**5. Friedel-Crafts reaction:** Undergoes FCR only with alkenes and not with other reactants.

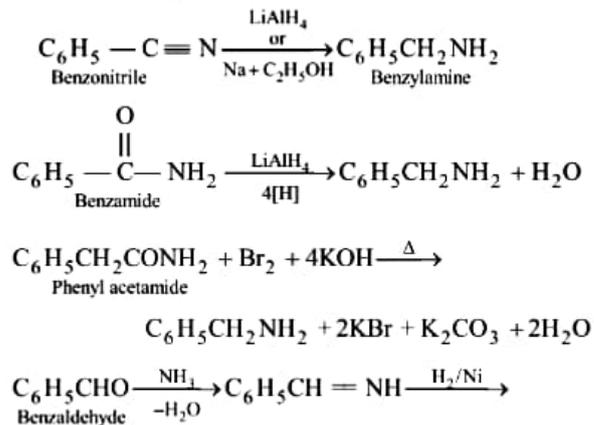


Aniline gives FCR with difficulty because an amino group (a basic group) undergoes reaction with Lewis acids to give a strongly deactivating group.

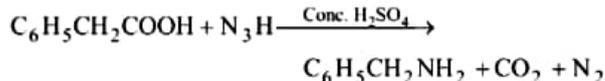


## BENZYL AMINE

It is a side chain primary amine. It is prepared as follows:



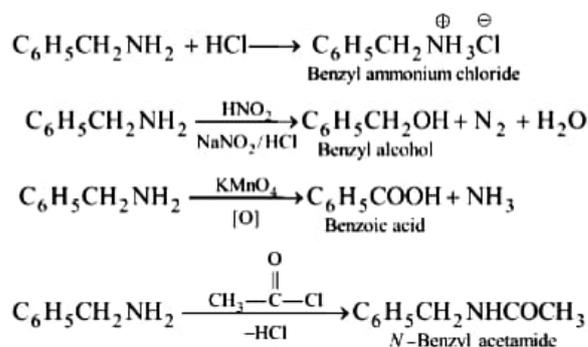
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  (Reductive amination)  
Benzylamine



## Physical Properties

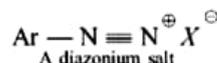
It is a colourless liquid, b. pt.  $185^\circ\text{C}$ . It is soluble in water and is more basic than aniline and isomeric toluidine but less basic than aliphatic amines.

## Chemical Properties



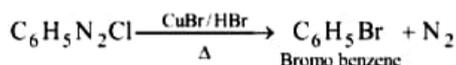
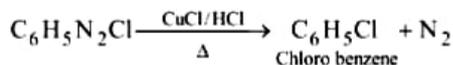
## DIAZONIUM SALTS

**J. Peter Griess** found that the reaction of primary aromatic amines with nitrous acid in presence of a suitable mineral acid at low temperature yields diazonium salts. These have the general formula  $\text{ArN}_2^+ \text{X}^-$  where  $\text{X}^-$  is an anion such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{HSO}_4^-$ , etc.

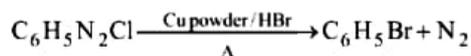
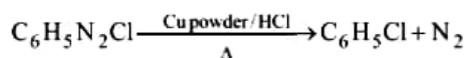




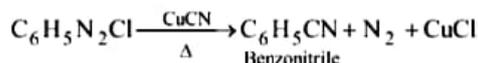
**4. Replacement of  $-\text{N}_2\text{Cl}$  by  $-\text{Cl}$  and  $-\text{Br}$  :** When diazonium salt solution is heated with cuprous halide dissolved in same hydrogen halide, the  $-\text{N}_2\text{Cl}$  is replaced by Cl or Br. It is known as **Sandmeyer's reaction**.



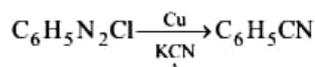
If a diazonium salt solution is heated with copper powder in presence of HCl or HBr we get corresponding halobenzene. This reaction is known as **Gattermann's reaction**.



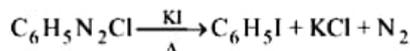
**5. Replacement of  $-\text{N}_2\text{Cl}$  by  $-\text{CN}$ :**



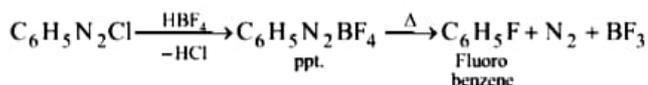
This is also called as **Sandmeyer's reaction**. However, the following reaction is Gattermann's reaction.



**6. Replacement of  $-\text{N}_2\text{Cl}$  by iodine atom:**

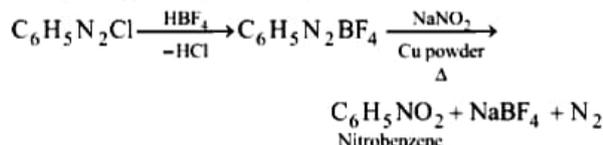


**7. Replacement by fluorine atom:**

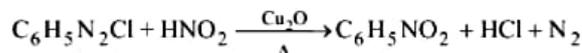
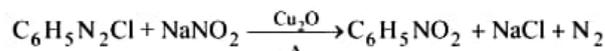


The preparation of fluoro benzene from benzene diazonium fluoroborate is known as **Balz-Schiemann reaction**.

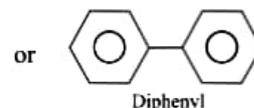
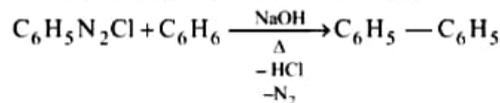
**8. Replacement of  $-\text{N}_2\text{Cl}$  by  $-\text{NO}_2$  group:** When benzene diazonium fluoroborate is heated with  $\text{NaNO}_2$  in presence of copper powder we get nitrobenzene.



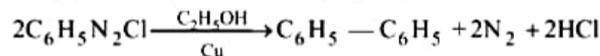
Nitrobenzene may also be obtained by heating benzene diazonium chloride with  $\text{NaNO}_2$  or  $\text{HNO}_2$  in presence of cuprous oxide.



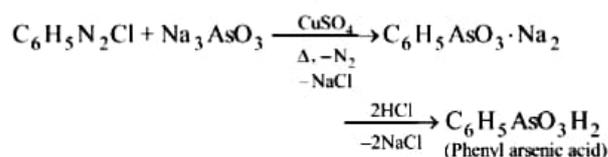
**9. Formation of diphenyl:** When an alkaline diazonium salt solution is heated with benzene, the diazonium group is replaced by phenyl group to yield diphenyl.



The above reaction is known as **Gomberg reaction**. Diphenyl can also be obtained by treating benzene diazonium chloride with ethanol and copper powder.

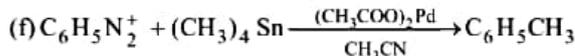
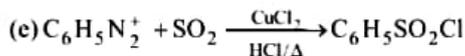
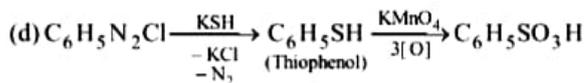
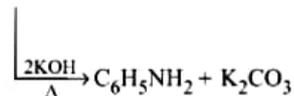
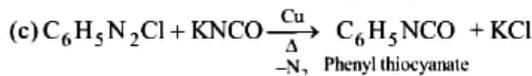
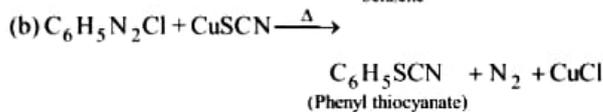
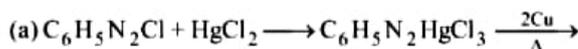


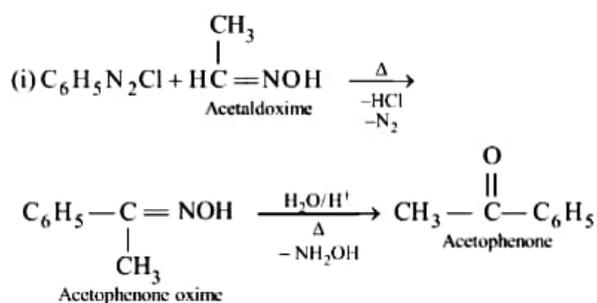
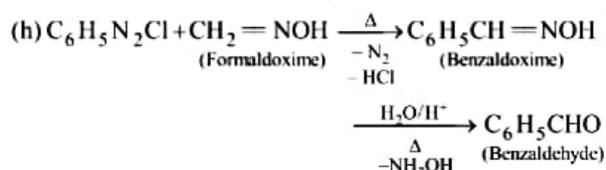
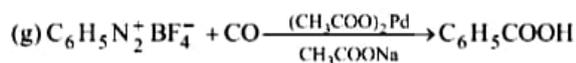
**10. Replacement by  $-\text{AsO}_3\text{H}_2$  group:**



The replacement by **arsenic acid group** is known as **BART'S reaction**.

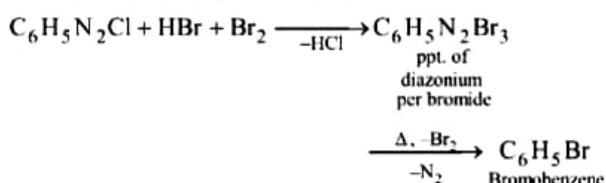
**11. Miscellaneous reactions:**





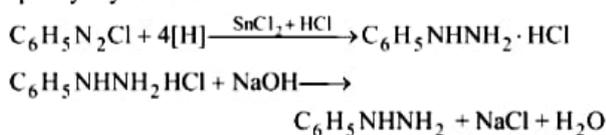
## II. Reactions of the Diazonium Salts in which the Nitrogen Atoms are Retained

### 1. Action of bromine and HBr:

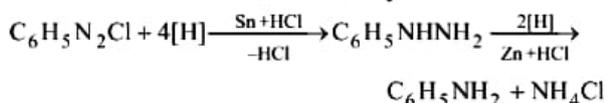


If the phenyl diazo per bromide is treated with aqueous ammonia, the azide ( $\text{C}_6\text{H}_5\text{N}_3$ ), is produced.

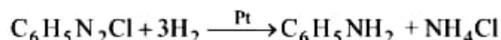
**2. Reduction:** When reduced with stannous chloride and conc. HCl, the group  $-\text{N}_2$  is converted into  $-\text{NHNH}_2$  to give phenyl hydrazine.



Reduction by  $\text{Na}_2\text{SO}_3$  also yields phenyl hydrazine. However reduction with metal and acid yields aniline.



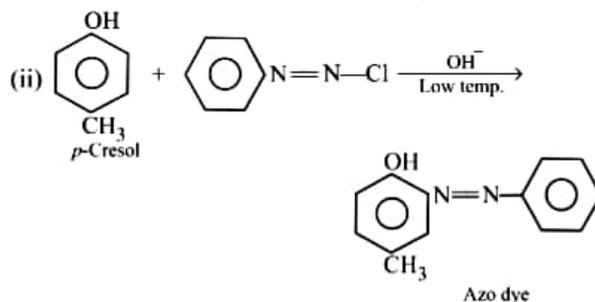
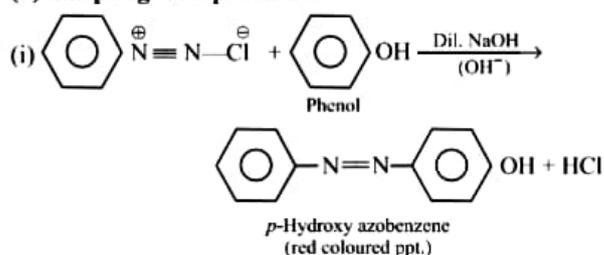
On catalytic reduction it gives aniline.



**3. Coupling reactions:** A condensation between diazonium salt and activated compound, *i.e.*, amine, dialkyl aniline or alkyl aniline in a weakly acidic solution and a phenol in a weakly alkaline medium, to give highly coloured **azo compounds** is known as **coupling**. These highly coloured compounds are known as **azodyes**. This process usually takes

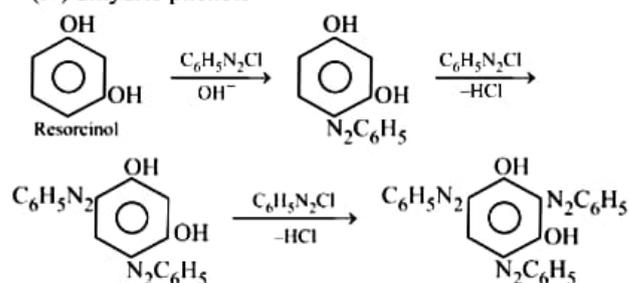
place at *para* position to the amino or phenolic group, in case the *para* position is occupied coupling takes place in the *ortho* positions. However, if both *ortho* and *para* positions are occupied, coupling either does not occur or a substituent like  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  present in the *p*-position is replaced by azo ( $-\text{N}=\text{N}-$ ) group. Coupling is an electrophilic substitution reaction and the electrophile is phenyl diazonium cation ( $\text{C}_6\text{H}_5\text{N}_2^+$ ).

### (a) Coupling with phenols:

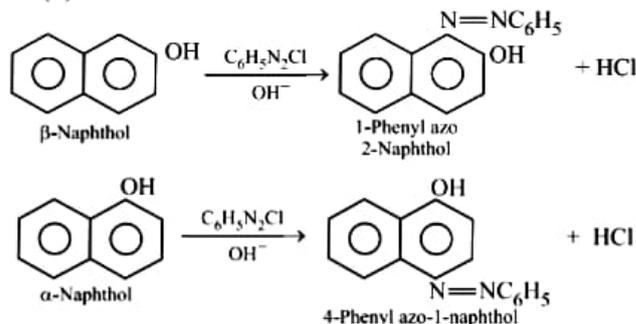


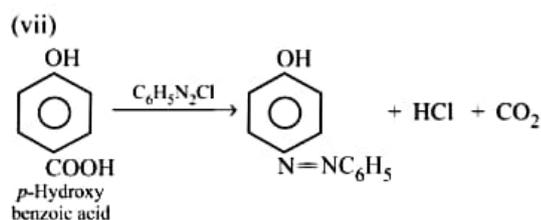
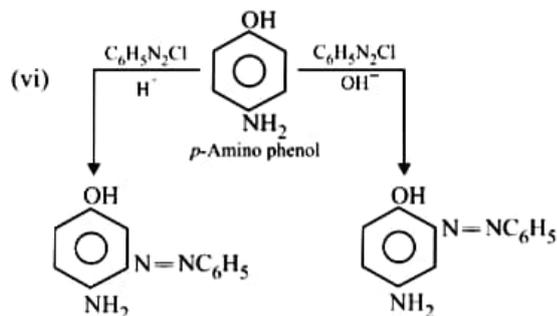
(iii) *o*- and *m*-cresol couples in *p*-position with diazonium salt.

### (iv) dihydric phenols



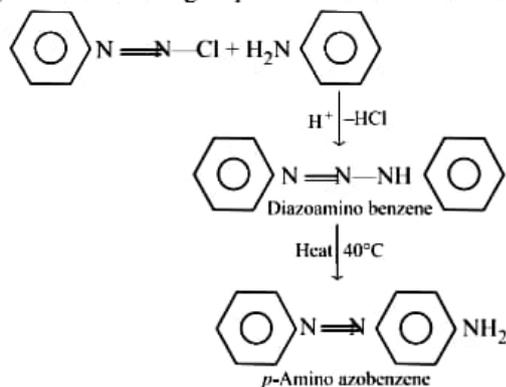
### (v)



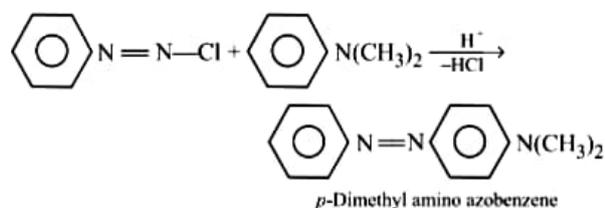


### (b) Coupling with amines:

(i) Aniline reacts to give *p*-amino azo benzene as follows :

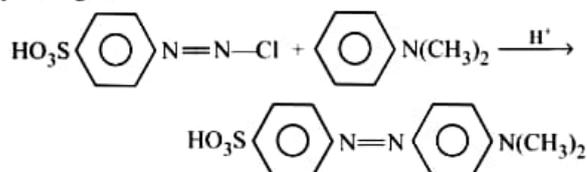


(ii) Coupling with *N,N*-dimethyl aniline



Electron attracting groups ( $-I$  groups) in the ring of benzene diazonium chloride facilitate coupling, while the presence of electron donating groups ( $+I$  groups) especially in the *m*- position of the original  $-\text{OH}$  or  $-\text{NH}_2$  group also facilitate coupling. A halogen or nitro group in the ring of aromatic amine or phenol lowers the electron density in the ring, hence such compounds do not undergo coupling with diazonium salts.

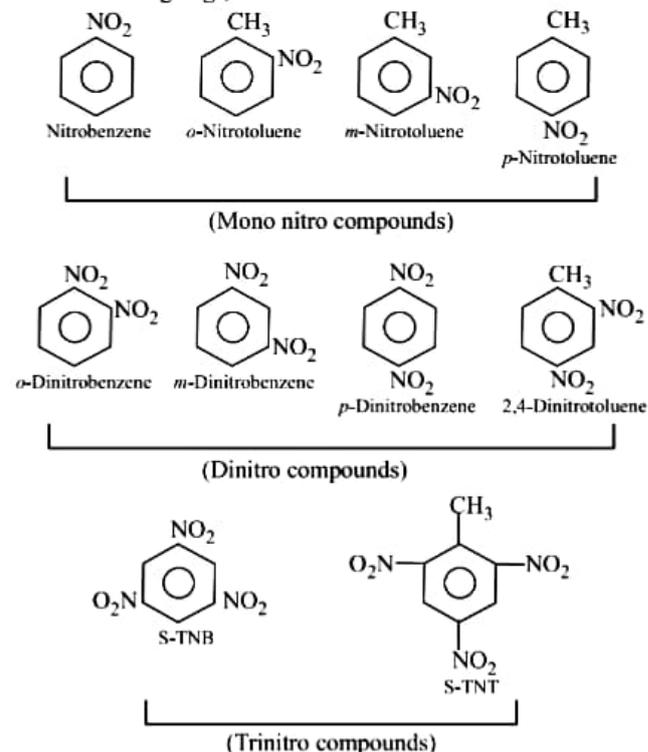
(iii) Coupling with diazotized sulphanilic acid gives methyl orange.



## NITRO COMPOUNDS

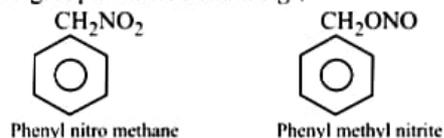
Organic compounds having nitro ( $-\text{NO}_2$ ) group are known as nitro compounds. These are of two types:

(a) **Nuclear nitro compounds** : When  $-\text{NO}_2$  is directly attached to ring *e.g.*,



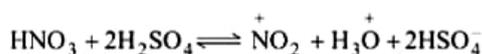
**(b) Aryl substituted nitro alkane and alkyl nitrites:**

When nitro group is in side chain *e.g.*,

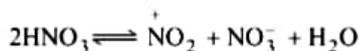
**Nitration**

The replacement of nuclear (ring) H by nitro group is known as nitration. It is carried out as follows:

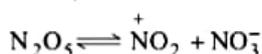
**(1) Direct nitration: (a)** A mixture of conc.  $\text{HNO}_3$  or fuming  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$  known as **nitration mixture** or **mixed acid** may be used. The function of conc.  $\text{H}_2\text{SO}_4$  is two fold, *i.e.*, as dehydrating agent and producer of electrophile nitronium ion ( $\text{NO}_2^+$ ) from conc.  $\text{HNO}_3$ .



(i) In concentrated  $\text{HNO}_3$  alone, one  $\text{HNO}_3$  molecule acts as base and other as acid in giving  $\text{NO}_2^+$  ion.



(ii) With  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  we have

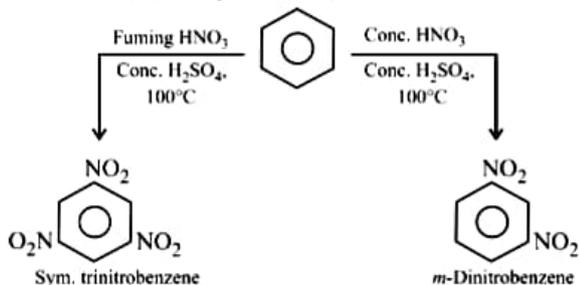


**(b)** A mixture of conc.  $\text{HNO}_3$  and acetic anhydride or  $\text{BF}_3$  may also be used. Here acetic anhydride acts as a dehydrating agent while  $\text{BF}_3$  is an effective catalyst because it forms solid hydrate with water.

**(c)** Nitrogen peroxide in presence of catalyst anhydrous  $\text{AlCl}_3$ , can also be used.

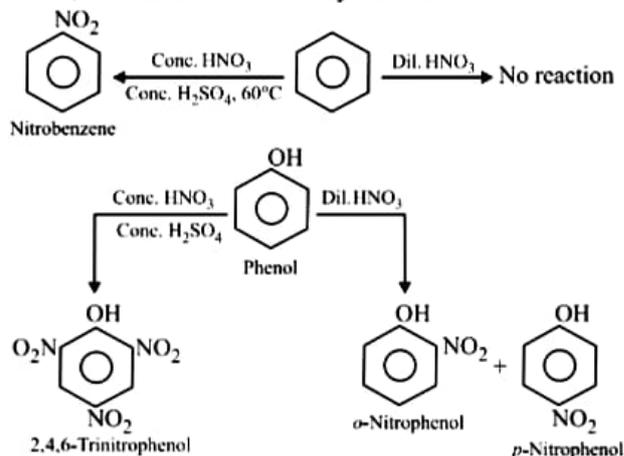
**(d)** Acetyl nitrile can be used for nitration of highly activated compounds.

The number of  $-\text{NO}_2$  introduced depends upon the nature of nitrating agent used, temperature of reaction as well as on the nature of compounds to be nitrated.



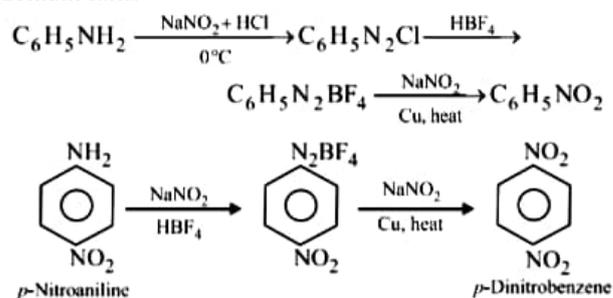
Similarly with conc.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$  at  $60^\circ\text{C}$  the product is nitrobenzene, but at  $100^\circ\text{C}$  it is *m*-dinitrobenzene.

Presence of electron-releasing groups ( $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{CH}_3$ ,  $-\text{OCH}_3$ , etc.) in the nucleus makes further nitration more easier. Thus, compounds like phenol, aniline, toluene, anisole, etc. can be nitrated easily than benzene.



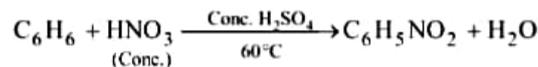
Compounds containing electron-withdrawing groups like  $-\text{NO}_2$ ,  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  requires powerful nitrating agent like fuming  $\text{HNO}_3$  +  $\text{H}_2\text{SO}_4$  and a higher temperature.

**(2) Indirect nitration:** This can be done by means of diazonium salts.

**NITROBENZENE****Methods of Preparation**

It is prepared as follows :

**(1) By the action of conc.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$  on benzene:**

**Note:**

For compounds containing **activating groups**, the reaction can be carried out with  $\text{HNO}_3$  alone or in water, acetic acid or acetic anhydride. It is because conc.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$  mixture would oxidise these compounds.

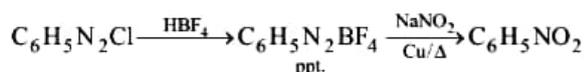
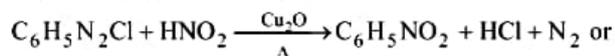
If anhydrous conditions are needed, nitration can be effected with  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  in the presence of  $\text{P}_2\text{O}_5$ , which removes the water formed in the reactions.

Nitration in alkaline media can be done with esters of HNO<sub>3</sub> like ethyl nitrate (C<sub>2</sub>H<sub>5</sub>ONO<sub>2</sub>)

Nitronium salts like NO<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>, NO<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> and NO<sub>2</sub><sup>+</sup>CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> can also be used for nitration.

BF<sub>3</sub> can be used for removing water as a solid hydrate.

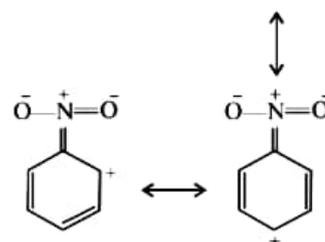
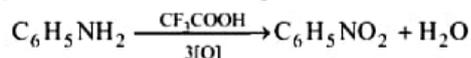
### (2) From benzene diazonium chloride:



### (3) Action of acetyl nitrite on benzene:

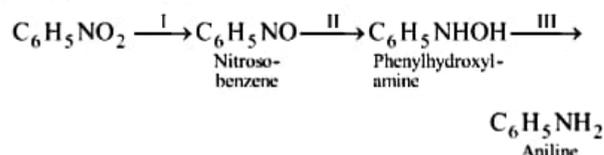


### (4) Oxidation of aniline by trifluoroacetic acid:



Due to  $-M$  (resonance) effect  $o$ -, and  $p$ -positions have low electron density while  $m$ -position becomes points of relatively more electron density hence incoming  $E^+$  enters in  $m$ -position.

**1. Reduction of nitro compounds:** It can be reduced in different media to yield different products. The reduction can be shown as follows :



## Physical Properties

- It is a pale-yellow, oily liquid (b. pt. 210°C) with a strong smell of bitter almond.
- It is insoluble in water but soluble in organic solvents.
- It is steam volatile and its vapours are poisonous.
- It is a good solvent for anhydrous AlCl<sub>3</sub> and hence used as a solvent in Friedel-Crafts reaction.

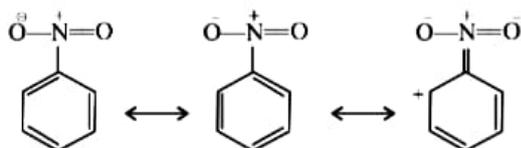
## Chemical Properties

It is less reactive than benzene. The presence of  $-\text{NO}_2$  group increases the stability of benzene ring. It is not affected by acids, alkalis and oxidising agents. Following points are important regarding its properties.

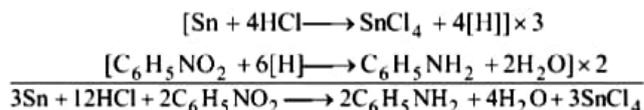
(i)  $-\text{NO}_2$  group is firmly attached with ring carbon (it is because of double bond character of carbon-nitrogen bond due to resonance), hence cannot be replaced by other groups, however in  $o$ - and  $p$ -dinitrobenzenes one  $-\text{NO}_2$  is easily replaced by  $-\text{OH}$  and  $-\text{NH}_2$  groups.

(ii) Due to the presence of oxygen in  $-\text{NO}_2$  group it shows only the reduction reactions.

(iii)  $-\text{NO}_2$  group being  $m$ -director gives all electrophilic substitution reactions in  $m$ -position with difficulty as compared to benzene.



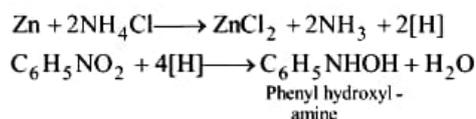
**(a) Reduction by metal and acids:** Sn + Conc. HCl or Fe + Conc. HCl reduces it to aniline.



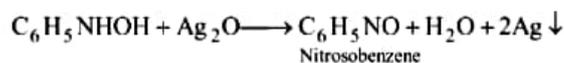
or, the reduction may be shown as follows:



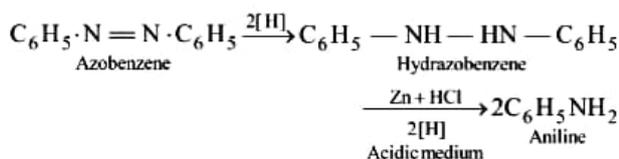
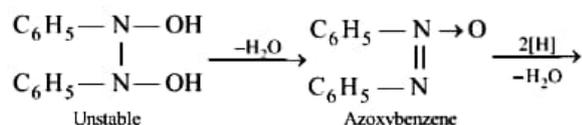
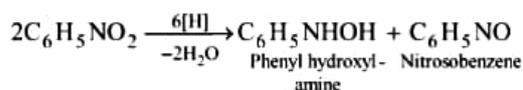
**(b) Reduction in neutral medium:** Neutral reducing agents like Al-Hg + H<sub>2</sub>O, zinc powder + NH<sub>4</sub>Cl or Zn powder + C<sub>2</sub>H<sub>5</sub>OH + CaCl<sub>2</sub> reduces it into phenyl hydroxylamine.



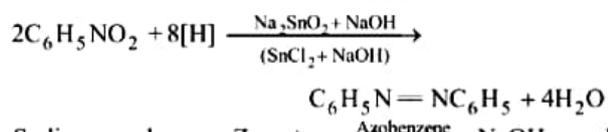
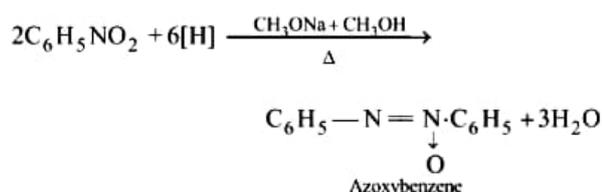
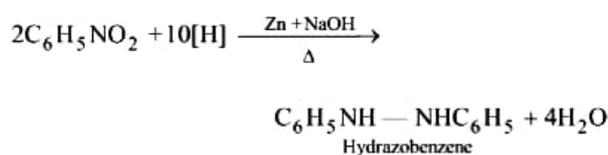
Other neutral reducing agent is zinc-copper couple and water. If the above hot solution is filtered into Tollen's reagent, a white ppt. is obtained. It is known as **Mullikan-Barker's test**.



**(c) Reduction in alkaline medium:** Depending upon the nature of alkaline reducing agent different products are obtained. It is believed that initially nitrosobenzene and phenyl hydroxyl amine are formed. These react together to produce a variety of compounds.

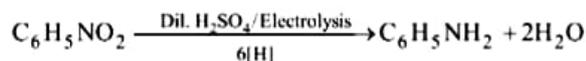


By using different alkaline reducing agents the final products are:

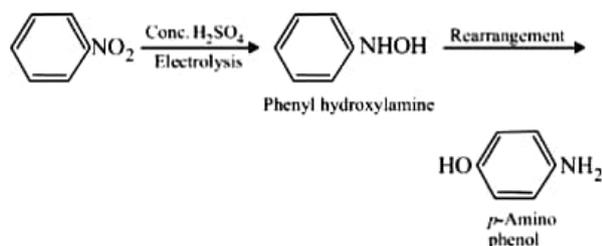


Sodium-amalgam, Zn + methanolic NaOH and  $\text{LiAlH}_4$  also reduce  $\text{C}_6\text{H}_5\text{NO}_2$  into azobenzene.

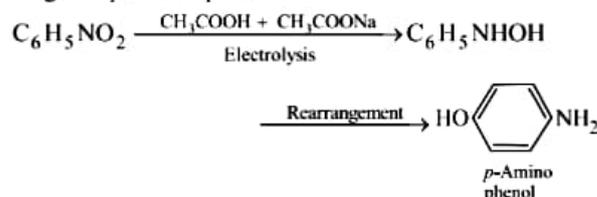
**(d) Electrolytic reduction:** (i) When electrolysed in a weakly acidic medium (dil.  $\text{H}_2\text{SO}_4$ ) it gives aniline.



(ii) When electrolysed in strongly acidic (conc.  $\text{H}_2\text{SO}_4$ ) medium it gives *p*-amino phenol. Presumably, initially phenyl hydroxylamine is produced which rearranges to *p*-amino phenol.

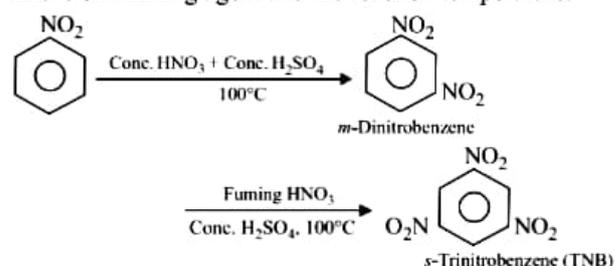


(iii) Electrolysis in aqueous solution of acetic acid and sodium acetate also gives phenyl hydroxylamine which rearranges to *p*-amino phenol.

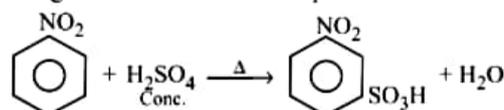


**2. Reactions of nucleus:** As a result of negative electromeric effect ( $-E$ ), negative inductive effect ( $-I$ ) and negative mesomeric effect ( $-M$ ) the *o*- and *p*-position becomes highly electron deficient leaving *m*-position unaffected. Thus, substitution in nitrobenzene takes place in *m*-position.

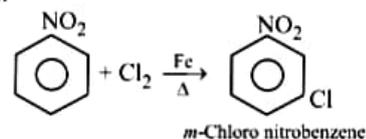
**(a) Nitration:** Gives different products depending upon the nature of nitrating agent and the reaction temperature.



**(b) Sulphonation:** On heating with conc.  $\text{H}_2\text{SO}_4$  nitrobenzene gives *m*-nitrobenzene sulphonic acid.

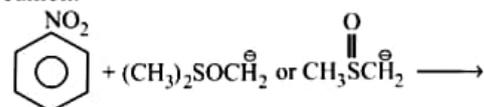


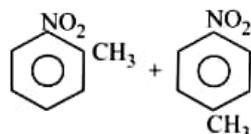
**(c) Halogenation:** In presence of halogen carriers (Fe powder,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , etc.) it reacts with halogen to give *m*-halo products.



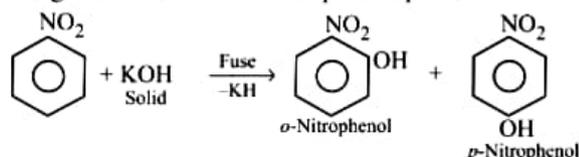
**(d)** It is so highly deactivated that there is no Friedel-Crafts reaction.

**(e)** Nitrobenzene can be methylated with the dimethylsulfonium methylide or methyl sulfinyl carbanion.





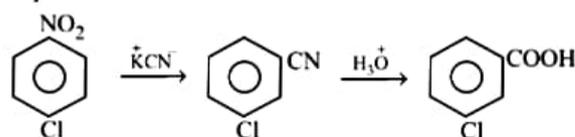
**3. Nucleophilic substitution:** When fused with solid KOH it gives a mixture of *o*- and *p*- nitrophenols.



**4. Formation of molecular addition compounds:** Certain nitro compounds, e.g., 1,3, 5- trinitrobenzene (TNB), picric acid, etc., react with polynuclear hydrocarbons (naphthalene, anthracene) to give crystalline addition compounds.

### Von-Richter Rearrangement

When nitro compounds are treated with cyanide ion, the  $\text{—NO}_2$  group is displaced and a carboxyl group enters with cine substitution, always *ortho* to the displaced group, never *m*- or *p*-.



### Uses of Nitrobenzene

- (1) As an oxidising agent in organic synthesis.
- (2) As a high boiling solvent.
- (3) In the manufacture of aniline, azo dyes, etc.
- (4) In the manufacture of floor polishes.
- (5) As a scent for cheap soaps and shoe polishes under the name of oil mirabane.



## Objective Problems

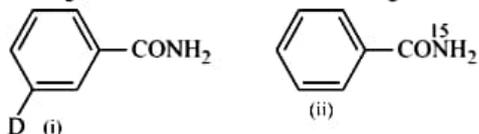


### Introduction and Methods of Preparation

1. When  $C_6H_5NO_2$  is treated with Zn dust and  $NH_4Cl$  we get:

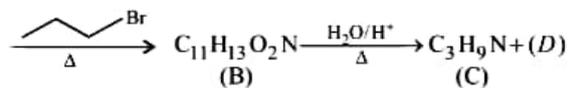
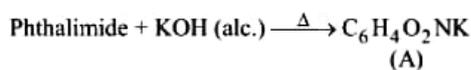
- aniline
- benzene
- phenyl hydroxyl amine
- azoxy benzene

2. Identify the products formed when mixture of (i) and (ii) undergoes intermolecular Hofmann degradation:



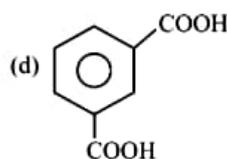
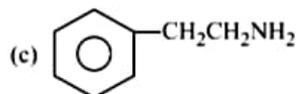
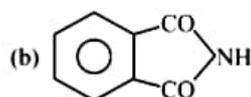
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3. In the reaction;

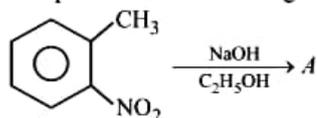


The product (D) is :

- 

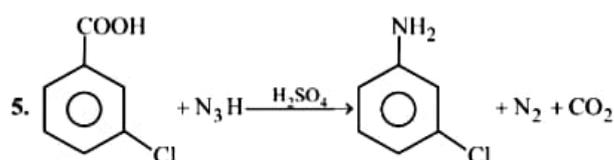


4. The product of the following reaction will be :



Reduction  $\rightarrow B \xrightarrow{H^+/H_2O} C$ ; will be :

- 
- 
- 
- 



The reaction is :

- Sandmeyer reaction
  - Schmidt reaction
  - Hunsdiecker
  - Friedel-Crafts reaction
6. On reduction in acidic medium, nitrobenzene gives:
- aniline
  - nitroso benzene
  - phenyl hydroxyl amine
  - hydrazobenzene

### Properties of Anilines and Benzylamine

7. Aniline has high boiling point, high vapour pressure at  $100^\circ\text{C}$  and is insoluble in water. Aniline is therefore separated by:

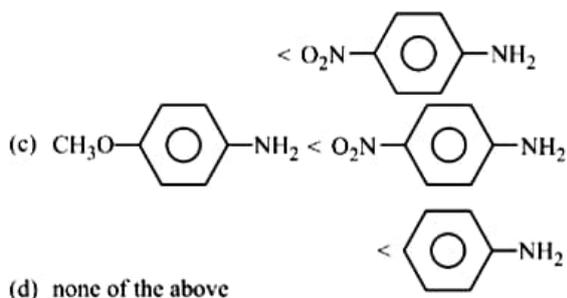
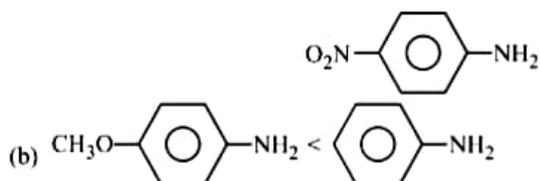
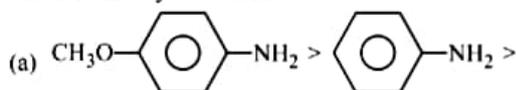
- steam distillation
- vacuum distillation
- simple distillation
- alkali treatment

8. The dipole moment of *p*-nitro aniline is :
- greater than that the nitrobenzene and aniline
  - smaller than that of nitrobenzene and aniline
  - greater than that of nitrobenzene but smaller than of aniline
  - equal to zero



The decreasing order of basicities of above mentioned amines is :

- $I > II > III > IV$
  - $I > III > II > IV$
  - $I > III > IV > II$
  - $III > IV > II > I$
10. Which of the following order is correct regarding the relative basicity of amines?



11. Aniline when treated with  $\text{NaNO}_2$  and cold conc.  $\text{HCl}$  gives:

- nitrobenzene
- benzene diazonium chloride
- chlorobenzene
- none of the above

12. Anils (Schiff's bases) are formed when aniline condenses with:

- benzophenone
- acetophenone
- benzaldehyde
- benzyl alcohol

13. Aniline reacts with chloroform in presence of  $\text{KOH}$  to give:

- o*-chlorobenzene
- phenyl cyanide
- carbylamine
- amino phenol

14. Aniline on sulphonation gives:

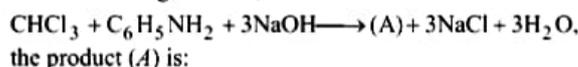
- sulphanilic acid

- m*-amino benzene sulphonic acid
- o*-amino benzene sulphonic acid
- none of the above

15. When aniline is heated with benzaldehyde the product is:

- benzoin
- Schiff's base
- unsaturated acid
- azoxy benzene

16. In the following reaction,



- phenyl cyanide
- phenyl isocyanide
- nitrobenzene
- none of these

17. Aniline  $\xrightarrow[0^\circ\text{C}]{\text{NaNO}_2/\text{HCl}}$  (A)  $\xrightarrow[\Delta]{\text{H}_2\text{O}}$  X,

compound X is :

- $\text{C}_6\text{H}_5\text{Cl}$
- $\text{C}_6\text{H}_5\text{COCl}$
- $\text{C}_6\text{H}_5\text{OH}$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$

18. Aniline is reacted with  $\text{Br}_2$  water and the resulting product is treated with an aqueous solution of  $\text{NaNO}_2$  in presence of dil.  $\text{HCl}$ . The resulting solution is converted into a tetra borofluorate which is subsequently heated dry. The final product is:

- 1,3,5-tribromobenzene
- p*-bromo fluorobenzene
- p*-bromo aniline
- 2,4,6-tribromo fluorobenzene

19. The reaction of aniline with  $\text{Br}_2$  in presence of carbon disulphide solvent gives:

- m*-bromo aniline
- 2,4,6-tribromo aniline
- o*- and *p*-bromo anilines
- N*-bromo aniline

20. Heating aniline with  $\text{CS}_2$  and  $\text{HgCl}_2$  gives:

- $\text{C}_6\text{H}_5\text{NCS}$
- $\text{C}_6\text{H}_5\text{NCO}$
- $\text{C}_6\text{H}_5\text{NC}$
- $\text{C}_6\text{H}_5\text{CN}$

21. Equimolecular mixture of aniline and phosgene on heating gives:

- phenyl isocyanate
- phenyl cyanate
- phenyl isocyanide
- phenyl cyanide

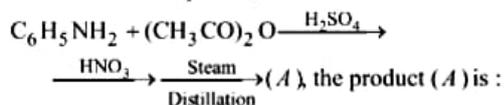
22. An excess of aniline and carbonyl chloride on heating gives:

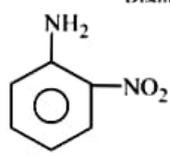
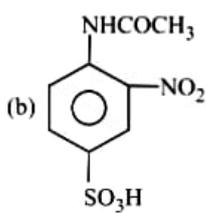
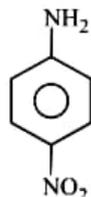
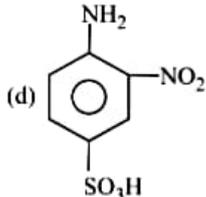
- $\text{C}_6\text{H}_5\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHC}_6\text{H}_5$
- $\text{C}_6\text{H}_5\text{NCO}$
- $\text{C}_6\text{H}_5\text{CNO}$
- $\text{C}_6\text{H}_5\text{CONH}_2$

23. On heating aniline with carbon disulphide in presence of solid KOH the product is:

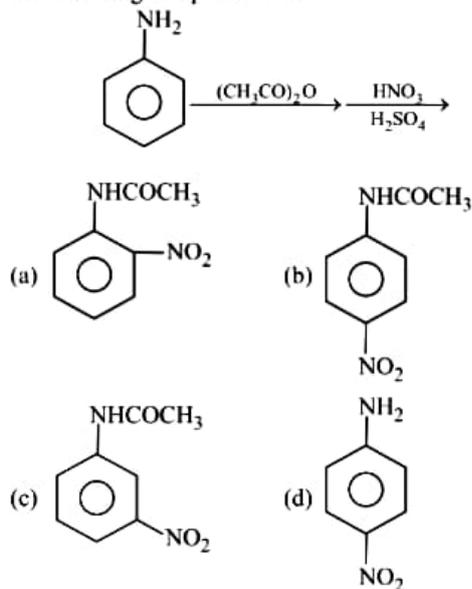
- (a)  $C_6H_5NH-C(=S)-NHC_6H_5$   
 (b)  $C_6H_5NCS$   
 (c)  $C_6H_5NCO$   
 (d) none of the above

24. In the reaction sequence,

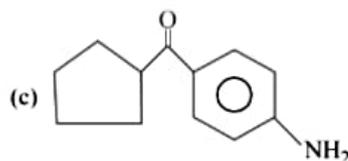
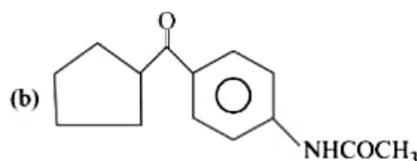
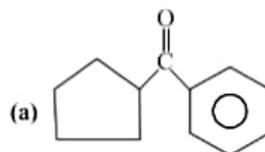
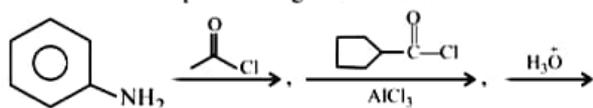


- (a)  (b)   
 (c)  (d) 

25. This reaction yields one main organic compound. Which of the following compound is it?

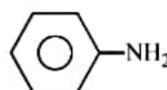
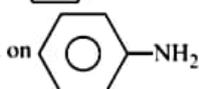
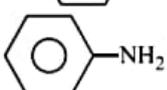
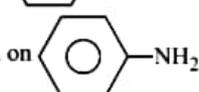


26. What is the end product of given reaction?

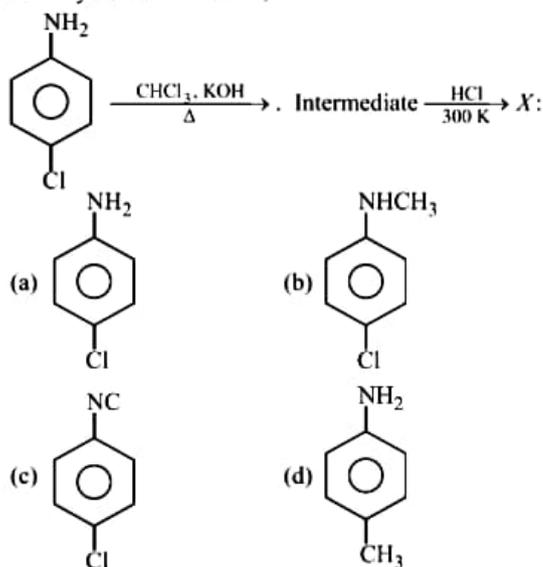


(d) none of the above

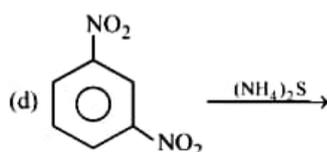
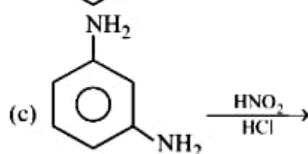
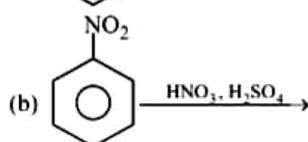
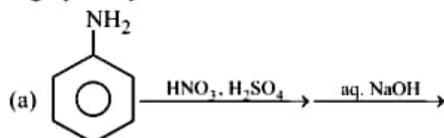
27. 2, 4, 6-tribromo aniline is a product of :

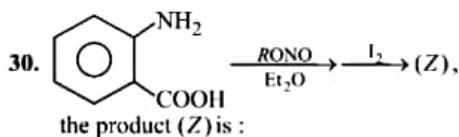
- (a) Electrophilic addition on   
 (b) Electrophilic substitution on   
 (c) Nucleophilic addition on   
 (d) Nucleophilic substitution on 

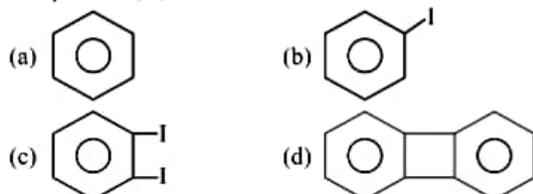
28. Identify X in the reaction.



29. Which of the following method is best suited as a high-yield synthesis of *m*-nitroaniline?



30.   
the product (Z) is:



31. Aniline when treated with bromine water gives:

- (a) *o*- and *p*-bromo anilines  
(b) *m*-bromo aniline  
(c) 2,4,6-tribromo aniline  
(d) 2,4-dibromo aniline

32. Aniline on reaction with  $\text{CH}_3\text{COCl}$  gives:

- (a) phenol (b) acetamide  
(c) acetanilide (d) benzene

33. Aniline in cold reacts with nitrous acid ( $\text{NaNO}_2 + \text{dil. HCl}$ ) to give:

- (a) phenol  
(b) benzene diazonium chloride  
(c) nitrobenzene  
(d) chlorobenzene

34. Aniline reacts with which of these to form Schiff's base?

- (a) acetic acid (b) benzaldehyde  
(c) acetone (d)  $\text{NH}_3$

### Diazonium Compounds

35. Which of the following reactants on reaction with  $\text{HNO}_2$  forms diazonium salts?

- (a)  $\text{C}_6\text{H}_5\text{NHC}_2\text{H}_5$  (b)  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$   
(c) *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{NHCH}_3$  (d) 2,5- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NH}_2$

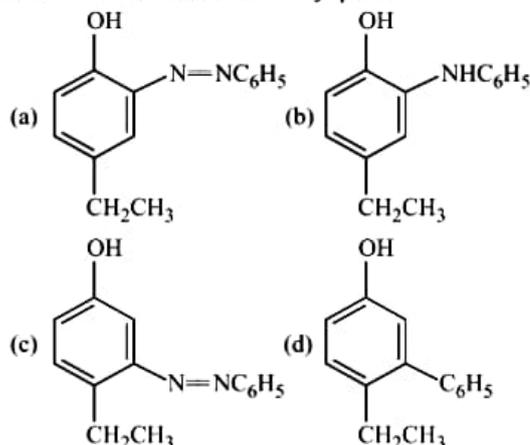
36. The conversion of 4-methyl benzene diazonium bromide to toluene is best carried out by using:

- (a)  $\text{H}^+$ ,  $\text{H}_2\text{O}$  (b)  $\text{H}_3\text{PO}_2$ ,  $\text{H}_2\text{O}$   
(c)  $\text{H}_2\text{O}$ ,  $\bar{\text{O}}\text{H}$  (d) Zn, NaOH

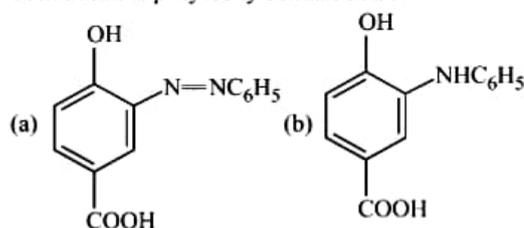
37. The transformation of 4-methyl benzene diazonium chloride to *p*-cresol is best carried out by using:

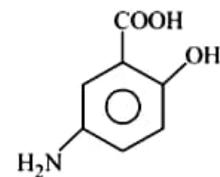
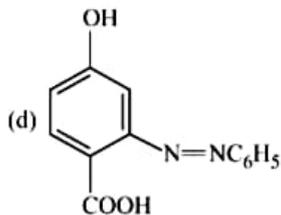
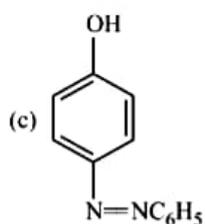
- (a)  $\text{H}_3\text{PO}_2$ ,  $\text{H}_2\text{O}$  (b)  $\text{H}^+$ ,  $\text{H}_2\text{O}$   
(c)  $\text{H}_2\text{O}$ ,  $\bar{\text{O}}\text{H}$  (d)  $\text{HBF}_4$

38. What is the principal product formed when the slurry obtained on treating aniline with potassium nitrite and HCl at  $0^\circ\text{C}$  has been added to 4-ethyl phenol?

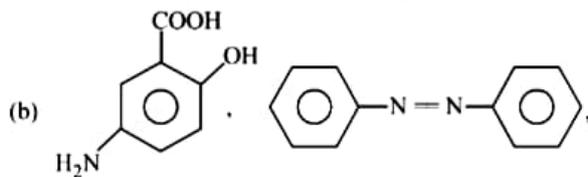
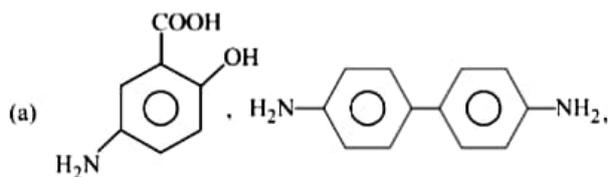
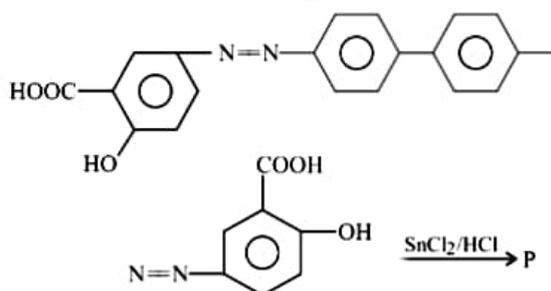


39. What is the principal product formed when slurry obtained on treating aniline with sodium nitrite and HCl at  $0^\circ\text{C}$  has been added to *p*-hydroxy benzoic acid?



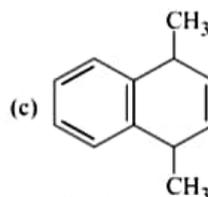
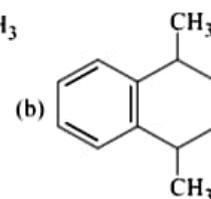
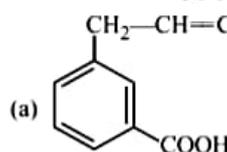
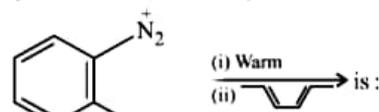


40. Identify the product/s formed when the following azo compound is reduced with  $\text{SnCl}_2/\text{HCl}$ :

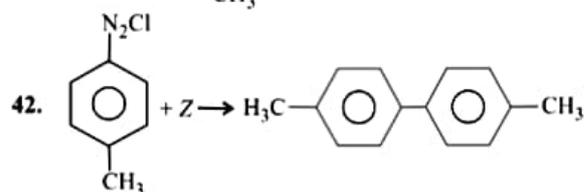


(d) none of the above

41. The product of the following reaction ,



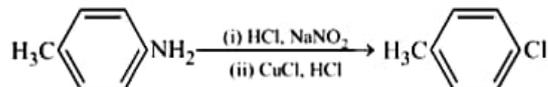
(d)  $\text{NO}_2$  and  $\text{CO}_2$



Which reagent is Z in the reaction given above?

- (a)  $\text{LiAlH}_4$  (b) Cu bronze powder  
(c)  $\text{Zn} + \text{aq. NH}_4\text{Cl}$  (d)  $\text{Zn} + \text{alc. NaOH}$

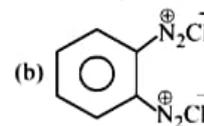
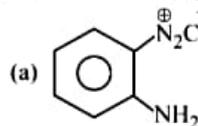
43. Consider the following reaction:

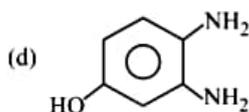
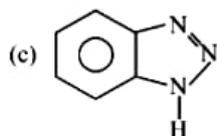


The name of the reaction and the intermediate *via* which it is known to proceed are, respectively :

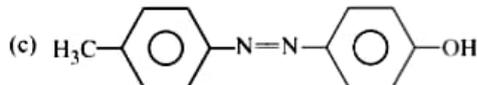
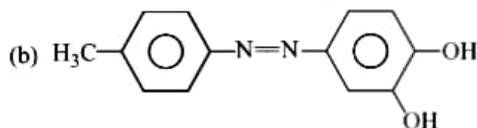
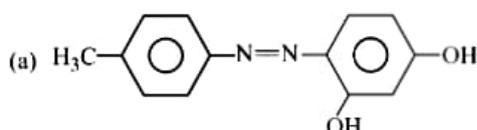
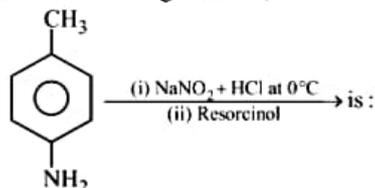
- (a) Hunsdiecker and benzyne  
(b) Sandmeyer and a free radical  
(c) Meerwein and a free radical  
(d) Sandmeyer and carbanion

44. Diazotization of *o*-phenylene diamine yields:





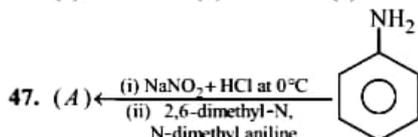
45. The product of the following reaction ;



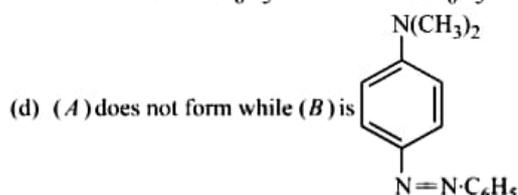
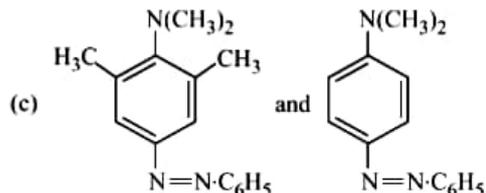
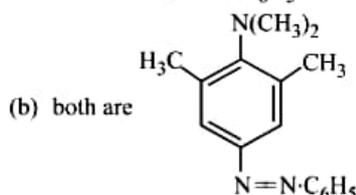
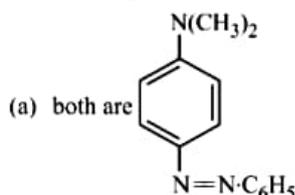
(d) none of the above

46. *p*-toluidine reacts with benzene-diazonium chloride to form a compound which, on boiling with  $\text{H}_2\text{SO}_4$  gives ..... product(s) :

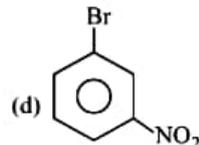
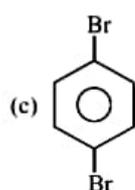
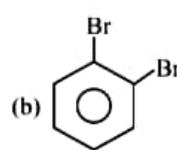
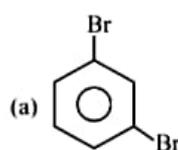
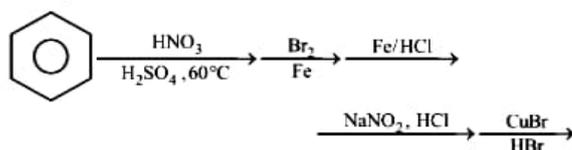
(a) one (b) two (c) three (d) four



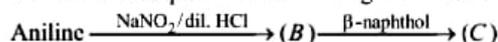
$\xrightarrow[\text{(ii) N,N-dimethyl aniline}]{\text{(i) NaNO}_2 + \text{HCl at } 0^\circ\text{C}}$  (B); (A) and (B) are :



48. Which of the following compounds would you expect to be major organic product of the five-step sequence shown here?



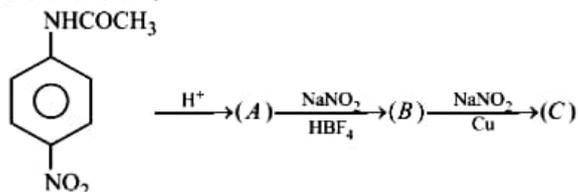
49. Consider the sequence of reactions given below:



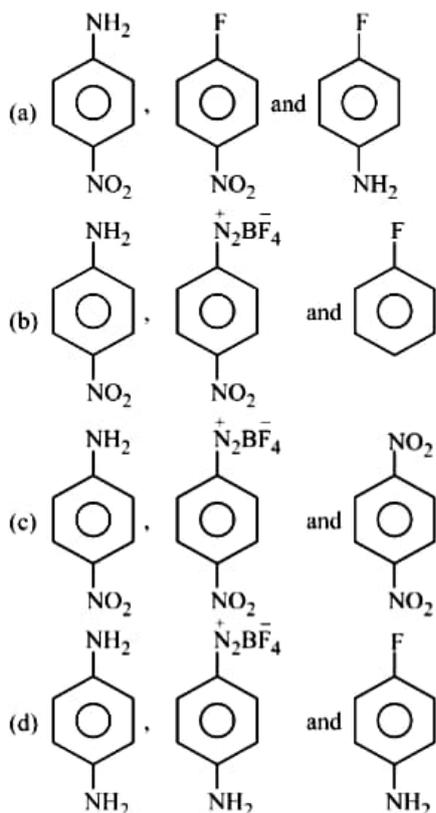
The product (C) has:

- (a) only an azo group  
 (b) only a phenolic group  
 (c) phenolic and azo groups  
 (d) amino and phenolic groups

50. In the reaction,



The products (A), (B) and (C) are:



51. Benzene diazonium chloride on reaction with phenol in a weakly basic solution gives:

- (a) diphenyl ether (b) *p*-hydroxy azobenzene  
(c) chlorobenzene (d) benzene

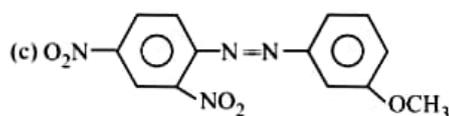
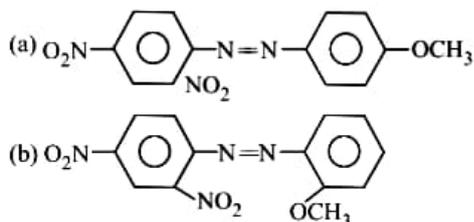
52. The high m. pt. and insolubility in organic solvents of sulphanic acid ( $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$ ) are due to its.....

.....structure.

- (a) Zwitter ion  
(b) ionic structure  $\text{H}_3\text{N}^+-\text{C}_6\text{H}_4-\text{SO}_3^-$   
(c) dipolar ion  
(d) none of the above

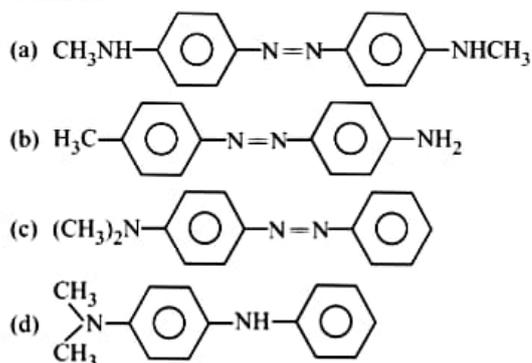
53. The product of following reaction,

2,4-dinitro aniline  $\xrightarrow[\text{(ii) Anisole}]{\text{(i) NaNO}_2 + \text{HCl at } 0^\circ\text{C}}$  is :



(d) none of the above

54. Aniline when diazotized in cold and then treated with dimethyl aniline gives a coloured product. Its structure would be:

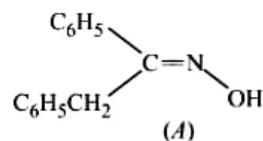


### Miscellaneous Problems

55. 2,4,6-tribromo aniline is obtained by:

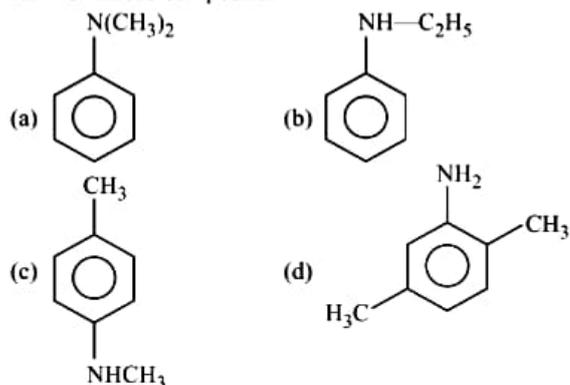
- (a) electrophilic addition  
(b) electrophilic substitution  
(c) nucleophilic addition  
(d) nucleophilic substitution

56. Beckmann transformation of *A* followed by hydrolysis will yield :

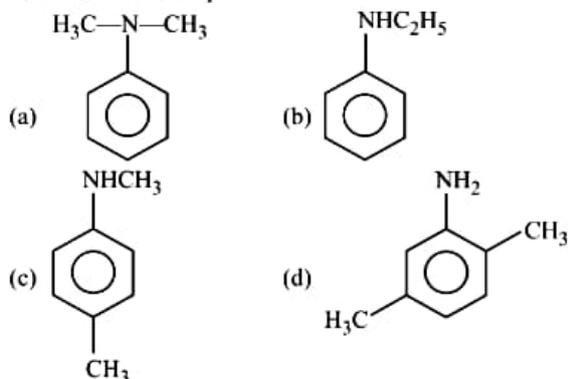


- (a) benzoic acid + benzylamine  
(b) phenyl acetic acid + benzyl amine  
(c) aniline + phenyl acetic acid  
(d) benzoic acid + aniline

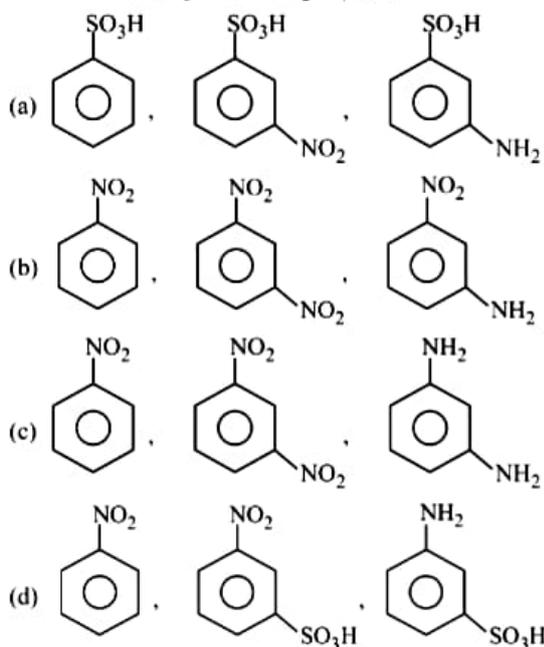
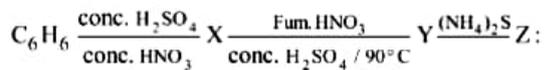
57. Which of the following reactants on reaction with  $\text{HNO}_2$  form C-nitroso compounds?



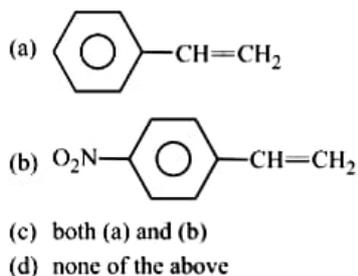
58. Which of the following reactants on reaction with  $\text{HNO}_2$  form *N*-nitroso compounds?



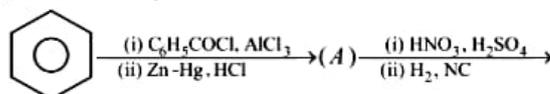
59. Identify the unknown compounds *X*, *Y* and *Z* in the following sequence of reaction;



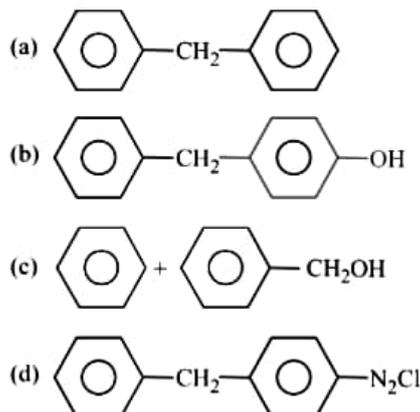
60. Which of the following reactants on reaction with  $(\text{C}_2\text{H}_5)_2\text{NH}$  forms *N*-alkylated products?



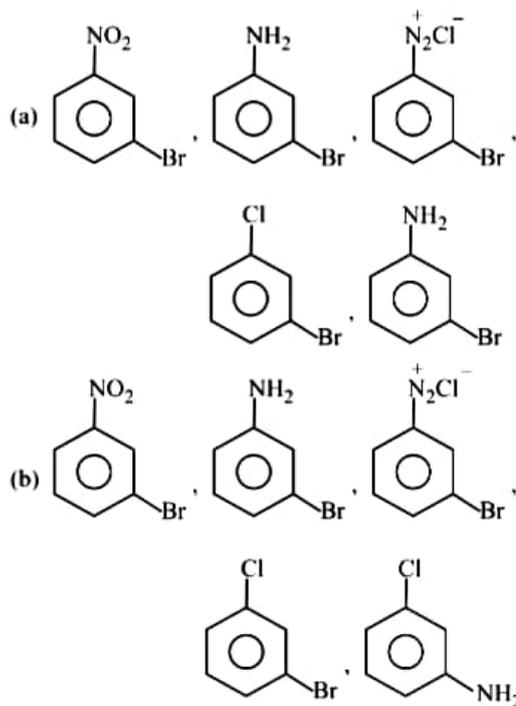
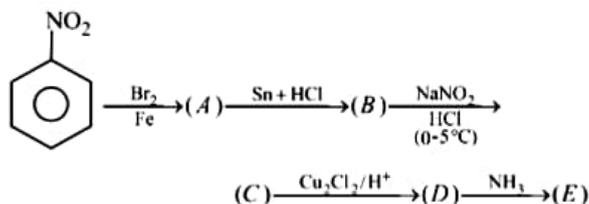
61. In the reaction,

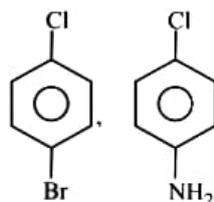
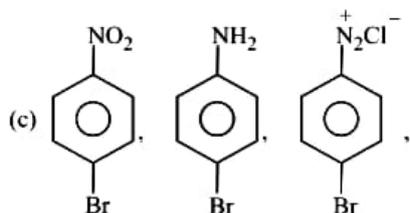


(B)  $\xrightarrow[\text{(ii) H}^+, \text{H}_2\text{O and } \Delta]{\text{(i) NaNO}_2/\text{HCl}}$  (C), the product (C) is :



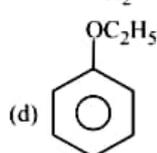
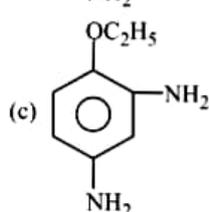
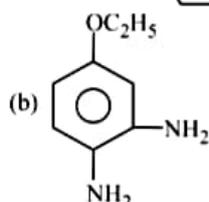
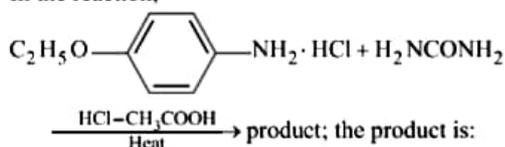
62. Identify (*A*), (*B*), (*C*), (*D*) and (*E*) in the following:



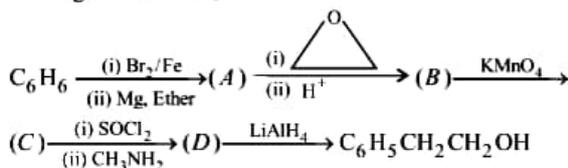


(d) none of the above

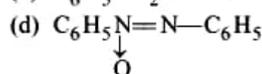
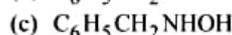
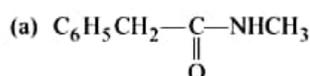
63. In the reaction,



64. In the given reaction:

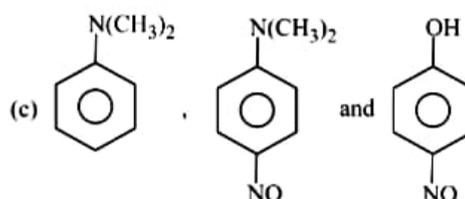
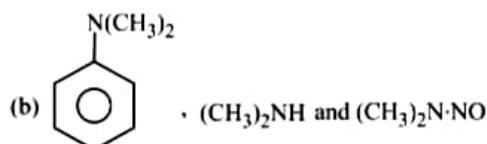
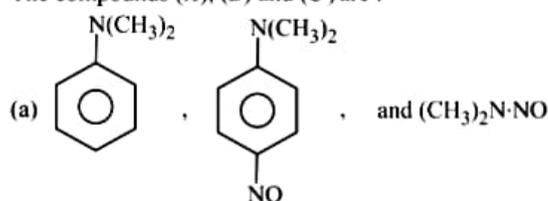


The product (D) is :



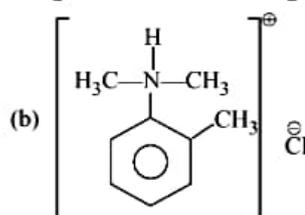
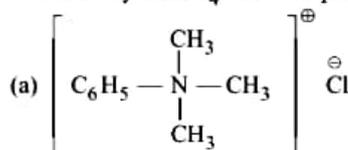
65. When compound (A)  $\text{C}_8\text{H}_{11}\text{N}$  is treated with  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  and aq. KOH, no any change takes place. Acidification of this mixture gives a clear solution. When (A) is treated with  $\text{NaNO}_2$  and HCl at  $0-5^\circ\text{C}$ , and the product is hydrolysed, a compound (B)  $\text{C}_7\text{H}_7\text{N}$  is obtained. (B) gives a ppt. with benzene sulphonyl chloride in the presence of aq. KOH. (B), on reaction with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  gives a yellow oily substance (C), which is a powerful carcinogen.

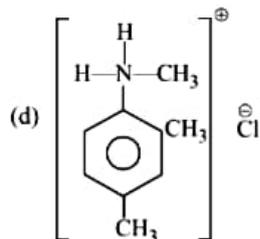
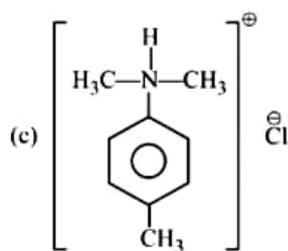
The compounds (A), (B) and (C) are :



(d) none of the above

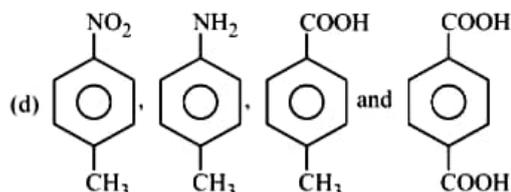
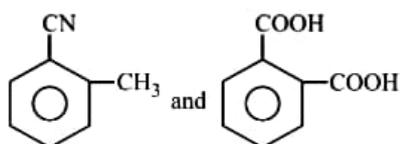
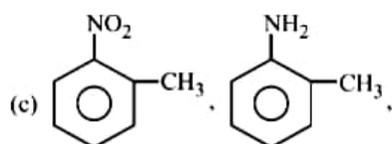
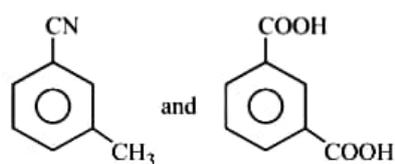
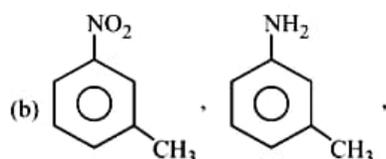
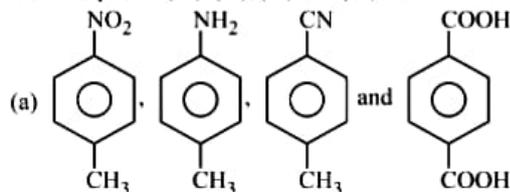
66. Compound (A)  $\text{C}_9\text{H}_{14}\text{NCl}$ , gives white ppt. with  $\text{AgNO}_3$  solution. It is resistant to bromination in either acid or alkaline solution. It is also resistant to heat, nitration and oxidation by  $\text{KMnO}_4$ . The compound (A) is :



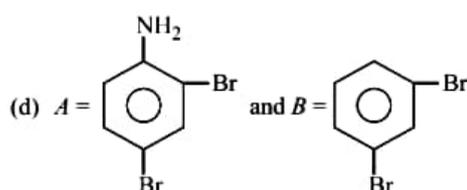
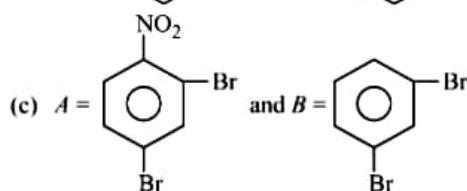
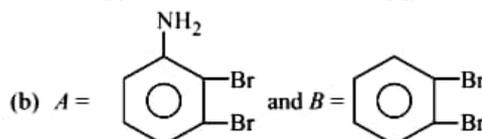
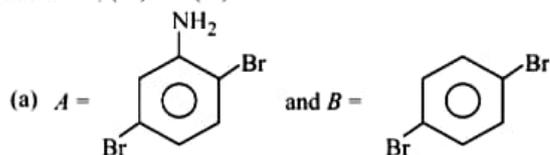


67. Compound (A),  $C_7H_7O_2N$  undergoes reduction to give (B),  $C_7H_9N$ . Compound (B) on diazotization followed by treatment with  $CuCN$  gives (C),  $C_8H_7N$ . Hydrolysis of (C) followed by oxidation gives (D),  $C_8H_6O_4$ . Compound (D) gives only one monosubstitution product.

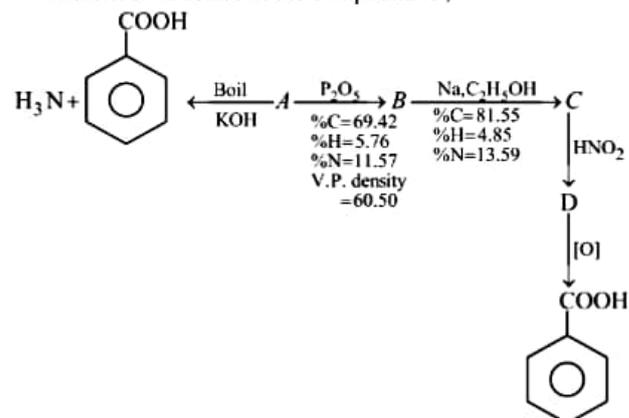
The compound (A), (B), (C) and (D) are:

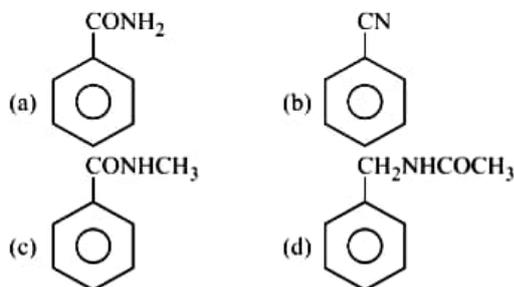


68. A compound (A) has molecular weight of 257 and contains 63.7% of bromine. Diazotization of (A) gives a diazonium salt, whose reduction gave a solid (B) containing 67.8% bromine. Only one mononitro derivative of (B) can be obtained, (A) and (B) are:

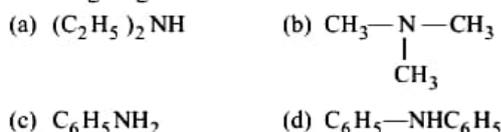


69. From the choices shown below pick the one which best describes structure of the compound A,





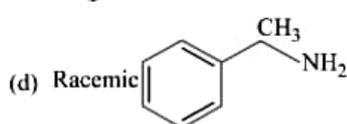
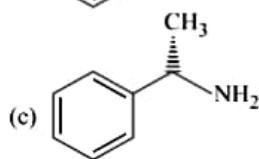
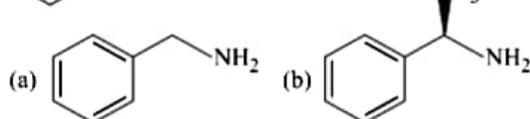
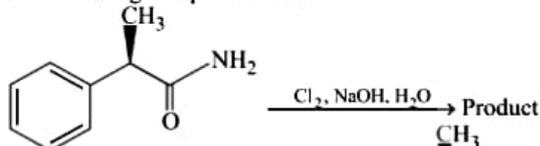
70. Which of the following compounds will dissolve in an alkali solution after it has undergone reaction with Hinsberg reagent?



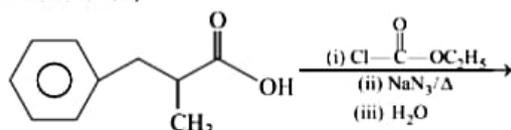
71. A compound *A* when reacted with  $PCl_5$  and then with ammonia gave *B*. *B* when treated with bromine and caustic potash produced *C*. *C* on treatment with  $NaNO_2$  and  $HCl$  at  $0^\circ C$  and then boiling produced *ortho*-cresol. Compound *A* is:



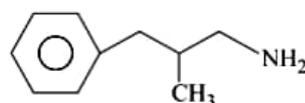
72. This reaction yields one main organic product. Which of the following compound is it?



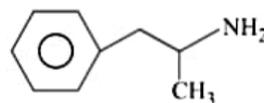
73. In the reaction,



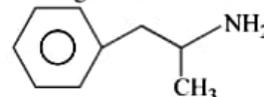
What is this reaction known as and which product is formed respectively?



(b) Curtius rearrangement, optically active



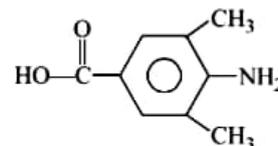
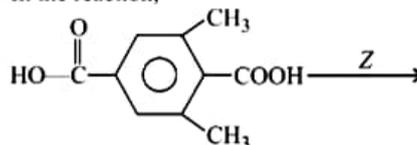
(c) Curtius rearrangement racemic



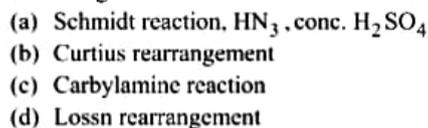
(d) Hofmann-Martius rearrangement



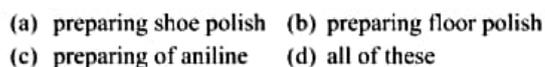
74. In the reaction,



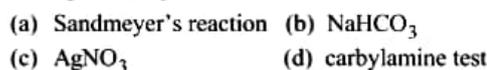
what is this reaction known and which reagent is *Z* in the reaction given above?



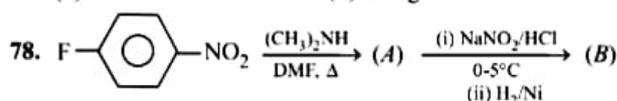
75.  $C_6H_5NO_2$  is generally used for:



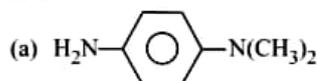
76. *p*-chloro aniline and anilinium hydrochloride can be distinguished by:

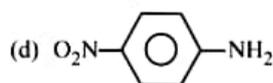
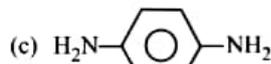
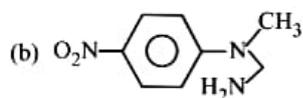


77. Which of the following is basic dye?

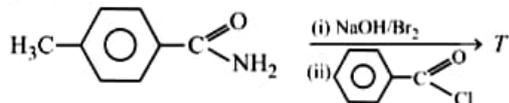


is:

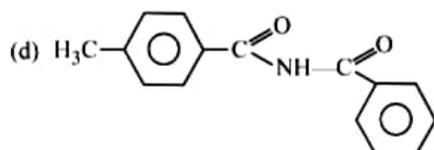
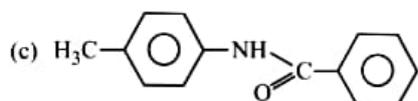
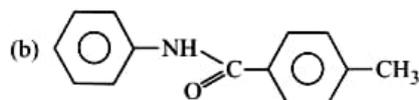
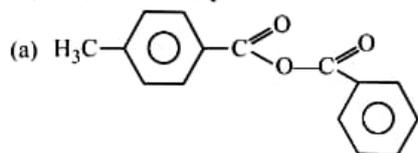




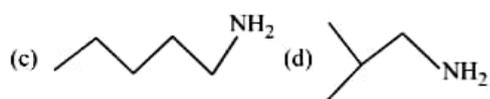
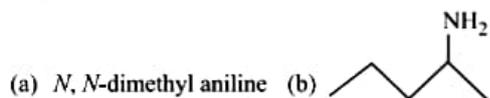
79. In the reaction,



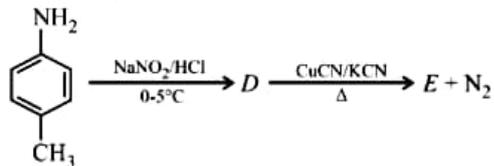
The structure of the product *T* is :



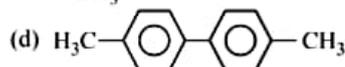
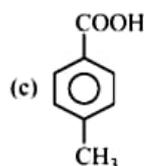
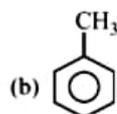
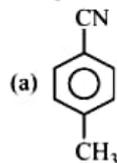
80. Which one of the following does not react with  $\text{CHCl}_3$  and  $\text{KOH}$ ?



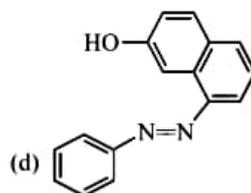
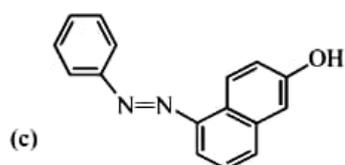
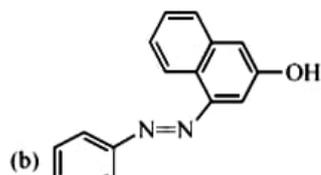
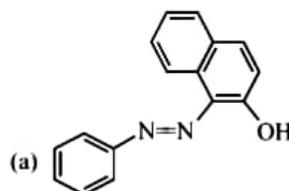
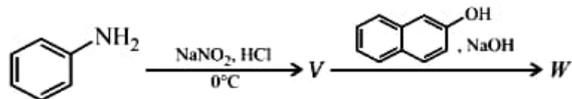
81. In the reaction,



The product (*E*) is :



82. In the following reactions, the major product *W* is :





### Objective Problems from Competitive Examination

1. Among the following, weakest base is :

(AIIMS 2003)

- (a)  $C_6H_5CH_2NH_2$       (b)  $C_6H_5CH_2NHCH_3$   
(c)  $O_2N-CH_2NH_2$       (d)  $HCONHCH_3$

2. Intermolecular hydrogen bonding is strongest in :

(AIIMS 2003)

- (a) methylamine      (b) phenol  
(c) formaldehyde      (d) methanol

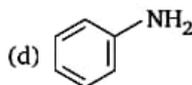
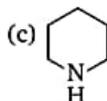
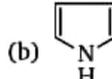
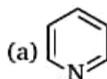
3. Among the following dissociation constant is highest for :

(AIIMS 2004)

- (a)  $C_6H_5OH$       (b)  $C_6H_5CH_2OH$   
(c)  $CH_3C \equiv CH$       (d)  $CH_3NH_3^+Cl^-$

4. The strongest base among the following is :

(AIIMS 2004)



5.  $C_6H_5CONHCH_3$  can be converted into  $C_6H_5CH_2NHCH_3$  by :

(AIIMS 2005)

- (a)  $NaBH_4$       (b)  $H_2$ - Pd/C  
(c)  $LiAlH_4$       (d)  $Zn-Hg/HCl$

6. Which of the following chemicals are used to manufacture methyl isocyanate that caused "Bhopal Tragedy"?

(AIIMS 2005)

- (i) Methylamine      (ii) Phosgene  
(iii) Phosphene      (iv) Dimethylamine  
(a) (i) and (iii)      (b) (iii) and (iv)  
(c) (i) and (ii)      (d) (ii) and (iv)

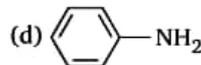
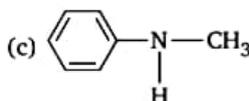
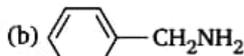
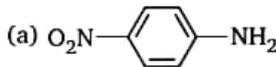
7. Acetamide is treated with the following reagents separately. Which one of these would yield methylamine ?

[AIPMT (Pre.) 2010]

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

8. Which of the following compounds is most basic ?

[AIPMT (Mains) 2011]



9. The compound which gives an oily nitrosoamine on reaction with nitrous acid at low temperature is :

(AIIMS 2008)

- (a)  $CH_3NH_2$       (b)  $(CH_3)_2CHNH_2$   
(c)  $CH_3-NH-CH_3$       (d)  $(CH_3)_3N$

10. An organic compound 'A' on treatment with  $NH_3$  gives 'B' which on heating gives 'C', 'C' when treated with  $Br_2$  in the presence of  $KOH$  produces ethylamine. Compound 'A' is :

[AIPMT (Mains) 2011]

- (a)  $CH_3COOH$       (b)  $CH_3CH_2CH_2COOH$   
(c)  $CH_3-CHCOOH$       (d)  $CH_3CH_2COOH$



11. Among the following compounds the one that is most reactive towards electrophilic nitration is :

[AIPMT (Pre.) 2012]

- (a) benzoic acid      (b) nitrobenzene  
(c) toluene      (d) benzene

12. Which of the following will be the most stable diazonium salt  $RN_2^+X^-$  ?

[AIPMT 2014]

- (a)  $CH_3N_2^+X^-$       (b)  $C_6H_5N_2^+X^-$   
(c)  $CH_3CH_2N_2^+X^-$       (d)  $C_6H_5CH_2N_2^+X^-$

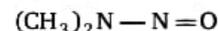
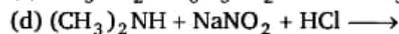
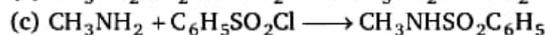
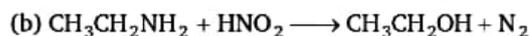
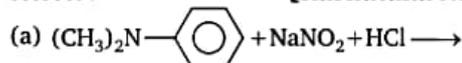
13. Which of the following will not give a primary amine ?

[AMU (Med.) 2013]



14. Some reactions of amines are given, which one is not correct ?

[Karnataka NEET 2013]

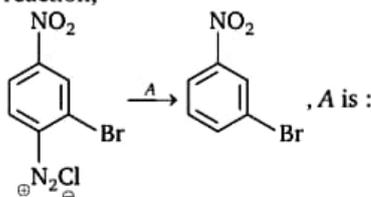


15. On hydrolysis of a "compound", two compounds are obtained. One of which on treatment with sodium nitrite and hydrochloric acid gives a product which does not respond to iodoform test. The second one

reduces Tollen reagent and Fehling solution. The "compound" is : **[Karnataka NEET 2013]**

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NC}$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$   
 (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{ON}=\text{O}$   
 (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CON}(\text{CH}_3)_2$

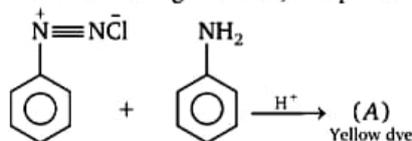
16. In the reaction,



**[Karnataka NEET 2013]**

- (a)  $\text{H}_3\text{PO}_2$  and  $\text{H}_2\text{O}$       (b)  $\text{H}^+/\text{H}_2\text{O}$   
 (c)  $\text{HgSO}_4/\text{H}_2\text{SO}_4$       (d)  $\text{Cu}_2\text{Cl}_2$

17. In the following reaction, the product 'A' is :



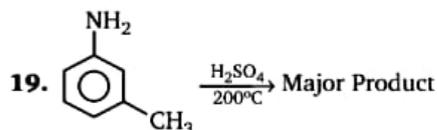
**[AIPMT 2014]**

- (a)
- (b)
- (c)
- (d)

18. Which of the following reactions is appropriate for converting acetamide to methanamine ?

**[NEET 2017]**

- (a) Hoffmann hypobromamide reaction  
 (b) Stephens reaction  
 (c) Gabriels phthalimide synthesis  
 (d) Carbylamine reaction

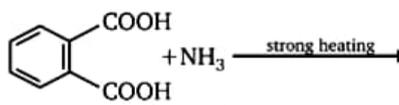


Major product of this reaction is : **[AIIMS 2017]**

- (a)
- (b)
- (c)
- (d)

20. The major product of the following reaction is :

**[NEET 2019]**



- (a)
- (b)
- (c)
- (d)

21. The correct order of the basic strength of methyl substituted amines in aqueous solution is :

**[NEET 2019]**

- (a)  $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$   
 (b)  $(\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$   
 (c)  $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2$   
 (d)  $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$

