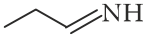
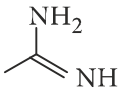
CHAPTER

26

Organic Compounds Containing Nitrogen

1. The increasing order of basicity of the following compounds is

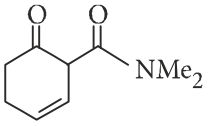
(1)  (2) 

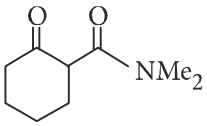
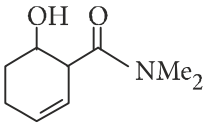
(3)  (4) 

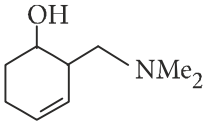
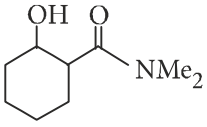
(a) (1) < (2) < (3) < (4) (b) (2) < (1) < (3) < (4)
(c) (2) < (1) < (4) < (3) (d) (4) < (2) < (1) < (3)

(2018)

2. The main reduction product of the following compound with $NaBH_4$ in methanol is

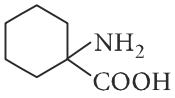
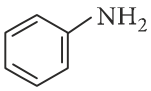


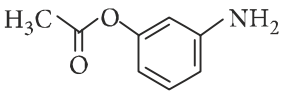
(a)  (b) 

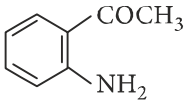
(c)  (d) 

(Online 2018)

3. The increasing order of diazotisation of the following compounds is

(*A*)  (*B*) 

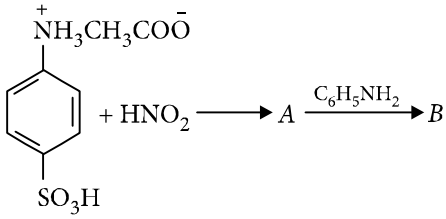
(*C*) 

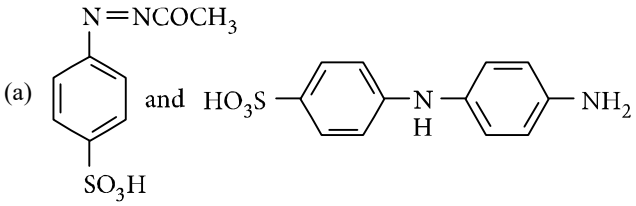
(*D*) 

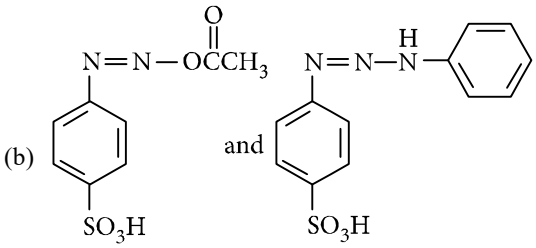
(a) (*A*) < (*D*) < (*B*) < (*C*) (b) (*D*) < (*C*) < (*B*) < (*A*)
(c) (*A*) < (*B*) < (*C*) < (*D*) (d) (*A*) < (*D*) < (*C*) < (*B*)

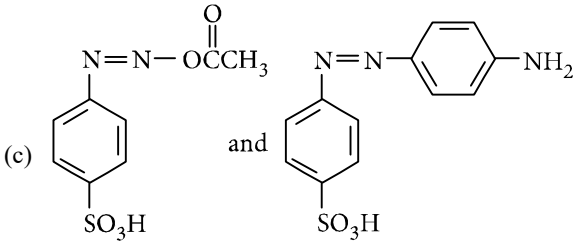
(Online 2018)

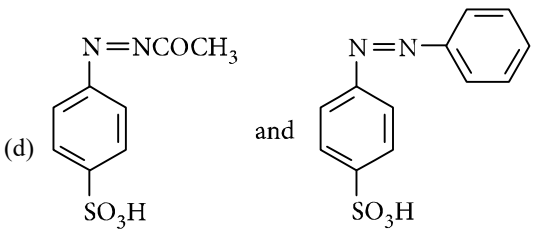
4. Products *A* and *B* formed in the following reactions are respectively



(a) 

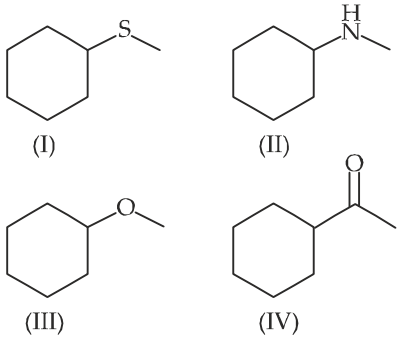
(b) 

(c) 

(d) 

(Online 2018)

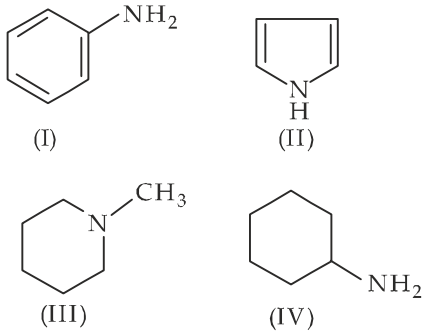
5. A mixture containing the following four compounds is extracted with 1 M HCl. The compound that goes to aqueous layer is



(I) (II) (III) (IV)

(a) (II) (b) (IV)
(c) (I) (d) (III) *(Online 2017)*

6. Among the following compounds the increasing order of their basic strength is



(I) (II) (III) (IV)

(a) (I) < (II) < (III) < (IV) (b) (I) < (II) < (IV) < (III)
(c) (II) < (I) < (III) < (IV) (d) (II) < (I) < (IV) < (III)

(Online 2017)

7. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are

(a) one mole of NaOH and one mole of Br_2
(b) four moles of NaOH and two moles of Br_2
(c) two moles of NaOH and two moles of Br_2
(d) four moles of NaOH and one mole of Br_2. *(2016)*

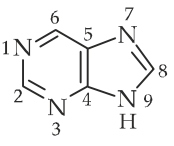
8. The test to distinguish primary, secondary and tertiary amines is

(a) Sandmeyer's reaction (b) Carbylamine reaction
(c) Mustard oil test (d) $C_6H_5SO_2Cl$ *(Online 2016)*

9. Fluorination of an aromatic ring is easily accomplished by treating a diazonium salt with HBF_4. Which of the following conditions is correct about this reaction?

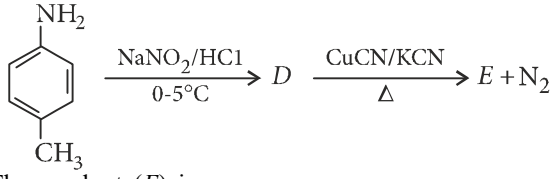
(a) NaF/Cu (b) Cu_2O/H_2O
(c) Only heat (d) $NaNO_2/Cu$ *(Online 2016)*

10. The "N" which does not contribute to the basicity for the compound is

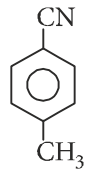


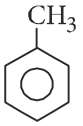
(a) N 9 (b) N 3
(c) N 1 (d) N 7 *(Online 2016)*

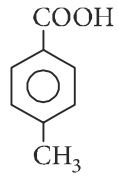
11. In the reaction,

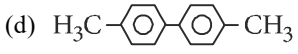


The product (*E*) is

(a) 

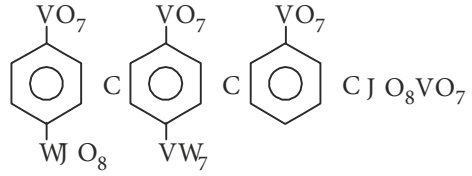
(b) 

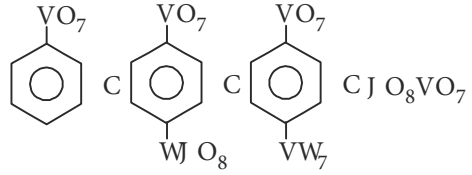
(c) 

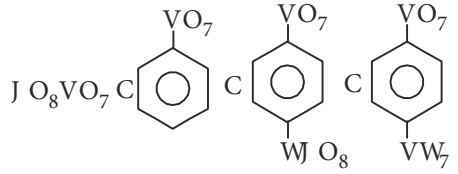
(d) 

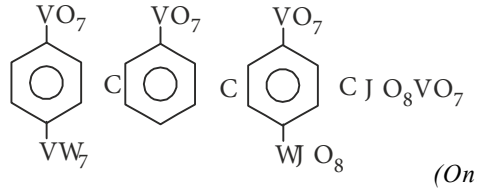
(2015)

12. Arrange the following amines in the order of increasing basicity.

(a) 

(b) 

(c) 

(d) 

(Online 2015)

13. Match the organic compounds in column-I with the Lassaigne's test results in column-II appropriately.

Column-I	**Column-II**
(A) Aniline	(i) Red colour with $FeCl_3$
(B) Benzenesulphonic acid	(ii) Violet colour with sodium nitroprusside
(C) Thiourea	(iii) Blue colour with hot and acidic solution of $FeSO_4$

(a) (A)-(ii); (B)-(i); (C)-(iii)
(b) (A)-(iii); (B)-(ii); (C)-(i)
(c) (A)-(ii); (B)-(iii); (C)-(i)
(d) (A)-(iii); (B)-(i); (C)-(ii) *(Online 2015)*

14. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is
(a) an alkyl isocyanide (b) an alkanol
(c) an alkanediol (d) an alkyl cyanide *(2014)*

15. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value?
(a) $C_6H_5NH_2$ (b) $(CH_3)_2NH$
(c) CH_3NH_2 (d) $(CH_3)_3N$ *(2014)*

16. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is
(a) 6 (b) 2
(c) 5 (d) 4 *(2013)*

17. In the chemical reaction,
$CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow (A) + (B) + 3H_2O$,
the compounds (*A*) and (*B*) are respectively
(a) C_2H_5NC and 3KCl (b) C_2H_5CN and 3KCl
(c) $CH_3CH_2CONH_2$ and 3KCl
(d) C_2H_5NC and K_2CO_3. *(2007)*

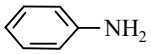
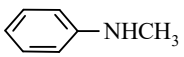
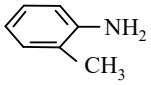
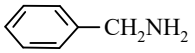
18. Which one of the following is the strongest base in aqueous solution?
(a) Methylamine (b) Trimethylamine
(c) Aniline (d) Dimethylamine *(2007)*

19. 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_3 alongwith a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is
(a) CH_3NCO (b) CH_3CONH_2
(c) $(NH_2)_2CO$ (d) $CH_3CH_2CONH_2$ *(2005)*

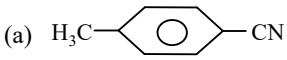
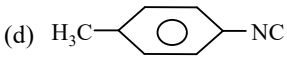
20. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as
(a) a Schiff's base (b) an enamine
(c) an imine (d) an amine. *(2005)*

21. Amongst the following the most basic compound is
(a) benzylamine (b) aniline
(c) acetanilide (d) *p*-nitroaniline. *(2005)*

22. Which one of the following methods is neither meant for the synthesis nor for separation of amines?
(a) Hinsberg method (b) Hofmann method
(c) Wurtz reaction (d) Curtius reaction *(2005)*

23. Which of the following is the strongest base?
(a)  (b) 
(c)  (d)  *(2004)*

24. Which one of the following does not have sp^2 hybridized carbon?
(a) Acetone (b) Acetic acid
(c) Acetonitrile (d) Acetamide *(2004)*

25. The reaction of chloroform with alcoholic KOH and *p*-toluidine forms
(a)  (b) 
(c) 
(d)  *(2003)*

26. Ethyl isocyanide on hydrolysis in acidic medium generates
(a) ethylamine salt and methanoic acid
(b) propanoic acid and ammonium salt
(c) ethanoic acid and ammonium salt
(d) methylamine salt and ethanoic acid. *(2003)*

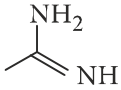
27. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is
(a) $CH_3NH_2 < NH_3 < (CH_3)_2NH$
(b) $(CH_3)_2NH < NH_3 < CH_3NH_2$
(c) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
(d) $CH_3NH_2 < (CH_3)_2NH < NH_3$ *(2003)*

28. When primary amine reacts with chloroform in ethanolic KOH then the product is
(a) an isocyanide (b) an aldehyde
(c) a cyanide (d) an alcohol. *(2002)*

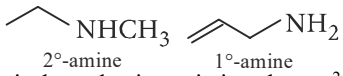
ANSWER KEY

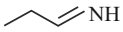
1. (c)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (d)	**8.** (d)	**9.** (c)	**10.** (a)	**11.** (a)	**12.** (d)
13. (b)	**14.** (a)	**15.** (b)	**16.** (c)	**17.** (a)	**18.** (d)	**19.** (c)	**20.** (b)	**21.** (a)	**22.** (c)	**23.** (d)	**24.** (c)
25. (d)	**26.** (a)	**27.** (c)	**28.** (a)								

Explanations

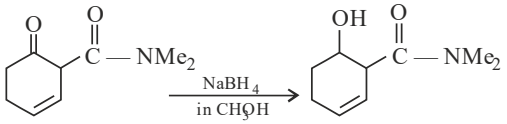
1. (c) :  strongest base as electrons of one nitrogen can easily donate due to –ve charge.

Now, out of 1 and 4, 4 is stronger as



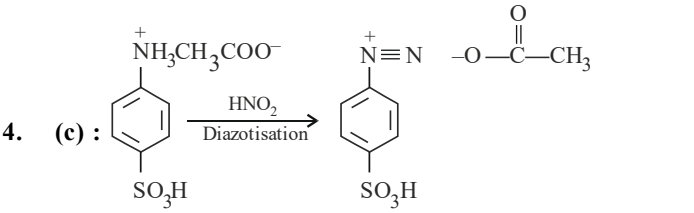
 is least basic as it involve sp^2 hybridised N-atoms.

So, the increasing order of basicity is (2) < (1) < (4) < (3).

2. (b) : 

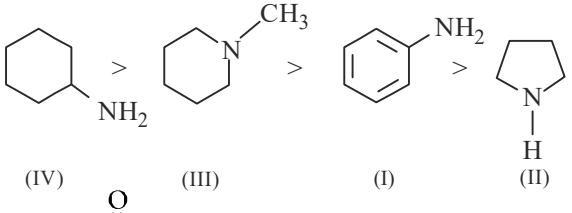
$NaBH_4$ does not reduce double bonds and amide groups.

3. (d)

4. (c) : 

5. (a)

6. (c) : Order of basicity :

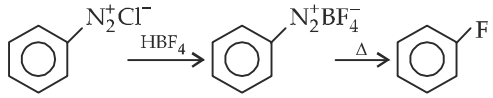


7. (d) : $R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow$

$$RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

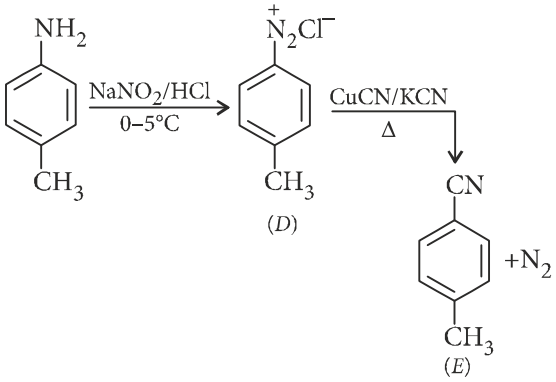
8. (d) : Hinsberg's reagent ($C_6H_5SO_2Cl$) forms monoalkyl sulphonamide with 1° amines which is soluble in KOH. With 2° amines it gives dialkyl sulphonamide which is insoluble in KOH and with 3° amines there is no reaction.

In mustard oil test, 1° amines on action of CS_2 and $HgCl_2$ give alkyl isothiocyanate having mustard oil smell. 2° amines react with CS_2 but not with $HgCl_2$ while 3° amines give no reaction. However, this test is not able to distinguish 2° and 3° amines.

9. (c) : 

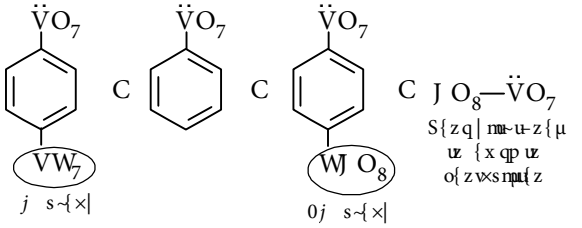
10. (a) : Lone pair of electrons on N 9 are involved in resonance so, it is not basic in nature.

11. (a) :

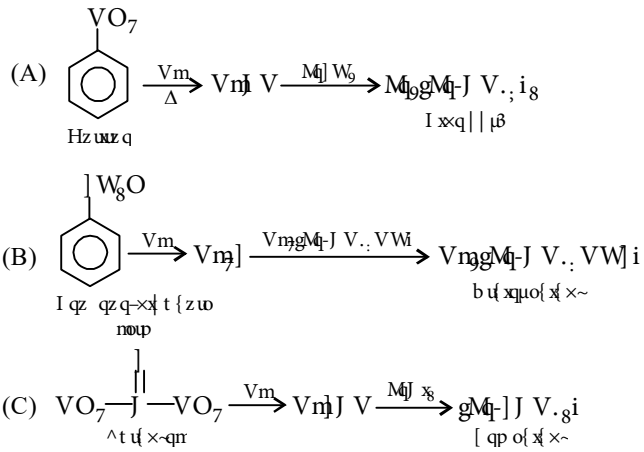


12. (d) : Aromatic amines like aniline are less basic than aliphatic amines because of the involvement of lone pair of electrons in resonance with the aromatic ring which now becomes less available for donation.

In substituted aromatic amines, electron withdrawing groups decrease the basic character and electron releasing group increase the basic character.



13. (b) : This is Lassaigne's test.



14. (a) : $\underset{\text{Aliphatic primary amine}}{R-NH_2} + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta}$

$R-N\equiv C + 3KCl + 3H_2O$

Alkyl isocyanide

15. (b) : Order of decreasing basic strength of amines in aqueous solution is

$\underset{2^\circ}{(CH_3)_2NH} > \underset{1^\circ}{CH_3NH_2} > \underset{3^\circ}{(CH_3)_3N} > \underset{\text{Aniline}}{C_6H_5NH_2}$

Basic strength $\propto K_b \propto \frac{1}{pK_b}$

Hence, $(CH_3)_2NH$ has the smallest pK_b value.

16. (c) : No. of amino groups $= \frac{390-180}{42} = 5$

17. (a) : $CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow$

$C_2H_5NC + 3KCl + 3H_2O$

This is called carbylamine reaction.

18. (d) : The increasing order of basicity of the given compounds is

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$

Due to the $+I$ effect of alkyl groups, the electron density on nitrogen increases and thus the availability of the lone pair of electrons to proton increases and hence the basicity of amines also increases. So aliphatic amines are more basic than aniline. In case of tertiary anine $(CH_3)_3N$, the covering of alkyl groups over nitrogen atom from all sides makes the approach and bonding by a proton relatively difficult, hence the basicity decreases. Electron withdrawing (C_6H_5 –) groups decreases electron density on nitrogen atom and thereby decreasing basicity.

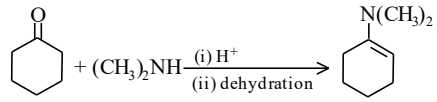
19. (c) :

Element	Percentage	Relative no. of atom	Simplest ratio
C	20.00	1.67	1
H	6.67	6.67	4
N	46.67	3.33	2
O	26.66	1.67	1

The molecular formula is CH_4N_2O. So, the compound is H_2NCONH_2.

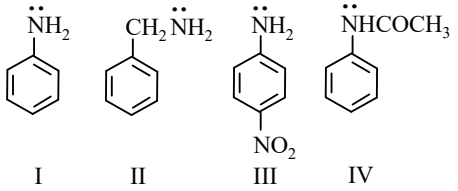
$\underset{\text{Urea}}{2NH_2CONH_2} \xrightarrow{\Delta} \underset{\text{Biuret}}{NH_2CONHCONH_2} + NH_3\uparrow$

Biuret gives violet colour with alkaline copper sulphate solution.

20. (b) : 

Enamine

21. (a) : Due to resonance of electron pair in aniline, basic strength decreases. In benzylamine electron pair is not involved in resonance. Further the presence of electron donating groups in the benzene ring increase the basic strength while electron withdrawing group decrease the basic strength of substituted aniline.



I II III IV

Decreasing order of basic strength is II > I > IV > III.

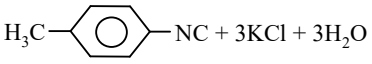
22. (c) : In Wurtz reaction alkyl halide reacts with sodium metal in the presence of dry ether to give alkane.

23. (d) : In this compound, the non-bonding electron pair of nitrogen does not take part in resonance. In other three compounds, the non-bonding electron pair of nitrogen is delocalized into benzene ring by resonance, as a result the electron density on the N atom decreases, due to which basicity decreases.

24. (c) : $\underset{\text{Acetone}}{\overset{sp^3}{CH_3}-\overset{sp^2}{CO}-\overset{sp^3}{CH_3}}$; $\underset{\text{Acetic acid}}{\overset{sp^3}{CH_3}-\overset{sp^2}{COOH}}$

$\underset{\text{Acetonitrile}}{\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv N}$; $\underset{\text{Acetamide}}{\overset{sp^3}{CH_3}-\overset{sp^2}{CONH_2}}$

25. (d) : 



The above reaction is known as carbylamine reaction and is generally used to convert primary amine into isocyanide.

26. (a) : Alkyl isocyanides are hydrolysed by dilute mineral acids to form primary amines.

$\underset{\text{Ethylisocyanide}}{C_2H_5N\equiv C} + 2H_2O \xrightarrow{H^+} \underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Methanoic acid}}{HCOOH}$

27. (c) : Except the amines containing tertiary butyl group, all lower aliphatic amines are stronger bases than ammonia because of $+I$ (inductive) effect. The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or Lewis acids and making the amine more basic. The observed order in the case of lower members is found to be as secondary > primary > tertiary. This anomalous behaviour of tertiary amines is due to steric factors *i.e.* crowding of alkyl groups cover nitrogen atom from all sides and thus makes it unable for protonation.

Thus the relative strength is in order :

$(CH_3)_2NH > CH_3NH_2 > NH_3$.

28. (a) : When a primary amine reacts with chloroform with ethanolic KOH, then a bad smell compound isocyanide is formed. This is called carbylamine reaction and this reaction is used as a test of primary amines.

$\underset{\text{Primary amine}}{RNH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Isocyanide}}{RNC} + 3KCl + 3H_2O$