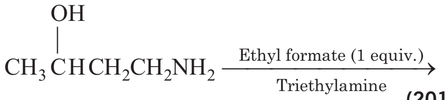
27

Aliphatic Compounds Containing Nitrogen

Objective Questions I (Only one correct option)

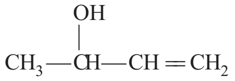
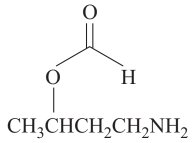
1. The major product of the following reaction is



$$\mathrm{CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2NH_2} \xrightarrow[\text{Triethylamine}]{\text{Ethyl formate (1 equiv.)}}$$

(2019 Main, 10 April I)

(a)  $\mathrm{CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2NHCHO}$ (b) $\mathrm{CH_3CH{=}CH{-}CH_2NH_2}$

(c)  $\mathrm{CH_3{-}\overset{\overset{OH}{|}}{C}H{-}CH{=}CH_2}$ (d) 

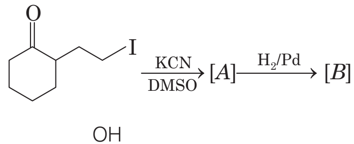
2. Ethylamine ($\mathrm{C_2H_5NH_2}$) can be obtained from *N*-ethylphthalimide on treatment with **(2019 Main, 10 April I)**

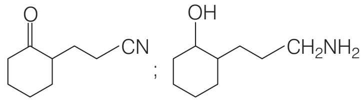
(a) $\mathrm{NaBH_4}$ (b) $\mathrm{NH_2NH_2}$ (c) $\mathrm{H_2O}$ (d) $\mathrm{CaH_2}$

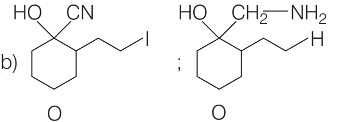
3. Hinsberg's reagent is **(2019 Main, 9 April II)**

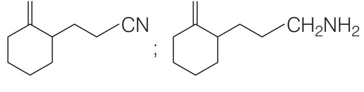
(a) $\mathrm{SOCl_2}$ (b) $\mathrm{C_6H_5COCl}$ (c) $\mathrm{C_6H_5SO_2Cl}$ (d) $\mathrm{(COCl)_2}$

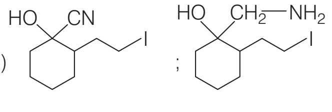
4. The major products *A* and *B* for the following reactions are, respectively **(2019 Main, 9 April II)**



(a) 

(b) 

(c) 

(d) 

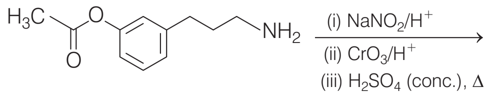
5. Which of the following amines can be prepared by Gabriel phthalimide reaction? **(2019 Main, 8 April I)**

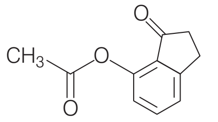
(a) *n* - butylamine
(b) triethylamine
(c) *t*-butylamine
(d) *neo* -pentylamine

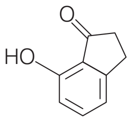
6. In the following compounds, the decreasing order of basic strength will be **(2019 Main, 8 April I)**

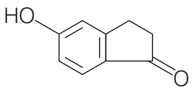
(a) $\mathrm{C_2H_5NH_2 > NH_3 > (C_2H_5)_2NH}$
(b) $\mathrm{(C_2H_5)_2NH > NH_3 > C_2H_5NH_2}$
(c) $\mathrm{(C_2H_5)_2NH > C_2H_5NH_2 > NH_3}$
(d) $\mathrm{NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH}$

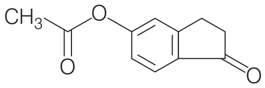
7. The major product of the following reaction is **(2019 Main, 12 Jan II)**



(a) 

(b) 

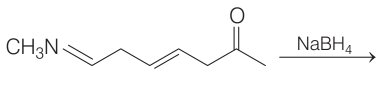
(c) 

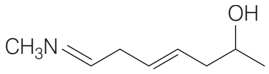
(d) 

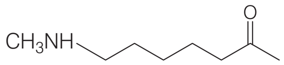
8. A compound '*X*' on treatment with $\mathrm{Br_2/NaOH}$, provided $\mathrm{C_3H_9N}$, which gives positive carbylamine test. Compound '*X*' is **(2019 Main, 11 Jan II)**

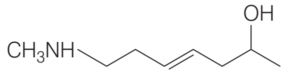
(a) $\mathrm{CH_3COCH_2NHCH_3}$
(b) $\mathrm{CH_3CH_2CH_2CONH_2}$
(c) $\mathrm{CH_3CON(CH_3)_2}$
(d) $\mathrm{CH_3CH_2COCH_2NH_2}$

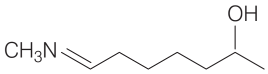
9. The major product of the following reaction is **(2019 Main, 10 Jan II)**



(a) 

(b) 

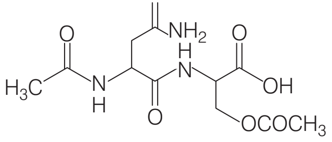
(c) 

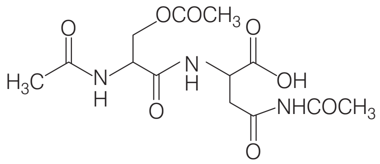
(d) 

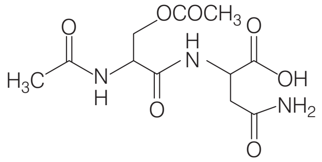
10. The correct structure of product '*P*' in the following reaction is

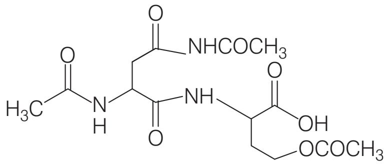
$$\text{Asn}-\text{Ser} + \underset{\text{(Excess)}}{(CH_3CO)_2O} \xrightarrow{NEt_3} P$$

(2019 Main, 10 Jan I)

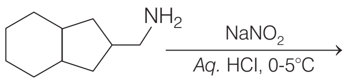
(a) 

(b) 

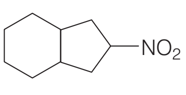
(c) 

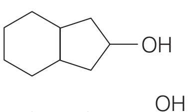
(d) 

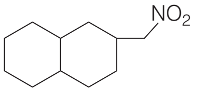
11. The major product formed in the reaction given below will be

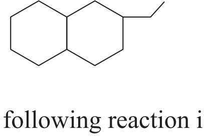


(2019 Main, 10 Jan I)

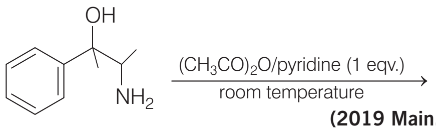
(a) 

(b) 

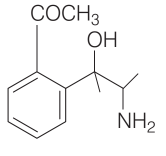
(c) 

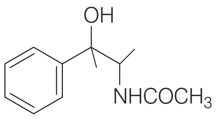
(d) 

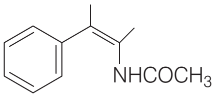
12. The major product obtained in the following reaction is

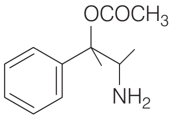


(2019 Main, 9 Jan II)

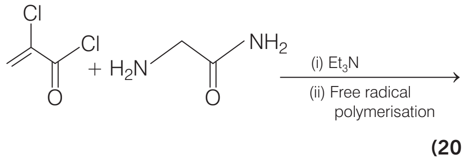
(a) 

(b) 

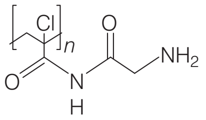
(c) 

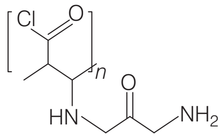
(d) 

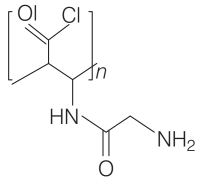
13. Major product of the following reaction is

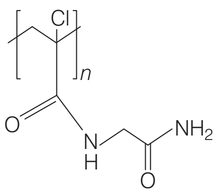


(2019 Main, 9 Jan I)

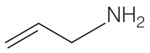
(a) 

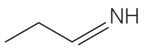
(b) 

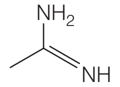
(c) 

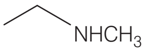
(d) 

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

I. 

II. 

III. 

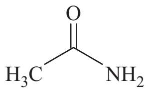
IV. 

(2018 Main)

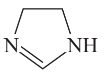
(a) (I) < (II) < (III) < (IV)
(b) (II) < (I) < (III) < (IV)
(c) (II) < (I) < (IV) < (III)
(d) (IV) < (II) < (I) < (III)

15. The order of basicity among the following compounds is

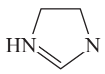
(2017 Adv.)



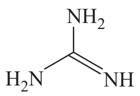
(I)



(II)



(III)



(IV)

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

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

(2016 Main)

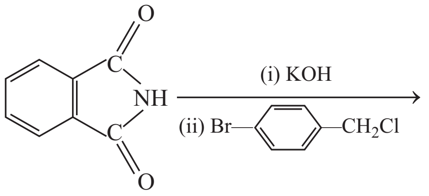
(a) four moles of NaOH and two moles of Br_2
(b) two moles of NaOH and two moles of Br_2
(c) four moles of NaOH and one mole of Br_2
(d) one mole of NaOH and one mole of Br_2

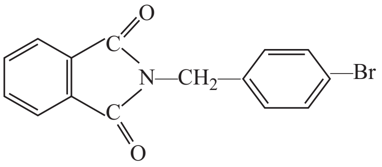
17. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **(2014 Main)**
(a) $(CH_3)_2NH$ (b) CH_3NH_2
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

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

19. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was **(2013 Main)**
(a) methyl isocyanate
(b) methylamine
(c) ammonia
(d) phosgene

20. The major product of the following reaction is **(2011)**



(a)


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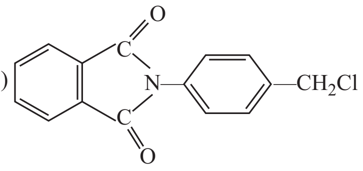

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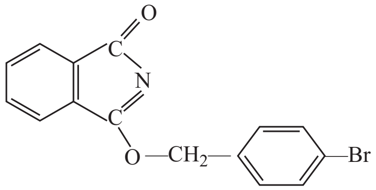

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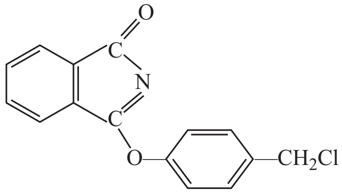
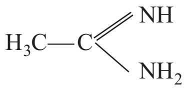


21. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Nitrogen containing compound + $KCl + H_2O$. Nitrogen containing compound is **(2006)**
(a) CH_3CN (b) CH_3NHCH_3
(c) $CH_3-\overset{-}{N}\equiv\overset{+}{C}$ (d) $CH_3-\overset{+}{N}\equiv\overset{-}{C}$

22. Benzamide on treatment with $POCl_3$ gives **(2004)**
(a) aniline (b) benzonitrile
(c) chlorobenzene (d) benzyl amine

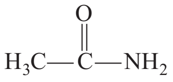
23. The correct order of basicities of the following compounds is



1

, $CH_3-CH_2-NH_2$,
2

$(CH_3)_2NH$,
3



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

4 **(2001, 1M)**

(a) $2>1>3>4$ (b) $1>3>2>4$ (c) $3>1>2>4$ (d) $1>2>3>4$

24. A positive carbylamine test is given by **(1999, 2M)**
(a) N, N-dimethylaniline (b) 2, 4-dimethylaniline
(c) N-methyl-*o*-methylaniline (d) *p*-methylbenzylamine

25. *p*-chloroaniline and anilinium hydrochloride can be distinguished by **(1998, 2M)**
(a) Sandmeyer reaction (b) $NaHCO_3$
(c) $AgNO_3$ (d) Carbylamine test

26. Carbylamine test is performed in alc. KOH by heating a mixture of **(1984, 1M)**
(a) chloroform and silver powder
(b) trihalogenated methane and a primary amine
(c) an alkyl halide and a primary amine
(d) an alkyl cyanide and a primary amine

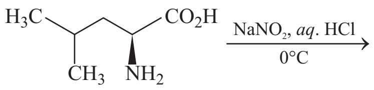
27. Acetamide is treated separately with the following reagents. Which of these would give methylamine? **(1983, 1M)**
(a) PCl_5 (b) Sodalime
(c) $NaOH + Br_2$ (d) Hot, conc. H_2SO_4

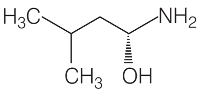
28. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine, is **(1981, 1M)**
(a) methylamine (b) ethylamine
(c) diethylamine (d) triethylamine

Objective Question II

(Only one more than one correct option)

29. The major product of the reaction is **(2015, Adv.)**



(a)


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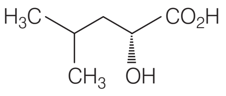

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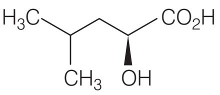
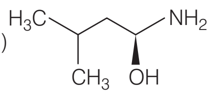


(d)


30. A positive carbylamine test is given by **(1999, 2M)**
(a) N, N-dimethyl aniline (b) 2, 4-dimethyl aniline
(c) N-methyl-*o*-methyl aniline (d) *p*-methyl benzyl amine

Fill in the Blanks

31. $(CH_3OH_2^+)$ is …… acidic than $(CH_3NH_3^+)$. **(1997 C, 1M)**

Match the Columns

32. Match each of the compounds in Column I with its characteristic reaction(s) in Column II. **(2016, Adv.)**

	Column I		Column II
(A)	$CH_3CH_2CH_2CN$	(p)	Reduction with Pd - C/ H_2
(B)	$CH_3CH_2OCOCH_3$	(q)	Reduction with $SnCl_2$ / HCl
(C)	$CH_3CH{=}CHCH_2OH$	(r)	Development of foul smell on treatment with chloroform and alcoholic KOH.
(D)	$CH_3CH_2CH_2CH_2NH_2$	(s)	Reduction with diisobutylaluminium hydride (DIBAL-H)
		(t)	Alkaline hydrolysis

Subjective Questions

33. $$\underset{\substack{\text{optically active}\\ X}}{C_5H_{13}N} \xrightarrow[-N_2]{NaNO_2,\ HCl} Y(\text{tertiary alcohol + other products})$$

Find *X* and *Y*. Is *Y* optically active ? Write the intermediate steps **(2005, 4M)**

34. Give reasons for the following in one or two sentences. Dimethylamine is a stronger base than trimethylamine. **(1998, 2M)**

35. Following reaction gives two products. Write the structures of the products.

$$CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\ \text{heat}}$$ **(1998, 2M)**

36. Give the structure of *A*. '*A* (C_3H_9N) reacts with benzenesulphonyl chloride to give a solid, insoluble in alkali'. **(1993, 1M)**

37. A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic KOH. A 0.295 g sample of the substance dissolved in *aq*. HCl and treated with $NaNO_2$ solution at 0°C, liberated a colourless, odourless gas whose volume corresponds to 112 mL at STP.

After evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance assuming that it contains one N-atom per molecule. **(1993, 4M)**

38. Arrange the following in increasing order of basic strength: methylamine, dimethylamine, aniline, N-methylaniline. **(1988, 1M)**

39. Give a chemical test and the reagent used to distinguish between the following : "Ethylamine and diethylamine". **(1988, 1M)**

40. For nitromethane molecule, write structures

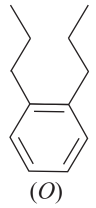
(i) showing significant resonance stabilisation

(ii) indicating tautomerism **(1986, 1M + 1M = 2M)**

41. State the equation for the preparation of following compounds : *n*-propyl amine from ethyl chloride. **(1982, 2 × 1M = 2M)**

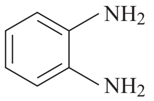
Passage Based Questions

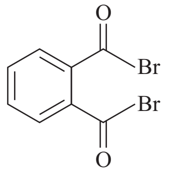
Treatment of compound *O* with $KMnO_4/H^+$ gave *P*, which on heating with ammonia gave *Q*. The compound *Q* on treatment with Br_2 / NaOH produced *R*. On strong heating, *Q* gave *S*, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound *T*.4 **(2016 Adv.)**

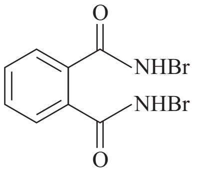


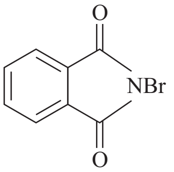
(*O*)

42. The compound *R* is

(a) 

(b) 

(c) 

(d) 

43. The compound *T* is

(a) glycine (b) alanine

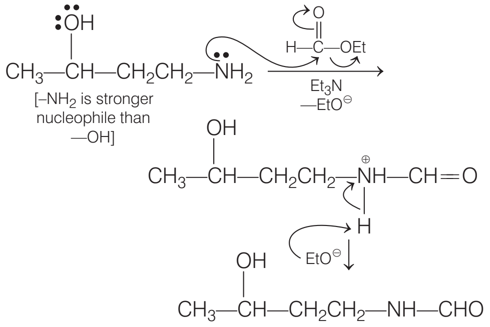
(c) valine (d) serine

Answers

1. (a) **2.** (b) **3.** (c) **4.** (c) **5.** (a) **6.** (c) **7.** (c) **8.** (b)
9. (c) **10.** (a) **11.** (*) **12.** (b) **13.** (d) **14.** (c) **15.** (d) **16.** (c)
17. (a) **18.** (d) **19.** (a) **20.** (a) **21.** (d) **22.** (b) **23.** (b) **24.** (d)
25. (c) **26.** (b) **27.** (c) **28.** (c) **29.** (c) **30.** (b,d) **31.** (more)
32. A → p, q, s, t; B → p, s, t; C → p; D → r **42.** (a) **43.** (b)

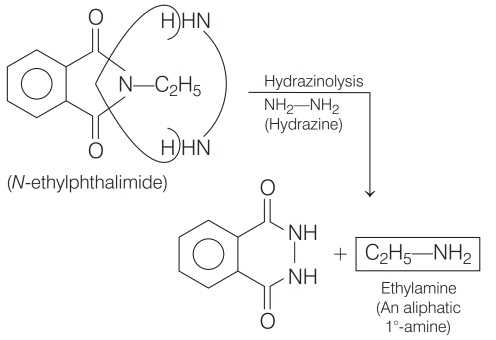
Hints & Solutions

1. The mechanism of the given reaction is as follows:



The basic mechanism of the reaction is acyl S_N2 because the nucleophile, $CH_3(OH)CH_2CH_2\ NH_2$ attacks the sp^2 carbon of the ester $(H—CO_2Et)$ and gets substituted.

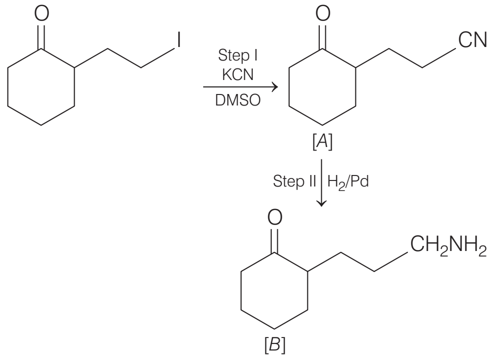
2. The reaction for the production of ethylamine from N-ethylphthalimide can be takes place as follows:



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.

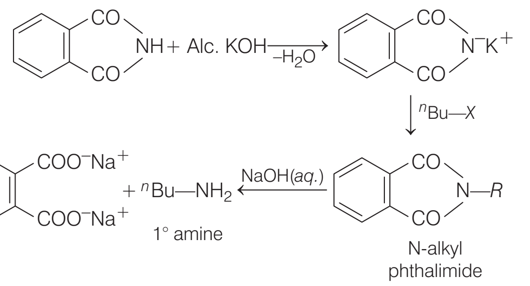
3. Hinsberg's reagent is $C_6H_5SO_2Cl$ (benzene sulphonyl chloride). This reagent is used to distinguish between primary, secondary and tertiary amines.

4.



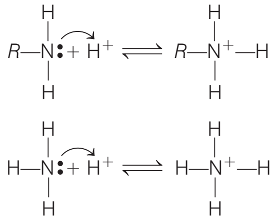
Step I involves the nucleophilic substitution reaction in which I (Iodine) is substituted by
— CN group. **In step II**, H_2/Pd reagent is used for reduction process. Here, — CN group reduces itself to $—CH_2NH_2$.

5. n-butylamine $(CH_3CH_2CH_2CH_2NH_2)$ can be prepared by Gabriel phthalimide reaction. This method produces only primary amines without the traces of secondary or tertiary amines. In this method, phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.



Triethylamine, t-butylamine and neo-pentylamine cannot be prepared by Gabriel phthalimide reaction.

6. Basic strength can be compared by the reaction of an alkanamine and ammonia with proton.

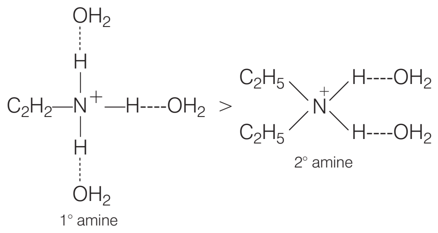


Basicity of an amine in aqueous solution depends upon the solubility of ammonium cation formed by accepting proton from water. The stability of ammonium cation depends upon the following factors.

(a) + I effect (b) Steric effect

(c) Solvation effect

In first case, on increasing the size of alkyl group + I effect increases and the positive charge of ammonium cation gets dispersed more easily, Therefore, order of basicity is 2º amine > 1º amine > ammonia. In second case, substituted ammonium cation is also stabilised by solvation with water molecules. Greater the size of ion, lesser will be the solvation and less stabilised is the ion.

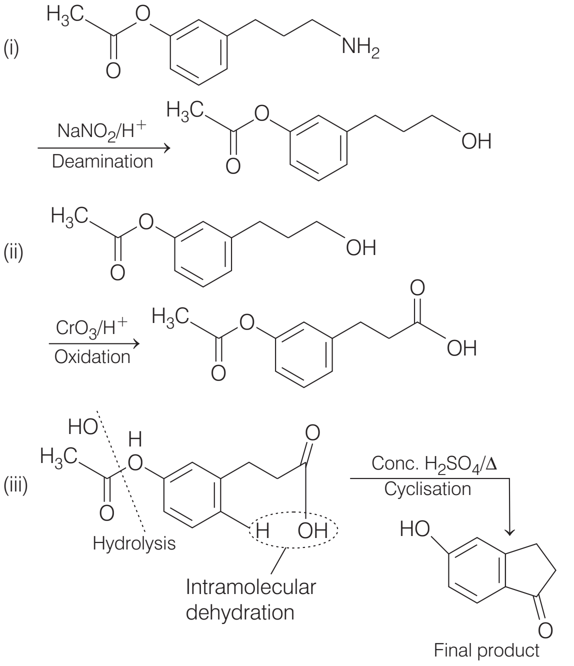


Considering both steric and solvation effect, it can be concluded that greater the number of H-atoms on the N-atom, greater will be the H-bonding and hence more stable is the ammonium cation. But in case of —C_2H_5 group, + *I* effect predominates over H-bonding. Therefore, order is 2º amine > 1° amine > ammonia i.e. $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$.

7. **Key Idea** The reaction involves:

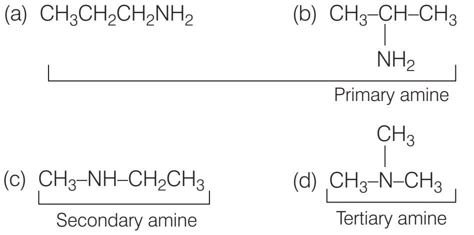
A. Deamination in step (i)
B. Oxidation in step (ii)
C. Hydroysis in step (iii)

The complete pathway of reactions is as follows:



Thus, option (c) is the correct answer.

8. The molecular formula, C_3H_9N refers to four structural isomers of amines



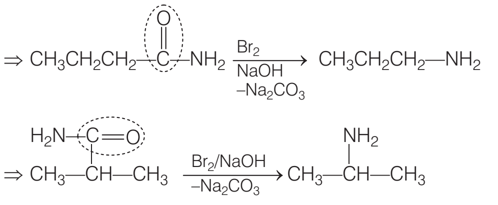
(a) $CH_3CH_2CH_2NH_2$ (b) $CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_3$

Primary amine

(c) $CH_3-NH-CH_2CH_3$ (d) $CH_3-\overset{CH_3}{\overset{|}{N}}-CH_3$

Secondary amine Tertiary amine

Here, only *a* and *b* (primary amines) can be prepared from their respective amides by Hoffmann bromamide (Br_2/NaOH) method and can give positive carbylamine test.



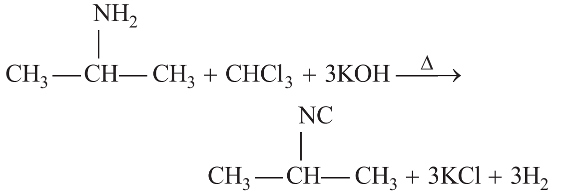
$$\Rightarrow CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[NaOH\ -Na_2CO_3]{Br_2} CH_3CH_2CH_2-NH_2$$

$$\Rightarrow CH_3-\overset{H_2N-C=O}{\overset{|}{CH}}-CH_3 \xrightarrow[-Na_2CO_3]{Br_2/NaOH} CH_3-\overset{NH_2}{\overset{|}{CH}}-CH_3$$

So, '*X*' can be $CH_3CH_2CH_2-CONH_2$ (a) or $CH_3CH(CONH_2)CH_3$ (b).

Carbylamine test given by (a) and (b)

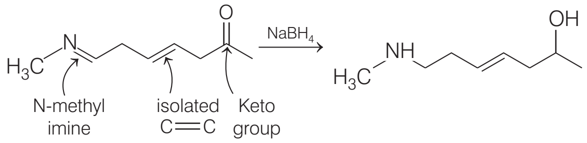
$$CH_3CH_2CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3(CH_2)_2NC + 3KCl + 3H_2$$



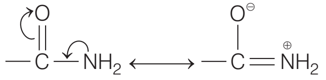
$$CH_3-\overset{NH_2}{\overset{|}{CH}}-CH_3 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-\overset{NC}{\overset{|}{CH}}-CH_3 + 3KCl + 3H_2$$

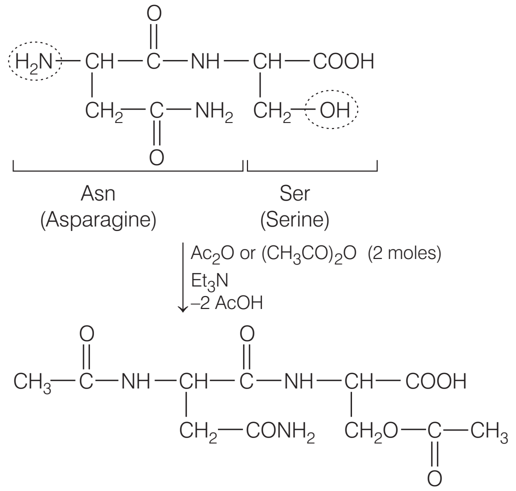
As (b) is not among the given options So, it is ruled out and compound (X) is $CH_3CH_2CH_2CONH_2$.

9. $NaBH_4$ is a selective reducing agent. It can reduce $>C=O$ group into alcohol, N-methyl imine group, Me—N═CH— into 2°-amine but cannot reduce an isolated C ═ C.



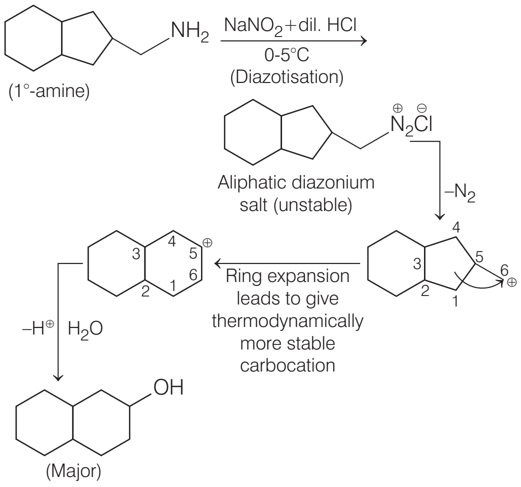
10 Acetylation by Ac_2O/Et_3N is possible with —NH_2 (1°-amine) and —OH (alcohol) groups only, but not with '—NH_2' part of $-\overset{O}{\overset{\|}{C}}-NH_2$ (amide) groups, because the *lp* of nitrogen in amide group is involved in resonance with $>C=O$ part.



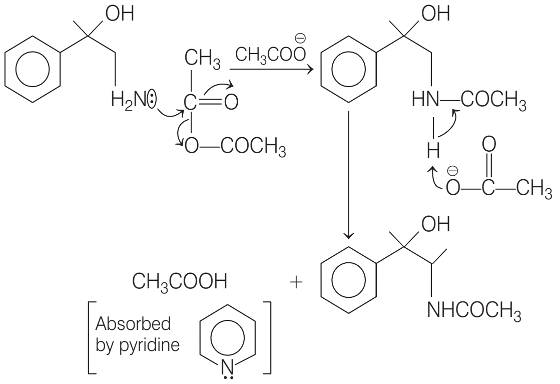


11. No option is the correct answer.

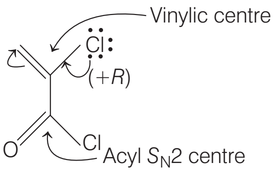
Amines in presence of $NaNO_2$ + dil. HCl undergoes diazotisation. The diazotised product readily loses nitrogen gas with the formation of carbocation. The resulting carbocation rearranges itself to give the expanded ring.

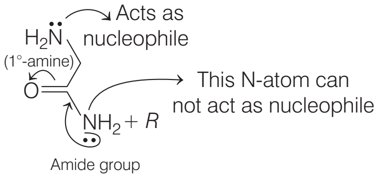


12. Rate of acetylation : $-NH_2 > -OH$ because N-bases are stronger than O-bases. Size of N-atom is larger than O-atom and at the same time, N atom is less electronegative than O-atom. So, N-atom of the $-\ddot{N}H_2$ group can donate its lone pair of electrons (Lewis basicity) more easily than that of O atom of the $-\ddot{O}H$ group.

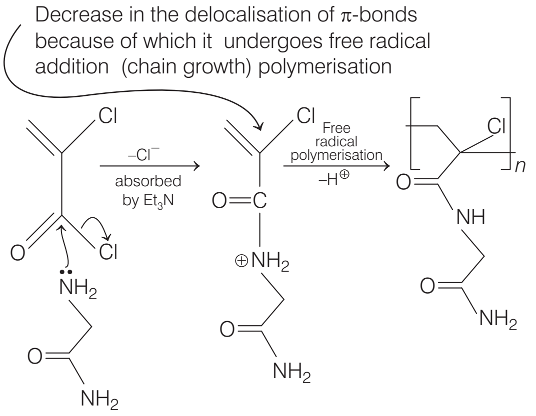


13. The analysis of both the substrates :

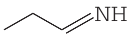


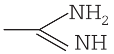


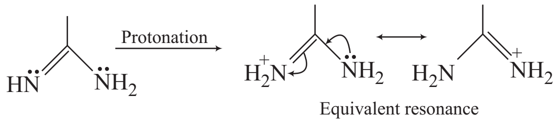
So, the reaction can take place as follows:

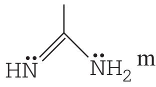


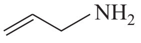
14. **Key Idea** Among the given compounds the basic nature depends upon their tendency to donate electron pair.

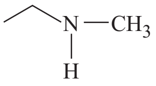
Among the given compounds in  , Nitrogen is sp^2-hybridised. This marginally increases the electronegativity of nitrogen which in turn decreases the electron donation tendency of nitrogen. Thus making compound least basic.

Among the rest  is totally different from others as in this compound lone pair of one nitrogen are in conjugation with π bond i.e. As a result of this conjugation the cation formed after protonation becomes resonance stabilised



This equivalent resonance in cation makes  most basic among all.

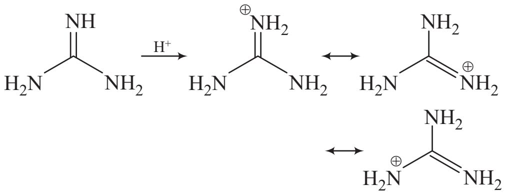
 Categorisation is very simple between rest two as

 (primary amine) is less basic than (secondary amine)

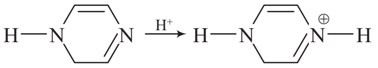
Hence, the correct order is

(II) < (I) < (IV) < (III) i.e. option (c) is correct.

15. IV is most basic as conjugate acid is stabilised by resonance of two — NH_2.



III is least basic as



Destablised by $-I$-effect of sp^2-carbons.

16. Hofmann-bromamide degradation reaction is given as:

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow \underset{(1^\circ\text{ amine})}{RNH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Hence, four moles of NaOH and one mole of Br_2 are used.

17. This problem can be solved by using the concept of effect of steric hindrance, hydration and H-bonding in basic strength of amines. Order of basic strength of aliphatic amine in aqueous solution is as follows (order of K_b)

$$(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N} > C_6H_5\ddot{N}H_2$$

As we know, $pK_b = -\log K_b$

So, $(CH_3)_2\ddot{N}H$ will have smallest pK_b value. In case of phenyl amine, N is attached to sp^2-hybridised carbon, hence it has highest pK_b and least basic strength.

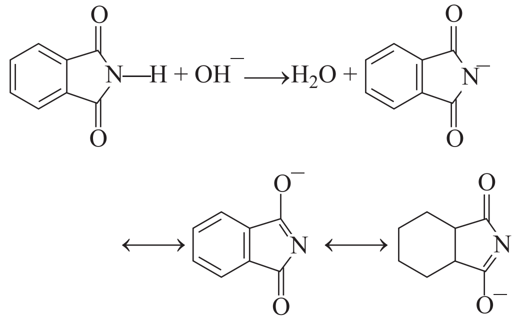
18. This reaction is an example of carbylamine test which includes conversion of amine to isocyanide.

$$\underset{1^\circ\text{ amine}}{R{-}\ddot{N}H_2} + CHCl_3 \xrightarrow[KOH]{C_2H_5OH} \underset{\text{Alkyl isocyanide}}{R{-}\overset{+}{N}{\equiv}\overset{-}{C}:}$$

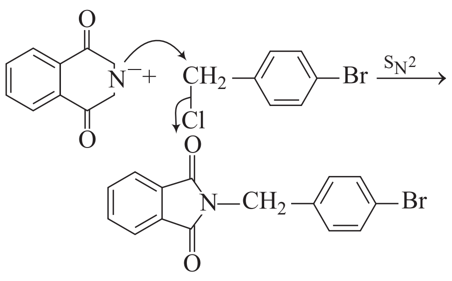
NOTE The mechanism of this reaction included rearrangement of nitrene in which migration of alkyl group from carbon to nitrogen takes place.

19. Methyl isocyanate $CH_3{-}N{=}C{=}O$ (MIC) gas was leaked from the storage tank of the union carbide plant in Bhopal gas tragedy.

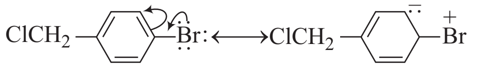
20. It is the first step of Gabriel's phthalimide synthesis. The hydrogen bonded to nitrogen is sufficiently acidic due to two α-carbonyls.



The conjugate base formed above act as nucleophile in the subsequent step of reaction. As shown above, the nucleophile exist in three resonating form, one may think of oxygen being the donor atom in the nucleophilic attack. However, nitrogen act as donor as it is better donor than oxygen.

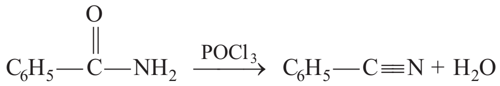


Bromine is not substituted in the above reaction as it is in resonance with benzene ring giving partial double bond character to C—Br bond, hence difficult to break.



21. $CH_3NH_2 + CHCl_3 + KOH \longrightarrow \underset{\text{isocyanide}}{CH_3{-}\overset{+}{N}{\equiv}\overset{-}{C}} + KCl + H_2O$

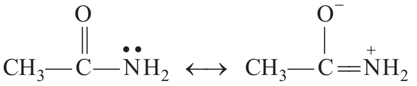
22.



$$C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 \xrightarrow{POCl_3} C_6H_5{-}C{\equiv}N + H_2O$$

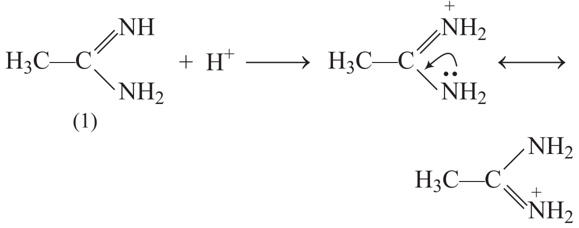
$POCl_3$ brings about dehydration of primary amide.

23. 4, (acetamide) is least basic because lone pair of nitrogen is involved in delocalisation.



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\ddot{N}H_2 \longleftrightarrow CH_3{-}\overset{\overset{\displaystyle O^-}{|}}{C}{=}\overset{+}{N}H_2$$

'1' is most basic due to formation of resonance stabilised conjugate acid.



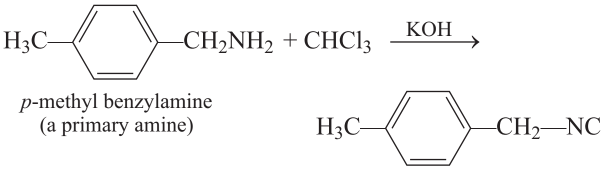
(1)

3 (secondary amine) is stronger base than 2 (primary amine).

Hence, overall order of basic strength is :

$$1 > 3 > 2 > 4$$

24.



p-methyl benzylamine
(a primary amine)

(isocyanide)

Carbylamine test is not given by secondary or tertiary amine.

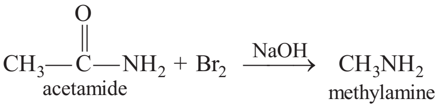
25. $\underset{\text{anilinium hydrochloride}}{C_6H_5\overset{+}{N}H_3Cl^-} + AgNO_3 \longrightarrow C_6H_5\overset{+}{N}H_3NO_3^- + AgCl(s)\downarrow$

No such precipitate of AgCl(*s*) would be formed with *p*-chloroaniline.

26. $R{-}NH_2 + CHCl_3 \xrightarrow{KOH} \underset{\substack{\text{isocyanide}\\\text{(foul smell)}}}{R{-}NC}$ 'Carbylamine test'

The above test is characteristic of primary amine and used to distinguish primary amine from other amines.

27.



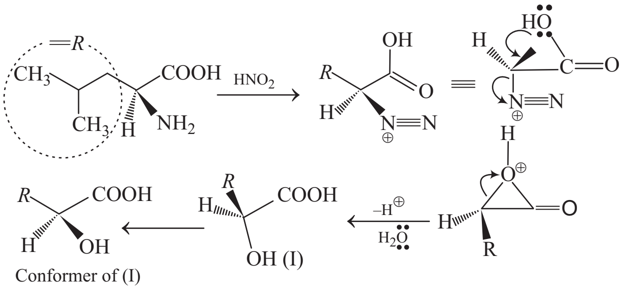
$$\underset{\text{acetamide}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2} + Br_2 \xrightarrow{NaOH} \underset{\text{methylamine}}{CH_3NH_2}$$

(Hofmann's bromamide reaction)

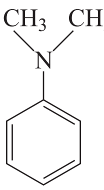
28. A secondary amine, on treatment with aqueous nitrous acid at low temperature produces oily nitrosamine.

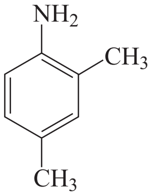
$$(C_2H_5)_2NH + HNO_2 \longrightarrow \underset{\text{nitrosamine}}{(C_2H_5)_2N-NO} + H_2O$$

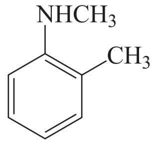
29. Reaction proceeds *via* diazonium salt with neighbouring group participation.

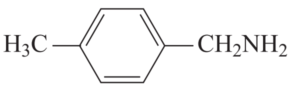


30. Carbylamine test is given by primary amines only.


N,N-dimethylaniline
(3°-amine)


2,4-dimethylaniline
(1°-amine)


N-methyl-*o*-methylaniline
(2°-amine)

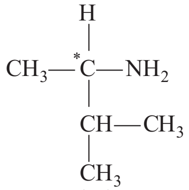

p-methyl benzylamine
(1°-amine)

31. More : CH_3NH_2 is stronger base than CH_3OH.

32.

	Column I	Column II
(A)	$CH_3CH_2CH_2CN$:	Gives amine with Pd-C/ H_2 Gives aldehyde with $SnCl_2$ / HCl Gives amide with diisobutyl- aluminium hydride. Gives carboxylic acid on alkaline hydrolysis.
(B)	$CH_3CH_2OCOCH_3$: ester	Reduced to alcohol with Pd - C/ H_2 Reduced with diisobutylaluminium hydride into aldehyde. Undergo alkaline hydrolysis.
(C)	$CH_3CH{=}CHCH_2OH$:	Reduced to butanol when treated with Pd-C/ H_2.
(D)	$CH_3CH_2CH_2CH_2NH_2$	A primary amine, gives carbylamine test.

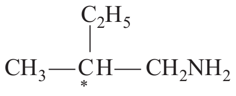
33.



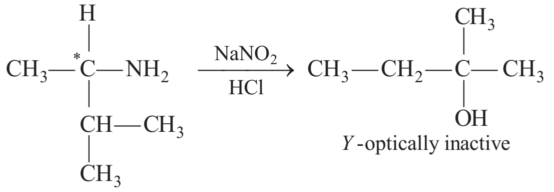
$$CH_3-\overset{*}{C}H(NH_2)-CH(CH_3)-CH_3$$

(*X*)

or



$$CH_3-\overset{*}{C}H(C_2H_5)-CH_2NH_2$$



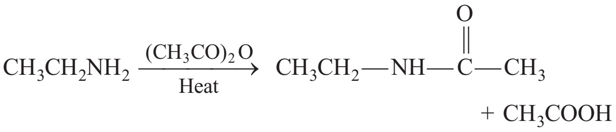
$$CH_3-\overset{*}{C}H(NH_2)-CH(CH_3)-CH_3 \xrightarrow[HCl]{NaNO_2} CH_3-CH_2-C(CH_3)(OH)-CH_3$$

Y-optically inactive

Above reaction proceeds *via* carbocation intermediate, hence rearrangement takes place.

34. Conjugate acid of dimethylamine is more stable than conjugate base of triethyl amine due to exhaustive H-bonding with water.

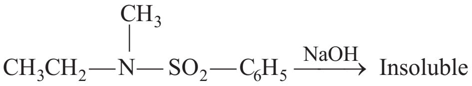
35.



$$CH_3CH_2NH_2 \xrightarrow[\text{Heat}]{(CH_3CO)_2O} CH_3CH_2-NH-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COOH$$

36. A must be a secondary amine :

$CH_3CH_2NHCH_3$ + benzene sulphonylchloride $\longrightarrow$



$$CH_3CH_2-\overset{CH_3}{\overset{|}{N}}-SO_2-C_6H_5 \xrightarrow{NaOH} \text{Insoluble}$$

37. Starting compound is a primary amine.

$$R-NH_2 + CHCl_3 + KCl \longrightarrow \underset{\text{foul smell}}{R-NC}$$

Also, $R-NH_2 + HNO_2 \longrightarrow R-OH + N_2$

Moles of $N_2 = \frac{112}{22500} = 5 \times 10^{-3}$

∵ One mole of N_2 is obtained from 1.0 mole of $R-NH_2$, mole of $R-NH_2 = 5 \times 10^{-3}$

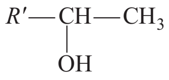
⇒ 5×10^{-3} mol $R-NH_2$ weigh = 0.295 g

1 mole of $R-NH_2$ will weigh $= \frac{0.295}{5 \times 10^{-3}} = 59$ g

In $R-NH_2$, $-NH_2$ has molar mass = 16

⇒ $R-$ has molar mass = 43

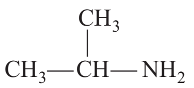
Also, the alcohol $R-OH$ gives iodoform test; it must has the following skeleton :



$$R'-\underset{OH}{\underset{|}{C}H}-CH_3$$

⇒ $R'-$ has molar mass = 15 (CH_3)

⇒ Original compound is



$$CH_3-\overset{CH_3}{\overset{|}{C}H}-NH_2$$

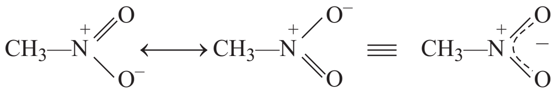
38. Aniline > N-methylaniline < methylamine < dimethylamine.

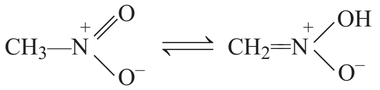
39. Carbylamine test given only by primary amine.

$$\underset{\text{primary amine}}{CH_3CH_2-NH_2} + CHCl_3 \xrightarrow{KOH} \underset{\text{foul smell}}{CH_3-CH_2-NC}$$

Nitrosamine test is given only by secondary amine.

$$(CH_3CH_2)_2NH + HNO_2 \longrightarrow \underset{\text{oily nitrosamine}}{(CH_3CH_2)_2N-NO}$$

40. (i) 

(ii) 

: Tautomerism

41. $CH_3CH_2Cl \xrightarrow[S_N2]{NaCN} CH_3CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$

42. (a)

43. Explanation