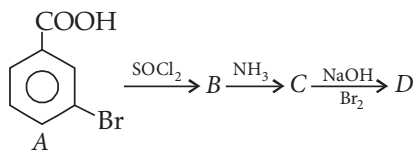


# Amines

## 13.4 Preparation of Amines

- Which of the following reactions is appropriate for converting acetamide to methanamine?
  - Hoffmann hypobromamide reaction
  - Stephen's reaction
  - Gabriel phthalimide synthesis
  - Carbylamine reaction (NEET 2017)
- Method by which aniline cannot be prepared is
  - degradation of benzamide with bromine in alkaline solution
  - reduction of nitrobenzene with  $H_2/Pd$  in ethanol
  - potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution
  - hydrolysis of phenylisocyanide with acidic solution. (2015)
- The electrolytic reduction of nitrobenzene in strongly acidic medium produces
  - azobenzene
  - aniline
  - p*-aminophenol
  - azoxybenzene. (2015, Cancelled)
- In a set of reactions *m*-bromobenzoic acid gave a product *D*. Identify the product *D*.



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- 
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(2011)

- Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine?
  - NaOH- $Br_2$
  - Sodalime
  - Hot conc.  $H_2SO_4$
  - $PCl_5$  (2010)
- Which one of the following on reduction with lithium aluminium hydride yields a secondary amine?
  - Methyl isocyanide
  - Acetamide
  - Methyl cyanide
  - Nitroethane (2007)
- In a set of reactions propionic acid yielded a compound *D*.
 
$$CH_3CH_2COOH \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow[\text{Br}_2]{KOH} D$$
 The structure of *D* would be
  - $CH_3CH_2NH_2$
  - $CH_3CH_2CH_2NH_2$
  - $CH_3CH_2CONH_2$
  - $CH_3CH_2NHCH_3$  (2006)
- Electrolytic reduction of nitrobenzene in weakly acidic medium gives
  - N*-phenylhydroxylamine
  - nitrosobenzene
  - aniline
  - p*-hydroxyaniline. (2005)

- Intermediates formed during reaction of  $RCONH_2$  with  $Br_2$  and KOH are
  - $RCONHBr$  and  $RNCO$
  - $RNHCOBr$  and  $RNCO$
  - $RNH - Br$  and  $RCONHBr$
  - $RCONBr_2$  (2001)
- Amides may be converted into amines by a reaction named after
  - Hoffmann
  - Claisen
  - Perkin
  - Kekule. (1999)

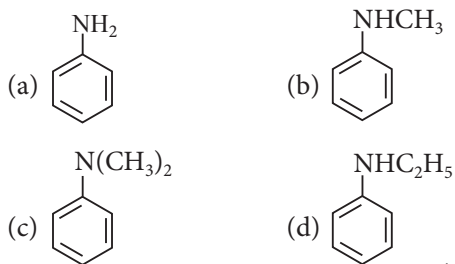
- Indicate which nitrogen compound amongst the following would undergo Hoffmann reaction (*i.e.*, reaction with  $Br_2$  and strong KOH) to furnish the primary amine ( $R-NH_2$ )?

- (a)  $RCONHCH_3$  (b)  $RCOONH_4$   
 (c)  $RCONH_2$  (d)  $R-CO-NHOH$

(1989)

### 13.6 Chemical Reactions

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

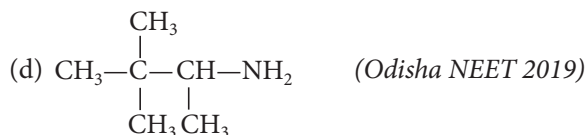
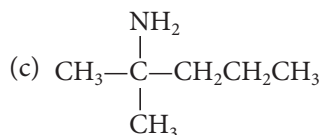
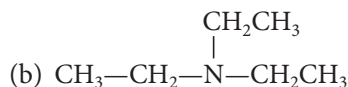
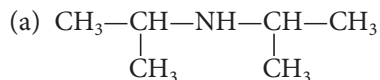


(NEET 2020)

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)

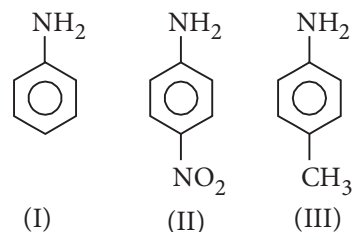
14. The amine that reacts with Hinsberg's reagent to give an alkali insoluble product is



15. Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because

- (a) in spite 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



- (a)  $\text{III} < \text{I} < \text{II}$  (b)  $\text{III} < \text{II} < \text{I}$   
 (c)  $\text{II} < \text{I} < \text{III}$  (d)  $\text{II} < \text{III} < \text{I}$

(NEET 2017)

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  $\pi$ -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  $\pi$ -electron system.

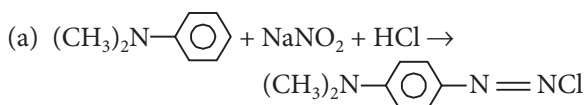
(NEET-I 2016)

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)  $CH_3CH_2CH_2NC$  (b)  $CH_3CH_2CH_2CN$   
 (c)  $CH_3CH_2CH_2ON=O$   
 (d)  $CH_3CH_2CH_2CON(CH_3)_2$

(Karnataka NEET 2013)

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



- (b)  $CH_3CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2OH + N_2$   
 (c)  $CH_3NH_2 + C_6H_5SO_2Cl \rightarrow CH_3NHOSO_2C_6H_5$   
 (d)  $(CH_3)_2NH + NaNO_2 + HCl \rightarrow (CH_3)_2N-N=O$  (Karnataka NEET 2013)

20. 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)  $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}-\text{NH}_2 \\ \diagdown \\ \text{CH}_3 \end{array}$   
 (b)  $\text{CH}_3\text{CH}_2-\text{NH}-\text{CH}_3$   
 (c)  $\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$   
 (d)  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$  (2012)

21. Which of the following compounds is most basic?

- (a)  $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$   
 (b)  $\text{C}_6\text{H}_5-\text{CH}_2\text{NH}_2$  (c)  $\text{C}_6\text{H}_5-\text{N}(\text{H})-\text{COCH}_3$   
 (d)  $\text{C}_6\text{H}_5-\text{NH}_2$  (Mains 2011)

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

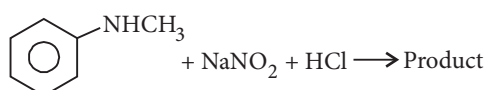
- (a) Alkyl amines are stronger bases than aryl amines.  
 (b) Alkyl amines react with nitrous acid to produce alcohols.  
 (c) Aryl amines react with nitrous acid to produce phenols.  
 (d) Alkyl amines are stronger bases than ammonia. (2010)

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.	$\text{CH}_3(\text{CH}_2)_3\text{NH}_2$	(i)	Alkaline hydrolysis
B.	$\text{CH}_3\text{C}\equiv\text{CH}$	(ii)	With KOH (alcohol) and $\text{CHCl}_3$ produces bad smell
C.	$\text{CH}_3\text{CH}_2\text{COOCH}_3$	(iii)	Gives white ppt. with ammoniacal $\text{AgNO}_3$
D.	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	(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)  
 (d) A-(iv), B-(ii), C-(iii), D-(i) (Mains 2010)

24. Predict the product.

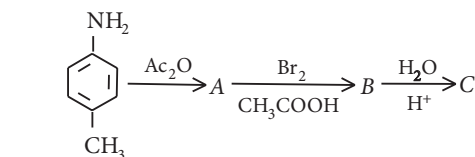


- (a)  $\text{C}_6\text{H}_5-\text{N}(\text{CH}_3)-\text{NO}_2$   
 (b)  $\text{C}_6\text{H}_5-\text{NO} + \text{C}_6\text{H}_5-\text{NHCH}_3$   
 (c)  $\text{C}_6\text{H}_5-\text{N}(\text{CH}_3)-\text{OH}$  (d)  $\text{C}_6\text{H}_5-\text{N}(\text{CH}_3)-\text{N}=\text{O}$  (2009)

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

- (a) Benzylamine (b) Diphenylamine  
 (c) Triphenylamine (d) *p*-Nitroaniline (2006)

26. The final product C, obtained in this reaction,



would be

- (a)  $\text{C}_6\text{H}_3(\text{NH}_2)(\text{CH}_3)(\text{COCH}_3)$  (b)  $\text{C}_6\text{H}_3(\text{NH}_2)(\text{CH}_3)(\text{COCH}_3)(\text{Br})$   
 (c)  $\text{C}_6\text{H}_3(\text{NH}_2)(\text{CH}_3)(\text{Br})$  (d)  $\text{C}_6\text{H}_3(\text{NHCOCH}_3)(\text{CH}_3)(\text{Br})$  (2003)

27.  $\text{A} \xrightarrow{\text{reduction}} \text{B} \xrightarrow{\text{CHCl}_3/\text{KOH}} \text{C} \xrightarrow{\text{reduction}} \text{N-methylaniline}$

then A is

- (a)  $\text{C}_6\text{H}_5-\text{NH}_2$  (b)  $\text{C}_6\text{H}_5-\text{NO}_2$   
 (c)  $\text{CH}_3\text{NH}_2$  (d)  $\text{C}_6\text{H}_5-\text{NC}$  (2000)

28. Phenyl isocyanides are prepared by which of the following reaction?

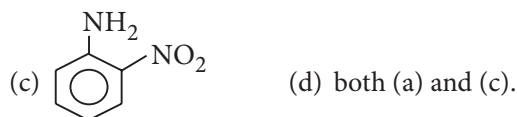
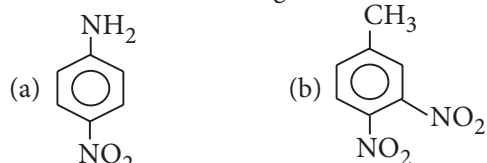
- (a) Reimer-Tiemann reaction  
 (b) Carbylamine reaction  
 (c) Rosenmund's reaction  
 (d) Wurtz reaction (1999)

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.

(1997)

30. An aniline on nitration gives



(1996)

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)

### 13.7 Methods of Preparation of Diazonium Salts

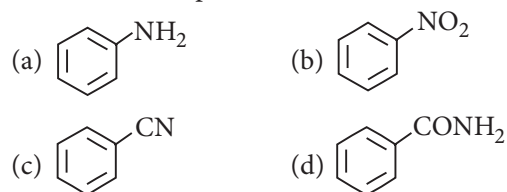
34. Which of the following will be most stable diazonium salt  $RN_2^+X^-$ ?

- (a)  $CH_3N_2^+X^-$  (b)  $C_6H_5N_2^+X^-$   
(c)  $CH_3CH_2N_2^+X^-$  (d)  $C_6H_5CH_2N_2^+X^-$  (2014)

### 13.9 Chemical Reactions

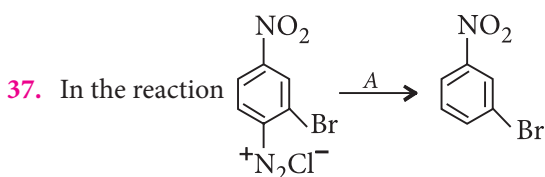
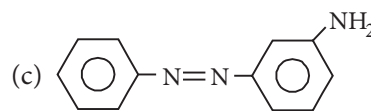
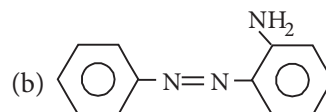
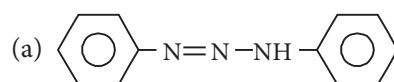
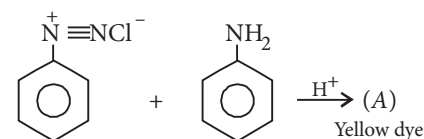
35. A given nitrogen-containing aromatic compound 'A' reacts with  $Sn/HCl$ , followed by  $HNO_2$  to give

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



(NEET-II 2016)

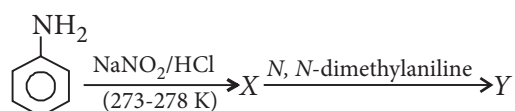
36. In the following reaction, the product (A) is



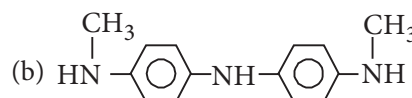
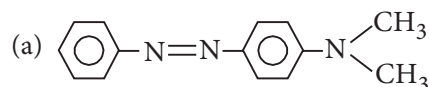
A is

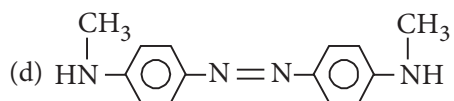
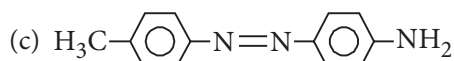
- (a)  $H_3PO_2$  and  $H_2O$  (b)  $H^+/H_2O$   
(c)  $HgSO_4/H_2SO_4$  (d)  $Cu_2Cl_2$  (NEET 2013)

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



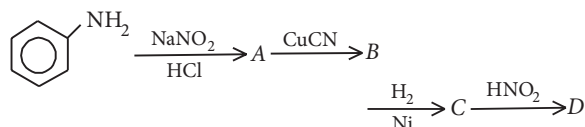
The structure of 'Y' would be





(2010, 2008, 2004)

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



The structure of the product D would be

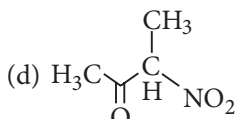
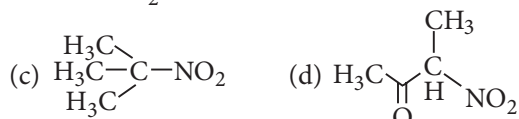
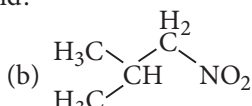
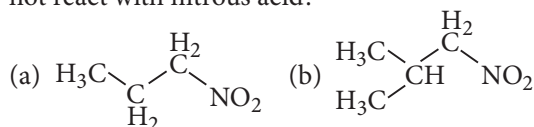
- (a)  $\text{C}_6\text{H}_5\text{NHOH}$  (b)  $\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_3$   
(c)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  (2005)

40. 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 to dry. The final product is

- (a) *p*-bromoaniline  
(b) *p*-bromofluorobenzene  
(c) 1, 3, 5-tribromobenzene  
(d) 2, 4, 6-tribromofluorobenzene. (1998)

### 13.A Other Nitrogen Containing Compounds

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



(NEET-II 2016)

42. Nitrobenzene on reaction with conc.  $\text{HNO}_3/\text{H}_2\text{SO}_4$  at  $80-100^\circ\text{C}$  forms which one of the following products?

- (a) 1, 4-Dinitrobenzene

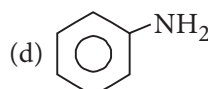
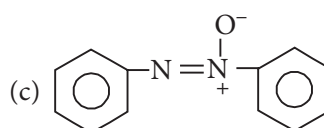
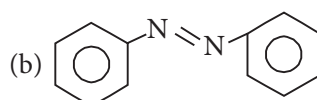
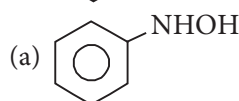
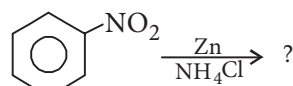
- (b) 1, 2, 4-Trinitrobenzene

- (c) 1, 2-Dinitrobenzene

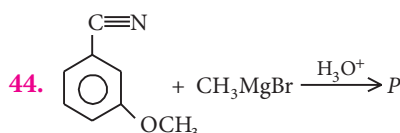
- (d) 1, 3-Dinitrobenzene

(NEET 2013)

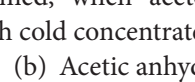
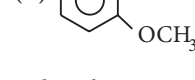
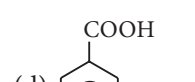
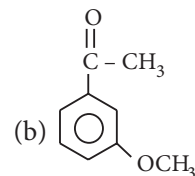
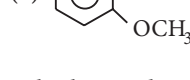
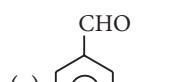
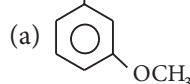
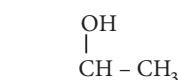
43. What is the product obtained in the following reaction?



(2011)



Product 'P' in the above reaction is



(2002)

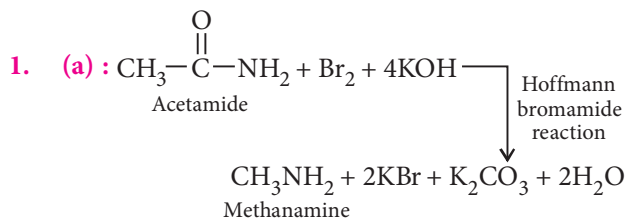
45. Which product is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl?

- (a) Methyl cyanide (b) Acetic anhydride  
(c) Acetic acid (d) Acetamide (1995)

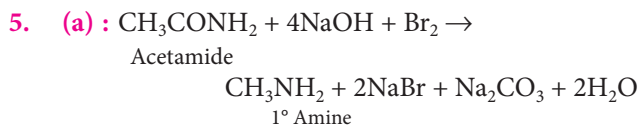
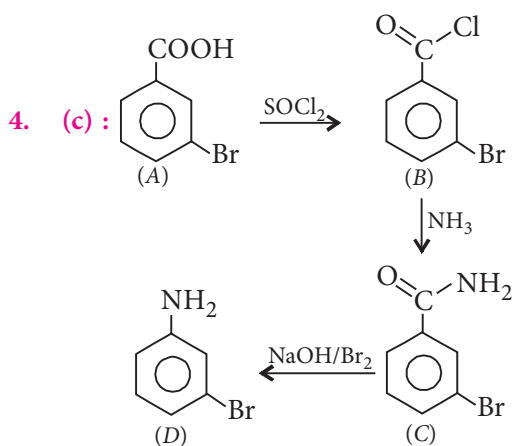
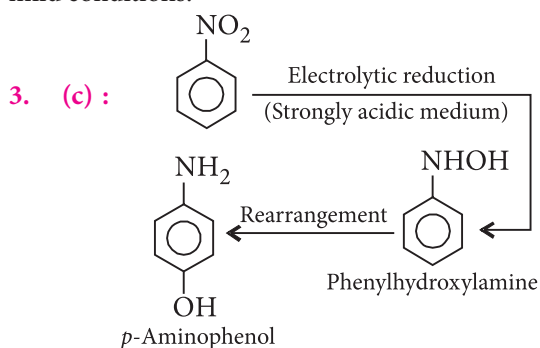
### ANSWER KEY

1. (a) 2. (c) 3. (c) 4. (c) 5. (a) 6. (a) 7. (a) 8. (c) 9. (a) 10. (a)  
11. (c) 12. (a) 13. (b) 14. (a) 15. (d) 16. (c) 17. (c) 18. (a) 19. (a) 20. (a)  
21. (b) 22. (c) 23. (c) 24. (d) 25. (a) 26. (c) 27. (b) 28. (b) 29. (c) 30. (d)  
31. (c) 32. (b) 33. (a) 34. (b) 35. (b) 36. (d) 37. (a) 38. (a) 39. (d) 40. (d)  
41. (c) 42. (d) 43. (a) 44. (b) 45. (d)

## Hints & Explanations

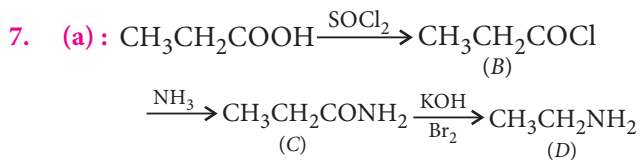
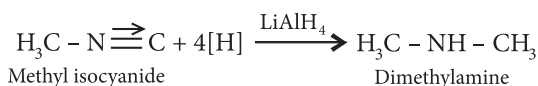
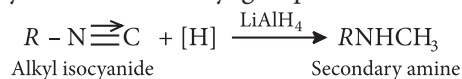


2. (c) : Aniline cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

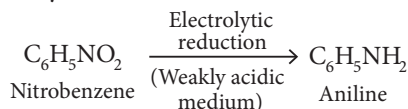


This reaction is called Hoffmann Bromamide degradation reaction.

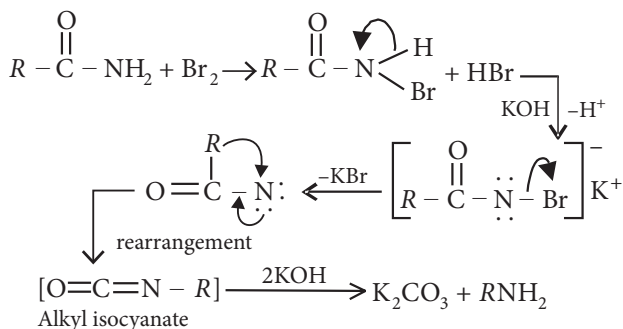
6. (a) : Alkyl isocyanide on reduction with lithium aluminium hydride forms secondary amine containing methyl as one of the alkyl groups.



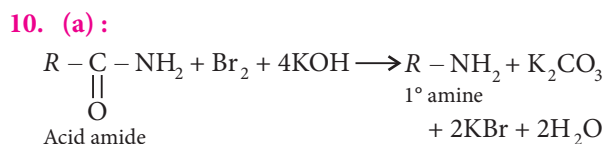
8. (c) : Electrolytic reduction of nitrobenzene in weakly acidic medium gives aniline but in strongly acidic medium it gives *p*-aminophenol through the acid-catalysed rearrangement of the initially formed phenylhydroxylamine.



9. (a) : The reaction,  $\text{RCONH}_2 + \text{Br}_2 + \text{KOH} \rightarrow \text{RNH}_2$  is known as Hoffmann bromamide degradation reaction. The mechanism of the reaction is

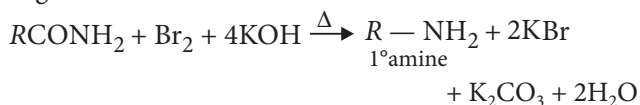


This reaction is used to descent the series, *i.e.*, for preparing a lower homologue from a higher one.



This reaction is called Hoffmann bromamide degradation reaction.

11. (c) : The amide ( $-\text{CONH}_2$ ) group is converted into primary amino group ( $-\text{NH}_2$ ) by Hoffmann's bromamide degradation reaction.



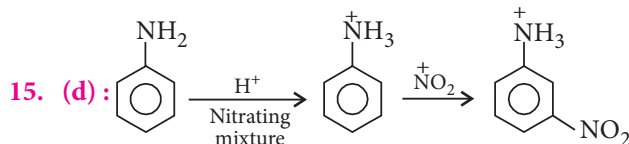
12. (a) : Aliphatic and aromatic primary amines give carbylamine test. Secondary and tertiary amines do not show this reaction.

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., CH<sub>3</sub> 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 —CH<sub>3</sub> group and hence primary amine is a stronger base than 3° amine. Hence, overall decreasing basic strength for methylamines in aqueous solution is (CH<sub>3</sub>)<sub>2</sub>NH > CH<sub>3</sub>NH<sub>2</sub> > (CH<sub>3</sub>)<sub>3</sub>N

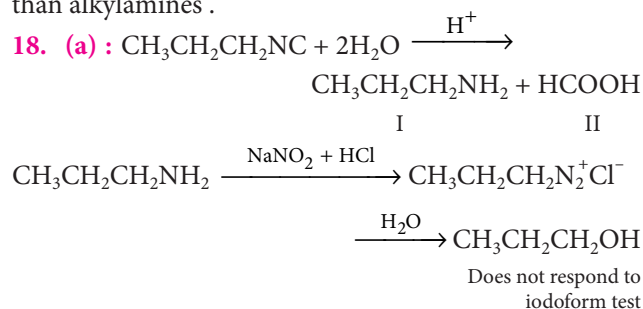
**14. (a) :** Secondary amines on reaction with Hinsberg's reagent gives *N*, *N*-dialkylbenzene sulphonamide which does not contain any hydrogen atom attached to N-atom, it is not acidic and hence, insoluble in alkali. Tertiary amines do not react with Hinsberg's reagent. Primary amines gives products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



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<sub>3</sub><sup>+</sup> is a *m*-directing group, therefore, a large amount of *m*-nitroaniline is also obtained.

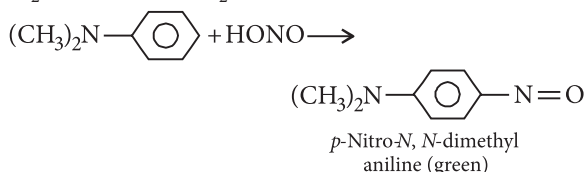
**16. (c) :** +I effect of substituted group increases the basic strength while —I effect of substituent decreases the basic strength of aniline.

**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.

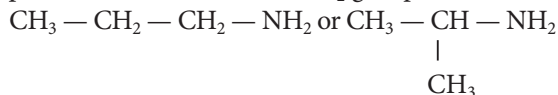


HCOOH reduces Tollens' reagent and Fehling's solution.

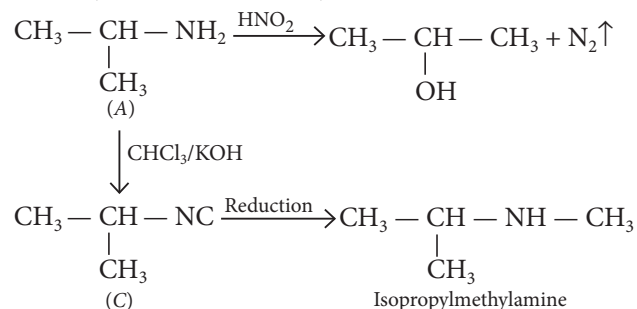
**19. (a) :** Aromatic tertiary amines undergo electrophilic substitution with nitrosonium ion at *p*-position of the phenyl ring to form green-coloured *p*-nitrosoamines.  $\text{NaNO}_2 + \text{HCl} \rightarrow \text{HNO}_2 + \text{NaCl}$



**20. (a) :** As A gives alcohol on treatment with nitrous acid thus, it should be primary amine. C<sub>3</sub>H<sub>9</sub>N has two possible structures with —NH<sub>2</sub> group.

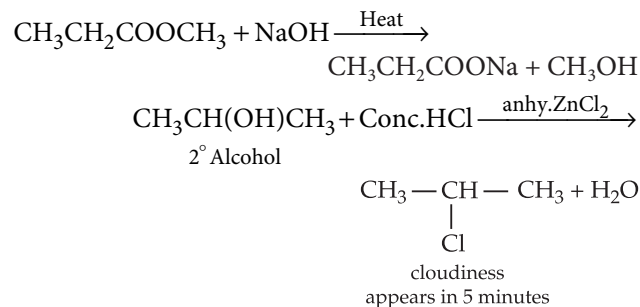
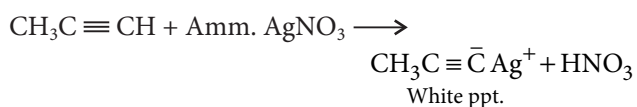
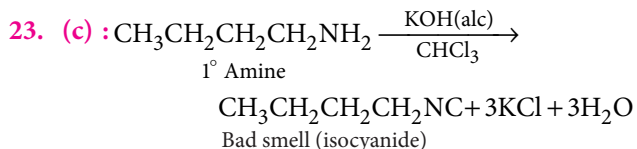
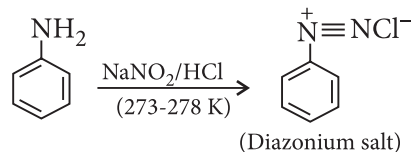


As it gives isopropylmethylamine thus, it should be isopropyl amine not *n*-propyl amine.

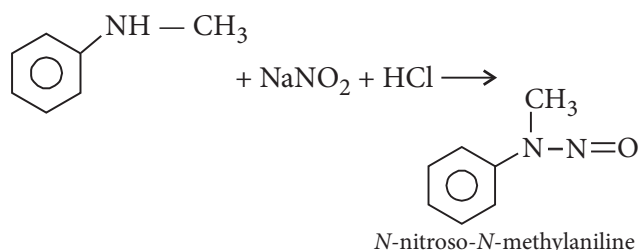


**21. (b) :** In benzylamine the electron pair present on the nitrogen is not delocalised with the benzene ring.

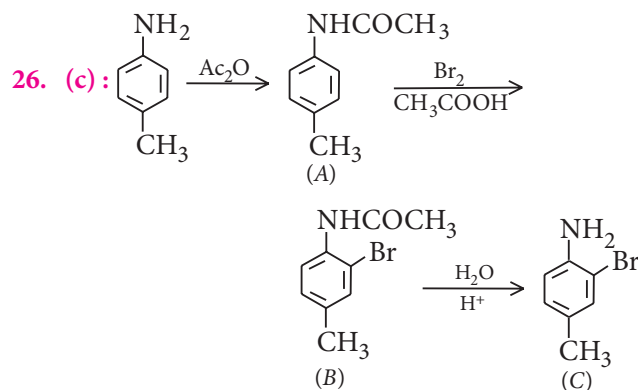
**22. (c) :** Aryl amines react with nitrous acid to produce diazonium salts.



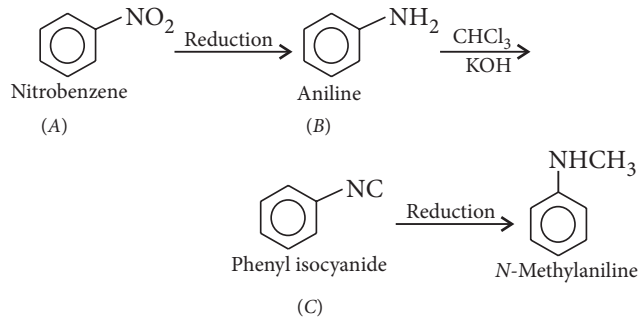
**24. (d) :** 2° aliphatic and aromatic amines react with nitrous acid to form *N*-nitrosoamine.



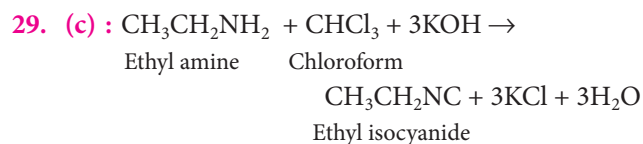
**25. (a) :** Any group which when present on benzene ring has electron withdrawing nature ( $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{Cl}$ ,  $-\text{C}_6\text{H}_5$ , etc.) decreases basicity of aniline e.g., aniline is more basic than nitroaniline. Lone 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.



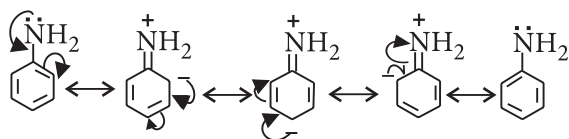
**27. (b) :** 'C' must be an isocyanide and it is obtained from a  $1^\circ$  amine by carbylamine reaction ( $\text{CHCl}_3 + \text{KOH}$ ). Further  $1^\circ$  amine can be obtained by reduction of nitro compound so 'A' is nitrobenzene.



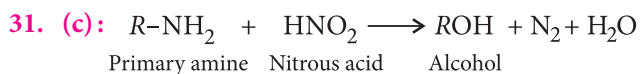
The above reaction is called carbylamine reaction, which is a specific reaction of  $1^\circ$ -amine.



**30. (d) :**



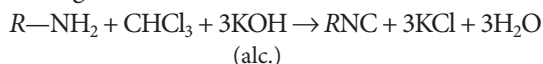
As,  $\text{NO}_2^+$  electrophile can attack both *ortho* and *para* positions, therefore both (a) and (c) product will be obtained.



**32. (b) :** Basic strength decreases as, cyclohexylamine > aniline > benzamide.

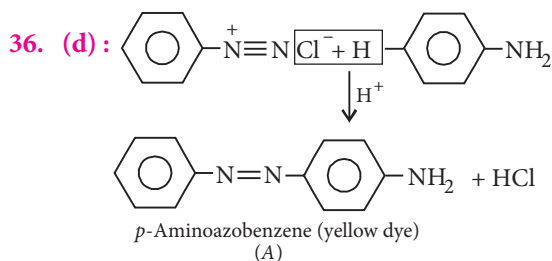
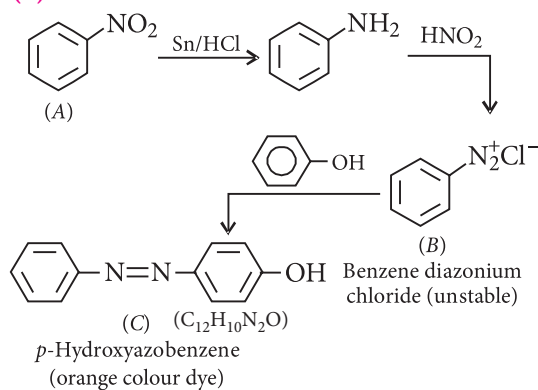
Lesser basicity in aniline and benzamide is due to participation of lone pair of electrons of  $-\text{NH}_2$  group in resonance.

**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  $1^\circ$  amines from  $2^\circ$  and  $3^\circ$  amines.

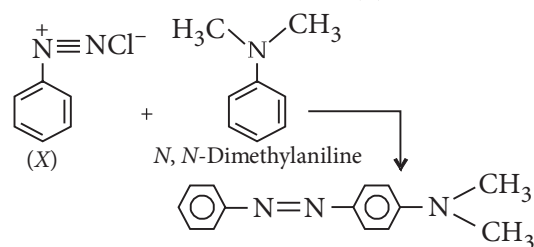
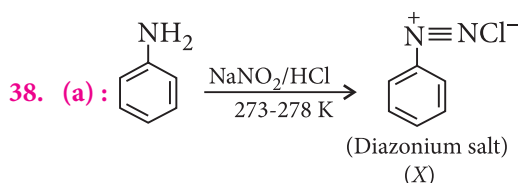


**34. (b) :** Aromatic diazonium salts are more stable due to dispersal of the positive charge in benzene ring.

**35. (b) :**

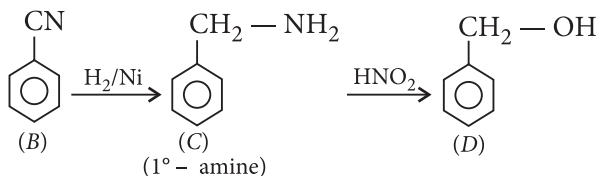
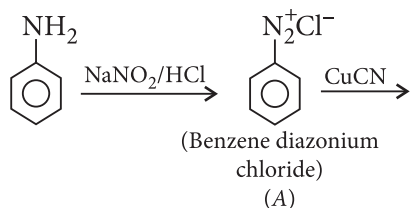


**37. (a) :**  $\text{H}_3\text{PO}_2$  and  $\text{H}_2\text{O}$  reduces the  $-\text{N}_2^+\text{Cl}^-$  to  $-\text{H}$ .

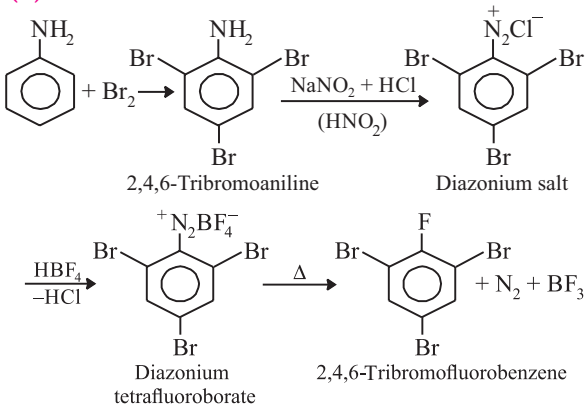
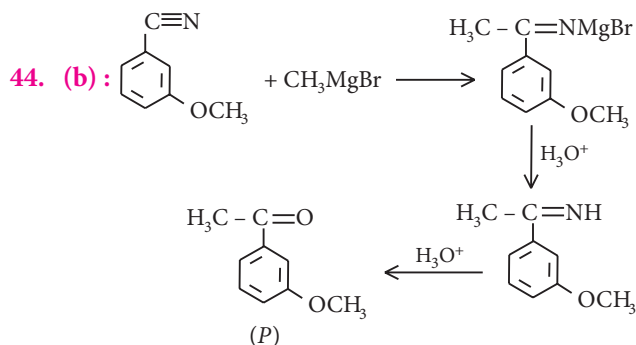
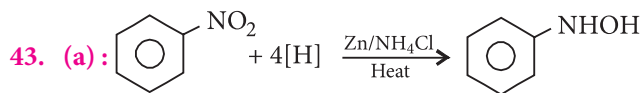
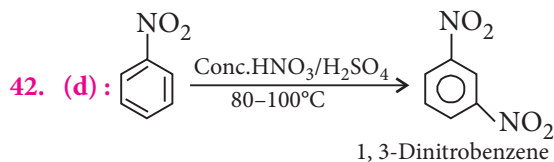




39. (d) :



40. (d) :

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

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