Chapter_13

Organic Compounds Containing Nitrogen

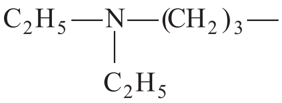
Practice Questions

1. The hybridisation and geometry of amines are sp^3 and pyramidal respectively due to the presence of
(a) divalent N-atom *(b)* trivalent N-atom
(c) monovalent N-aom *(d)* tetravalent N-atom

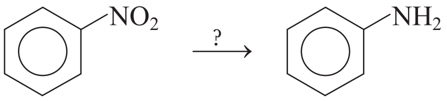
2. What is the bond angle of $C — N — E$ (E = C or H) in case of trimethylamine?
(a) 109.5° *(b)* More than 109.5°
(c) 108° *(d)* 90°

3. If one H-atom of ammonia is replaced by alkyl group, the amine, thus obtained is known as
(a) secondary amine *(b)* primary amine
(c) tertiary amine *(d)* quaternary amine

4. Which of the following is an aromatic amine?
(a) Aniline
(b) N-methyl aniline
(c) 2-phenyl ethanamine
(d) None of the above

5. The IUPAC name of 
$C_2H_5—\underset{\substack{|\\C_2H_5}}{N}—(CH_2)_3—CH_3$ is
(a) N-ethylbutan-2-amine
(b) N-diethylbutan-1-amine
(c) N, N-diethylbutan-1-amine
(d) N, N-diethylbutan-2-amine

6. Which of the following reagents is/are used in the given reaction?



(a) H_2/Pd, ethanol *(b)* $Sn + HCl$
(c) $Fe + HCl$ *(d)* All of these

7. What is the correct order of reactivity of halides with amines?
(a) $RCl > RBr > RI$ *(b)* $RI > RBr > RCl$
(c) $RCl > RI > RBr$ *(d)* $RI > RCl > RBr$

8. Which of the following can be prepared using Gabriel phthalimide synthesis?
(a) Primary aromatic amines
(b) Secondary amines
(c) Primary aliphatic amines
(d) Tertiary amines

9. Ethylamine $(C_2H_5HN_2)$ can be obtained from N-ethylphthalimide on treatment with
(a) $NaBH_4$ *(b)* NH_2NH_2
(c) H_2O *(d)* CaH_2

10. Which of the following reactions is appropriate for converting acetamide to methanamine?
(a) Carbylamine reaction
(b) Hofmann bromamide reaction
(c) Stephen's reaction
(d) Gabriel's phthalimide synthesis

11. Which of the following can form H-bond?
(a) NH_3 *(b)* $R—CH_3$
(c) $R—O—R$ *(d)* $R—Br$

12. Amines behave as a nucleophile because of
(a) the presence of unshared pair of electrons on N-atom
(b) the absence of unshared pair of electrons on N-atom
(c) the vacant p-orbital of N-atom
(d) All of the above

13. Amines on treatment with acids yield salt because they are
(a) basic in nature *(b)* acidic in nature
(c) amphoteric in nature *(d)* None of these

14. The correct order of the basic strength of methyl substituted amines in aqueous solution is
(a) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$
(b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
(c) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
(d) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

15. Aniline is more stable than anilinium ion because
(a) it has more resonating structures.
(b) it has less resonating structures.
(c) it has more π-bonding.
(d) it has less π-bonding

16. The carbylamine reaction is given by
(a) $(C_2H_5)_3N$ *(b)* $(C_2H_5)_2NH$
(c) $C_2H_5NH_2$ *(d)* $C_3H_7NHC_2H_5$

17. Name the product(s) formed during the reaction of primary aliphatic amines with nitrous acid at room temperature?
(a) RNO_2 *(b)* ROH
(c) Both (a) and (b) *(d)* None of these

18. The chemical formula of Hinsberg's reagent is
(a) HNO_2 *(b)* $NaOH + CaO$
(c) $C_6H_5SO_2Cl$ *(d)* CH_3CONH_2

19. $—NH_2$ group in aniline is activating group and, hence reaction occurs at
(a) *para* position *(b)* *ortho* position
(c) *meta* position *(d)* Both (a) and (b)

20. Aniline does not undergo Friedel-Crafts reaction due to
(a) less reactivity of aniline
(b) salt formation with $AlCl_3$

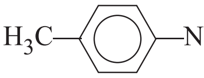
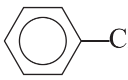
(c) electron accepting effect of —NH_2 group present in aniline
(d) None of the above

21. Which of the following amine will form stable diazonium salt at 273-278 K?
(a) $C_2H_5NH_2$ *(b)* $C_6H_5NH_2$
(c) $C_6H_5CH_2NH_2$ *(d)* $C_6H_5N(CH_3)_2$

22. Which of the following compound is water insoluble and stable at room temperature?
(a) Benzene diazonium chloride
(b) Benzene diazonium fluoroborate
(c) Both (a) and (b)
(d) None of the above

23. The reagent used to form aryl fluoride from arene diazonium chloride is
(a) HF *(b)* KF
(c) HBF_4 *(d)* None of these

24. Coupling reaction is an example of
(a) nucleophilic addition reaction.
(b) nucleophilic substitution reaction.
(c) electrophilic substitution reaction.
(d) electrophilic addition reaction.

25. The compounds  NH_2 and  CH_2NH_2 are distinguished by
(a) $C_6H_5SO_2Cl$ and OH^- in H_2O
(b) $AgNO_3$ in H_2O
(c) dilute HCl
(d) HNO_2 and β-naphthol

ANSWERS

1.	(b)	**2.**	(c)	**3.**	(b)	**4.**	(a)	**5.**	(c)	**6.**	(d)	**7.**	(b)	**8.**	(c)	**9.**	(b)	**10.**	(b)
11.	(a)	**12.**	(a)	**13.**	(a)	**14.**	(d)	**15.**	(a)	**16.**	(c)	**17.**	(b)	**18.**	(c)	**19.**	(d)	**20.**	(b)
21.	(b)	**22.**	(b)	**23.**	(c)	**24.**	(c)	**25.**	(d)										

Hints & Solutions

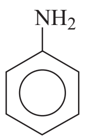
1. *(b)* Due to the presence of trivalent N-atom and unshared pair of electrons in amines, hybridisation and geometry become sp^3 and pyramidal respectively.

2. *(c)* The C—N—*E* angle is 108° in case of trimethylamine due to the presence of unshared pair of electrons in it.

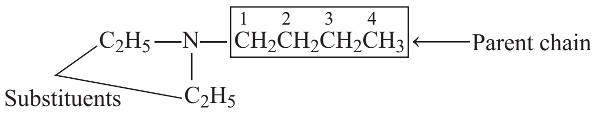
3. *(b)* If one H-atom of NH_3 is replaced by alkyl or aryl group, the primary (1°) amine is obtained.

$$\underset{\text{Ammonia}}{NH_3} \xrightarrow[-\text{H}]{+R/Ar} \underset{1^\circ \text{ amine}}{R/ArNH_2}$$

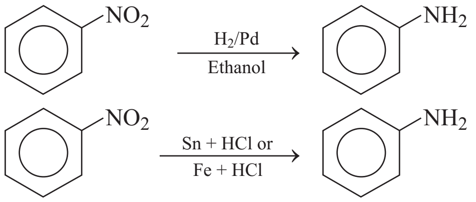
4. *(a)* Aromatic amine is aniline and its IUPAC name is benzamine. The structure of aniline is



5. *(c)* The IUPAC name of the given compound is N, N-diethylbutan-1-amine.

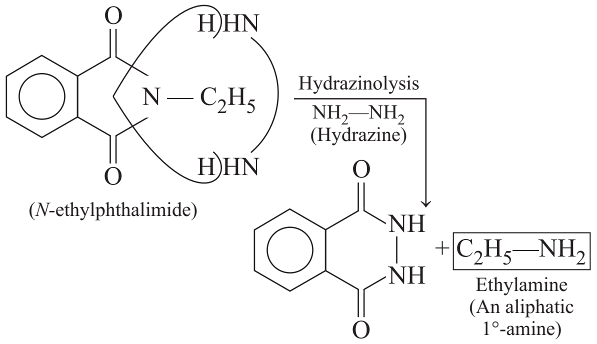


6. *(d)* The reagents used to reduce nitro compounds to corresponding amines are hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. The reactions are as follows :



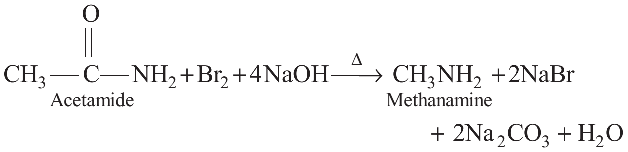
8. *(c)* Primary aliphatic amines can be prepared by Gabriel phthalimide synthesis. Secondary and tertiary amines cannot be prepared by this method due to steric hindrance. Aromatic primary amines cannot be prepared because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

9. *(b)* The reaction for the production of ethylamine from *N*-ethylphthalimide can be takes place as follows :



This reaction is the second step of Gabriel phthalimide synthesis for the preparation of aliphatic 1°-amines and amino acid. In this step, concentrated alkali can also be used in place of hydrazine.

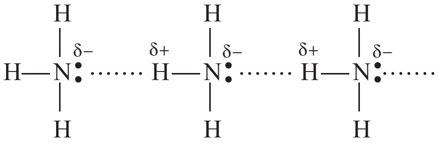
10. (*b*) The conversion of acetamide to methanamine can be achieved by Hofmann bromamide reaction. It involves the migration of alkyl or aryl with its electron pair to electron deficient N from adjacent carbon. The reaction involves the intermediate isocyanate. Complete reaction is shown below :



$$\underset{\text{Acetamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{Methanamine}}{CH_3NH_2} + 2NaBr + 2Na_2CO_3 + H_2O$$

11. (*a*) The attractive electrostatic force between a hydrogen atom and an electronegative atom (F, O, N) is known as hydrogen bond.

Thus, ammonia (NH_3) forms hydrogen bond as shown below :

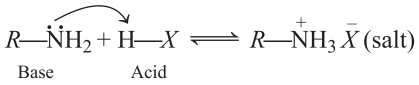


Intermolecular H-bonding in NH_3

12. (*a*) Amines behave as a nucleophile because of the presence of unshared pair of electrons on N-atom.

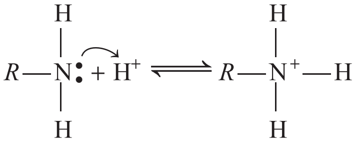
13. (*a*) Amines being basic in nature form salt on treatment with acids.

The reaction is as follows :



$$\underset{\text{Base}}{R-\ddot{N}H_2} + \underset{\text{Acid}}{H-X} \rightleftharpoons R-\overset{+}{N}H_3\overset{-}{X}\text{ (salt)}$$

14. (*d*) Basic strength of methyl substituted amines in aqueous solution depends upon the ease of formation of cation by accepting a proton from the acid.



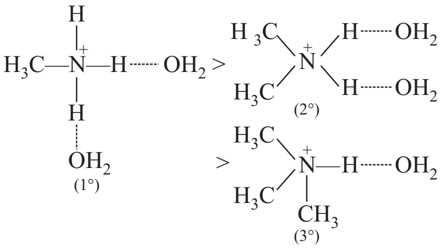
The basic strength can be decided by both inductive effect and solvation effect of alkyl group.

In aqueous phase, the substituted $\overset{+}{N}H_4$ cations get stabilised not only by electron releasing effect of alkyl group ($+I$) but also by solvation with water molecules. Greater the size of ion, lesser will be solvation and less stabilised is the ion.

The order is as follows :

Inductive effect $(CH_3)_3N > (CH_3)_2(NH) > CH_3NH_2$

Solvation effect



Strong + *I*-effect and hydrogen bonding favours higher basic strength of 2° amine. Thus, the correct order of basic strength in aqueous medium will be

$(CH_3)_2NH(2^\circ) > CH_3NH_2(1^\circ) > (CH_3)_3N(3^\circ)$

15. (*a*) Aniline is a resonance hybrid of five resonating structures and anilinium ion is obtained when aniline accept a proton and has only two resonating structures. Greater the number of resonating structures, greater is the stability. Therefore, aniline is more stable than anilinium ion.

16. (*c*) The carbylamine reaction is given by $C_2H_5NH_2$.

Only primary aliphatic and aromatic primary amine on heating with $CHCl_3$ and ethanolic KOH gives isocyanides. 2° and 3° amines do not show this reaction.

17. (*b*) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, form alcohol and liberate nitrogen gas quantitatively .

So, the product formed is $R-OH$.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2\,+\,HCl} [R\overset{+}{N}_2Cl^-] \xrightarrow{H_2O} ROH + N_2\uparrow + HCl$$

18. (*c*) The chemical formula of Hinsberg's reagent is $C_6H_5SO_2Cl$, i.e. benzene sulphonyl chloride.

19. (*d*) *ortho* and *para*-positions to the NH_2 group becomes centre of high electron density. Thus, NH_2 group is *ortho* and *para*-directing and act as powerful activating group.

20. (*b*) Aniline does not undergo Friedel-Craft's reaction (alkylation and acetylation) due to salt formation with $AlCl_3$, the Lewis acid, which is used as a catalyst.

Due to this, nitrogen of aniline acquires positive charge and, hence acts as a strong deactivating group.

21. (*b*) Primary aromatic amines ($C_6H_5NH_2$) form arene diazonium salts which are stable for a short time in solution at low temperatures (273-278 K).

22. (*b*) Benzene diazonium fluoroborate is water insoluble and stable at room temperature, whereas benzene diazonium chloride is soluble in water and is stable in cold but reacts with water, when warmed.

23. (*c*) The reagent used to form aryl fluoride from arene diazonium chloride is HBF_4.

Here, arene diazonium chloride on treatment with fluoroboric acid (HBF_4) give arene diazonium fluoroborate which on heating decomposes to yield aryl fluoride.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + HBF_4 \longrightarrow Ar\overset{+}{N}_2\overset{-}{B}F_4 \xrightarrow{\Delta} Ar - F + BF_3 + N_2\uparrow$$

24. (*c*) Coupling reaction is an example of electrophilic substitution reaction. In this reaction, benzene diazonium chloride reacts with phenol/aniline in which the phenol/aniline molecule at its *para* position is coupled with the diazonium salt to form *p*-hydroxy azobenzene/*p*-amino azobenzene.

25. (*d*) Given compounds can be distinguish by using HNO_2 and β-naphthol as shown in following reaction :