- When primary amine reacts with chloroform in ethanolic KOH then the product is [2002]
  - (a) an isocyanide
- (b) an aldehyde
- (c) a cyanide
- (d) an alcohol.
- The reaction of chloroform with alcoholic KOH 2. and p-toluidine forms [ 2003]

(c) 
$$H_3C$$

- 3. The correct order of increasing basic nature for the bases NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>NH is [2003]
  - (CH<sub>3</sub>)<sub>2</sub>NH < NH<sub>3</sub> < CH<sub>3</sub>NH<sub>2</sub>
  - (b)  $NH_3 < CH_3NH_2 < (CH_3)_2NH$
  - (c)  $CH_3NH_2 < (CH_3)_2NH < NH_3$
  - (d)  $CH_3NH_2 < NH_3 < (CH_3)_2NH$
- Ethyl isocyanide on hydrolysis in acidic medium [2003]
  - (a) propanoic acid and ammonium salt
  - (b) ethanoic acid and ammonium salt
  - (c) methylamine salt and ethanoic acid
  - (d) ethylamine salt and methanoic acid
- 5. Which one of the following methods is neither meant for the synthesis nor for separation of [2005] amines?

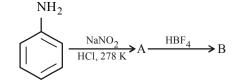
- (a) Curtius reaction (b) Wurtz reaction
- Hofmann method (d) Hinsberg method
- 6. Amongst the following the most basic compound is [2005]
  - (a) p-nitroaniline
- (b) acetanilide
- aniline
- (d) benzylamine
- 7. An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating it gives NH<sub>3</sub> along with a solid residue. The solid residue give violet colour with alkaline copper sulphate solution. The compound is [2005]
  - CH<sub>3</sub>CH<sub>2</sub>CONH<sub>2</sub> (b) (NH<sub>2</sub>)<sub>2</sub>CO
  - (c) CH<sub>3</sub>CONH<sub>2</sub>
- (d) CH<sub>3</sub>NCO
- 8. Which one of the following is the strongest base in aqueous solution?

[2007]

- (a) Methylamine
- (b) Trimethylamine
- (c) Aniline
- (d) Dimethylamine
- 9. In the chemical reaction,

 $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow$ 

- (A) + (B) + 3H<sub>2</sub>O, the compounds (A) and (B)are respectively [2007]
- (a)  $C_2H_5NC$  and 3KCl
- (b) C<sub>2</sub>H<sub>5</sub>CN and 3KCl
- (c) CH<sub>3</sub>CH<sub>2</sub>CONH<sub>2</sub> and 3KCl
- (d)  $C_2H_5NC$  and  $K_2CO_3$ .
- 10. In the chemical reactions,



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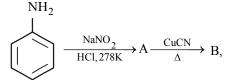
the compounds 'A' and 'B' respectively are

### [2010]

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

### In the chemical reactions:

[2011RS]



the compounds A and B respectively are:

- (a) Benzene diazonium chloride and benzonitrile
- Nitrobenzene and chlorobenzene
- (c) Phenol and bromobenzene
- (d) Fluorobenzene and phenol
- 12. A compound with molecular mass 180 is acylated with CH<sub>2</sub>COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is:

[2013]

- (a) 2
- (b) 5
- (c) 4
- (d) 6
- 13. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is: [2014]
  - (a) an alkanol
- (b) an alkanediol
- (c) an alkyl cyanide (d) an alkyl isocyanide
- 14. Considering the basic strength of amines in aqueous solution, which one has the smallest [2014]  $pK_b$  value?
  - (a)  $(CH_3)_2NH$
- (b) CH<sub>3</sub>NH<sub>2</sub>
- (c)  $(CH_3)_3N$
- (d)  $C_6H_5NH_2$
- **15.** In the reaction

[JEE M 2015]

### Chemistry

$$\xrightarrow{\text{NaNO}_2/\text{HCl}} D \xrightarrow{\text{CuCN/KCN}} E + N_2$$

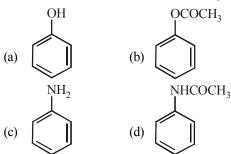
the product E is:

(a) 
$$CN$$
 $CH_3$ 

In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br<sub>2</sub> used per mole of amine produced are:

## [JEE M 2016]

- Two moles of NaOH and two moles of Br<sub>2</sub>.
- (b) Four moles of NaOH and one mole of Br<sub>2</sub>.
- One mole of NaOH and one mole of Br<sub>2</sub>.
- (d) Four moles of NaOH and two moles of Br<sub>2</sub>.
- Which of the following compounds will form significant amount of meta product during mononitration reaction? [2017]



Amines	
Allillics	

	Answer Key													
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(a)	(c)	(b)	(d)	(b)	(d)	(b)	(d)	(a)	(c)	(a)	(b)	(d)	(a)	(a)
16	17													
(b)	(c)													

## SOLUTIONS

1. (a) 
$$C_2H_5NH_2 + CHCl_3 + 3KOH$$
  
 $\rightarrow C_2H_5N \equiv C + 3KCl + 3HCl$   
(Ethyl isocyanide)

2. (c) 
$$\stackrel{\text{NH}_2}{\longleftrightarrow}$$
 +CHCl<sub>3</sub>+ 3KOH $\longrightarrow$ 

$$N = C$$

$$+3KCl+3H_2O$$

$$CH_3$$

3. **(b)** The alkyl groups are electron releasing group (+ I), thus increases the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or lewis acid and making the amine more basic. Hence more the no. of alkyl group more basic is the amine. Therefore the correct order is

$$NH_3 < CH_3NH_2 < (CH_3)_2NH$$

**4. (d)** Ethyl isocyanide on hydrolysis form primary amines.

$$CH_3CH_2N \stackrel{=}{\to} C + H_2O \xrightarrow{H^+}$$
 $CH_3CH_2NH_2 + HCOOH$ 

Therefore it gives only one mono chloroalkane.

**5. (b)** Wurtz reaction is for the preparation of hydrocarbons from alkyl halide

$$RX + 2Na + XR \longrightarrow R - R + 2NaX$$

**6. (d)** Benzylamine  $CH_2NH_2$  is most

basic. In others the basic character is suppressed due to Resonance (see applications of resonance).

- 7. **(b)** 
  - (a) (b) (c) (d) C 20% 20/12 = 1.66 1.66 / 1.66 = 1 H 6.67% 6.67 / 1 = 6.67 6.67 / 1.66 = 4.16 N 46.67% 46.67/14 = 3.33 3.33 / 1.66 = 2.02

O 26.64% 26.64 / 16 = 1.66 1.66 / 1.66 = 1.0

The compound is  $CH_4N_2O$ Empirical weight = 60; Mol. wt. = 60;

$$\therefore n = \frac{60}{60} = 1$$

 $\begin{array}{c} O \\ \parallel \\ Molecular formula = CH_4N_2O; NH_2 - C - NH_2 \end{array}$ 

On heating urea loses ammonia to give Biuret

 $2\mathsf{NH}_2\mathsf{CONH}_2 {\longrightarrow} \mathsf{H}_2\mathsf{NCO}.\mathsf{NH}.\mathsf{CONH}_2 + \mathsf{NH}_3$ 

Biuret with alkaline CuSO<sub>4</sub> gives violet colour. Test for –CONH– group.

aliphatic amines. Among aliphatic amines the order of basicity is  $2^{\circ} > 1^{\circ} > 3^{\circ}$ . The electron density is decreased in  $3^{\circ}$  amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton

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relatively difficult. Therefore the basicity decreases. Further Phenyl group show - I effect, thus decreases the electron density on nitrogen atom and hence the basicity.

- dimethylamine (2° aliphatic amine) is strongest base among given choices.
- The correct order of basic strength is Dimethylamine > Methyl amine > Trimethyl amine>Aniline.
- 9. (a) This is carbylamine reaction. CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> + CHCl<sub>3</sub> + 3KOH

$$\longrightarrow$$
 C<sub>2</sub>H<sub>5</sub>NC + 3KCl + 3H<sub>2</sub>O

10. (c) Primary aromatic amines react with nitrous acid to yield arene diazonium salts.

ArNH<sub>2</sub> + NaNO<sub>2</sub> + 2HX 
$$\xrightarrow{\text{cold}}$$
 1° Aromatic amine

$$Ar$$
— $N = N^+X^- + NaX + 2H_2O$   
Arene diazonium salt

The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF<sub>4</sub>). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as

### **Balz-Schiemann reaction.**

$$\begin{array}{c} \text{Ar--N}_2^+\text{X}^- \xrightarrow{\text{HBF}_4} \text{Ar--N}_2^+\text{BF}_4^- \downarrow \xrightarrow{\text{heat}} \\ \text{Ar--F} + \text{BF}_3 + \text{N}_2 \end{array}$$

11. (a)

$$\begin{array}{c|c}
NH_2 & N_2^+Cl^-\\
\hline
NaNO_2 & CuCN
\end{array}$$
Diazotization

Benzene diazonium chloride

(A)

$$C \equiv N$$
Benzonitrile
(B)
Sandmayer reaction

## Chemistry

12. **(b)** 
$$R - \underbrace{NH_2}_{Mol.Mass=16} + CH_3 - C - Cl \xrightarrow{-HCl} O$$

Now since the molecular mass increases by 42 unit as a result of the reaction of one mole of CH<sub>3</sub>COCl with one-NH<sub>2</sub> group and the given increase in mass is 210. Hence the number of  $-NH_2$  groups is = 210/42 = 5.

**13.** (d)  $R - CH_2 - NH_2 + CHCl_3 + 3KOH (alc)$ Carbyl amine reaction

$$\longrightarrow$$
 R-CH<sub>2</sub>-NC+3KCl+3H<sub>2</sub>O

Alkyl isocynide

14. (a) Arylamines are less basic than alkyl amines and even ammonia. This is due to resonance. In aryl amines the lone pair of electrons on N is partly shared with the ring and is thus less available for sharing with a proton.

> In alkylamines, the electron releasing alkyl group increases the electron density on nitrogen atom and thus also increases the ability of amine for protonation. Hence more the no. of alkyl groups higher should be the basicity of amine. But a slight discrepancy occurs in case of trimethyl amines due to steric effect. Hence the correct order is

$$(CH_3)_2 NH > CH_3 NH_2$$
  
>  $(CH_3)_3 N > C_6 H_5 NH_2$ 

15. (a)

$$\begin{array}{c} NH_2 \\ \hline \\ CH_3 \end{array} \xrightarrow{NaNO_2/HCl} \begin{array}{c} N = \stackrel{+}{NCl}^- \\ \hline \\ CH_3 \end{array} \xrightarrow{CuCN/KCN} \begin{array}{c} CN \\ \hline \\ CH_3 \end{array}$$

Amines \_\_\_\_\_c-137

4 moles of NaOH and one mole of Br<sub>2</sub> is required during production of one mole of amine during Hoffmann's bromamide degradation reaction.

$$\begin{array}{l} \text{R-C-NH}_2 + \text{Br}_2 + 4 \text{NaOH} \rightarrow \text{R-NH}_2 + \text{K}_2 \text{CO}_3 + 2 \text{NaBr} \\ + 2 \text{H}_2 \text{O} \end{array}$$

17. (c) Nitration takes place in presence of concentratedHNO<sub>3</sub> + concentrated H<sub>2</sub>SO<sub>4</sub>

In strongly acidic nitration medium, the amine is converted into anilinium ion  $(-NH_3^+)$ ; substitution is thus controlled not by  $-NH_2$  group but by  $-NH_3^+$  group which, because of its positive charge, directs the entering group to the metaposition instead of ortho, and para.

$$\begin{array}{c|c} : \mathrm{NH_2} & \overset{\oplus}{\mathrm{NH_3}} \\ & & \overset{\mathrm{Conc.\,HNO_3}}{\longrightarrow} & & \\ -\mathrm{NH_2\,gp}: \mathit{o,p} \text{-directing} & -\mathrm{NH_3^+gp}: \mathit{m\text{-}directing} \end{array}$$