CHAPTER

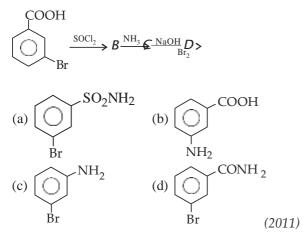
Amines

13.4 Preparation of Amines

- **1.** 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)
- 2. Method by which aniline cannot be prepared is
 - (a) degradation of benzamide with bromine in alkaline solution
 - (b) reduction of nitroben zene with $H_2/Pdine than ol$
 - (c) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution
 - (*d*) hydrolysis of phenylisocyanide with acidic solution. (2015)
- **3.** The electrolytic reduction of nitrobenzene in strongly acidic medium produces
 - (a) azobenzene (b) aniline
 - (c) *p*-aminophenol (d) azoxybenzene.

(2015, Cancelled)

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



- 5. Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine?
 - (a) NaOH-Br₂ (b) Sodalime
 - (c) Hot conc. H_2SO_4 (d) PCl₅ (2010)
- 6. 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)
- 7. In a set of reactions propionic acid yielded a compound *D*.

 $\begin{array}{c} \text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{SOCl}_2} B \xrightarrow{\text{NH}_3} & \xrightarrow{\text{KOH}} \\ \text{The structure of } D \text{ would be} & & & \\ \end{array}$

(a) $CH_3CH_2NH_2$ (b) $CH_3CH_2CH_2NH_2$ (c) $CH_3CH_2CONH_2$ (d) $CH_3CH_2NHCH_3$

(2006)

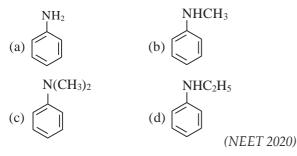
- 8. Electrolytic reduction of nitrobenzene in weakly acidic medium gives
 - (a) *N*-phenylhydroxylamine
 - (b) nitrosobenzene
 - (c) aniline
 - (d) p-hydroxyaniline. (2005)
- 9. Intermediates formed during reaction of RCONH₂ with Br₂ and KOH are
 - (a) RCONHBr and RNCO
 - (b) RNHCOBr and RNCO
 - (c) RNH Br and RCONHBr
 - (d) RCONBr_2 (2001)
- **10.** Amides may be converted into amines by a reaction named after
 - (a) Hoffmann(b) Claisen(c) Perkin(d) Kekule. (1999)
- **11.** Indicate which nitrogen compound amongst the following would undergo Hoffmann reaction (*i.e.*, reaction with Br₂ and strong KOH) to furnish the primary amine (*R*–NH₂)?

Amines

(a) RCONHCH ₃	(b) RCOONH ₄
(c) RCONH ₂	(d) $R - CO - NHOH$
	(1989)

13.6 Chemical Reactions

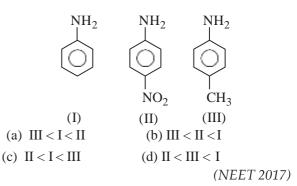
12. Which of the following amines will give the carbylamine test?



- **13.** The correct order of the basic strength of methyl substituted amines in aqueous solution is
 - (a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
 - (b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$
 - (c) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$
 - (d) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$ (*NEET* 2019)
- **14.** The amine that reacts with Hinsberg's reagent to give an alkali insoluble product is

(a)
$$CH_{3}$$
— CH — NH — CH — CH_{3}
 CH_{3} CH_{3}
(b) CH — CH — CH — N — CH CH_{3}
(c) CH_{3} — C — $CH_{2}CH_{2}CH_{3}$
 CH_{3}
(d) CH_{3} — C — CH — NH_{2} (Odisha NEET 2019)
 I
 CH_{3} CH_{3}

- **15.** Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because
 - (a) inspite of substituents nitro group always goes to only *m*-position
 - (b) in electrophilic substitution reactions amino group is *meta* directive
 - (c) in absence of substituents nitro group always goes to *m*-position
 - (d) in acidic (strong) medium aniline is present as anilinium ion. (NEET 2018)
- **16.** The correct increasing order of basic strength for the following compounds is



- **17.** 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)

18. 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) CH₃CH₂CH₂NC (b) CH₃CH₂CH₂CN

(c)
$$CH_3CH_2CH_2ON \underline{--}O$$

(d) CH₃CH₂CH₂CON(CH₃)₂

3 2

(Karnataka NEET 2013)

19. Some reactions of amines are given. Which one is not correct?

(a)
$$(CH_3)_2N \longrightarrow + NaNO_2 + HCl \rightarrow (CH_3)_2N \longrightarrow -N - NCl$$

(b) $CH_3CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2OH + N_2$
(c) $CH_3NH_2 + C_2H_4SO_2C_1 \rightarrow CH_3NHSO_2C_4H_5$
(d) $(CH_1)NH_2 + NaNO_2 + HCl \rightarrow (CH_1)N_2 - N_2 - N_2$

(Karnataka NEET 2013)

20. An organic compound (C_3H_9N) (*A*), when treated with nitrous acid, gave an alcohol and N₂ gas was evolved. (*A*) on warming with CHCl₃ and caustic potash gave (*C*) which on reduction gave isopropylmethylamine. Predict the structure of (*A*).

(a)
$$\begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \end{array} \begin{array}{c} CH - NH_2 \\ CH_3 CH_2 - NH - CH_3 \\ (c) \\ CH_3 N \\ CH_3 \\ CH_3 \end{array}$$

(d) $CH_3 CH_2 CH_2 - NH_2$ (2012)

21. Which of the following compounds is most basic?

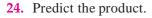
(a)
$$O_2N \longrightarrow NH_2$$

(b) $\swarrow -CH_2NH_2(c) \qquad \bigcirc N \in OCH_3$
(d) $\swarrow -NH_2$ (Mains 2011)

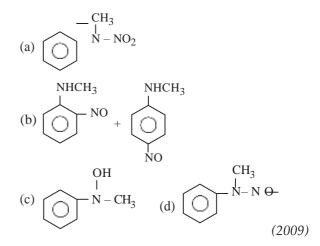
- 22. Which of the following statements about primary amines is false?
 - (a) Alkyl amines are stronger bases than aryl amines.
 - (b) Alkyl amines react with nitrous acid to produce alcohols.
 - (c) Aryl amines react with nitrous acid to produce phenols.
 - (d) Alkyl amines are stronger bases than ammonia. (2010)
- 23. Match the compounds given in List I with their characteristic reactions given in List II. Select the correct option.

	List I (Compounds)	List II (Reactions)				
A.	CH ₃ (CH ₂) ₃ NH ₂	(i)	Alkaline hydrolysis			
B.	CH₃C €Ħ	(ii)	With KOH (alcohol) and CHCl ₃ produces bad smell			
C.	CH ₃ CH ₂ COOCH ₃	(iii)	Gives white ppt. with ammoniacal AgNO ₃			
D.	CH ₃ CH(OH)CH ₃	(iv)	With Lucas reagent cloudiness appears after 5 minutes			

- (a) A-(ii), B-(i), C-(iv), D-(iii)
- (b) A-(iii), B-(ii), C-(i), D-(iv)
- (c) A-(ii), B-(iii), C-(i), D-(iv)
- (Mains 2010) (d) A-(iv), B-(ii), C-(iii), D-(i)



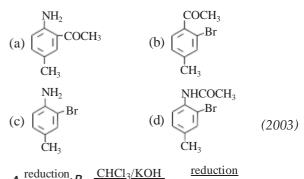
+ NaNO₂ + HCl \longrightarrow Product



- 25. Which of the following is more basic than aniline?
 - (b) Diphenylamine (a) Benzylamine
 - (c) Triphenylamine (d) *p*-Nitroaniline (2006)
- **26.** The final product *C*, obtained in this reaction,

$$(\downarrow I \\ (\downarrow I \\ CH_3) \xrightarrow{Ac_2O} A \xrightarrow{Br_2} (H_2O) \xrightarrow{H_2O} C$$

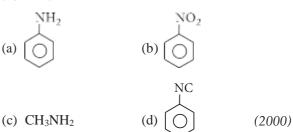
would be



A reduction 27.

N-methylaniline,

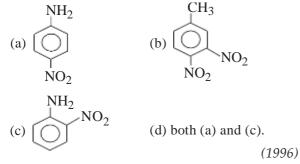
then A is



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

Amines

- **29.** The compound obtained by heating a mixture of ethylamine 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.
- **30.** An aniline on nitration gives



- **31.** The action of nitrous acid on an aliphatic primary amine gives
 - (a) secondary amine (b) nitro alkane
 - (c) alcohol (d) alkyl nitrite. (1994)
- **32.** 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)
- **33.** 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)

(1997)

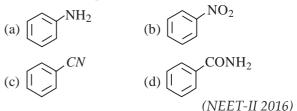
13.7 Methods of Preparation of Diazonium Salts

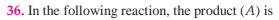
34. Which of the following will be most stable diazonium salt $RN_2^+X^-$?

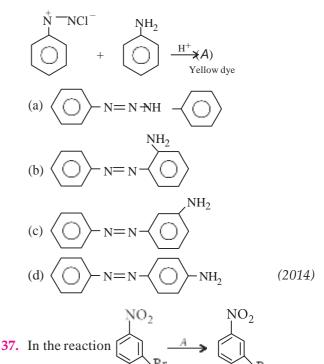
(a) $CH_3N_2 X$ (b) $C_6H_5N_2 X$ (c) $CH_3CH N^+X^-$ (d) $C H CH N^+X^-$ (2014) $_{6} 5 2 2$

13.9 Chemical Reactions

35. A given nitrogen-containing aromatic compound '*A*' reacts with Sn/HCl, followed by HNO₂ 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



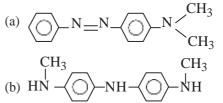


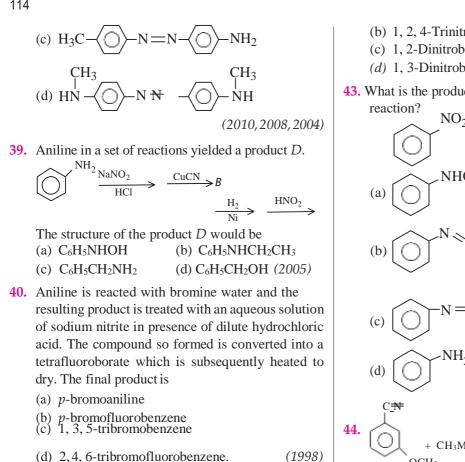


- $^+N_2Cl^-$ *A* is (a) H₃PO₂ and H₂O (b) H⁺/H₂O
 - (c) $HgSO_4/H_2SO_4$ (d) Cu_2Cl_2 (*NEET* 2013)
- Aniline in a set of the following reactions yielded a coloured product Y.

$$\underbrace{NH_2}_{(273-278 \text{ K})} X \xrightarrow{N, N-\text{dimethylaniline}} Y$$

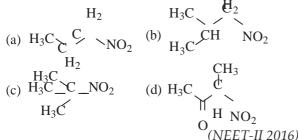
The structure of 'Y' would be





13.A) Other Nitrogen Containing Compounds

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



- **42.** 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

(c)

(a)

(c)

(b)

(d)

23.

33.

43.

(c)

(a)

(a)

24.

34.

44.

(d)

(b)

(b)

2.

12.

22.

32.

42.

(a)

(c)

(b)

(c)

(c)

1.

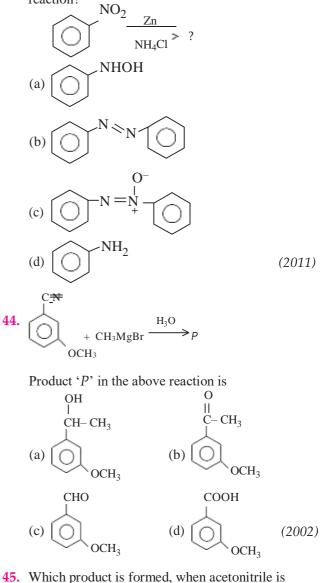
11.

21.

31.

41.

- (b) 1, 2, 4-Trinitrobenzene
- (c) 1, 2-Dinitrobenzene
- (d) 1, 3-Dinitrobenzene (NEET 2013)
- **43.** What is the product obtained in the following



hydrolysed partially with cold concentrated HCl? (a) Methyl cyanide (b) Acetic anhydride

28.

38.

(b)

(a)

(c) Acetic acid

(b)

(a)

(d) Acetamide (1995)

29.

39.

(c)

(d)

30.

40.

(d)

(d)

		_(ANSV		=v					
	(c)	5.	(a)	6.	(a)	7.			10. 20.	

27.

37.

26.

36.

(c)

(d)

25.

35.

45.

(a)

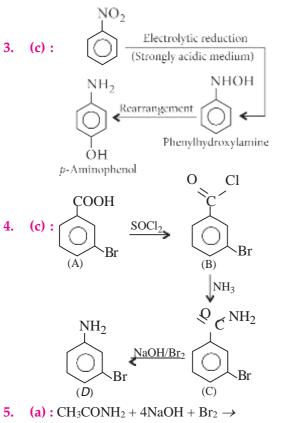
(b)

(d)

Hints & Explanations

1. (a) : CH
$$_ \overset{O}{\underbrace{CH}}_{3} \underset{Acetamide}{\overset{O}{\underbrace{CH}}_{2}} \overset{O}{\underbrace{CH}}_{2} \overset{O}{\underbrace{CH}}_{3} \overset{O}{\underbrace{CH}}_{2} \overset{O}{\underbrace{CH}}_{3} \overset{O}{\underbrace{CH}}_{3}$$

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



Acetamide

$$CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O_1^{\circ} Amine$$

This reaction is called Hoffmann Bromamide degradation reaction.

6. (a) : Alkyl isocyanide on reduction with lithium aluminium hydride forms secondary amine containing methyl as one of the alkyl groups.

$$\begin{array}{c} R - N \stackrel{\Longrightarrow}{\Longrightarrow} C + [H] \xrightarrow{\text{LiAlH}_4} RNHCH_3 \\ \text{Alkyl isocyanide} & \text{Secondary amine} \\ H_3C - N \stackrel{\Longrightarrow}{\Longrightarrow} C + 4[H] \xrightarrow{\text{LiAlH}_4} H_3C - NH - CH_3 \\ \text{Methyl isocyanide} & \text{Dimethylamine} \end{array}$$

7. (a): CH₃CH₂COOH
$$\xrightarrow{\text{SOCl}_2}$$
 CH₃CH₂COCl
(B)
 $\xrightarrow{\text{NH}_3}$ CH₃CH₂CONH₂ $\xrightarrow{\text{KOH}}_{\text{Br}_2}$ CH₃CH₂NH₂
(C)

8. (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.

 $\begin{array}{c} & \text{Electrolytic} \\ \text{C}_{6}\text{H}_{5}\text{NO}_{2} & \hline \\ \text{Nitrobenzene} & (Weakly acidic \\ \text{medium}) & \text{Aniline} \end{array}$

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

This reaction is used to descent the series, *i.e.*, for preparing a lower homologue from a higher one. **10. (a)**:

$$R - C - NH_2 + Br_2 + 4KOH \longrightarrow R - NH_2 + K_2CO_3$$

O
Acid amide + 2KBr + 2H 2O

This reaction is called Hoffmann bromamide degradation reaction.

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

$$RCONH_2 + Br_2 + 4KOH \longrightarrow R - NH_2 + 2KBr$$

1°amine
+ K2CO3 + 2H2O

12. (a) : Aliphatic and aromatic primary amines give carbylamine test. Secondary and tertiary amines do not show this reaction.

13. (b) : The basicity of amines in aqueous solution depends on the stability of the ammonium cation or conjugate acid formed by accepting a proton from water which in turn depends on the + I-effect of alkyl group,

extent of hydrogen bonding and steric factor. All these factors are favourable for 2° amines. Therefore, 2° amines are the strongest bases. If the alkyl group is small *i.e.*, CH₃ then there is no steric hindrance to H-bonding. Thus, the stability due to hydrogen bonding predominates over the stability due to + *I*-effect of —CH₃ group and hence primary amine is a stronger base than 3° amine. Hence, overall decreasing basic strength for methylamines in aqueous solution is

 $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

14. (a) : Secondary amines on reaction with Hinsberg's reagent gives N, N-dialkylbenzene sulphonamide which does not contain any hydrogen atom attached to N-atom, it is not acidic and hence, insoluble in alkali.

Tertiary amines do not react with Hinsberg's reagent. Primary amines gives products which are soluble in alkali.

15. (d) :
$$\bigcirc^{2} \xrightarrow{H^{+}}_{\text{Nitrating mixture}} \bigcirc^{3} \xrightarrow{\text{NH}}_{\text{NO}_{2}} \longrightarrow \bigcirc^{\text{NH}_{3}}_{\text{NO}_{2}}$$

The reason for formation of an unexpected amount of *m*-nitroaniline is that under strongly acidic condition of nitration, most of the aniline is converted into anilinium ion and since, $-NH_3$ is a *m*-directing group, therefore, a large amount of *m*-nitroaniline is also obtained. **16.** (c) : +*I* effect of substituted group increases the

basic strength while -I effect of substitutent decreases the basic strength of aniline.

17. (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 .

18. (a): CH₃CH₂CH₂NC + 2H₂O
$$\xrightarrow{\text{H}^{+}}$$

CH₃CH₂CH₂NH₂ + HCOOH
I II
CH CH CH NH NaNO₂ + HCI $\xrightarrow{+-}$
CH₃CH₂CH₂CH₂N₂Cl $\xrightarrow{+-}$
CH₃CH₂CH₂CH₂OH
Does not respond to
iodoform test

HCOOH reduces Tollens' reagent and Fehling's solution. **19.** (a) : Aromatic tertiary amines undergo electrophilic substitution with nitrosonium ion at *p*-position of the phenyl ring to form green-coloured *p*-nitrosoamines. NaNO₂ + HCl \rightarrow HNO₂ + NaCl

$$(CH_3)_2N \longrightarrow +HONO \longrightarrow$$

 $(CH_3)_2N \longrightarrow N = O$
 p -Nitro N , N-dimethyl
aniline (green)

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

$$CH_3 - CH_2 - CH_2 - NH_2 \text{ or } CH_3 - CH - NH_2$$

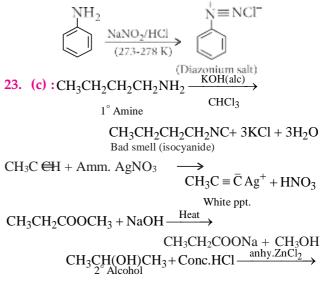
 $|$
 CH_3

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

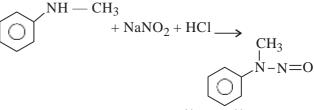
$$\begin{array}{c} CH_{3} \longrightarrow CH \longrightarrow NH_{2} \xrightarrow{HNO_{2}} CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} + N_{2} \uparrow \\ \downarrow \\ CH_{3} & OH \\ \downarrow \\ CHCl_{3}/KOH \\ CH_{3} \longrightarrow CH \longrightarrow NC \xrightarrow{Reduction} CH_{3} \longrightarrow CH \longrightarrow NH \longrightarrow CH_{3} \\ \downarrow \\ CH_{3} & CH_{3} \\ \downarrow \\ CD \\ CH_{3} & CH_{3} \\ \downarrow \\ CD \\ Isopropylmethylamine \end{array}$$

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

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



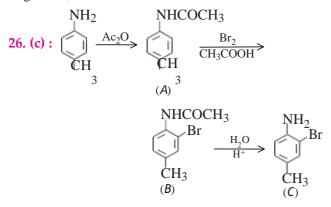
24. (d) : 2° aliphatic and aromatic amines react with nitrous acid to form *N*-nitrosoamine.



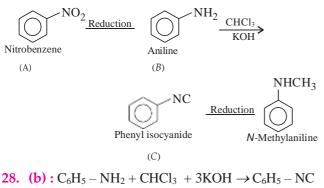
N-nitroso-N-methylaniline

Amines

25. (a) : Any group which when present on benzene ring has electron withdrawing nature (-NO₂, -CN, $-SO_3H$, -COOH, -Cl, $-C_6H_5$, etc.) decreases basicity of aniline *e.g.*, aniline is more basic than nitroaniline. Lone pair of electrons are more delocalised in diphenylamine and triphenylamine, thus these are less basic than aniline. In benzylamine the electron pair present on nitrogen is not delocalised with the benzene ring hence, it is more basic than aniline.



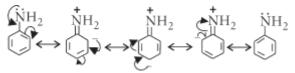
27. (b): 'C' must be an isocyanide and it is obtained from a 1° amine by carbylamine reaction (CHCl₃ + KOH). Further 1° amine can be obtained by reduction of nitro compound so 'A' is nitrobenzene.



$$+ 3KCl + 3H_20$$

The above reaction is called carbylamine reaction, which is a specific reaction of 1°-amine.

30. (d) :



As, NO $\frac{1}{2}$ electrophile can attack both *ortho* and *para* positions, therefore both (a) and (c) product will be obtained.

31. (c) :
$$R-NH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$$

Primary amine Nitrous acid Alcohol

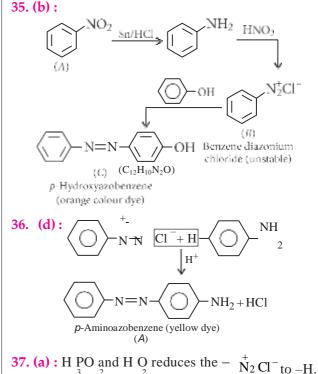
32. (b) : Basic strength decreases as, cyclohexylamine > aniline > benzamide. Lesser basicity in aniline and benzamide is due to

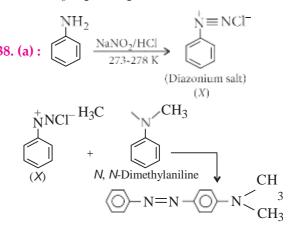
participation of lone pair of electrons of - NH₂ group in resonance.

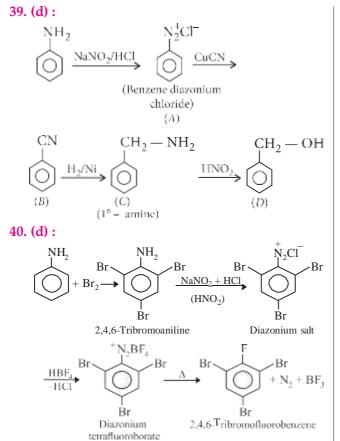
33. (a) : In carbylamine reaction, primary amines on heating with chloroform in presence of alcoholic KOH form isocyanides (or carbylamines). It is used to distinguish 1° amines from 2° and 3° amines.

$$R \longrightarrow RNC + 3KCl + 3H_2O$$
(alc.)

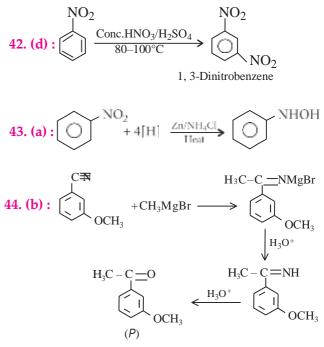
34. (b) : Aromatic diazonium salts are more stable due to dispersal of the positive charge in benzene ring.







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



45. (d): $CH_3 - C \equiv N \xrightarrow[Acetonitrile]{\text{conc. HCl}} CH_3 - CONH_2$ Acetonitrile