Amines

Case Study Based Questions

Case Study 1

Amines constitute one of the most important class of organic compounds. In nature, they occur among vitamins, proteins, alkaloids and hormones. These are the derivatives of ammonia, obtained by the replacement of one, two or three hydrogen atoms by alkyl/aryl groups. Amines are very reactive due to the difference in electronegativity between nitrogen and hydrogen atoms and due to the presence of unshared pair of electrons over N-atom. The number of hydrogen atoms attached to the N-atom decides the course of reactions of amine, that is why amines differ in many reactions. In aromatic amines like aniline, electron density at ortho and para positions with respect to NH_2 group is high. Therefore, this group is ortho or para directing and a powerful activating group.

Read the given passage carefully and give the answer of the following questions:

Q1. Carbylamine test is done for:

a. detection of NO_2 group

b. confirming the presence of secondary amine

c. confirming the presence of primary amine

d. for confirming the basic nature of $-NH_2$ group

Q2. Which of the following on reduction with lithium aluminium hydride yields secondary amine?

a. Methyl cyanide

b. Nitroethane

c. Methyl isocyanide d. Acetamide

Q3. Which of the following amines cannot be prepared by Gabriel phthalimide synthesis?

a. Ethylamine

b. Isopropyl amine

c. Propylamine

d. Ethyl methyl amine

Q4. The solubility of water for C6 H5 NH_2 (1), (C_2 H5)2 NH (II) and C_2H5 NH_2 (III) increases in the order:

a. | | < | < |
b. I<II < III
c. | | | < | <I
d. II<I< III

Answers

1. (d) for confirming the basic nature of -NH_2 group
2. (d) Acetamide
3. (c) Propylamine
4. (a) | <<I

Case Study 2

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/ aryl groups. Amines are usually formed from nitro compounds, halides, amides, etc. They exhibit hydrogen bonding which influences their physical properties. Alkyl amines are found to be stronger bases than ammonia. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Reactivity of aromatic amines can be controlled by acylation process.

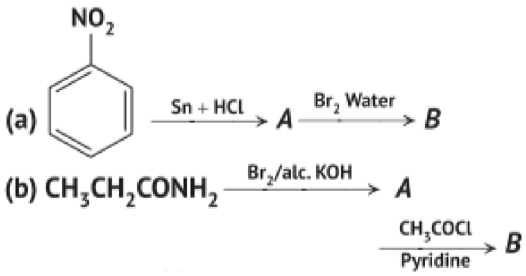
Read the given passage carefully and give the answer of the following questions:

Q1. Why does aniline not give Friedel-Crafts reaction?

Q2. Arrange the following in the increasing order of their pk, values:
$C_6H_5NH_2$, NH_3 C_2H_5NH2,$(CH_3)_3N$

Q3. (i) How can you distinguish between
$CH_3CH_2NH_2$ and $(CH_3CH_2)_2$ NH by Hinsberg test?

(ii) Write the structures of A and B in the following reactions:



OR

How will you convert the following:
(i) Benzoic acid to aniline
(ii) Aniline to p-bromoaniline

Answers

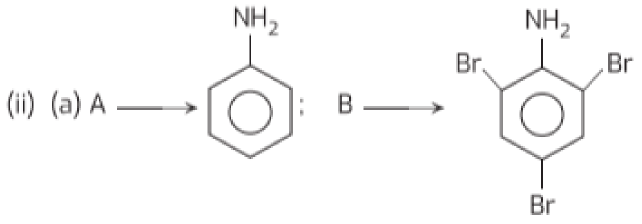
1. Aniline forms salt with the lewis acid catalyst i.e.. $ALCl_3$ which is used in Friedel-crafts reaction. Further, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

2. $C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (CH_3)_3N$

3. (i) When ethylamine is shaken with benzene sulphonyl chloride (Hinsberg's reagent) and aqueous KOH solution, it gives a clear solution.
$C_6H_5SO_2CL + CH_3\ CH_2\ NH_2 \longrightarrow C_6\ H_5\ SO_2\ NHCH_2CH_3$

$$\xrightarrow{KOH} \underset{\text{Potassium salt (Clear solution)}}{[C_6H_5SO_2-N-CH_2CH_3]\,K + H_2O}$$

While diethylamine is 2° amine, on similar treatment it forms an insoluble substance.



(b) $A \longrightarrow CH_3CH_2NH_2$; $B \longrightarrow CH_3CH_2NHCOCH_3$

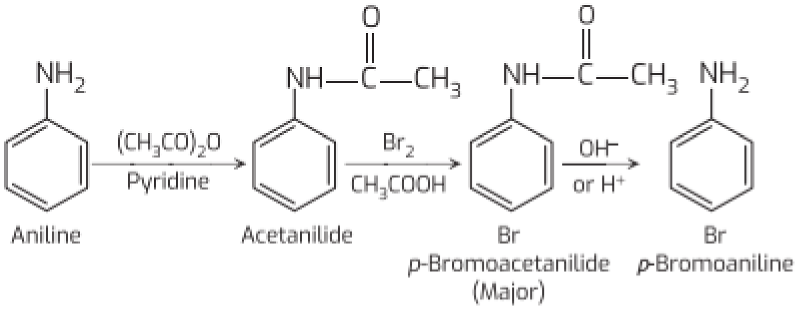
OR

(i) $\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaOH \longrightarrow C_6H_5COONa$

$$\xrightarrow[\text{Dry distillation}]{\text{Sodalime}} C_6H_5$$

$$\xrightarrow[323-333\text{ K}]{\text{conc. }HNO_3/H_2SO_4} C_6H_5NO_2 \xrightarrow[(6H)]{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2}$$

(ii)



Case Study 3

Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and hydrogen bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Aryl diazonium salts provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group.

Read the given passage carefully and give the answer of the following questions:

Q1. Arrange the following in the increasing order of their pk_b values in aqueous solution: $C_2H_5NH_2$,$(C_2H5)2NH$, $(C_2H_5)_3N$

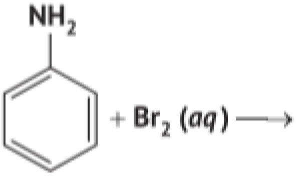
Q 2. Aniline on nitration gives a substantial amount of m-nitroaniline, though amino group is o/p directing. Why?

Q3. An aromatic compound 'A' of molecular formula $C_7H_6O_2$ on treatment with aqueous ammonia and heating forms compound 'B'. Compound 'B' on heating with Br, and aqueous KOH gives a compound 'C' of molecular formula C,H,N. Write the structures of A, B and C.

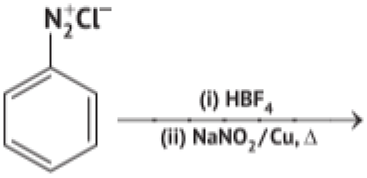
OR

Complete the following reactions giving main products:

(i)



(ii)



(CBSE 2023)

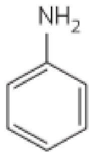
Answers

1. $C_2H_5NH_2 < (C_2H_5)_2$ NH $(C_2H_5)_3N$

2. Nitration is carried out in an acidic medium. In a strongly acidic medium, aniline is protonated to give anilinium ion (which is meta-directing). Hence, it gives a substantial amount of m-nitro aniline on nitration.

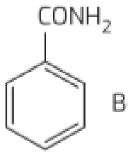
3. Compound C has the molecular formula C_6H_7N which is formed by heating compound 'B' with Br_2 and KOH. This is a Hoffmann bromamide degradation reaction. Therefore,

compound B is an amide and compound C is an amine. The only amine with the molecular formula, C_6H_7N is aniline i.e., $C_6H_5NH_2$.



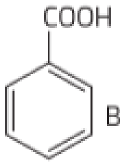
Aniline

So, the compound *'B'* must be benzamide ($C_6H_5CONH_2$).



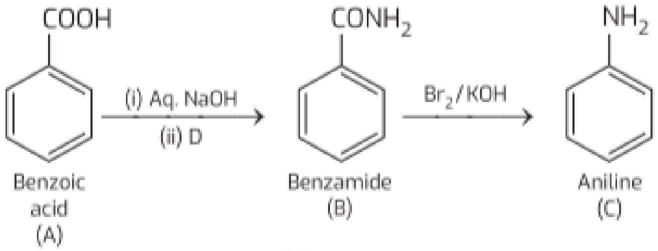
Benzamide

Further, benzamide is formed by heating compound 'A' with aqueous ammonia. Therefore, compound 'A' must be benzoic acid.

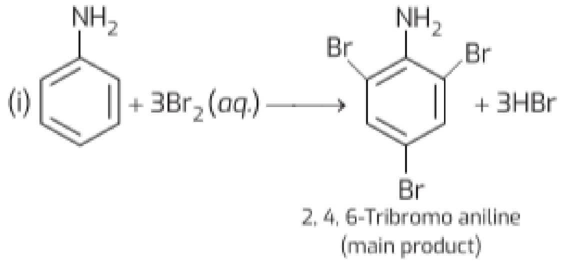


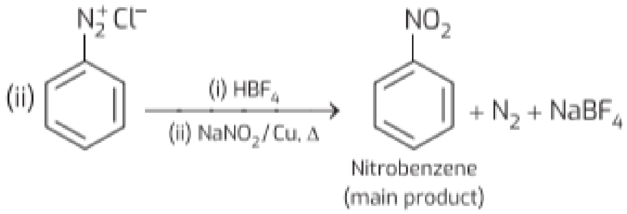
Benzoic acid

The given reactions are explained as under:



OR



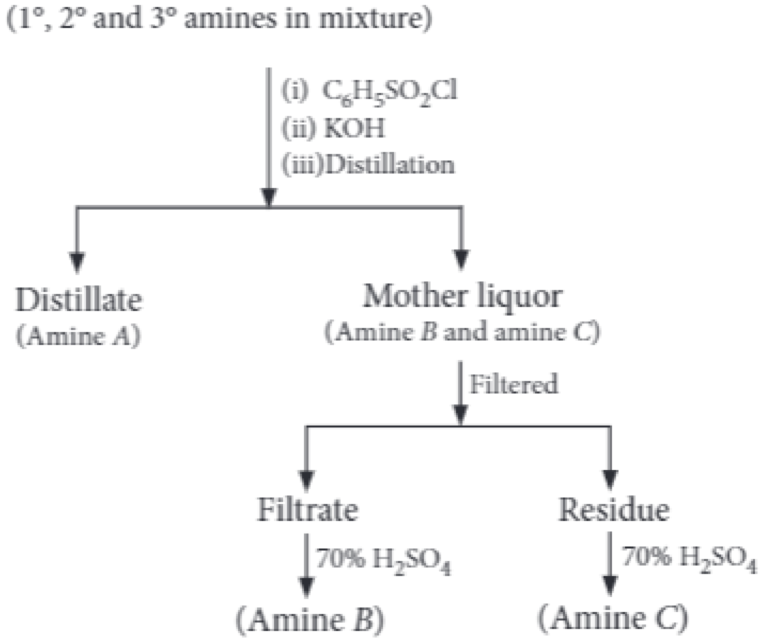


Solutions for Questions 4 to 11 are Given Below

Case Study 4

Read the passage given below and answer the following questions :

When the mixture contains the three amine salts (1°, 2° and 3°) along with quaternary salt, it is distilled with KOH solution. The three amines distill, leaving the quaternary salt unchanged in the solution. Then the mixture of amines is separated by fractional distillation, Hinsberg's method and Hoffmann's method.



The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Hinsberg reagent is
- (a) aliphatic sulphonyl chloride
- (b) phthalamide
- (c) aromatic sulphonyl chloride
- (d) anhydrous $ZnCl_2$ + conc. HCl.

(ii) Primary amine with Hinsberg's reagent forms
- (a) *N*-alkyl benzene sulphonamide soluble in KOH solution
- (b) *N*-alkyl benzene sulphonamide insoluble in KOH solution
- (c) *N,N*-dialkyl benzene sulphonamide soluble in KOH solution
- (d) *N,N*-dialkyl benzene sulphonamide insoluble in KOH solution.

OR

Secondary amine with Hinsberg's reagent forms

(a) *N*-alkyl benzene sulphonamide soluble in KOH solution

(b) *N*-alkyl benzene sulphonamide insoluble in KOH solution

(c) *N,N*-dialkyl benzene sulphonamide soluble in KOH solution

(d) *N,N*-dialkyl benzene sulphonamide insoluble in KOH solution.

(iii) To separate amines in a mixture Hoffmann's method is used. The Hoffmann's reagent is

(a) benzenesulphonyl chloride

(b) diethyl oxalate

(c) benzeneisocyanide

(d) *p*-toulenesulphonic acid.

(iv) 3° amines with Hinsberg's reagent give

(a) no reaction

(b) product which is same as that of 1° amine

(c) product which is same as that of 2° amine

(d) products which is a quaternary salt.

Case Study 5

Read the passage given below and answer the following questions :

A mixture of two aromatic compounds (*A*) and (*B*) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound (*A*), when heated with alcoholic solution of KOH produce C_7H_5N (*C*) associated with unpleasant odour.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) What is *A*?

(a) $C_6H_5NH_2$

(b) $C_6H_5CH_3$

(c) C_6H_5CHO

(d) None of these

OR

The reaction of (*A*) with alcoholic solution of KOH to produce (*C*) of unpleasant odour is called

(a) Sandmeyer reaction

(b) Carbylamine reaction

(c) Ullmann reaction

(d) Reimer-Tiemann reaction.

(ii) The alkaline aqueous layer (*B*) when heated with chloroform and then acidified give a mixture of isomeric compounds of molecular formula $C_7H_6O_2$. (*B*) is

(a) C_6H_5CHO

(b) C_6H_5COOH

(c) $C_6H_5CH_3$

(d) C_6H_5OH

(iii) In the chemical reaction, $CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow (A) + (B) + 3H_2O$, the compounds (*A*) and (*B*) are respectively

(a) C_2H_5NC and KCl

(b) C_2H_5CN and KCl

(c) $CH_3CH_2CONH_2$ and KCl

(d) C_2H_5NC and K_2CO_3

(iv) Direct nitration of an aromatic compound (*A*) is not feasible because

(a) the reaction cannot be stopped at the mononitration stage

(b) a mixture of *o*, *m* and *p*-nitroaniline is always obtained

(c) nitric acid oxidises most of the aromatic compound to give oxidation products along with only a small amount of nitrated products

(d) all of the above

Case Study 6

Read the passage given below and answer the following questions :

The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the $-NH_2$ group, which it can donate to electron deficient compounds. Aliphatic amines are stronger bases than NH_3 because of the +*I* effect of the alkyl groups. Greater the number of alkyl groups attached to N-atom, higher is the electron density on it and more will be the basicity. Thus, the order of basic nature of amines is expected to be 3° > 2° > 1°, however the observed order is 2° > 1° > 3°. This is explained on the basis of crowding on N-atom of the amine by alkyl groups which hinders the approach and bonding by a proton, consequently, the electron pair which is present on N is unavailable for donation and hence 3° amines are the weakest bases.

Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as $-CH_3$, $-OCH_3$, etc. increase the basicity while electron-withdrawing substitutes such as $-NO_2$, $-CN$, halogens, etc. decrease the basicity of amines. The effect of these substituents is more at *p* than at *m*-positions.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which one of the following is the strongest base in aqueous solution?

(a) Methyl amine
(b) Trimethyl amine
(c) Aniline
(d) Dimethyl amine

(ii) Which order of basicity is correct?

(a) Aniline > *m*-toluidine > *o*-toluidine
(b) Aniline > *o*-toluidine > *m*-toluidine
(c) *o*-toluidine > aniline > *m*-toluidine
(d) *o*-toluidine < aniline < *m*-toluidine

(iii) What is the decreasing order of basicity of primary, secondary and tertiary ethylamines and NH_3?

(a) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$
(b) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(c) $(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N > NH_3$
(d) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

(iv) The order of basic strength among the following amines in benzene solution is

(a) $CH_3NH_2 > (CH_3)_3N > (CH_3)_2NH$
(b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
(c) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
(d) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$

OR

Choose the correct statement.

(a) Methylamine is slightly acidic.
(b) Methylamine is less basic than ammonia.
(c) Methylamine is a stronger base than ammonia.
(d) Methylamine forms salts with alkalies.

Case Study 7

Read the passage given below and answer the following questions :

Amines are alkyl or aryl derivatives of ammonia formed by replacement of one or more hydrogen atoms. Alkyl derivatives are called aliphatic amines and aryl derivatives are known as aromatic amines. The presence of aromatic amines can be identified by performing dye test. Aniline is the simplest example of aromatic amine. It undergoes electrophilic substitution reactions in which $—NH_2$ group strongly activates the aromatic ring through delocalisation of lone pair of electrons of N-atom. Aniline undergoes electrophilic substitution reactions. *Ortho* and *para* positions to the $-NH_2$ group become centres of high electrons density. Thus, $-NH_2$ group is *ortho* and *para*-directing and powerful activating group.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Cyclohexylamine and aniline can be distinguished by

(a) Hinsberg test (b) carbylamine test (c) Lassaigne test (d) azo dye test.

(ii) Which of the following compounds gives dye test?

(a) Aniline (b) Methyl amine (c) Diphenyl amine (d) Ethyl amine

OR

Aniline when acetylated, the major product on nitration followed by alkaline hydrolysis gives

(a) acetanilide (b) *o*-nitroacetanilide (c) *p*-nitroaniline (d) *m*-nitroaniline.

(iii) Oxidation of aniline with manganese dioxide and sulphuric acid produces

(a) phenylhydroxylamine (b) nitrobenzene (c) *p*-benzoquinone (d) phenol.

(iv) Aniline when treated with conc. HNO_3 and H_2SO_4 gives

(a) *p*-phenylenediamine (b) *m*-nitroaniline (c) *p*-benzoquinone (d) nitrobenzene.

Case Study 8

Read the passage given below and answer the following questions :

Amines are basic in nature. The basic strength of amines can be expressed by their dissociation constant, K_b or pK_b.

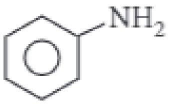
$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$

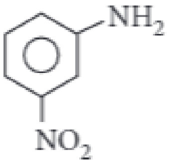
$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]} \text{ and } pK_b = -\log K_b$$

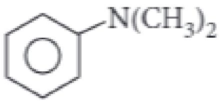
Greater the K_b value or smaller the pK_b value, more is the basic strength of amine. Aryl amines such as aniline are less basic than aliphatic amines due to the involvement of lone pair of electrons on N-atom with the resonance in benzene. In derivatives of aniline, the electron releasing groups increase the basic strength while electron withdrawing groups decrease the basic strength. The base weakening effect of electron withdrawing group and base strengthening effect of electron releasing group is more marked at *p*-position than at *m*-position. *o*-Substituted aniline is less basic than aniline due to ortho effect and is probable due to combination of electronic and steric effect.

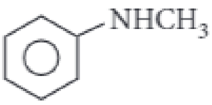
The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following has lowest pK_b value?

(a) 

(b) 

(c) 

(d) 

(ii) The strongest base among the following is

(a) $C_6H_5NH_2$ (b) $p\text{-}NO_2-C_6H_4NH_2$ (c) $m\text{-}NO_2-C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$

(iii) Maximum pK_b value of

(a) 

(b) 

(c) $(CH_3CH_2)_2NH$ (d) $(CH_3)_2NH$

(iv) Which of the following statements is not correct?

(a) Methylamine is more basic than NH_3.
(b) Amines form hydrogen bonds.
(c) Ethylamine has higher boiling point than propane.
(d) Dimethylamine is less basic than methylamine.

OR

$CH_3CH_2NH_2$ contains a basic $-NH_2$ group, but CH_3CONH_2 does not because

(a) acetamide is amphoteric in character

(b) in ethylamine the electron pair on N-atom is delocalised by resonance

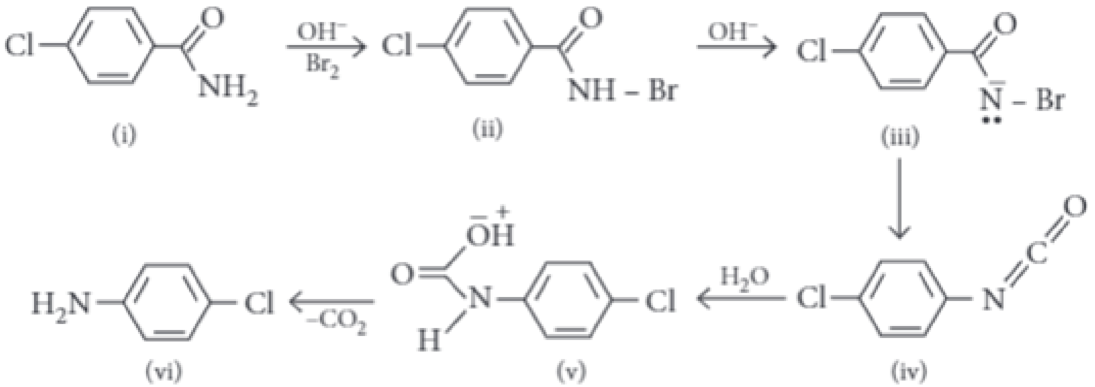
(c) in ethylamine there is no resonance while in acetamide the lone pair of electrons on N-atom is delocalised and is less available for protonation

(d) none of these.

Case Study 9

Read the passage given below and answer the following questions :

$RCONH_2$ is converted into RNH_2 by means of Hoffmann bromamide degradation. During the reaction amide is treated with Br_2 and alkali to get amine. This reaction is used to descend the series in which carbon atom is removed as carbonate ion (CO_3^{2-}). Hoffmann bromide degradation reaction can be written as :



The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Hoffmann bromamide degradation is used for the preparation of

(a) primary amines (b) secondary amines

(c) tertiary amines (d) secondary aromatic amines.

(ii) Which is the rate determining step in Hoffmann bromamide degradation?

(a) Formation of (i) (b) Formation of (ii) (c) Formation of (iii) (d) Formation of (iv).

(iii) Which of the following are used for the conversion of (i) to (ii)?

(a) KBr (b) KBr + CH_3ONa (c) KBr + KOH (d) Br_2 + KOH

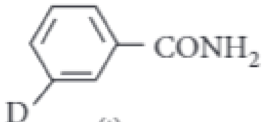
OR

Identify *B* in the following reaction.

$$R-C\equiv N \xrightarrow[\text{(Partially hydrolysis)}]{\text{Conc. HCl}} A \xrightarrow{Br_2/KOH} B$$

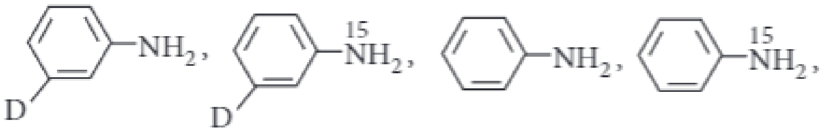
(a) $RCONH_2$ (b) RNH_2 (c) $RNHBr$ (d) $R=N=C=O$

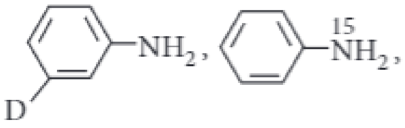
(iv) What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hoffmann bromamide degradation?

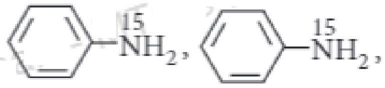


(i)

(ii)

(a) 

(b) 

(c) 

(d) 

Case Study 10

Read the passage given below and answer the following questions :

Amines are produced when an alcoholic solution of ammonia and an alkyl or a benzyl halide is heated in a sealed tube at 373 K. This reaction is called ammonolysis and usually gives a mixture of primary, secondary and tertiary amines along with some quarternary ammonium salts. This reaction is an example of nucleophilic substitution reaction in which ammonia acts as a nucleophile due to the presence of a lone pair of electrons on the nitrogen atom. However this method cannot be used for the preparation of aryl amines. One of the most convenient methods for the preparation of aryl amines is reduction of nitro compounds. Aryl amines can also be prepared by reduction of nitrites or Gabriel phthalimide synthesis.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Ammonolysis of alkyl halides only produces 2° amines.
Reason : Ammonolysis of alkyl halides involves the reaction between alkyl halides and alcoholic ammonia.

OR

Assertion : Gabriel-phthalimide reaction can be used to prepare both aryl and alkyl primary amines.
Reason : Aryl halides are more reactive alkyl halides towards nucleophilic substitution reactions.

(ii) **Assertion :** Ammonolysis method cannot be used for the preparation of aryl amines.
Reason : Aryl halides are much less reactive than alkyl halides towards nucleophilic substitution reaction.

(iii) **Assertion :** Ammonolysis can be used to prepare pure primary amines.
Reason : Ammonolysis of haloalkanes lead to multiple ammonium salts.

(iv) **Assertion :** Aromatic 1° amines can not be prepared by Gabriel phthalimide synthesis.
Reason : Aryl halides do not undergo nucleophilic substitution with anion formed by phthalimide.

Case Study 11

Read the passage given below and answer the following questions :

Aniline activates the benzene ring by increasing electron density at *ortho*- and *para*-positions. Hence, it is *o*-, *p*-directing. –NH_2 group strongly activates the ring therefore it is difficult to stop the reaction at monosubstitution stage. Among electrophilic substitution reaction, direct nitration of aniline is not done to get *o*- and *p*-nitroaniline because lone pair of electrons present at nitrogen atom will accept proton from nitrating mixture to give anilinium ion which is *meta*-directing.

Aniline with $NaNO_2$ and HCl forms benzene diazonium chloride at very low temperature. Aromatic amines react with nitrous acid to form a yellow oily liquid known as *N*-nitrosoamines.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) Assertion : Nitrating mixture used for carrying out nitration of benzene consists of conc. HNO_3 + conc. H_2SO_4.
Reason : In presence of H_2SO_4, HNO_3 acts as a base and produces NO_2^+ ions.

(ii) Assertion : Anilinium chloride is more acidic than ammonium chloride.
Reason : Anilinium ion is not resonance-stabilised.

(iii) Assertion : Nitrobenzene can be prepared from benzene by using mixture of conc. HNO_3 and conc. H_2SO_4.
Reason : In the mixture, H_2SO_4 act as a acid.

(iv) Assertion : In strongly acidic solution, aniline becomes less reactive towards electrophilic reagents.
Reason : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

OR

Assertion : Nitration of aniline can be done conveniently by protecting $-NH_2$ group through acetylation.
Reason : Acetylation of aniline results in the increase of electron density in the benzene ring.

HINTS & EXPLANATIONS

4. (i) (c)

(ii) (a) : A primary amine forms *N*-alkylbenzene sulphonamide which because of the presence of an acidic hydrogen on the N-atom dissolves in aqueous KOH.

OR

(d) : A secondary amine forms *N,N*-dialkylbenzene sulphonamide which due to absence of acidic hydrogen on N-atoms does not dissolve in aqueous KOH.

(iii) (b)

(iv) (a) : Tertiary amine does not contain a replaceable hydrogen on the nitrogen atom. So, 3° amine does not react with Hinsberg's reagent.

5. **(i) (a) :** Given, mixture of (*A*) and (*B*) $\xrightarrow[+\text{ KOH }(aq)]{CHCl_3}$ organic layer (*A*) + alkaline aqueous layer (*B*)

Organic layer on treating with KOH (alc.) produces (C_7H_5N) (*C*) of unpleasant odour and thus (*C*) is C_6H_5NC. Therefore, (*A*) is $C_6H_5NH_2$.

OR

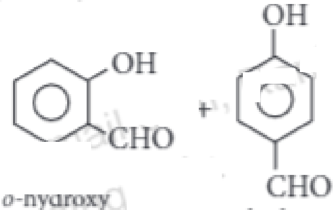
(b) : Carbylamine reaction

$$\underset{\substack{\text{Aniline}\\(A)}}{C_6H_5NH_2} + CHCl_3 + 3KOH\text{ (alc.)} \longrightarrow \underset{\text{Phenyl isocyanide }(C)}{C_6H_5NC} + 3KCl + 3H_2O$$

(ii) (d): Alkaline layer on treating with $CHCl_3$ followed by acidification gives two isomers having formula ($C_7H_6O_2$). This is Reimer-Tiemann reaction and thus (*B*) is C_6H_5OH.

$C_6H_5OH + CHCl_3 + KOH \xrightarrow{H^+}$

Phenol (*B*)



o-hydroxy benzaldehyde

p-hydroxy benzaldehyde

(iii) (a): $CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$

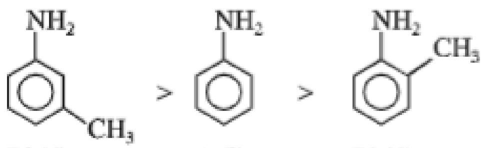
This is called carbylamine reaction.

(iv) (c): Direct nitration of aniline is not a feasible process because nitric acid oxidises most of aniline to give oxidation products along with only a small amount of nitrated products.

6. **(i) (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 amine $(CH_3)_3N$, 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 groups decrease electron density on nitrogen atom and thereby decreasing basicity.

(ii) (d): In general, electron donating (+*R*) group which when present on benzene ring ($-NH_2$, $-OR$, $-R$, etc.) at the *para* position increases the basicity of aniline.

Ortho substituted anilines are weaker bases than aniline due to *ortho* effect.



m-Toluidine Aniline *o*-Toluidine

(iii) (d): In case of ethylamines, the combined effect of inductive effect, steric effect and solvation effect gives the order of basic strength as

$$\underset{(2^\circ)}{(C_2H_5)_2NH} > \underset{(3^\circ)}{(C_2H_5)_3N} > \underset{(1^\circ)}{C_2H_5NH_2} > NH_3$$

(iv) (b): In non-aqueous solvents the basic strength of alkyl amines follows the order :

tertiary amines > secondary amines > primary amines.

OR

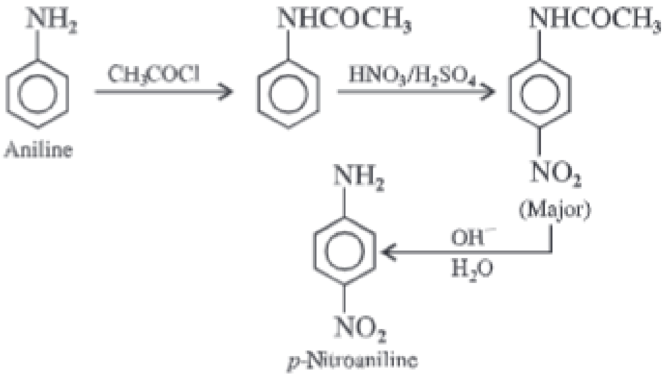
(c) : Methyl amine is stronger base than ammonia due to electron releasing inductive effect of methyl group.

7. **(i) (d)**

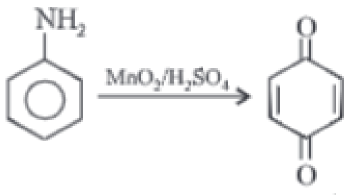
(ii) (a): Aromatic primary amines give dye test.

OR

(c) :

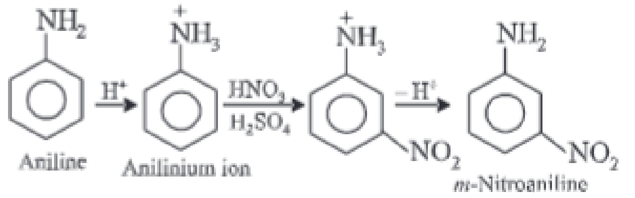


(iii) (c) :



p-Benzoquinone

(iv) (b): In acidic medium aniline gets protonated to anilinium ion which is *meta*-directing.



8. **(i) (c)**

(ii) (d)

(iii) (a)

(iv) (d): Dimethylamine is more basic than methyl amine.

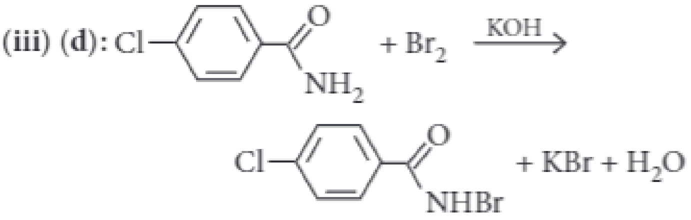
OR

(c)

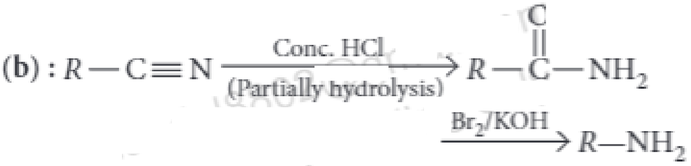
9. **(i) (a)**

(ii) (d): The rate determining step is probably loss of Br^- to form isocyanate as this is the slowest step.

(iii) (d):

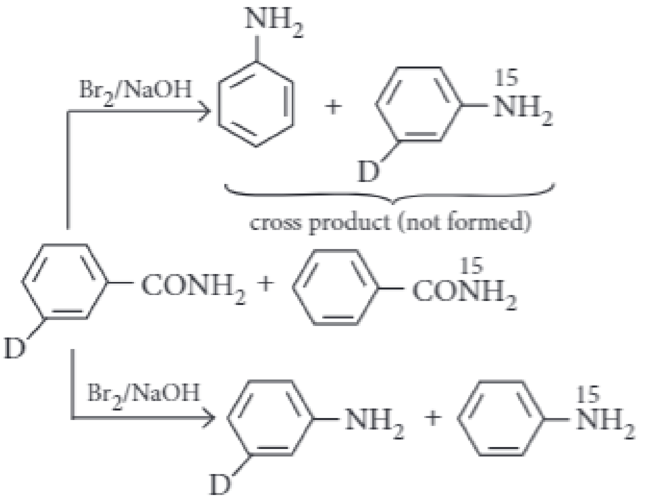


OR



$$\textbf{(b)}: R—C\equiv N \xrightarrow[\text{(Partially hydrolysis)}]{\text{Conc. HCl}} R—\overset{\text{C}}{\overset{\|}{C}}—NH_2 \xrightarrow{Br_2/KOH} R—NH_2$$

(iv) (b): Since, the overall reaction is intermolecular, hence there will be no effect on product formation.



10. **(i) (d):** Reaction can be used to prepare 1°, 2°, 3° amines and finally quaternary ammonium salts.

OR

(c) : Aryl halides are less reactive than aralkyl halides towards nucleophilic substitution reactions.

(ii) (a)

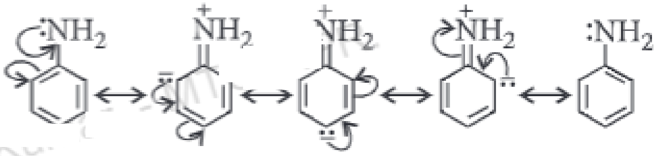
(iii) (d): Ammonolysis cannot be used to prepare pure primary amines. This method usually gives a mixture of primary, secondary and tertiary amines along with some quaternary ammonium salts.

(iv) (a)

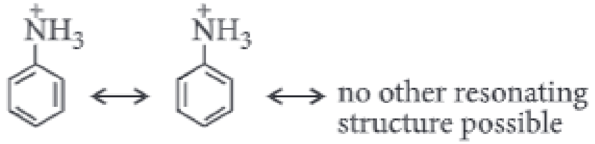
11. **(i) (a):** $HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3O^+$

(ii) (c): $\underset{\substack{\text{anilinium ion} \\ \text{stronger acid}}}{C_6H_5\overset{+}{N}H_3} \longrightarrow \underset{\substack{\text{aniline} \\ \text{weaker conjugated base}}}{C_6H_5NH_2} + H^+$

Aniline is weaker base than ammonium chloride. In NH_4Cl or aliphatic amines, the non-bonding electron pair of N is localized and is fully available for coordination with a proton. On the other hand, in aniline or other aromatic amines, the non-bonding electron pair is delocalised into benzene ring by resonance.



But anilinium ion is less resonance stabilised than aniline.



(iii) (b)

(iv) (a)

OR

(c)