# CHAPTER 19 - ORGANIC COMPOUNDS CONTAINING NITROGEN (AMINES)

## **Single Correct Type**

- (A) a hydrocarbon
- (B) a cyanide
- (C) primary amine
- (D) Isocupmate
- 2. Which of the following sequence of reagent is the good means to furnish the conversion?

$$R-CH_2OH \longrightarrow R-CH_2NH_2$$

- (I)  $KMnO_4$ ;  $SOCl_2$ ;  $NH_3$ ,  $\Delta$ ; NaOBr
- (II)  $SOCl_2$ ; NaCN;  $H_2$ , Ni
- (III) cro<sub>3</sub> in dilute acetone; NH<sub>3</sub>; H<sub>2</sub>,Ni

(IV)

Cu,300°C; NH<sub>3</sub>; LiAlH<sub>4</sub>

(A) I, II, III, IV

(B) I, II, III

(C) II, III, IV

- (D) III, IV
- 3. In nitration of aniline, -NH<sub>2</sub> group is protected by the following process:
  - (A) Alkylation

(B) Acylation

(C) Diazotization

(D) Decarboxylation

4. Which of the following reactions will produce a secondary amine?

$$(A) \xrightarrow{\text{NH}_2} \xrightarrow{\text{1.LiAlH}_4.\text{diethylether}}$$

$$(B) \quad \bigcirc_{N} \xrightarrow{\stackrel{O}{\longleftarrow} \frac{1.\text{LiAlH}_{4}.\text{diethylether}}{2.\text{H}_{2}\text{O}}}$$

(C) 
$$\stackrel{\text{HO}}{\longrightarrow}$$
  $\stackrel{\text{CH}_3}{\longrightarrow}$   $\stackrel{\text{1.LiAlH}_4.diethylether}{\longrightarrow}$ 

(D) 
$$\stackrel{\parallel}{\underset{\stackrel{}{\underset{}}{\bigvee}}} CH_3$$
 $\stackrel{1.\text{LiAlH}_4.\text{diethylether}}{\underset{2.\text{H}_2O}{\longrightarrow}}$ 

5. Molecular formula of chloropicrin is

(A)CHCl<sub>3</sub>NO<sub>2</sub>

(B) CCl<sub>3</sub>NO<sub>3</sub>

(C)CCl<sub>2</sub>NO<sub>2</sub>

(D) CCl<sub>3</sub>NO<sub>2</sub>

6. Identify (Z) in the following sequence of reactions.

$$(B) \xrightarrow{H_3C} \xrightarrow{N_2^+CI}_{CH_3}$$

$$(C)$$
 $OCH_3$ 
 $OH$ 
 $OH$ 

(D) 
$$\bigcirc$$
 OCH<sub>3</sub>

## 7. Which of the following compound is most basic?

$$(A)_{NH_2}$$
  $NH_2$   $NH_2$   $NH_2$   $NH_3$   $NH_4$   $NH_4$   $NH_4$   $NH_5$   $NH_5$   $NH_6$   $N$ 

$$(C)_{Me-NH}$$
  $NH-Me$   $(D)$   $(CH_3)_2NH$ 

 $NH_2$ 

 $\dot{\rm N}{\rm O}_2$ 

$$(C)$$
 $NH_2$ 
 $NO_2$ 

$$(B) \bigvee_{NO_2}^{NH_2}$$

$$(D) \bigcup_{NO_2}^{NHI}$$

9. 
$$NO_2$$
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 
 $NO_2$ 

$$(C)$$
 $NH_2$ 
 $NH_2$ 

$$(B) \bigcirc_{NO_2}^{NH_2}$$

$$(D) \qquad \qquad \bigvee_{\mathsf{HS}}^{\mathsf{NH}_2}$$

10. 
$$\downarrow^{O}$$
 + H<sub>3</sub>C-CH<sub>2</sub>-NHCH<sub>2</sub>CH<sub>3</sub> -----?

$$(C) 
\downarrow N 
\downarrow C_2H_5 
\downarrow C_2H_5$$

$$N \subset C_2H_5$$

$$(D) \qquad \bigwedge^{\mathsf{N} \subset \mathsf{QH}_{\mathsf{E}}} \mathsf{C}_{\mathsf{QH}_{\mathsf{E}}}$$

# **Multiple Correct Type**

- 11. CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> is soluble in
  - (A) dilute HCl

(B) Cuso<sub>4</sub> solution

(C)  $AgNO_3$ 

(D) dil. H<sub>2</sub>SO<sub>4</sub>

- 12. Which of the following compound cannot be prepared by Gabirielphthalimide synthesis?
  - $(A) CH_3 CH_2 NH_2$

 $(B) (\mathsf{CH}_{\scriptscriptstyle 3})_{\scriptscriptstyle 3} \mathsf{C} \!-\! \mathsf{NH}_{\scriptscriptstyle 2}$ 

 $(C) \, \, \mathsf{Ph} \! - \! \mathsf{NH}_{_{\! 2}}$ 

- (D)  $\langle \bigcirc \rangle$  NH CH<sub>3</sub>
- 13. Aspirin and oil of wintergreen can be distinguished by
  - (A) Neutral Fecl<sub>3</sub>

(B) Aq. NaOH

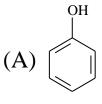
(C) Aq. NaHCO<sub>3</sub>

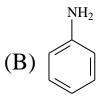
- (D)  $Br_2/CCl_4$
- 14. The reagent (s) used to convert phenol in to Anisole is/are.
  - (A)  $NaOH, CH_3I$

(B)  $CH_2N_2, BF_3$ 

(C)  $(CH_3)_2 SO_4$ , NaOH

- (D)  $NaHCO_3, CH_3I$
- 15. Which of the following undergo reaction with alcoholic KOH and chloroform?







(D)

- 16. Which of the following compounds give carbylamines reaction?
- 17. Which of the following reaction represent the major product :

(A) 
$$CH_3$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

(B) 
$$Ph - C - NH_2 \xrightarrow{Br_2 + KOH} Ph - NH_2$$

(C) 
$$\xrightarrow{\text{Br}_2 + \text{KOH}}$$
  $\xrightarrow{\text{NH}_2}$ 

(D) 
$$COC1 \xrightarrow{(i)N_{NaN_3}} COC1 \xrightarrow{(i)i)H_2O} C$$

- A mixture of primary, secondary and tertiary amines can be 18. separated by

  - (A) Nitrous acid test (B) Carbylamine reaction
  - (C) Hinsberg's method (D) reaction with chloride (Acylation)
    - acetyl
- 19. By which of the following reactions can methyl cyanide be prepared?

(A) 
$$CH_3Br \xrightarrow{KCN} DMF$$

$$(B)$$
  $CH_3NH_2 \frac{CHCl_3}{KOH}$ 

(C) 
$$H_3C - CH = N - OH \xrightarrow{P_2O_5} \Delta$$

$$(A) \ \mathsf{CH_3Br} \xrightarrow{\mathsf{KCN}} \qquad \qquad (B) \ \ \mathsf{CH_3NH_2} \xrightarrow{\mathsf{CHCl_3}} \qquad \\ (C) \ \mathsf{H_3C-CH=N-OH} \xrightarrow{\mathsf{P_2O_5}} \qquad (D) \ \ \mathsf{H_3C-C-NH_2} \xrightarrow{\mathsf{P_4O_{13}}} \qquad \\$$

- 20. Which of the following arrangements are correct with respect to the property of the compounds indicated in the parentheses?
  - $(A) \ \mathsf{HCOOH} > \mathsf{CH_3COOH} > \mathsf{CH_3CH_2COOH}(\mathsf{Acidic\ strength})$

$$(B) \ \, \text{F} \qquad \text{COOH} > \ \, \text{CI} \qquad \text{COOH} > \ \, \text{Br} \qquad \text{COOH} \, (\text{Acidic strength})$$

(C)

(D)

$$NH_2$$
  $NH_2$   $C-NH_2$   $>$   $O$  (Base strength)

## **Integer Type**

- 21. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitroso amine. The compound must have how many minimum carbon atom.
- 22. What is the number of benzene derivatives having the molecular formula C<sub>7</sub>H<sub>9</sub>N that would respond to carbyl amine test.
- 23. The Gabriel synthesis of amines is out lined the following way,

$$\begin{array}{c|c}
O & O & O \\
NH & KOH & N^{-}K^{+} & RX/DMF
\end{array}$$

$$\begin{array}{c|c}
N-R & \xrightarrow{Ethanol reflux} RNH_{2}
\end{array}$$

Out of the given amines, how many cannot be prepare by this method.

(1) CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>

(2) CH<sub>3</sub>NHCH<sub>3</sub>

(3)  $CH_2 = CH - NH_2$ 

(7) 
$$(8)$$
  $(8)$ 

- 24. Certain nitrogenous compound with molecular mass (180) show an increase in its molecular mass to 348 after treatment with acetyl chloride. The number of possible NH<sub>2</sub> groups in the molecule is:
- 25. A nitrogenous compound with molecular mass 180 shows an increase in molecular mass to 348 after treatment with acetyl chloride. The number of possible NH<sub>2</sub> group in the molecule is.
- 26. Among R–CH<sub>2</sub>–NO<sub>2</sub>, Ph–NO<sub>2</sub>, Ph–CH<sub>2</sub>–NO<sub>2</sub>, R<sub>2</sub>CH–NO<sub>2</sub> and R<sub>3</sub>C–NO<sub>2</sub>, how many compounds with give blue colour when treated with HNO<sub>2</sub> followed by NaOH
- 27. Of the following amines how many can be separated by Hoffmann's mustard oil reaction?

28. How many of the following compound are more basic than aniline?

- 29. A compound with molecular formula C<sub>9</sub>H<sub>24</sub>N<sub>4</sub> is converted by the action of acetyl chloride to a compound with molecular mass 314. The number of NH<sub>2</sub> groups in the compound is\_\_\_\_\_.
- 30. Number of isomeric primary amines obtained from  $c_4H_{11}N$  are

#### **SOLUTIONS**

## **Single Correct Type**

1. (C)

$$\begin{array}{c|c} O \\ \parallel \\ CH_2-C-NH_2 \\ \hline \\ C-OCH_3 \\ \hline \\ O \end{array} \qquad \begin{array}{c} Br_2/NaOH \\ \hline \\ C-OCH_3 \\ \parallel \\ O \end{array}$$

The reaction above is a case of Hoffman Bromamide degradation reaction which converts an amide to a primary amine.

2. (D)

For (a),

$$\mathsf{R} - \mathsf{CH_2} - \mathsf{OH} \xrightarrow{\mathsf{KMnO_4}} \mathsf{RCOOH} \xrightarrow{\mathsf{SOCl_2}} \mathsf{RCoCl} \xrightarrow{\mathsf{NH_3}} \mathsf{RCONH_2} \xrightarrow{\mathsf{NaOBr}} \mathsf{RNH_2}$$

This result in R-NH<sub>2</sub> and not R-CH<sub>2</sub>-NH<sub>2</sub>

For (b),

$$\mathsf{R}-\mathsf{CH}_2-\mathsf{OH} \xrightarrow{\mathsf{SOCl}_2} \mathsf{R}-\mathsf{CH}_2-\mathsf{CI} \xrightarrow{\mathsf{NaCN}} \mathsf{R}-\mathsf{CH}_2-\mathsf{CN} \xrightarrow{\mathsf{H}_2} \mathsf{R}-\mathsf{CH}_2-\mathsf{CH}_2-\mathsf{NH}_2$$

This result in R-CH2-CH2-NH2 and not R-CH2-NH2

For (c),

$$\mathsf{R} - \mathsf{CH}_2 - \mathsf{OH} \xrightarrow{\mathsf{CrO}_3} \mathsf{R} - \mathsf{CHO} \xrightarrow{\mathsf{NH}_3} \mathsf{R} - \mathsf{CH} = \mathsf{NH} \xrightarrow{\mathsf{Ni}} \mathsf{R} - \mathsf{CH}_2 - \mathsf{NH}_2$$

This result in R-CH<sub>2</sub>-NH<sub>2</sub>

For (d),

$$R - CH_2 - OH \xrightarrow{Cu} R - CHO \xrightarrow{NH_3} R - CH = NH \xrightarrow{LiAlH_4} R - CH_2 - NH_2$$

This is also result in R—CH<sub>2</sub>—NH<sub>2</sub>

## 3. (B)

-NH<sub>2</sub> group is first converted to -NHCOCH<sub>3</sub> group through acylation and then after nitration it is converted back to -NH<sub>2</sub> group through Hydrolysis as shown below.

#### 4. (D)

$$CH_3$$
 $CH_3$ 
 $CH_3$ 

## 5. (D)

Chloropicrin, also known as nitrochloroform, is a chemical compound currently used as a broad-spectrum antimicrobial, fungicide, herbicide, insecticide, and nematicide. It's chemical structural formula is Cl<sub>3</sub>CNO<sub>2</sub>.

 $HOC_6H_2(NO_2)_3 + 11 NaOCl \rightarrow 3 Cl_3CNO_2 + 3 Na_2CO_3 + 3 NaOH + 2 NaCl$ 

6. (D)

7. (C)

The conjugate acid of Me—NH—NH—Me is the most stabilized, indicating that Me—NH—NH—Me is the most basic.

8. (B)

Wijs solution (ICl in acetic acid) is used to produce (Iodonium ion) which adds to aromatic compounds.

(As  $_{-NH_2}$  is ortho/para directing and  $_{-NO_2}$  is meta directing, will result in the given product.)

## 9. (B)

NH<sub>4</sub>HS reduces the nitrobenzene to Aniline. However, when we have two  $-NO_2$  groups, it reduces only one  $-NO_2$  group.

$$NO_2$$
 $NH_2$ 
 $NO_2$ 
 $NH_4HS$ 
 $NO_2$ 

## 10. (A)

$$C_{2}H_{5}$$
 $C_{2}H_{5}$ 
 $C_{2}H_{5}$ 
 $C_{2}H_{5}$ 
 $C_{2}H_{5}$ 
 $C_{2}H_{5}$ 

2º Amine on reaction with aldehyde or ketone gives enamine.

## **Multiple Correct Type**

11. (A, B, C, D)

Amines being basic in nature dissolve in dilute HCl and dil. H<sub>2</sub>SO<sub>4</sub>. They can also coordinate with cu<sup>2+</sup> and Ag<sup>+</sup> ions to form soluble complexes as they can act as good ligands.

12. (B, C, D)

Primary aliphatic amines are prepared by Gabrielphthalimide synthesis.

cannot be prepared because it is a secondary amine.

(CH<sub>3</sub>)<sub>3</sub>C-NH<sub>2</sub> and Ph-NH<sub>2</sub> cannot be prepared because 3° alkyl halides and arylhalides cannot be used in this reaction.

13. (A, C)

$$\begin{array}{c|c}
OH & OCOCH_3 \\
\hline
OCOOH & (CH_3CO)_2O \\
\hline
& pyridine
\end{array}$$

$$\begin{array}{c}
OCOCH_3 \\
\hline
COOH
\end{array}$$

14. (A, B, C)

(A) 
$$\frac{1) \operatorname{Hg}(OAC)_{2} - \operatorname{Hhr}/H_{2}O}{2) \operatorname{NCBH}_{4}/H_{2}O} \xrightarrow{OH}$$
(B) 
$$\frac{\operatorname{H}^{+}/H_{2}O}{OH}$$

#### 15. (A, B, C, D)

Alcoholic solution produces an electrophile :CCl<sub>2</sub>. Hence are likely to show reaction.

### 16. (A, B, C)

Carbylamine reaction is given by 1° amines

#### 17. (A, B, D)

(A) Beckmann rearrangement

(D) 
$$C = O \xrightarrow{H_2O} C = O \xrightarrow{H_$$

#### 18. (A, C, D)

#### **Nitrous acid Test**

1°, 2° and 3° amines can be separated by using HNO<sub>2</sub>.

1° amines form alcohol with evolution of N<sub>2</sub>.

2° amines form nitroso amine which gives green colour with phenol and conc. H<sub>2</sub>SO<sub>4</sub>.

3° amines forms nitrites which on heating gives nitroso amine which responds to **Liebermann's test.** 

1° amine reacts with benzene sulphonyl chloride (Hinsberg's reagent) to form mono alkyl sulphonamide which is soluble in KOH.

2° amines forms similar compound with Hinsberg's reagent but it is insoluble in NaOH.

3° amines does not combine with Hinsberg's reagent.

### **Reaction with Acetyl Chloride**

1° amine reacts with acetyl chloride to form N-substituted amides.

2° amines reacts with acid chlorides to form N, N-disubstituted amides.

3° amines does not react since they do not have replaceable hydrogen on nitrogen.

$$H_3CBr \xrightarrow{KCN} H_3CCN$$

$$CH_3NH_2 \xrightarrow{CHCI_3/KOH} H_3C \xrightarrow{P} C$$

$$\begin{array}{c} O \\ || \\ H_3C - C - NH_2 \xrightarrow{P_4O_{10}} H_3C - C \equiv N \end{array}$$

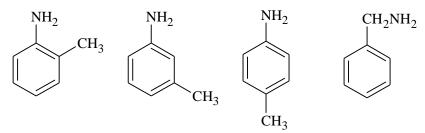
#### 20. (A, B, C)

- group increases and +I group decreased acidic strength.

Carboxylic group are more acidic than alcohol. And aromatic alcohols are more acidic than aliphatic alcohol.

## **Integer Type**

- 21. (2)
- 22. (4)



23. (5)

Only primary amines can be prepared by this method. The second step involves  $S_N2$  reaction. Therefore

and  $CH_2 = CH - X$  are not expected to give  $S_N2$ .

24. (4)

The chemical reaction involved is as follows:

$$-NH_2 + Cl - \overset{O}{C} - CH_3 \xrightarrow{-H} -NH - \overset{O}{C} - CH_3$$

Net increase in mol. Mass on acylation of one  $-NH_2$  group = Mol. Mass of  $CH_3CO$  group - At. Mass of H = 43 - 1 = 42

Actual increase in mol. Mass on acylation

$$=348-180=168$$

no.  $CH_3CO$  group added = 168/42 = 4Hence the compound has  $4 - NH_2$  groups.

$$-NH_2$$
 +  $CI$   $-CH_3$   $\xrightarrow{-H}$   $-NH$   $-C$   $-CH_3$ 

Increase in molecular mass on acylation of one  $-NH_2$  group is 42. Increase in Molecular mass = 348-180 = 168No. of  $-NH_2$  group =  $\frac{168}{42} = 4$ 

- 26. (1) only R<sub>2</sub>CH–NO<sub>2</sub> will give this reaction
- 27. (4)
  Primary amine gives positive test for Hoffmann's mustard oil reaction.
- 28. (5)

Aliphatic amines and compound containing + M group are more basic than aniline.

29. (3)

$$R-NH_{2} + CH_{3} Cl \longrightarrow HCl + R-NH CH_{3}$$

$$Compoound_{1}(C_{9}H_{24}N_{4}) + Cl \longrightarrow Compoound_{2}$$

$$Molar\ mass = M_1 = 188$$

 $Molar\ mass = M_2 =$ 

314

The reaction involves loss of one H and it is replaced by – COCH<sub>3</sub> group.

$$\therefore M_1 - n + 43n = M_2$$

$$188 + 42n = 314$$

$$n = 3$$

30. (4)

Four 1° amines are possible

CH<sub>3</sub>CH(NH<sub>2</sub>)CH<sub>2</sub>CH<sub>3</sub>,(CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub>