CHAPTER 27

# Organic Compounds Containing Nitrogen

## Key Notes and Formulae

### Amines

Amines constitute an important class of organic compounds derived by replacing one or more-hydrogen atoms of $NH_3$ molecule by alkyl/aryl group(s). They are derivatives of $NH_3$.

### Types of Amines

1. Primary amines ($R\text{-}NH_2$)
2. Secondary amines ($R_2\text{-}NH$)
3. Teritiary amines ($R_3\text{-}N$)

### Basicity of Amines

1. In gases: $3^o > 2^o > 1^o > NH_3$ > Aniline (321 NA)
2. In aqueous solution:
   - If R > $CH_3$ $\Rightarrow$ $2^o > 3^o > 1^o > NH_3$ > Aniline
   - If R = $CH_3$ $\Rightarrow$ $2^o > 1^o > 3^o > NH_3$ > Aniline

### Descending-Hoffmann Bromamide Reaction

$$RCONH_2 \xrightarrow{Br_2, KOH} RNH_2$$

### Benzene Diazonium Chloride ($C_6H_5N_2^+Cl^-$)

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N = N - Cl + NaCl + 2H_2O$$

### Acylation

$$CH_3COCl + CH_3NH_2 \rightarrow CH_3CONHCH_3 + HCl$$

### Carbylamine Reaction

Primary amines react with chloroform and NaOH/KOH to give a foul smell (isocyanide).

$$RNH_2 \xrightarrow{CHCl_3, KOH} RNC$$

### Reactions of Aniline

Aniline undergoes electrophilic substitution reaction at o, p (2, 4, 6) positions.

### Nitrobenzene

It is known as oil of Mirbane.
It is also known as artificial oil of the bitter almonds.

### Reduction of Nitrobenzene

In acidic medium (Sn or Zn + HCl)

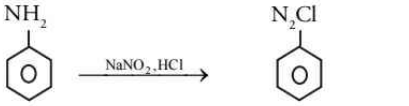
$$C_6H_5NO_2 + 6H \xrightarrow[HCl]{Sn \text{ or } Zn} \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

Nitrobenzene is used in the manufacture of aniline, benzidine azodyes. It is used as an oxidising agent in organic synthesis. It is also used fro scenting cheap soap and shoe polishes.

### Reason for Basicity

Due to resonance in aromatic amines, the lone pair of electrons on nitrogen atom is less available for coordination with proton, as a result electron density on nitrogen decreases and basicity also decreases. Such resonance does not exist in aliphatic amines. So they are more basic than aromatic amines.

### Diazonium Salts




diazotisation
Benzene diazonium chloride

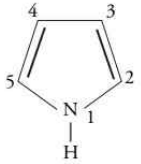
### Alkyl Cyanides

These compound have formula RCN. These are the derivatives of HCN. According to IUPAC system, cyanides are named as 'alkane nitrile'.

## Previous Years' Questions

### NEET

**1.** In pyrrole **[July 2016]**

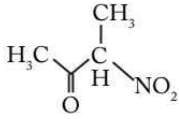


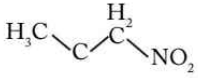

the electron density is maximum on

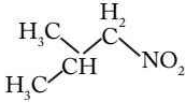
(a) 2 and 5 (b) 2 and 3

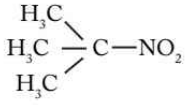
(c) 3 and 4 (b) 2 and 4

**2.** Which one of the following nitro-compounds does not react with nitrous acid ? **[July 2016]**

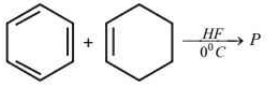
(a) 


(b) 

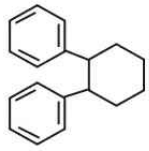

(c) 

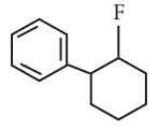

(d) 

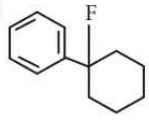

**3.** In the given reaction **[July 2016]**

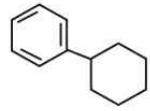



the product P is

(a) 

(b) 


(c) 


(d) 

**4.** The product formed by the reaction of an aldehyde with a primary amine is **[May 2016]**

(a) Schiff base

(b) Ketone

(c) Carboxylic acid

(d) Aromatic acid

**5.** The correct statement regarding the basicity of arylamines is. **[May 2016]**

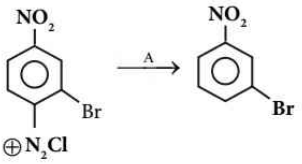
(a) Arylamines are generally less basic than al kaylamines because the nitrogen lone-pair electrons are delocaized by interaction with the aromatic ring $\pi$ electron system

(b) Arylamines are generally more basic than alkaylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring $\pi$ electron system

(c) Arylamines are generally more basic than alkaylamines because of aryl group.

(d) Arylamines are generally more basic than alkaylamines because the nitrogen atom in arylamine is sp- hybridized.

**6.** In the reaction, A is: **[2013]**

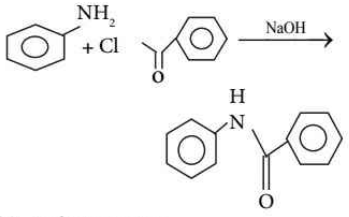



(a) $H_3PO_4$ and $H_2O$
(b) $H^+/H_2O$
(c) $HgSO_4/H_2SO_4$
(d) $Cu_2Cl_2$

**7.** Nitobenzene on reaction with conc. $HNO_3/H_2SO_4$ at 80 - 100°C forms which one of the following products? **[2013]**
(a) 1, 2 Dinitobenzene
(b) 1, 3 Dinitrobenzene
(c) 1, 4 Dinitrobenzene
(d) 1, 2, 4 Trinitrobemzene

## AIPMT

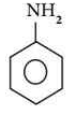
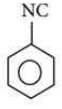
**8.** The following reaction **[2015]**

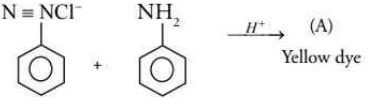



(a) Perkins reaction
(b) Acetyl reaction
(c) Schotten - Baumann Reaction
(d) Friedel - Craft's reaction

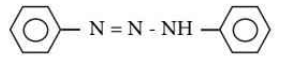
**9.** $A \xrightarrow{\text{reduction}} B \xrightarrow{CHCl_3/KOH} C \xrightarrow{\text{reduction}}$ N-methylaniline

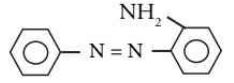
then A is **[2015]**

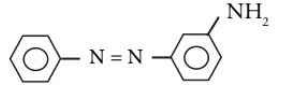
(a) 
(b) 
(c) $CH_3NH_2$
(c) 

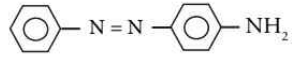
**10.** 


**[2014]**

(a) 

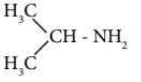
(b) 

(c) 

(d) 


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

**12.** 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 iso- propylmethylamine. Predict the structure of (A). **[2012]**

(a) 

(b) $CH_3CH_2$ - NH - $CH_3$

(c) $CH_3$-N-$CH_3$ (with $CH_3$ below N)

(d) $CH_3CH_2CH2 - NH_2$

**13.** Which of the following compounds is most basic ? **[2011]**

(a) $O_2N$–C$_6$H$_4$–$NH_2$

(b) C$_6$H$_5$–$CH_2NH_2$

(c) C$_6$H$_5$–N(H)–$COCH_3$

(d) C$_6$H$_5$–$NH_2$

**14.** Which of the following statement about primary amines is false ? **[2010]**

(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.

**15.** Nitrobenzene can be prepared from benzene by using mixture of conc. $HNO_3$ and conc. $H_2SO_4$. In the mixture, nitric acid acts as a/an **[2009]**

(a) Acid (b) Base

(c) Catalyst (c) Reducing Agent

**16.** Which one of the following on reduction with lithium aluminium hydride yields a secondary amine? **[2007]**

(a) Methyl isocyanide

(b) Acetamide

(c) Methyle Cyanide

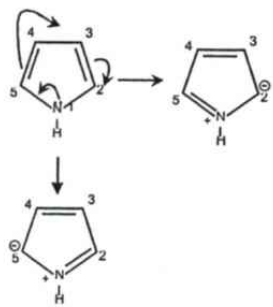
(d) Nitroethane

## Answer key

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | (a) | 2. | (d) | 3. | (d) | 4. | (a) | 5. | (a) | 6. | (a) | 7. | (b) | 8. | (c) |
| 9. | (b) | 10. | (d) | 11. | (b) | 12. | (a) | 13. | (b) | 14. | (c) | 15. | (b) | 16. | (a) |

## Detailed Solutions

**1. (a).**



Electron density is maximum on-2 & 5th carbon because -ve charge present at carbon 2 and 5 so electrophilic substitution reaction takes place at 2nd and 5th carbon.

**2. (d).**

$1^0$ nitro compound, $2^0$ nitrocompound react with $HNO_2$ acid but $3^0$ nitro compound does not react with nitrous acid.

(i) $CH_3$-C(=O)-C($CH_3$)H-$NO_2$ $\xrightarrow{HNO_2}$ $CH_3$-C(=O)-C($CH_3$)(N=OH)-$NO_2$

(ii)

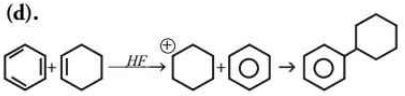
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}NO_2 \xrightarrow{HO\text{-}N=O} CH_3\text{-}CH_2\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}NO_2$$

(iii)

$$CH_3\text{-}\underset{\underset{CH_3}{|}}{C}H\text{-}CH_2\text{-}NO_2 \xrightarrow{HO\text{-}N=O} CH_3\text{-}\underset{\underset{CH_3}{|}}{C}H\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}NO_2$$

$3^0$nitro $\xrightarrow{HNO_2}$ No reaction

**3. (d).**



This is a Freidal - Craft reaction

**4. (a).**

Aldehyde +Primary Amine →Schiff base

**5. (a).**

R - $NH_2$
Alkylamine

- Aryl amine
- De-localized lone pair of nitrogen
- Less basic

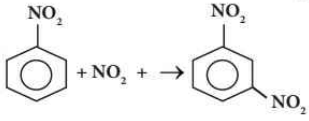
**6. (a):** $H_3PO_2$ and $H_2O$ reduces the- $\overset{+}{N}_2\overset{-}{Cl}$ to -H

**7. (b):** $NO_2$ group being electron withdrawing reduces electron density at positions. Hence, now the meta - position becomes electron rich on which the electrophile (nitronium ion) attacks during nitration.

$$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2O + NO_2^+$$

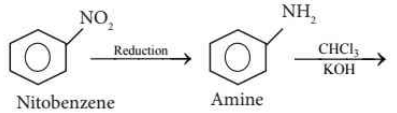
electrophile



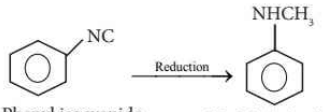
m - dinitrobenzene
or 1, 3 - dinitrobenzne

**8. (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.

**9. (b):** 'C' must be an isocyanide and obtained from a $1^0$ amine by carbylamine reaction ($CHCl_3$ + KOH). Further $1^0$ amine must be obtained by reduction of nitrohydrocarbon. So 'A' is nitrobenzene.

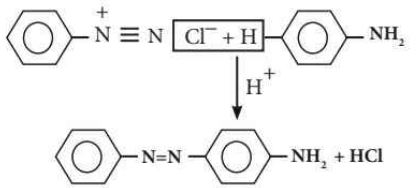


Nitobenzene Amine



Phenyl isocyanide N - Methylaniline

**10. (d):**



p - Aminoazobenzene (yellow dye)
(A)

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

**12. (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.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2 \quad \text{or} \quad CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}NH_2$$

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

$$CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}NH_2 \xrightarrow{HNO_2} CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3 + N_2\uparrow$$

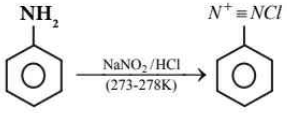
(A)

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{CH}}} - NC \xrightarrow{HNO_2} CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{CH}}} - NH - CH_3$$

(C) Isopropylmethylamine

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

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




**15.** **(b).** $H^+ + HO - NO_2 \rightarrow [H_2O^+ - NO_2]$

$\downarrow$

$H_2O + NO_2^+$

**16.** **(a).** Alkyl isocyanide on reduction with lithium aluminium hydride forms secondary amines containing methyl as one of the alkyl groups.

$$R - N \rightleftarrows C + [H] \xrightarrow{LiAlH_4} RNHCH_3$$

Alkyl amines Secondary amine

$$H_3C - N \rightleftarrows + 4\,[H] \xrightarrow{LiAlH_4} H_3C\text{-}NH\text{-}CH_3$$

Methyl isocyanide Dimethylamine