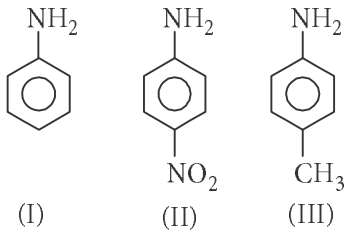
Chapter 27. Organic Compounds Containing Nitrogen

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



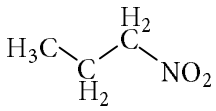
(I) (II) (III)

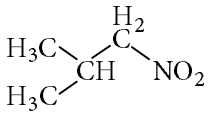
(a) III < I < II (b) III < II < I
(c) II < I < III (d) II < III < I

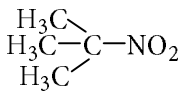
(NEET 2017)

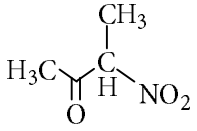
2. Which of the following reactions is appropriate for converting acetamide to methanamine?
(a) Hoffmann hypobromamide reaction
(b) Stephen's reaction
(c) Gabriel phthalimide synthesis
(d) Carbylamine reaction *(NEET 2017)*

3. Which one of the following nitro-compounds does not react with nitrous acid?

(a) 

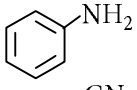
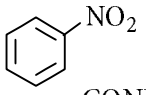
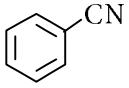
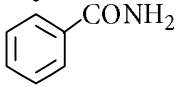
(b) 

(c) 

(d) 

(NEET-II 2016)

4. A given nitrogen-containing aromatic compound '*A*' reacts with Sn/HCl, followed by HNO_2 to give an unstable compound '*B*'. '*B*', on treatment with phenol, forms a beautiful coloured compound '*C*' with the molecular formula $C_{12}H_{10}N_2O$. The structure of compound '*A*' is

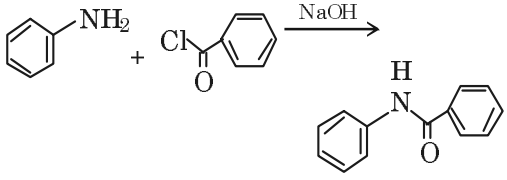
(a) 
(b) 
(c) 
(d) 

(NEET-II 2016)

5. The correct statement regarding the basicity of arylamines is
(a) arylamines are generally more basic than alkylamines because of aryl group
(b) arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is *sp*-hybridised
(c) arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalised by interaction with the aromatic ring π-electron system
(d) arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalised by interaction with the aromatic ring π-electron system.
(NEET-I 2016)

6. The product formed by the reaction of an aldehyde with a primary amine is
(a) carboxylic acid (b) aromatic acid
(c) Schiff's base (d) ketone.
(NEET-I 2016)

7. The following reaction



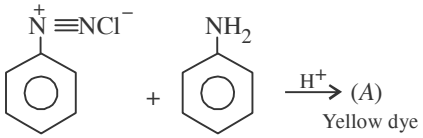
is known by the name
(a) Perkin's reaction
(b) Acetylation reaction
(c) Schotten-Baumann reaction
(d) Friedel-Craft's reaction. *(2015)*

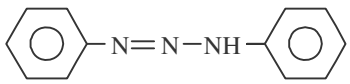
8. Method by which aniline cannot be prepared is
(a) degradation of benzamide with bromine in alkaline solution
(b) reduction of nitrobenzene with H_2/Pd in ethanol
(c) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution
(d) hydrolysis of phenylisocyanide with acidic solution. *(2015)*

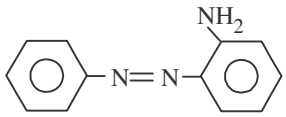
9. The number of structural isomers possible from the molecular formula C_3H_9N is
(a) 5 (b) 2
(c) 3 (d) 4 *(2015)*

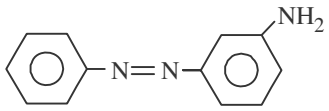
10. The electrolytic reduction of nitrobenzene in strongly acidic medium produces
(a) azobenzene (b) aniline
(c) *p*-aminophenol (d) azoxybenzene.
(2015, Cancelled)

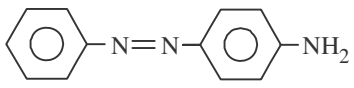
11. In the following reaction, the product (*A*) is



(a) 

(b) 

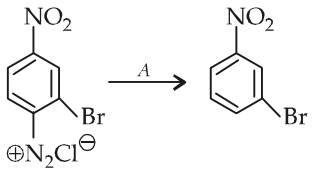
(c) 

(d) 

(2014)

12. Which of the following will be most stable diazonium salt $RN_2^+X^-$?
(a) $CH_3N_2^+X^-$ (b) $C_6H_5N_2^+X^-$
(c) $CH_3CH_2N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$
(2014)

13. Nitrobenzene on reaction with conc. HNO_3/H_2SO_4 at 80–100°C forms which one of the following products?
(a) 1, 4-Dinitrobenzene
(b) 1, 2, 4-Trinitrobenzene
(c) 1, 2-Dinitrobenzene
(d) 1, 3-Dinitrobenzene *(NEET 2013)*

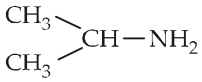
14. In the reaction 

A is
(a) H_3PO_2 and H_2O (b) H^+/H_2O
(c) $HgSO_4/H_2SO_4$ (d) Cu_2Cl_2
(NEET 2013)

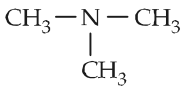
15. On hydrolysis of a "compound", two compounds are obtained. One of which on treatment with sodium nitrite and hydrochloric acid gives a product which does not respond to iodoform test. The second one reduces Tollens reagent and Fehling's solution. The "compound" is
(a) $CH_3CH_2CH_2NC$
(b) $CH_3CH_2CH_2CN$
(c) $CH_3CH_2CH_2ON{=}O$
(d) $CH_3CH_2CH_2CON(CH_3)_2$
(Karnataka NEET 2013)

16. Some reactions of amines are given. Which one is not correct?
(a) $(CH_3)_2N$–C$_6$H$_4$– + $NaNO_2$ + HCl →
$(CH_3)_2N$–C$_6$H$_4$–N=NCl
(b) $CH_3CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2OH + N_2$
(c) $CH_3NH_2 + C_6H_5SO_2Cl \rightarrow CH_3NHSO_2C_6H_5$
(d) $(CH_3)_2NH + NaNO_2 + HCl \rightarrow (CH_3)_2N{-}N{=}O$
(Karnataka NEET 2013)

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

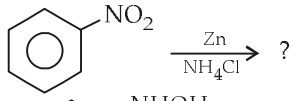
(a) 

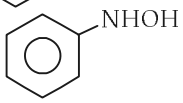
(b) $CH_3CH_2 - NH - CH_3$

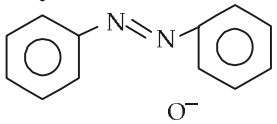
(c) 

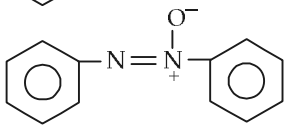
(d) $CH_3CH_2CH_2 - NH_2$ *(2012)*

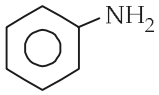
18. What is the product obtained in the following reaction?



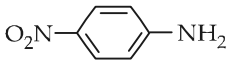
(a) 

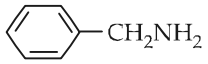
(b) 

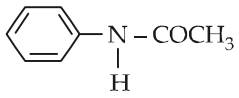
(c) 

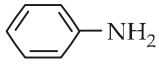
(d)  *(2011)*

19. Which of the following compounds is most basic?

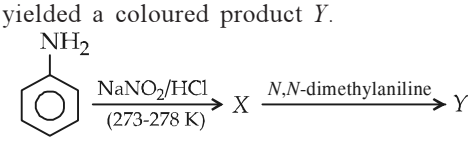
(a) 

(b) 

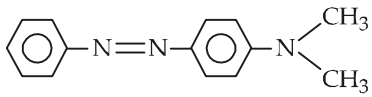
(c) 

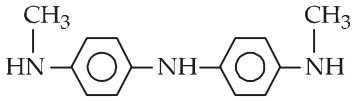
(d)  *(Mains 2011)*

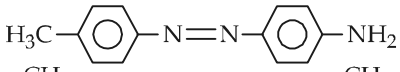
20. Aniline in a set of the following reactions yielded a coloured product *Y*.

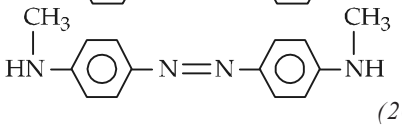


The structure of '*Y*' would be

(a) 

(b) 

(c) 

(d)  *(2010)*

21. Which of the following statements about primary amines is false?

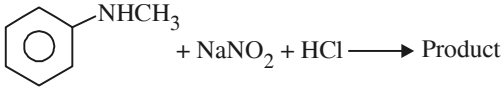
(a) Alkyl amines are stronger bases than aryl amines.

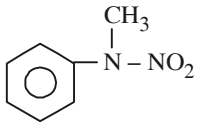
(b) Alkyl amines react with nitrous acid to produce alcohols.

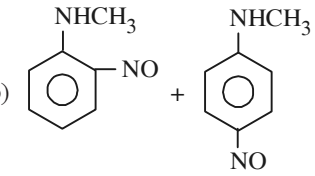
(c) Aryl amines react with nitrous acid to produce phenols.

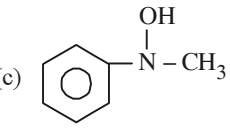
(d) Alkyl amines are stronger bases than ammonia. *(2010)*

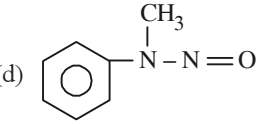
22. Predict the product.



(a) 

(b) 

(c) 

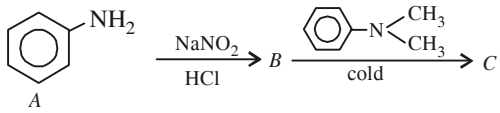
(d)  *(2009)*

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

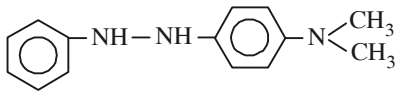
(a) acid (b) base

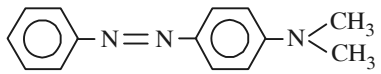
(c) catalyst (d) reducing agent. *(2009)*

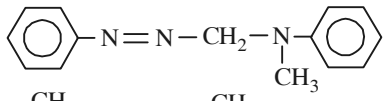
24. In a reaction of aniline a coloured product *C* was obtained.

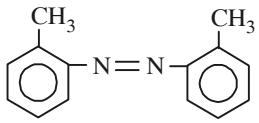


The structure of *C* would be

(a) 

(b) 

(c) 

(d) 

(2008, 2004)

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

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

(2007)

26. Which of the following is more basic than aniline?

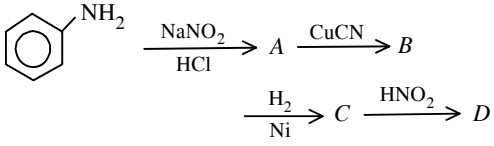
(a) Benzylamine (b) Diphenylamine
(c) Triphenylamine (d) *p*-Nitroaniline

(2006)

27. Electrolytic reduction of nitrobenzene in weakly acidic medium gives

(a) *N*-phenylhydroxylamine
(b) nitrosobenzene
(c) aniline
(d) *p*-hydroxyaniline. *(2005)*

28. Aniline in a set of reactions yielded a product *D*.

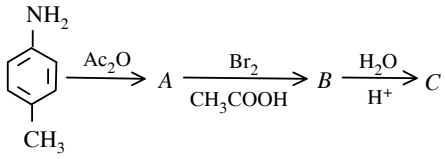


The structure of the product *D* would be

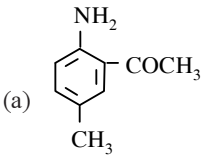
(a) C_6H_5NHOH (b) $C_6H_5NHCH_2CH_3$
(c) $C_6H_5CH_2NH_2$ (d) $C_6H_5CH_2OH$

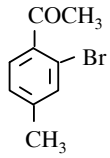
(2005)

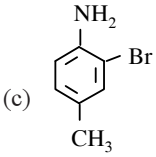
29. The final product *C*, obtained in this reaction

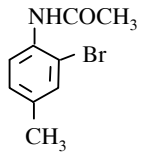


would be

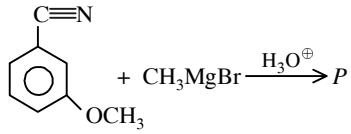
(a) 

(b) 

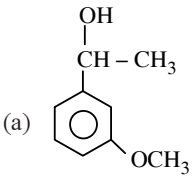
(c) 

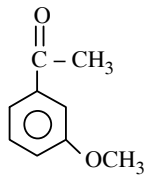
(d) 

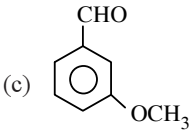
(2003)

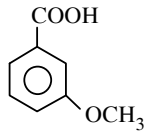
30. 

Product '*P*' in the above reaction is

(a) 

(b) 

(c) 

(d) 

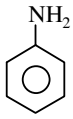
(2002)

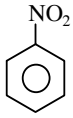
31. Intermediates formed during reaction of $R\overset{\overset{O}{\|}}{C}NH_2$ with Br_2 and KOH are

(a) *R*CONHBr and *R*NCO
(b) *R*NHCOBr and *R*NCO
(c) *R*NH – Br and *R*CONHBr
(d) $RCONBr_2$ *(2001)*

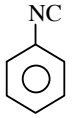
32. $A \xrightarrow{\text{reduction}} B \xrightarrow{CHCl_3/KOH} C \xrightarrow{\text{reduction}}$ *N*-methylaniline,

then *A* is

(a) 

(b) 

(c) CH_3NH_2

(d)  *(2000)*

33. Amides may be converted into amines by a reaction named after
(a) Hoffmann (b) Claisen
(c) Perkin (d) Kekule

(1999)

34. Phenyl isocyanides are prepared by which of the following reaction?
(a) Reimer-Tieman reaction
(b) Carbylamine reaction
(c) Rosenmund's reaction
(d) Wurtz reaction

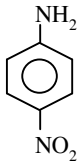
(1999)

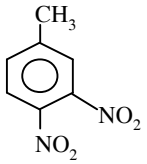
35. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated dry. The final product is
(a) *p*-bromoaniline
(b)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

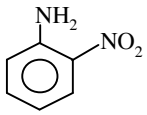
(1998)

36. The compound obtained by heating a mixture of ethyl amine and chloroform with ethanolic potassium hydroxide (KOH) is
(a) an amide
(b) an amide and nitro compound
(c) an ethyl isocyanide
(d) an alkyl halide. *(1997)*

37. An aniline on nitration gives

(a) 

(b) 

(c) 

(d) both (a) and (c). *(1996)*

38. Which product is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl?
(a) Methyl cyanide
(b) Acetic anhydride
(c) Acetic acid
(d) Acetamide *(1995)*

39. When aniline reacts with oil of bitter almonds (C_6H_5CHO) condensation takes place and benzal derivative is formed. This is known as
(a) Schiff's base
(b) Benedict's reagent
(c) Million's base
(d) Schiff's reagent. *(1995)*

40. The action of nitrous acid on an aliphatic primary amine gives
(a) secondary amine (b) nitro alkane
(c) alcohol (d) alkyl nitrite.

(1994)

41. Which one of the following order is wrong, with respect to the property indicated?
(a) Benzoic acid > phenol > cyclohexanol (acid strength)
(b) Aniline > cyclohexylamine > benzamide (basic strength)
(c) Formic acid > acetic acid > propanoic acid (acid strength)
(d) Fluoroacetic acid > chloroacetic acid > bromoacetic acid (acid strength)

(1994)

42. For carbylamine reaction, we need hot alcoholic KOH and
(a) any primary amine and chloroform
(b) chloroform and silver powder
(c) a primary amine and an alkyl halide
(d) a monoalkylamine and trichloromethane.
(1992)

43. Indicate which nitrogen compound amongst the following would undergo Hofmann reaction (*i.e.*, reaction with Br_2 and strong KOH) to furnish the primary amine (R–NH_2)?
(a) RCONHCH$_3$ (b) RCOONH$_4$
(c) RCONH$_2$ (d) $R - CO - NHOH$
(1989)

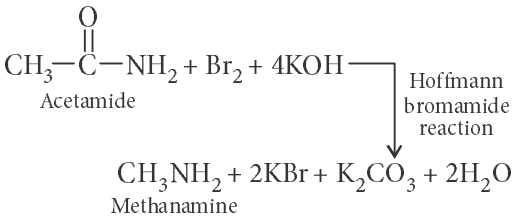
Answer Key

1.	(c)	**2.**	(a)	**3.**	(c)	**4.**	(b)	**5.**	(c)	**6.**	(c)	**7.**	(c)	**8.**	(c)	**9.**	(d)	**10.**	(c)
11.	(d)	**12.**	(b)	**13.**	(d)	**14.**	(a)	**15.**	(a)	**16.**	(a)	**17.**	(a)	**18.**	(a)	**19.**	(b)	**20.**	(a)
21.	(c)	**22.**	(d)	**23.**	(b)	**24.**	(b)	**25.**	(a)	**26.**	(a)	**27.**	(c)	**28.**	(d)	**29.**	(c)	**30.**	(b)
31.	(a)	**32.**	(b)	**33.**	(a)	**34.**	(b)	**35.**	(d)	**36.**	(c)	**37.**	(d)	**38.**	(d)	**39.**	(a)	**40.**	(c)
41.	(b)	**42.**	(a)	**43.**	(c)														

EXPLANATIONS

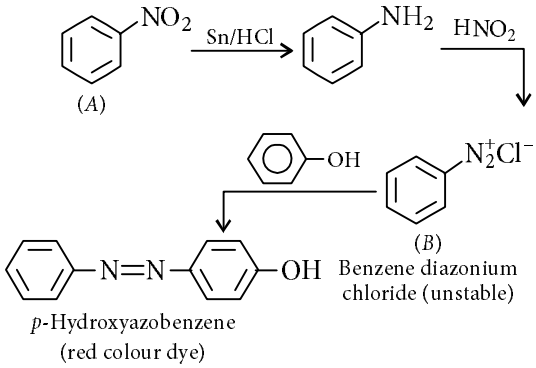
1. (c)

2. (a) :



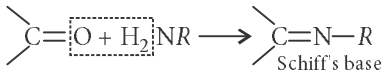
3. (c) : Tertiary nitroalkanes do not react with nitrous acid as they do not contain α-hydrogen atom.

4. (b) :



5. (c) : In arylamines, lone pair of electrons on nitrogen atom is delocalised over the benzene ring, thus, not available for donation. So, arylamines are less basic than alkylamines .

6. (c) :



7. (c) : Benzoylation of compounds containing an active hydrogen atom such as alcohols, phenols and amines with benzoyl chloride in the presence of dilute aq. NaOH solution is called Schotten-Baumann reaction.

8. (c) : Aniline cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

9. (d) : The possible structural isomers are :

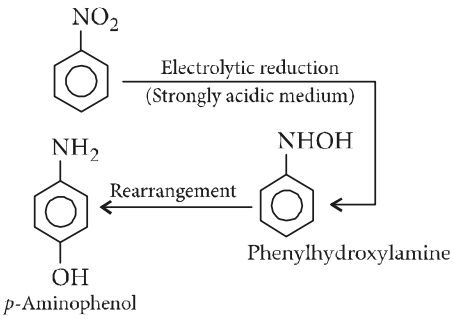
1. $CH_3CH_2CH_2NH_2$
   Propanamine

2. $CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$
   Propanamine

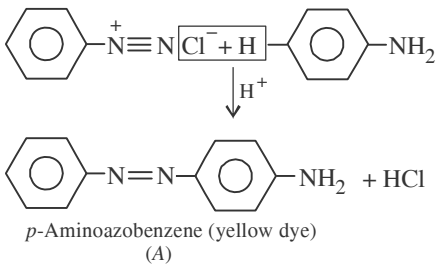
3. $CH_3CH_2NHCH_3$
   N-Methylethanamine

4. $CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$
   N,*N*-Dimethylmethanamine

10. (c) :

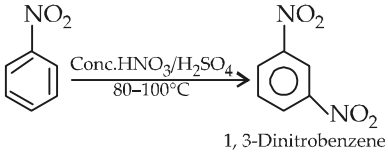


11. (d) :



12. (b) : Aromatic diazonium salts are more stable due to dispersal of the positive charge in benzene ring.

13. (d) :



14. (a) : H_3PO_2 and H_2O reduces the $-\overset{+}{N}_2\overset{-}{Cl}$ to –H.

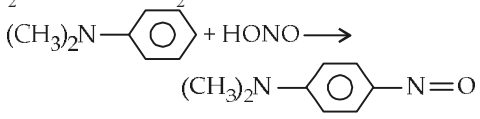
15. (a) : $CH_3CH_2CH_2NC + 2H_2O \xrightarrow{H^+}$

$CH_3CH_2CH_2NH_2 + HCOOH$
I II

II (HCOOH) reduces Tollens' reagent and Fehling's solution.

16. (a) : Aromatic tertiary amines undergo electrophilic substitution with nitrosonium ion at *p*-position of the phenyl ring to form green-coloured *p*-nitrosoamines.

$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$

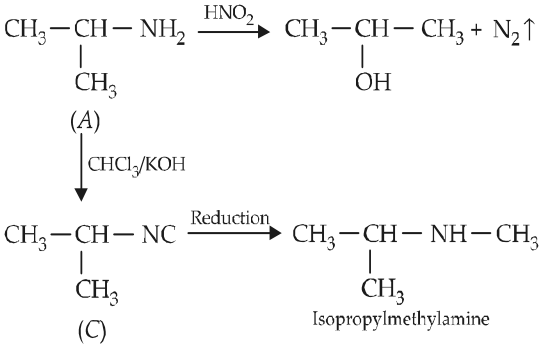


p-Nitro-*N*, *N*-dimethyl aniline (green)

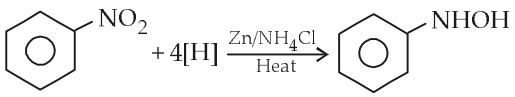
17. (a) : As *A* gives alcohol on treatment with nitrous acid thus it should be primary amine. C_3H_9N has two possible structure with $-NH_2$ group.

$CH_3-CH_2-CH_2-NH_2$ or $CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-NH_2$

As it gives isopropylmethylamine thus it should be isopropyl amine not *n*-propyl amine.

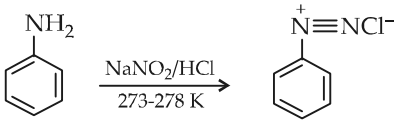


18. (a) :

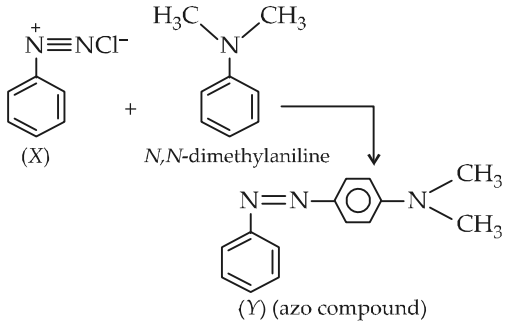


19. (b) : In benzylamine the electron pair present on the nitrogen is not delocalised with the benzene ring.

20. (a) :

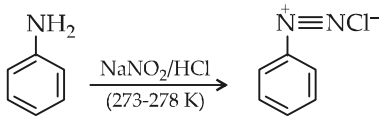


(diazonium salt)
(*X*)



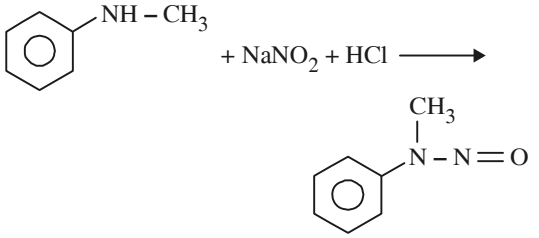
(*Y*) (azo compound)

21. (c) : Aryl amines react with nitrous acid to produce diazonium salts.



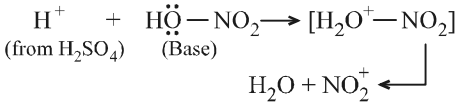
(diazonium salt)

22. (d) : 2° aliphatic and aromatic amines react with nitrous acid to form *N*-nitrosoamine.

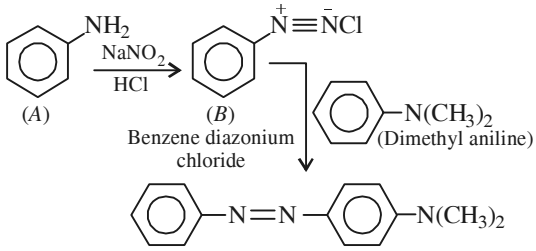


N-nitroso-*N*-methylaniline

23. (b) :



24. (b) :



p-Dimethyl amino azobenzene (Butter yellow)
(*C*)

25. (a) : Alkyl isocyanides on reduction with lithium aluminium hydride forms secondary amines containing methyl as one of the the alkyl groups.

$$R-N\rightleftarrows C \;+[H] \xrightarrow{LiAlH_4} RNHCH_3$$
Alkyl isocyanide — Secondary amine

$$H_3C-N\rightleftarrows C + 4[H] \xrightarrow{LiAlH_4} H_3C-NH-CH_3$$
Methyl isocyanide — Dimethylamine

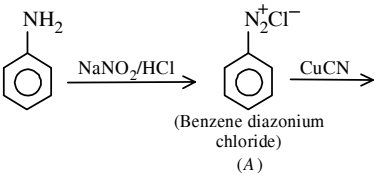
26. (a) : Any group which when present on benzene ring has electron withdrawing ($-NO_2$, $-CN$, $-SO_3H$, $-COOH$, $-Cl$, $-C_6H_5$, etc.) group decreases basicity of aniline. *e.g.* Aniline is more basic than nitroaniline and diphenyl amine. While a group which has electron repelling effect ($-NH_2$, $-OR$, $-R$, etc.) increases basicity of aniline.

Thus, benzylamine is more basic than aniline.

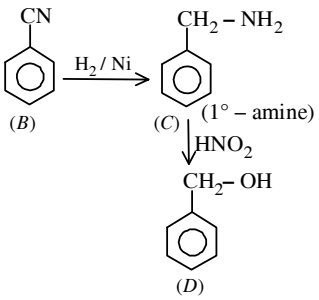
27. (c) : Electrolytic reduction of nitrobenzene in weakly acidic medium gives aniline but in strongly acidic medium it gives *p*-aminophenol through the acid-catalysed rearrangement of the initially formed phenylhydroxylamine.

$$C_6H_5NO_2 \xrightarrow[\text{Weakly acidic medium}]{\text{Electrolytic reduction}} C_6H_5NH_2$$
Nitrobenzene — Aniline

28. (d) :

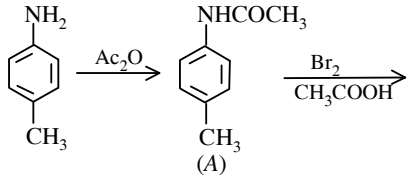


(Benzene diazonium chloride) (*A*)

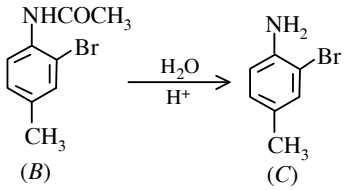


(*B*) (*C*) (*D*)

29. (c) :

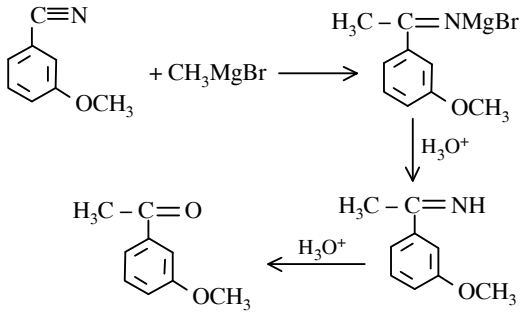


(*A*)



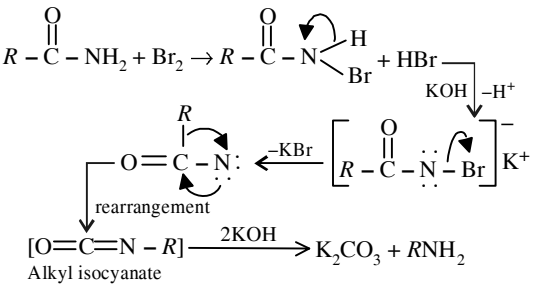
(*B*) (*C*)

30. (b) :



(*P*)

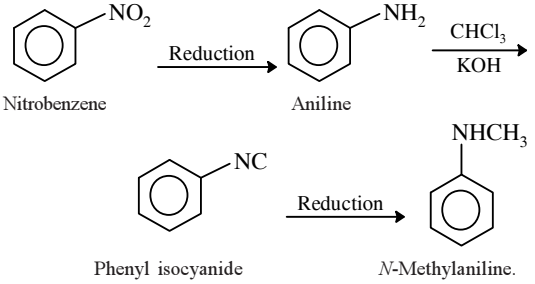
31. (a) : The reaction $RCONH_2 + Br_2 + KOH \rightarrow RNH_2$ is known as Hoffmann-bromamide reaction. The mechanism of the reaction is



Alkyl isocyanate

This reaction is used in the descent of series, *i.e.* for preparing a lower homologue from a higher one.

32. (b) : '*C*' must be an isocyanide and obtained from a 1° amine by Carbylamine reaction ($CHCl_3$ + KOH). Further 1° amine must be obtained by reduction of nitrohydrocarbon. So '*A*' is nitrobenzene.



Nitrobenzene — Aniline — Phenyl isocyanide — *N*-Methylaniline.

33. (a) :

$$R-\underset{\underset{O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow \underset{1^\circ \text{ amine}}{R-NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

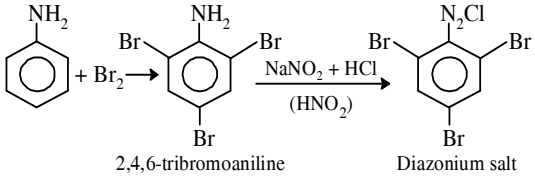
Acid amide

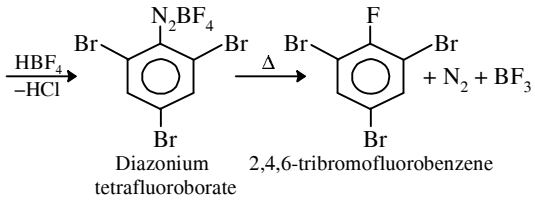
This reaction is called Hoffmann bromamide reaction.

34. (b) : $C_6H_5-NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5-NC + 3KCl + 3H_2O$

The above reaction is called as carbylamine reaction, which is a specific reaction of 1°-amine. In this reaction aniline is treated with an alkaline solution of chloroform to give phenyl isocyanide.

35. (d) :

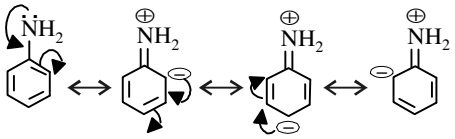




36. (c) : $\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$

Isocyanide can be easily characterised by their offensive odour. The reaction is called carbylamine test.

37. (d) :



As, NO_2^+ electrophile can attack both *ortho* and *para* positions, therefore both (a) and (c) product will be obtained.

38. (d): $\underset{\text{Acetonitrile}}{CH_3-C\equiv N} \xrightarrow[H_2O]{\text{conc. HCl}} \underset{\text{Acetamide}}{CH_3-CO-NH_2}$

39. (a) : Benzaldehyde reacts with primary aromatic amines to form Schiff's base (Benzylidene aniline).

$\underset{\text{Benzaldehyde}}{C_6H_5HC=O} + \underset{\text{Aniline}}{C_6H_5NH_2} \rightarrow \underset{\text{Benzylidene aniline}}{C_6H_5HC=NC_6H_5} + H_2O$

40. (c) :

$$\underset{\text{Primary amine}}{R-NH_2} + \underset{\text{Nitrous acid}}{HNO_2} \longrightarrow \underset{\text{Alcohol}}{ROH} + N_2 + H_2O$$

41. (b) : Basic strength decreases as,

cyclohexylamine > aniline > benzamide.

Lesser basicity in aniline and benzamide is due to participation of lone pair of electron of $-NH_2$ group.

42. (a) : In carbylamine reaction, primary amines on heating with chloroform in presence of alcoholic KOH form isocyanides (or carbylamines). It is used to distinguish 1° amines from 2° and 3° amines.

$R-NH_2 + CHCl_3 + 3KOH \xrightarrow[\text{(alc.)}]{} RNC + 3KCl + 3H_2O$

43. (c) : The amide ($-CONH_2$) group is converted into primary amino group ($-NH_2$) by Hofmann's bromamide reaction.

$$RCONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} \underset{1^\circ \text{ amine}}{R-NH_2} + KBr + K_2CO_3 + 2H_2O$$