DAY THIRTY ONE

Organic Compounds Containing Nitrogen

Learning & Revision for the Day

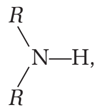
- Amines
- Diazonium Salts

Amines

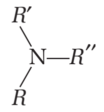
These are the derivatives of ammonia in which one, two or all the three hydrogen atoms are replaced by alkyl or aryl groups. Amines are classified as primary, secondary and tertiary according to the replacement of one, two or three hydrogen atoms from ammonia respectively.

RNH_2,

Primary

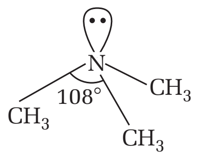


Secondary



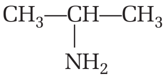
Tertiary

- Nitrogen, in amines, contains four sp^3-hybridised orbitals. Out of these four, the three sp^3-hybridised orbitals of nitrogen overlap either with s-orbitals of hydrogen or sp^3- orbitals carbon depending upon the composition of amines. The fourth hybridised orbital of nitrogen in all amines has unshared pair of electrons. Due to the presence of lone pair of electrons, lone pair-bond pair repulsions increases due to which the bond angle C—N—E of nomenclature (where, E is C or H) 109.5° and shape is pyramidal.



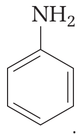
Pyramidal shape of trimethylamine

- In common system of nomenclature, an aliphatic amine is named by prefixing alkyl group to amine, i.e. alkylamine. In **IUPAC system**, amines are named as alkanamines, derived by replacement of 'e' of alkane by the word amine. While naming arylamine suffix 'e' of arene is replaced by 'amine'.



$$\underset{NH_2}{CH_3—\underset{|}{CH}—CH_3}$$

Propan-2-amine

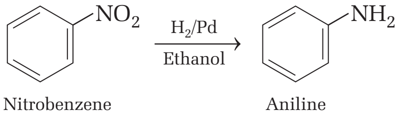


Benzenamine

Preparation of Amines

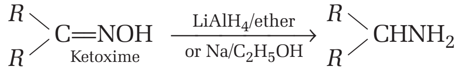
Several methods can be used to prepare aliphatic amines, out of which some are specific for 1°, 2°, 3° amines while some gives mixtures of all the three. These are as follows:

(i) Alkyl nitriles, nitroalkanes, oximes of aldehydes, ketones and amides, all on reduction give primary amines. Reduction of nitriles to primary amines by using Na and alcohol is called **Mendius reaction**.

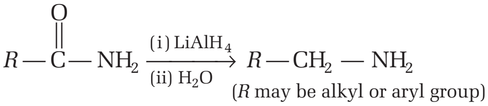
(a) 

(b) $R{-}NO_2 \xrightarrow[\text{or Fe + HCl}]{\text{Sn + HCl}} \underset{\substack{\text{Primary}\\\text{amine}}}{R{-}NH_2}$

(c) $R{-}C{\equiv}N \xrightarrow[\text{Na(Hg) / } C_2H_5OH]{H_2/Ni} R{-}CH_2{-}NH_2$

(d) 

$\begin{matrix}R\\R\end{matrix}\!\!>\underset{\text{Ketoxime}}{C{=}NOH} \xrightarrow[\text{or Na/}C_2H_5OH]{LiAlH_4\text{/ether}} \begin{matrix}R\\R\end{matrix}\!\!>CHNH_2$

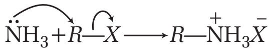
(e) 

$R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R{-}CH_2{-}NH_2$

(R may be alkyl or aryl group)

NOTE $\underset{\text{Isocyanide}}{R{-}N{\equiv}C} \xrightarrow[\text{or Na (Hg) + } C_2H_5OH]{H_2/Ni} \underset{(2°\text{ amine})}{R{-}NH{-}CH_3}$

(ii) When alkyl halide is heated with alcoholic solution of ammonia in a sealed tube at about 393 K, a mixture of amines is obtained. This reaction is called **Hofmann's ammonolysis method.**



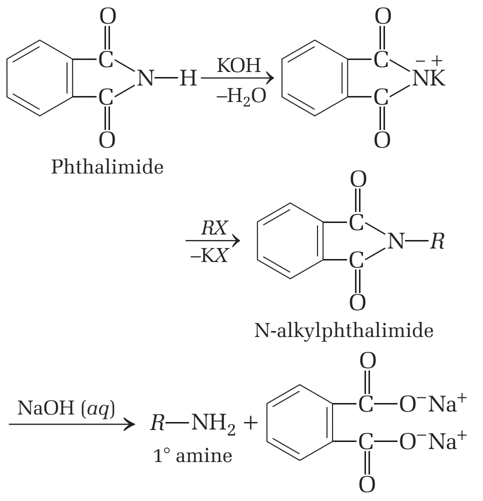
$\ddot{N}H_3 + R{-}X \longrightarrow R{-}\overset{+}{N}H_3\overset{-}{X}$

$\underset{1°}{RNH_2} \xrightarrow{RX} \underset{2°}{R_2NH} \xrightarrow{RX} \underset{3°}{R_2N} \xrightarrow{RX} \underset{\substack{\text{Quaternary}\\\text{ammonium salt}}}{R_4\overset{+}{N}\overset{-}{X}}$

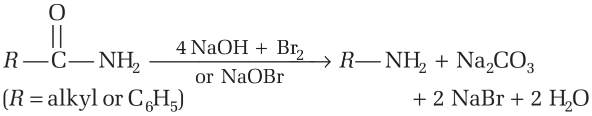
The free amine can be obtained from ammonium salt by treatment with a strong base.

$$R\overset{+}{N}H_3X^- + NaOH \longrightarrow R{-}NH_2 + H_2O + Na^+X^-$$

(iii) **Gabriel phthalimide synthesis** is used for the preparation of 1° amine. In this reaction, phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with RX followed by either alkaline hydrolysis or hydrazinolysis with hydrazine ($H_2N \cdot NH_2$) produces the corresponding 1° amine. Primary aromatic amine (except those containing electron withdrawing group at *o*- and *p*-positions, e.g. $-NO_2$ group) cannot be synthesised by this method because ArX do not undergo S_N reaction with anion formed by phthalimide.



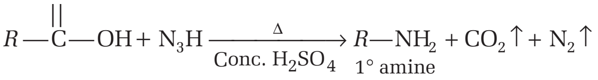
(iv) Amides on reaction with Br_2 in an aqueous or ethanolic solution of NaOH give 1° amine with one C-atom less than that present in the amide. This reaction is called **Hofmann-Bromamide degradation reaction.**



$R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \xrightarrow[\text{or NaOBr}]{4\,NaOH + Br_2} R{-}NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O$

(R = alkyl or C_6H_5)

(v) Carboxylic acid, when warmed with hydrazoic acid (N_3H) in the presence of concentrated sulphuric acid, gives a high yield of primary amines. This reaction is called **Schmidt reaction**.



$R{-}\overset{\overset{O}{\|}}{C}{-}OH + N_3H \xrightarrow[\text{Conc. } H_2SO_4]{\Delta} \underset{1°\text{ amine}}{R{-}NH_2} + CO_2\uparrow + N_2\uparrow$

Instead of N_3H and conc. H_2SO_4, a mixture of NaN_3 and conc. H_2SO_4 can also be used.

Physical Properties

Some important physical properties of amines are discussed below :

- The lower aliphatic amines are gases with fishy odour. Aniline and other arylamines are usually colourless but develop colour on keeping it in air for a long time due to atmospheric oxidation.
- Boiling points and solubility of isomeric amines decrease with branching, i.e.

$$\underset{\substack{1°\text{ amine}\\(2\text{H-bonding})}}{CH_3{-}CH_2{-}CH_2{-}NH_2} > \underset{\substack{2°\text{ amine}\\(1\text{H-bonding})}}{CH_3{-}NH{-}CH_2{-}CH_3} > \underset{\substack{3°\text{ amine}\\(\text{No H-bonding})}}{(CH_3)_3N}$$

- Amines have lower boiling point than corresponding alcohols.

Chemical Properties

Amines are reactive and behave as nucleophiles due to the presence of one unshared pair of electrons. Some important chemical properties of amines are discussed below:

1. Basic Nature of Amines

- Amines are basic in nature, so react with acids and form salt. Larger the value of K_b or smaller the value of pK_b, stronger is the base.

  In $R\,NH_2$, $RN=CHR$ and RCN, nitrogen is sp^3, sp^2 and sp-hybridised respectively. More the s-character of hybridised orbital containing lone pair, lesser is the basic character. Hence, RNH_2 is most basic and RCN is least basic among these.
- The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

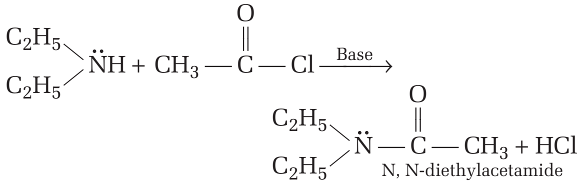
  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- Electron donating substituent such as $—CH_3$, $—OCH_3$ increases the basicity while electron withdrawing group such as $—NO_2$, $—COOH$ decreases the basicity.

NOTE In gaseous phase, the order of basicity would be 3° amine > 2° amine > 1° amine > NH_3.

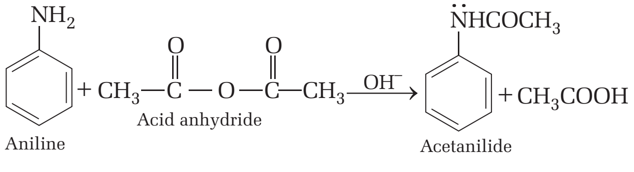
2. Acylation

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydride and esters by nucleophilic substitution reaction. This reaction is known as acylation. In this reaction, 1° amines give N-substituted amide, while 2° amines give N,N-disubstituted amides.

$$C_2H_5—NH_2 + \underset{\text{(Acyl chloride)}}{CH_3COCl} \xrightarrow{OH^-} \underset{\text{N-ethylethanamide}}{C_2H_5—NHCOCH_3} + HCl$$



$$(C_2H_5)_2\ddot{N}H + CH_3—\overset{\overset{O}{\|}}{C}—Cl \xrightarrow{\text{Base}} \underset{\text{N, N-diethylacetamide}}{(C_2H_5)_2\ddot{N}—\overset{\overset{O}{\|}}{C}—CH_3} + HCl$$



3. Carbylamine Reaction

Aliphatic and aromatic primary amines on heating with $CHCl_3$ and KOH(alc.) form isocyanide or carbylamine which is a foul smelling substance. Secondary ($R—NH—R$) and tertiary amines (R_3N) do not show this reaction. This reaction is known as carbylamine reaction and it is used as a test for primary amines.

$$R—NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underset{\text{Carbylamine}}{R—NC} + 3KCl + 3H_2O$$

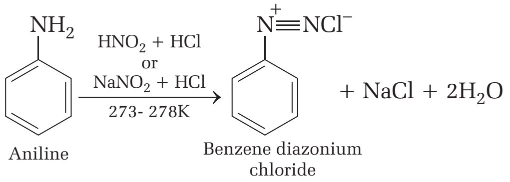
4. Reaction with Nitrous Acid

Primary, secondary and tertiary amines react differently with nitrous acid which is prepared *in situ* from a mineral acid and sodium nitrite.

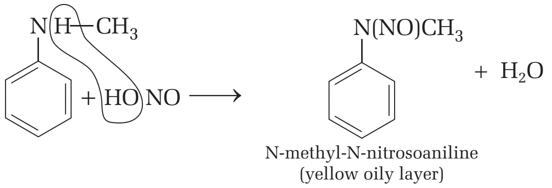
(i) Aliphatic primary amines when react with HNO_2, gives alcohol.

$$R—NH_2 \xrightarrow[NaNO_2 + HCl]{(HNO_2)} [R\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2\uparrow + HCl$$

(ii) Aromatic primary amines when react with HNO_2 at low temperatures, give diazonium salts.



(iii) Secondary amines both aliphatic and aromatic on reaction with HNO_2 give an oily nitroso compound.



(iv) Tertiary aliphatic amines dissolve in a cold solution of nitrous acid to form water soluble nitrite salts which decompose on warming to give nitrosoamine and alcohol.

$$\underset{3^\circ\text{ amine}}{(C_2H_5)_3N} + HONO \xrightarrow{\text{Cold}} \underset{\text{Trimethylammonium nitrite salt}}{[(C_2H_5)_3N^+H]\,NO_2^-}$$

$$\xrightarrow{\text{Warm}} (C_2H_5)_2N—N=O + C_2H_5OH$$

(v) Aromatic amines react with nitrous acid to form aliphatic diazonium salts at low temperatures (273-278 K).

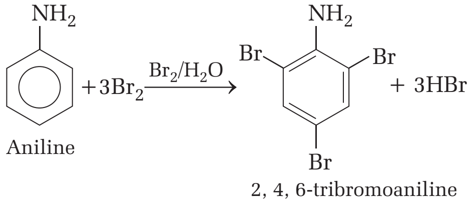
$C_6H_5—NH_2 \xrightarrow[273–278\,K]{NaNO_2 + 2HCl} C_6H_5—\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$ This reaction is used to distinguish 1°, 2° and 3° amines.

5. Electrophilic Substitution Reaction

In electrophilic substitution reaction, an atom that is attached to an aromatic system is replaced by an electrophile. In case of aniline, $—NH_2$ group is *ortho* and *para* directing and a powerful activating group. These positions become the centre of high electron density.

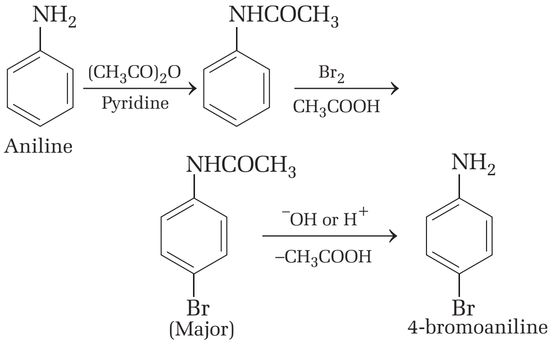
Some of the most important electrophilic aromatic substitution, i.e. bromination, nitration, sulphonation etc., are given below:

(i) Due to strong activating effect of the amino group, halogenation (or bromination) of amines occur very fast.

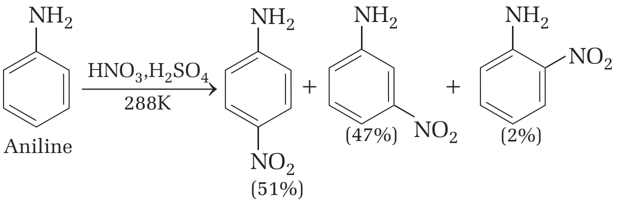


The main problem encountered during electrophilic substitution reactions of aromatic amines is that these have very high reactivity.

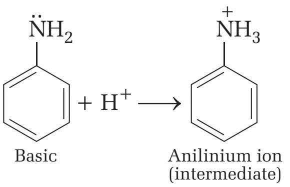
A monohalogenated (or monobrominated) product can be obtained by selective bromination. This can be done by protecting the —NH_2 group by acetylation with acetic anhydride then carrying out the desired substitution followed by hydrolysis of amide.



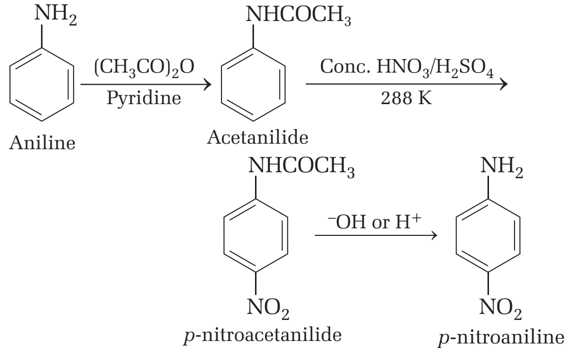
(ii) Aniline can be treated with nitric acid and sulphuric acid to give nitrobenzene *via* nitration process.



This is due to the fact that aniline gets protonated to form anilinium ion which is *meta*-directing.

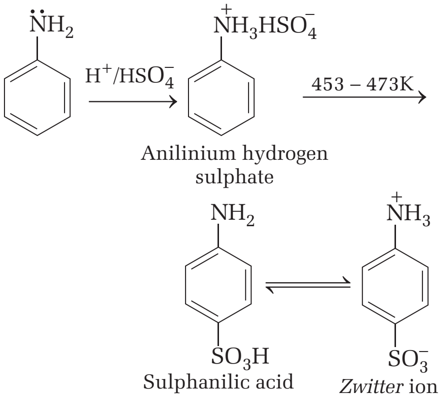


By protecting the —NH_2 group through acetylation with acetic anhydride, the nitration can be controlled and *p*-nitroaniline is obtained as a major product.



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

(iii) Aniline can be treated with a conc. H_2SO_4 to give anilinium hydrogen sulphate which on heating with sulphuric acid at 453-473 K produces sulphanilic acid in a reversible reaction *via* sulphonation.



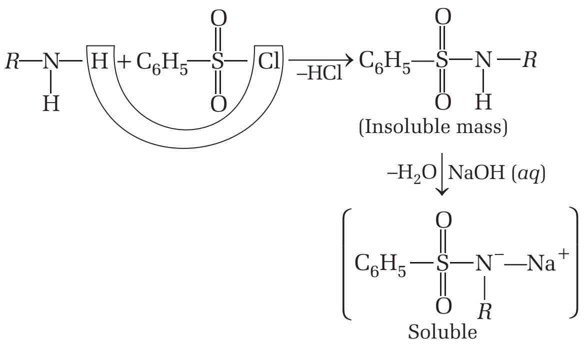
Identification of 1°, 2° and 3° Amines

Several reactions can be used to identify 1°, 2° and 3° amines. Some important test are as follows:

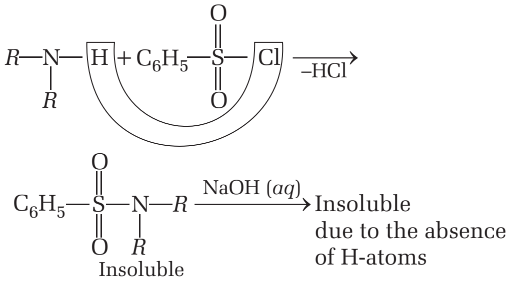
Hinsberg's Test

Distinction between primary, secondary and tertiary amines is made by $C_6H_5SO_2Cl$, which is known as Hinsberg's reagent.

(i) **Primary amines** give an insoluble mass which is soluble in alkali.



(ii) **Secondary amines** give an insoluble substance, which remains unaffected by alkali.



(iii) **Tertiary amines** do not react with benzene sulphonyl chloride because of the absence of replaceable H-atoms on N-atom.

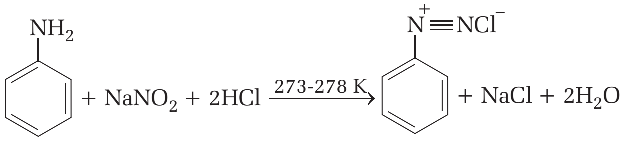
Carbylamine reaction and reaction with nitrous acid can also be used to distinguish between 1°, 2° and 3° amines as discussed before in this chapter.

Uses of Amines

Amines are used as intermediates in drug manufacturing and as reagents in organic synthesis. Aromatic amines are used for manufacture of polymers, dyes and as intermediates for additives in rubber industry. Quaternary ammonium salts of long chain aliphatic tertiary amines are used as detergents.

Diazonium Salts

- Diazonium salts are obtained when primary aromatic amines react with nitrous acid. These salts are used in the preparation of azo dyes and a number of useful halogen substituted arenes.
- Benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278 K. The conversion of primary aromatic amines into diazonium salt is known as diazotisation.



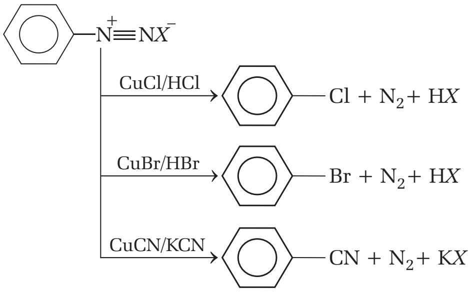
- Benzene diazonium chloride is a colourless crystalline solid. It is readily soluble in water. It is stable in cold but reacts with water when warmed.

Diazonium salts mainly show two types of reactions. These are as follows:

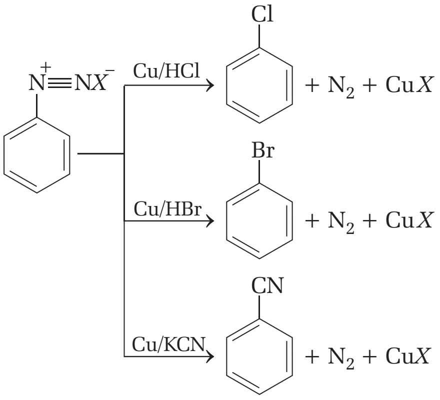
1. Reactions Involving Displacement of Diazo Group

The following reactions are involved in the displacement of diazo group in the benzene can be given as :

(i) Benzene diazonium chloride heated with cuprous chloride or bromide respectively dissolved in HCl or HBr yield chlorobenzene or bromobenzene, respectively. This reaction is called **Sandmeyer's reaction.**



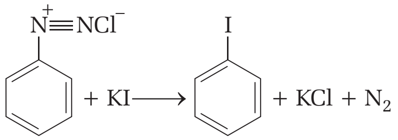
(ii) In **Gattermann reaction**, benzene diazonium chloride is warmed with copper powder and HCl, HBr and KCN to produce chlorobenzene, bromobenzene and cyanobenzene respectively.



The yield in Sandmeyer's reaction is found to be greater than the Gattermann reaction.

(iii) Some other reactions of diazonium salt involving displacement of diazo group.

(a)



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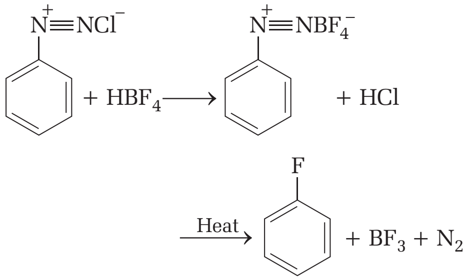

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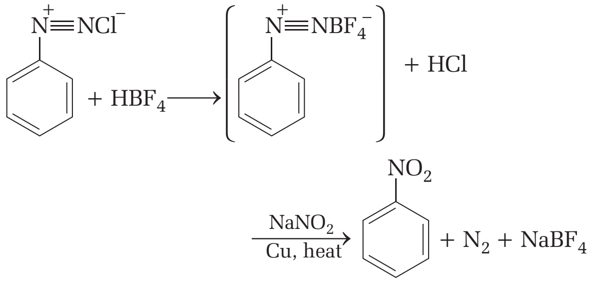

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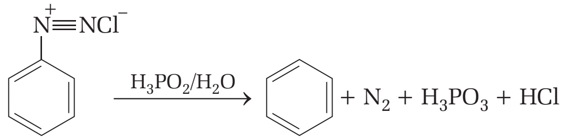

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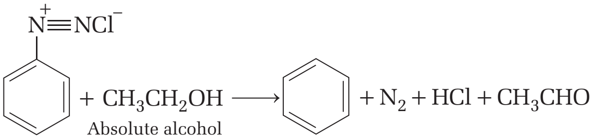

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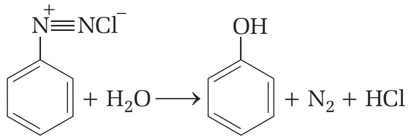
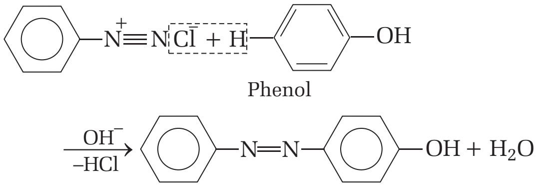


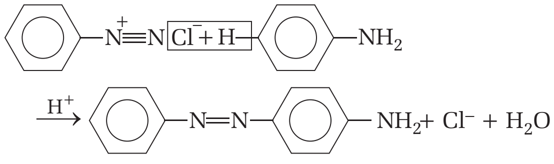
2. Reactions Involving Retention of Diazo Group

Coupling reactions are the example of electrophilic substitution reaction.

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the —N = N— bond.



p-hydroxyazobenzene (Orange dye)



p-aminoazobenzene (Yellow dye)

Coupling with phenols is carried out in weakly alkaline medium (pH 9 to 10) because phenolate ion produced is coupled with diazonium salt more readily. Above pH 10, diazonium salt reacts with hydroxide ion to form diazotate ion which does not take part in coupling reaction.

Uses of Diazonium Salts

Diazonium salts are used for the preparation of a large number of aromatic compounds *viz* substitution and coupling compounds.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

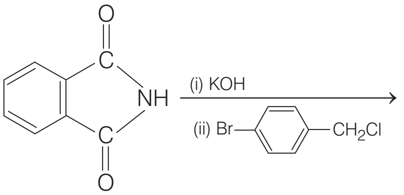
1 Reduction of aromatic nitro compounds using Fe and HCl gives

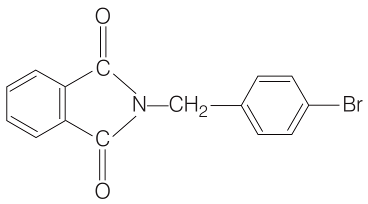
(a) aromatic oxime (b) aromatic hydrocarbon
(c) aromatic primary amine (d) aromatic amide

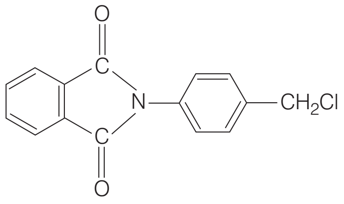
2 In which of the following reaction, tertiary amine is obtained?

(a) Aniline $\xrightarrow{CH_3I}\xrightarrow{CH_3I}$ (b) Aniline $\xrightarrow{CH_3I}$
(c) Nitrobenzene $\xrightarrow{Sn/HCl}$ (d) None of these

3 The major product of the following reaction is



(a)


(b)


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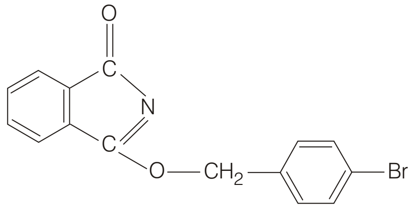

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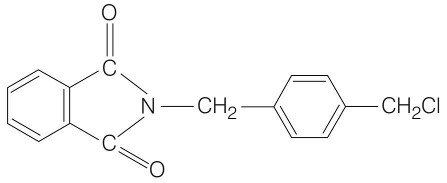


4 The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is

(a) excess H_2
(b) Br_2 in aqueous NaOH
(c) iodine in the presence of phosphorus
(d) $LiAlH_4$ in ether

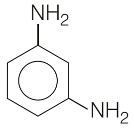
5 Acetamide is treated separately with the following reagents. Which one of these would give methylamine?

(a) PCl_5
(b) $NaOH + Br_2$
(c) Soda lime
(d) Hot conc. H_2SO_4

6 In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are → JEE Main 2016

(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 two moles of Br_2

7 The major product of the reaction between *m*-dinitrobenzene and NH_4SH is

(a)


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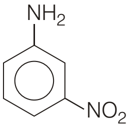

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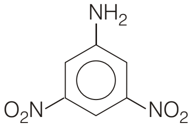

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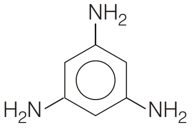
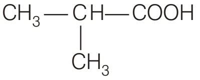
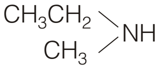


8 An organic compound *A* on reacting with NH_3 gives *B*. On heating, *B* gives *C*. *C* in the presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. *A* is → Online JEE Main 2013

(a) CH_3COOH
(b) $CH_3CH_2CH_2COOH$
(c)

$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—COOH$
(d) CH_3CH_2COOH

9 Which of the following should be most volatile?

I. $CH_3CH_2CH_2NH_2$
II. $(CH_3)_3N$
III.

$\begin{matrix} CH_3CH_2 \\ CH_3 \end{matrix}\!\!>NH$
IV. $CH_3CH_2CH_3$

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

10 Amongst the following, the strongest base in aqueous medium is

(a) CH_3NH_2
(b) $NCCH_2NH_2$
(c) $(CH_3)_2NH$
(d) $C_6H_5NHCH_3$

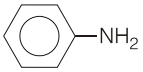
11. Which one of the following is the strongest base in aqueous solution?

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

12. The order of basicity of amines in gaseous state is → JEE Main (Online) 2013

(a) $1° > 2° > 3° > NH_3$
(b) $3° > 2° > NH_3 > 1°$
(c) $3° > 2° > 1° > NH_3$
(d) $NH_3 > 1° > 2° > 3°$

13. Which of the following is the strongest base?

(a)


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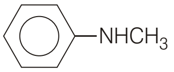

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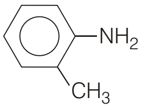
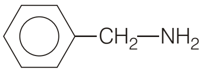
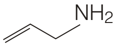


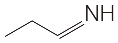
(d)


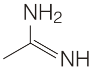
14. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? → JEE Main 2014

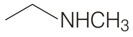
(a) $(CH_3)_2NH$
(b) CH_3NH_2
(c) $(CH_3)_3N$
(d) $C_6H_5NH_2$

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

I.


II.


III.


IV.


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

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 → JEE Main (Online) 2013

(a) 2
(b) 5
(c) 4
(d) 6

17 On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is → JEE Main 2014

(a) an alkanol
(b) an alkanediol
(c) an alkyl cyanide
(d) an alkyl isocyanide

18 Carbylamine forms from aliphatic or aromatic primary amine *via* which of the following intermediates?

➞ JEE Main (Online) 2013

(a) Carbanion (b) Carbene
(c) Carbocation (d) Carbon radical

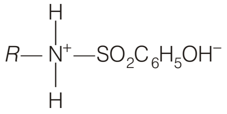
19 Which of the following is formed when $R\,NH_2$ reacts with $R\,CHO$?

(a) Hemiacetals (b) Acetals
(c) Ketals (d) Imines

20 The compound, which on reaction with aqueous nitrous acid at low temperature, produces an oily nitrosoamine, is

(a) diethylamine (b) ethylamine
(c) aniline (d) methyl amine

21 $R\,NH_2$ reacts with $C_6H_5SO_2Cl$ in aqueous KOH to give a clear solution. On acidification a precipitate is obtained which is due to the formation of

(a) 
$R—\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N^+}}—SO_2C_6H_5OH^-$
(b) $R—N^-SO_2C_6H_5K^+$
(c) $C_6H_5SO_2NH_2$ (d) $R—NH—SO_2—C_6H_5$

22 Which one of the following methods is neither meant for the synthesis nor for separation of amines?

(a) Curtius reaction (b) Wurtz reaction
(c) Hofmann method (d) Hinsberg method

23 Match the following and choose the correct option.

Column I	Column II
A. Ammonolysis	1. Amine with lesser number of carbon atoms
B. Gabriel phthalimide synthesis	2. Detection test for primary amines
C. Hofmann bromamide reaction	3. Reaction of phthalimide with KOH and $R—X$
D. Carbylamine reaction	4. Reaction of alkyl halides with NH_3

Codes

	A	B	C	D		A	B	C	D
(a)	2	1	3	4	(b)	4	3	1	2
(c)	3	2	4	1	(d)	4	1	3	2

24 On heating aniline with fuming sulphuric acid at 180°C, the compound formed will be

(a) aniline disulphate (b) aniline-2,4,6-trisulphonic acid
(c) sulphanilic acid (d) None of these

25 Nitration of aniline also gives *m*-nitroaniline in strong acidic medium because

(a) in electrophilic substitution reaction amino group is *meta*-directive
(b) inspite of substituents nitro group always goes to *m*-position
(c) in acidic (strong) medium aniline is present as anilinium ion
(d) None of the above

26 Which of the following will give only one monosubstituted product?

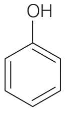
(a) *o*-dinitrobenzene (b) *m*-dinitrobenzene
(c) *p*-dinitrobenzene (d) None of these

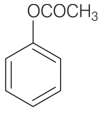
27 Acetanilide on nitration followed by alkaline hydrolysis mainly gives

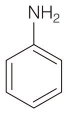
(a) *o*-nitroacetanilide (b) *p*-nitroaniline
(c) *m*-nitroaniline (d) 2, 4, 6-trinitroaniline

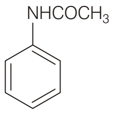
28 Which of the following compounds will give significant amount of *meta-product* during mononitration reaction?

➞ JEE Main 2017

(a) 

(b) 

(c) 

(d) 

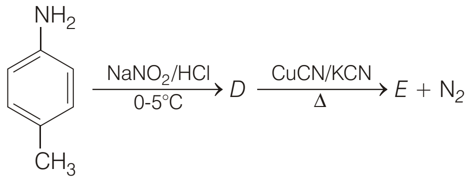
29 Benzene diazonium chloride reacts with hypophosphorous acid to produce

(a) benzene (b) phenol
(c) cyanobenzene (d) chlorobenzene

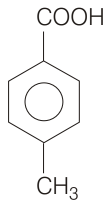
30 Fluorobenzene (C_6H_5F) can be synthesised in the laboratory

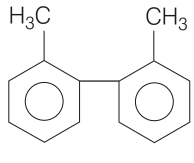
(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4
(c) by direct fluorination of benzene with F_2 gas
(d) by reacting bromobenzene with NaF solution

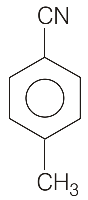
31 In the reaction,

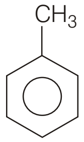


The product *E* is ➞ JEE Main 2015

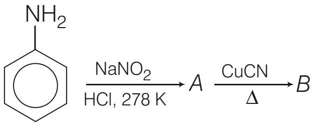
(a) 

(b) 

(c) 

(d) 

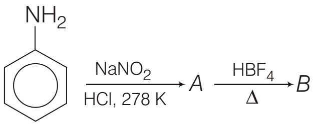
32 In the chemical reaction,



Compounds *A* and *B* respectively are

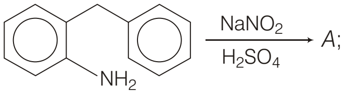
(a) fluorobenzene and phenol
(b) benzene diazonium chloride and benzonitrile
(c) nitrobenzene and chlorobenzene
(d) phenol and bromobenzene

33 In the chemical reactions,

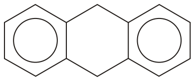
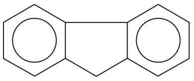
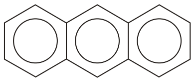
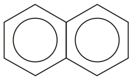


the compounds '*A*' and '*B*' respectively are ➞ **AIEEE 2010**

(a) nitrobenzene and fluorobenzene
(b) phenol and benzene
(c) benzene diazonium chloride and fluorobenzene
(d) nitrobenzene and chlorobenzene

34 

Product of this reaction is

(a) 
(b) 
(c) 
(d) 

Direction (Q. Nos. 35-36) *In the following questions, Assertion* (A) *followed by a Reason* (R) *is given. Choose the correct answer out of the following choices.*

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct incorrect and Reason is incorrect
(d) Both Assertion and Reason are incorrect

35 **Assertion** (A) Hofmann's bromamide reaction is given by primary amides.

Reason (R) Primary amines in Hofmann's bromamide reaction follows acidic hydrolysis.

36 **Assertion** (A) Acylation of amine gives a monosubstituted product whereas alkylation of amines gives polysubstituted product

Reason (R) Acyl group sterically hinders the approach of further acyl groups

Direction (Q. Nos. 37-40) *Each of these questions contains two statements :* Statement I (Assertion) *and* Statement II (Reason). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true

37 **Statement I** Amines are pyramidal in shape.

Statement II N-atom is sp^3-hybridised.

38 **Statement I** Aromatic amines are generally less basic than alkyl amines.

Statement II π-electrons in the ring decreases basic character.

39 **Statement I** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Statement II The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

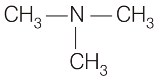
40 **Statement I** Aniline on reaction with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate.

Statement II The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation.

DAY PRACTICE SESSION 2

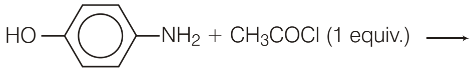
PROGRESSIVE QUESTIONS EXERCISE

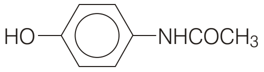
1 Compound '*A*' (C_3H_9N) reacts with benzene sulphonyl chloride to form a solid insoluble in alkali. The structure of compound '*A*' is

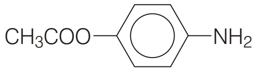
(a) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$

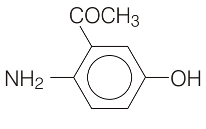
(b) $CH_3-CH_2-NH-CH_3$
(c) $CH_3-CH_2-CH_2-NH_2$
(d) All of these

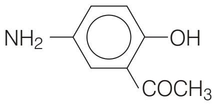
2 The main product formed in the reaction is



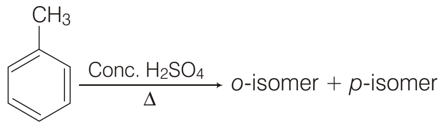
(a) 

(b) 

(c) 

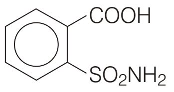
(d) 

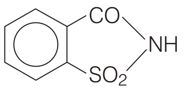
3 Consider the following reaction sequence

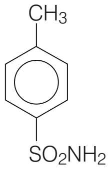


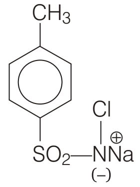
$$o\text{-isomer} \xrightarrow{PCl_5} \xrightarrow{NH_3} \xrightarrow[35°C]{aq.\ KMnO_4} \xrightarrow{\Delta} A$$

The structure of compound '*A*' is

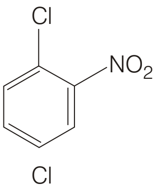
(a) 

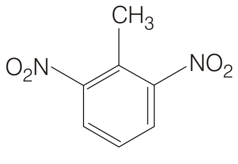
(b) 

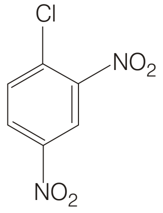
(c) 

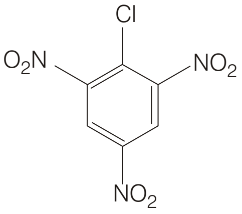
(d) 

4 A major component of Borsch reagent is obtained by reacting hydrazine hydrate with which of the following?
→ JEE Main (Online) 2013

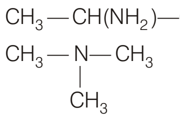
(a) 

(b) 

(c) 

(d) 

5 An organic compound containing C, H and N only was found to contain C = 61.03, N = 23.71. Its vapour density is 29.5. On treatment with nitrous acid, it gave nitrogen. The compound is

(a) $CH_3-CH(NH_2)-CH_3$
(b) $CH_3-CH_2-NH-CH_3$
(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$
(d) $CH_3-HC{=}CH-NH_2$

6 Reactants of reaction I are CH_3CONH_2, KOH, Br_2

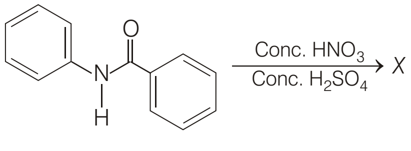
Reactants of reaction II are CH_3NH_2, $CHCl_3$, KOH

The intermediate species of reaction I and reaction II are respectively

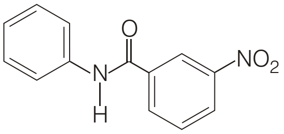
(a) carbonium ion, carbene
(b) carbene, nitrene
(c) nitrene, carbene
(d) carbocation, nitrene

7 Which of the following reactions belong to electrophilic aromatic substitution?

(a) Bromination of acetanilide
(b) Coupling reaction of aryldiazonium salts
(c) Diazotisation of aniline
(d) Both (a) and (b)

8 

The structure of the major product X is

(a) 

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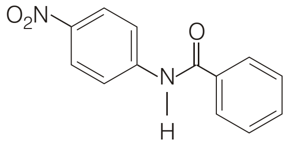

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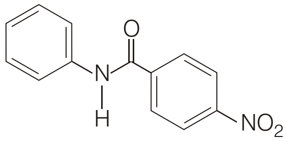

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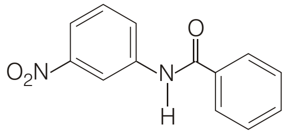

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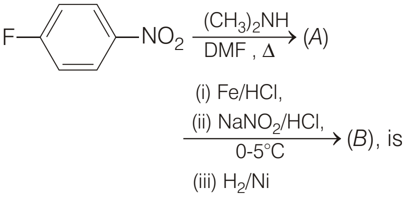

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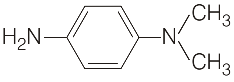

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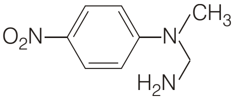

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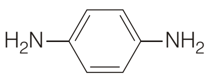

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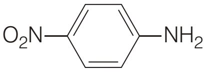


10. The best method to synthesise *m*-dibromobenzene is by using the reaction

(a) Benzene $\xrightarrow{Br_2/FeBr_3/\text{heat}}$

(b) Aniline $\xrightarrow{Br_2,\ H_2O} [\ \ ] \xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

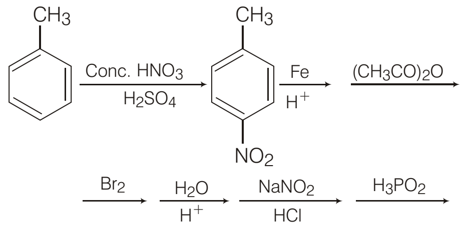
(c) Nitrobenzene $\xrightarrow[H_2SO_4,\ \Delta]{\text{Fuming } HNO_3} [\ \ ] \xrightarrow[C_2H_5OH,\ \text{heat}]{Fe/HCl} [\ \ ] \xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

(d) Bromobenzene $\xrightarrow[H_2SO_4]{HNO_3} [\ \ ] \xrightarrow[C_2H_5OH,\ \text{heat}]{Fe/HCl} [\ \ ] \xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

13 Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide solution. The reaction mixture so obtained contains

(a) mixture of *o*-and *p*-bromotoluenes
(b) mixture of *o*-and *p*-dibromobenzenes
(c) mixture of *o*-and *p*-bromoanilines
(d) mixture of *o*-and *m*-bromotoluenes

12 Consider the following reaction sequence
The final product of this reaction sequence is



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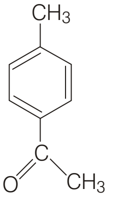

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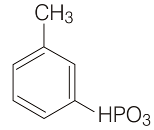

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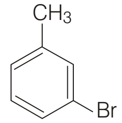

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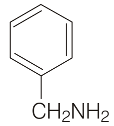
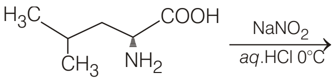


13 The major product of the reaction is



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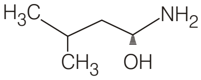

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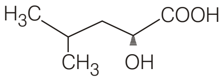

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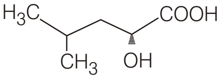

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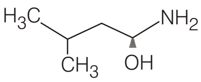


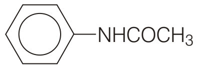
14 A compound (*X*) has the molecular formula C_7H_7NO. On treatment with Br_2 and KOH. (*X*) gives an amine (*Y*); (*Y*) gives carbylamine test. *(Y)* upon diazotisation and coupling with phenol gives an azodye (*Z*). (*X*) is

(a) $PhCONH_2$
(b) $PhCONHCOCH_3$
(c) $PhNO_2$
(d) $PhCOONH_4$

15 *(A)* is subjected to reduction with Zn-Hg/HCl and the product formed is N-methylmethanamine *(A)* can be

(a) ethane nitrile
(b) Nitroethane
(c) carbylamino ethane
(d) carbylamino methane

16 The correct order of basic strength of the following are



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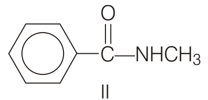
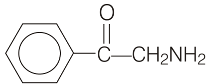
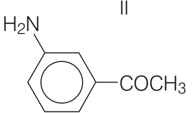


II



III



IV

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

ANSWERS

SESSION 1
1 (c) **2** (a) **3** (a) **4** (d) **5** (b) **6** (c) **7** (b) **8** (d) **9** (b) **10** (c)
11 (c) **12** (c) **13** (d) **14** (a) **15** (c) **16** (b) **17** (d) **18** (b) **19** (d) **20** (a)
21 (b) **22** (b) **23** (b) **24** (c) **25** (c) **26** (c) **27** (b) **28** (c) **29** (a) **30** (b)
31 (c) **32** (b) **33** (c) **34** (b) **35** (c) **36** (c) **37** (b) **38** (c) **39** (d) **40** (a)

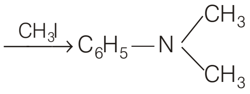
SESSION 2
1 (b) **2** (a) **3** (b) **4** (c) **5** (a) **6** (c) **7** (d) **8** (b) **9** (a) **10** (c)
11 (a) **12** (c) **13** (d) **14** (a) **15** (c) **16** (d)

Hints and Explanations

SESSION 1

1 $C_6H_5-NO_2 \xrightarrow[\text{Reduction}]{\text{Fe/HCl}} \underset{\text{Aromatic primary (1°) amine}}{C_6H_5-NH_2}$

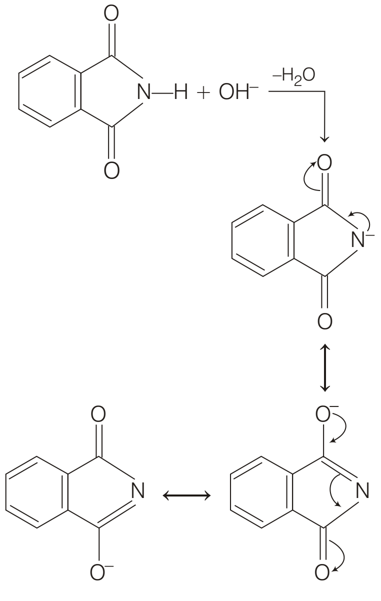
2 $C_6H_5NH_2 \xrightarrow{CH_3I} \underset{\text{Secondary amine}}{C_6H_5NHCH_3}$



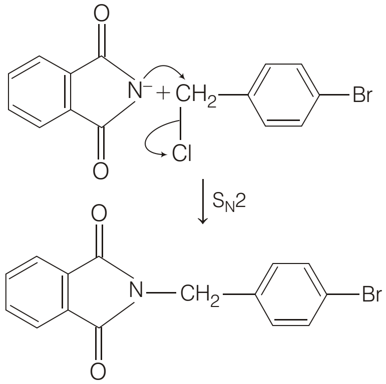
$\xrightarrow{CH_3I} C_6H_5-N\begin{matrix}CH_3\\CH_3\end{matrix}$

Tertiary amine

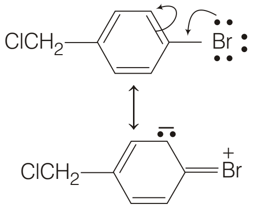
3 It is the first step of Gabriel's phthalimide synthesis, the hydrogen bonded to nitrogen is sufficiently acidic due to two α-carbonyls.



The conjugate base formed above act as nucleophile in the subsequent step of reaction. 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.



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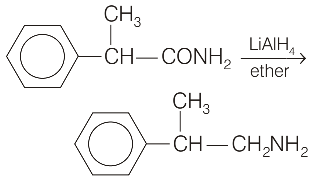


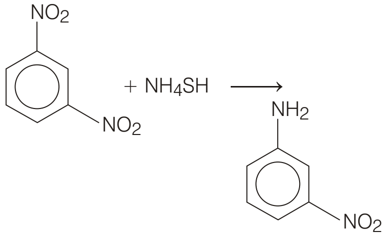
5 $\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{NaOH + Br_2} \underset{\text{Methylamine}}{CH_3NH_2}$

6 Hofmann-bromamide degradation reaction is given as:

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow RNH_2 + NaCO_3 + 2NaBr + 2H_2O$$

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

7



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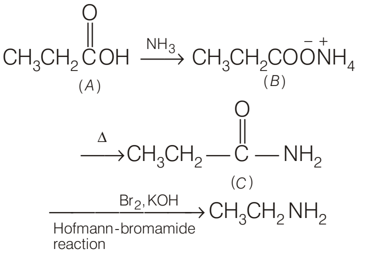


$\underset{(A)}{CH_3CH_2\overset{O}{\overset{\|}{C}}OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2COO\overset{-}{}\overset{+}{N}H_4}$
$\xrightarrow{\Delta} \underset{(C)}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2}$
$\xrightarrow[\text{Hofmann-bromamide reaction}]{Br_2, KOH} CH_3CH_2NH_2$

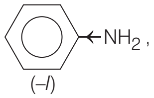
9 1° and 2° amines due to intermolecular H-bonding have higher boiling points (and hence less volatile) than 3° amines and hydrocarbons of comparable molecular mass. Further, due to polar C—N bonds, 3° amines are more polar than hydrocarbons which are almost non-polar. Therefore, due to weak dipole-dipole interactions, 3° amines have higher boiling point (i.e. less volatile) than hydrocarbons. In other words, $CH_3CH_2CH_3$ has the least boiling point and hence, is most volatile.

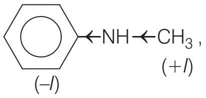
10 $(CH_3)_2$ NH acts as strong base, due to presence of two methyl groups with $+I$-effect, which intensifies negative charge on N-atom.

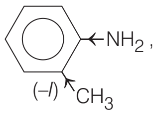
11 Dimethyl amine is the strongest base in aqueous solution due to solvation and inductive effect.

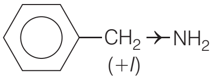
12 In gaseous state, as the number of alkyl group increases, electron density also increases and hence, the availability of electrons for donation increases, thus, basicity increases.
Hence, the correct order of basicity of amines in gaseous state is
$3° > 2° > 1° > NH_3$.

13 $—CH_3$ ($+I$-effect) increases electron density at N-atom, hence basic nature is increased. C_6H_5 decreases electron density at N-atom, thus basic nature is decreased.

(a) 

(b) 

(c) 

(d) 

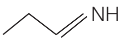
Thus, benzylamine (d) is the strongest base.

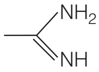
14 Order of basic strength of aliphatic amine in aqueous solution is as follows (order of K_b)

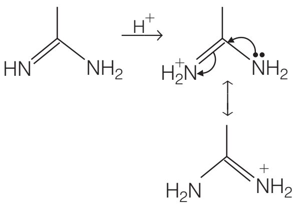
$$(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N} > C_6H_5\ddot{N}H_2$$

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.

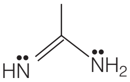
15 Among the given compounds the basic nature depends upon their tendency to donate electron pair.

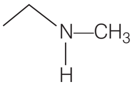
Since  is sp^2-hybridised. This marginally increases the electron negativity of nitrogen which in turn decreases the electron donating tendency of nitrogen. Thus making compound least basic.

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 become resonance stabilised.

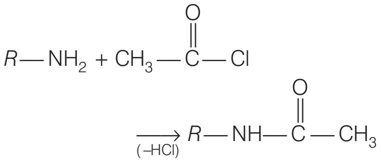


Equivalent resonance

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.

16 

$$R—NH_2 + CH_3—\overset{O}{\overset{\|}{C}}—Cl \xrightarrow[(-HCl)]{} R—NH—\overset{O}{\overset{\|}{C}}—CH_3$$

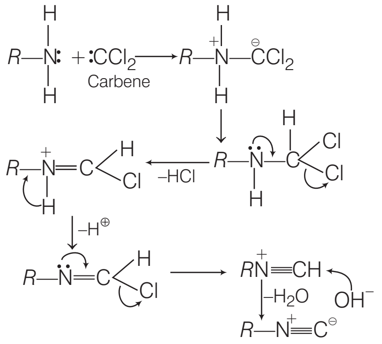
Since, each $—COCH_3$ group displace one H atom in the reaction of one mole of $CH_3—\overset{O}{\overset{\|}{C}}—Cl$ with one $—NH_2$ group, the molecular mass increases with 42 unit. Since, the mass increases by $(390 - 180) = 210$ hence the number of $—NH_2$ group is $\frac{210}{42} = 5$.

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

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

18 The mechanism of carbylamine reaction is given below :

$$CHCl_3 \xrightarrow[\alpha\text{-elimination}]{OH^-} \underset{\text{Dichlorocarbene}}{:CCl_2}$$



19 When amines reacts with an aldehyde then imines are formed.

$$R—NH_2 + R\overset{O}{\overset{\|}{C}}—H \longrightarrow R—CH=N—R\text{(Imine)}$$

20 $(C_2H_5)_2NH + HNO_2 \xrightarrow[-H_2O]{} \underset{\text{Nitrosoamine}}{(C_2H_5)_2N \cdot N=O}$

21 $C_6H_5SO_2Cl + RNH_2 \longrightarrow RNHSO_2C_6H_5 + HCl$

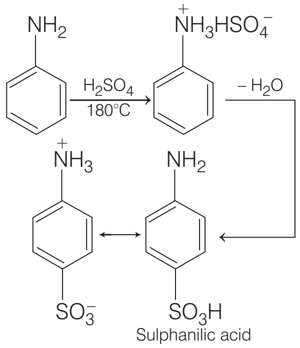
N- alkyl benzene sulphonamide (Soluble in KOH)

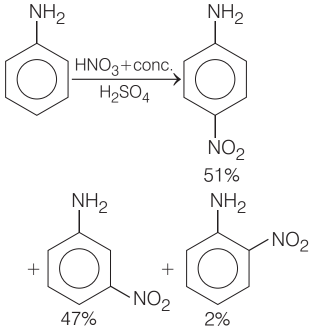
$\xrightarrow{KOH} [R—\overset{-}{N}SO_2C_6H_5]K^+ + H_2O$

22 Wurtz reaction is used to prepare alkanes from alkyl halides.

$$2R—X + 2Na \xrightarrow{\text{Dry ether}} R—R + 2NaX$$

23 A ⟶ 4; B ⟶ 3; C ⟶ 1; D ⟶ 2

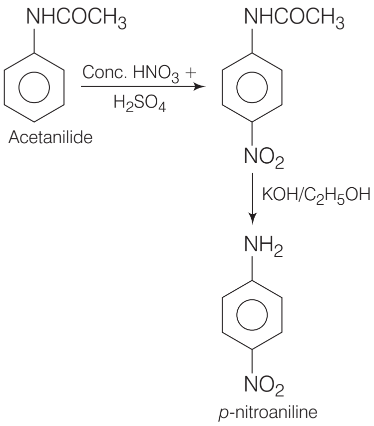
24. 

25. 

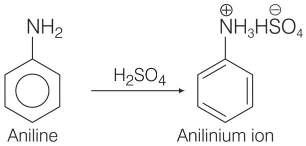
Nitration of aniline also gives *m*-nitroaniline in strong acidic medium because in strong acidic conditions, protonation of —NH_2 group gives anilinium ion (NH_3^+) which is deactivating and *m*-directive in nature.

26 The disubstituted benzene in which all the four hydrogen atoms are identical, will give only one monosubstituted product. i.e. *p*-dinitrobenzene.

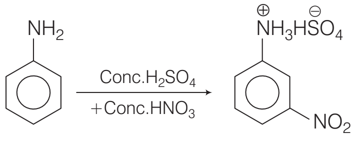
27 *p*-nitroaniline is obtained as a major product by the nitration of acetanilide followed by alkaline hydrolysis.



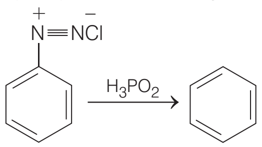
28 Aniline in presence of nitrating mixture (conc. HNO_3 + conc. H_2SO_4) gives significant amount(≈ 47%) of *meta*-product because in presence of H_2SO_4 its protonation takes place and anilinium ion is formed.



Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.



29 Benzene diazonium chloride undergoes deamination upon reaction with hypophosphorus acid and gives benzene.



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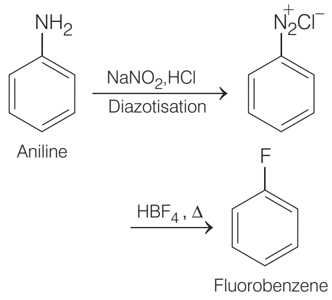

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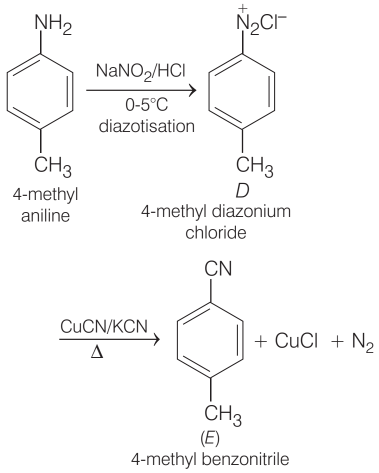
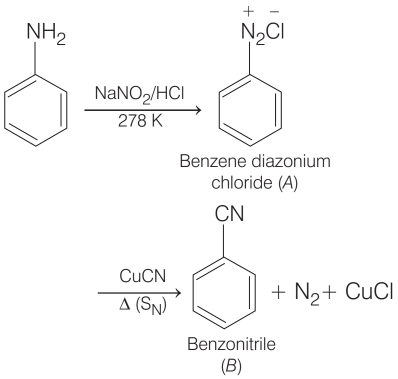


32 Formation of (*A*) is by diazotisation and formation of *B* from *A* is by S_N reaction.



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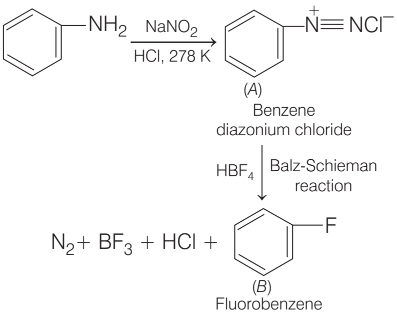

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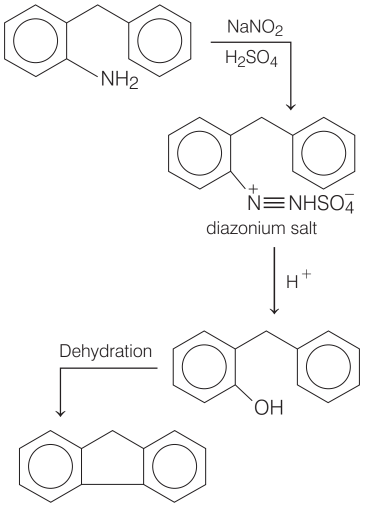


35 **Correct Reason** With Br_2 / NaOH, primary amides are converted into isocyanates which upon alkaline hydrolysis give primary amines.

36 **Correct Reason** Due to delocalisation of the lone pair of electrons of the N-atom over the carbonyl group in the acyl derivative, the electron density on the N-atom decreases to such an extent that it does not act as a nucleophile at all and hence, does not react with another molecule of the acylating agent.

37 It is true that nitrogen atom in amine is sp^3-hybridised but due to the presence of lone pair of electrons, the angle C—N—*E* (where, *E* is C or H) is less than 109.5°. It is 108° in case of trimethyl amine (pyramidal shape).

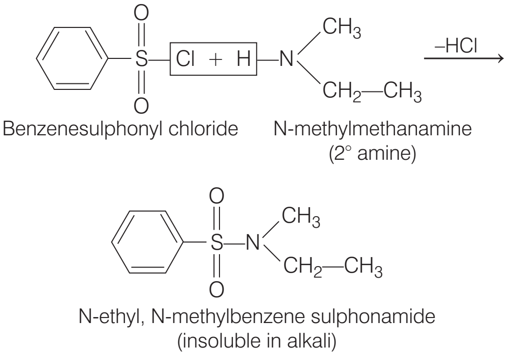
38 Aromatic amines are less basic than alkyl amines and ammonia due to the electron withdrawing nature of the aryl group. π-electrons are responsible for resonance effect.

39 In strongly acidic medium, aniline gets protonated, so lone pair of electrons are not available to produce mesomeric or electromeric effects. Thus, aniline becomes less reactive.

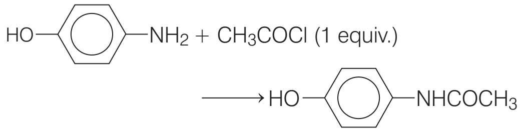
40 Aniline on reaction with $NaNO_2$ + HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate is due to the extended conjugation.

SESSION 2

1



2 —NH_2 is more activated than —OH. Hence, —NH_2 is attacked by CH_3COCl.



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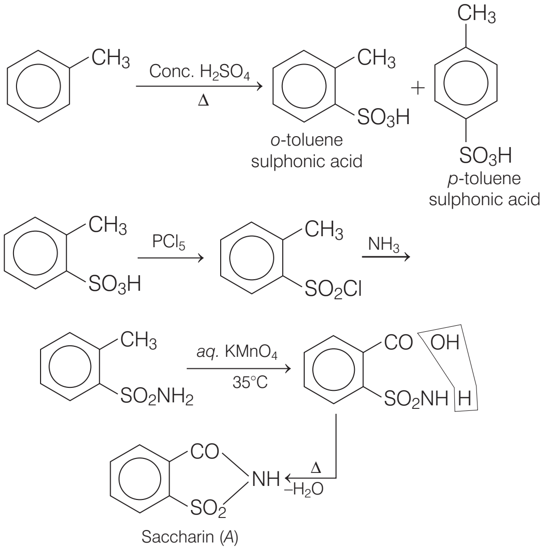
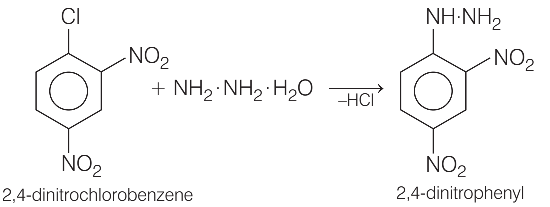


4 Borsch reagent is 2,4-dinitrophenyl hydrazine, thus, it is obtained by treating 2,4-dinitrochlorobenzene with hydrazine hydrate.



5. (i) For empirical formula

Element	%	Molar ratio	Simplest ratio
C	61.03	$\frac{61.03}{12} = 5.08$	$\frac{5.08}{1.69} = 3$
H	15.26	$\frac{15.26}{1} = 15.26$	$\frac{15.26}{1.69} = 9$
N	23.71	$\frac{23.71}{14} = 1.69$	$\frac{1.69}{1.69} = 1$

$\therefore$ Empirical formula is C_3H_9N and empirical formula weight = 59

Given, molecular weight = Vapour density × 2 = 29.5 × 2 = 59

$$\therefore \quad n = \frac{59}{59} = 1$$

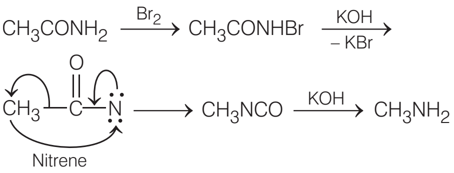
$\therefore$ Molecular formula is C_3H_9N.

(ii) The amine loses N_2 on treatment with HNO_2 and thus, it is a primary amine. Thus, compound is

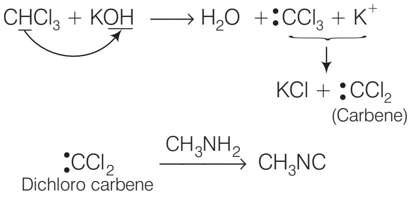
$CH_3—CH_2—CH_2—NH_2$ (Propanamine) or $CH_3—CH(NH_2)—CH_3$ (Propan-2-amine)

$$(CH_3)_2CHNH_2 + HNO_2 \longrightarrow N_2 + (CH_3)_2CHOH + H_2O$$

6 Reaction I

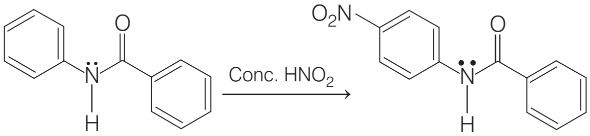


Reaction II

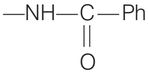


7 Bromination of acetanilide and coupling reactions of diazonium salts both are the examples of electrophilic substitution reaction.

8



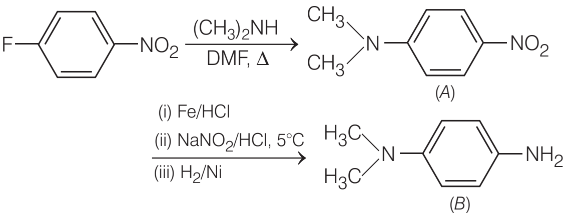
Since, ring 1 is more active, electrophilic substitution takes place over ring 1. Further more



$—NH—\underset{\underset{O}{\|}}{C}—Ph$

is *ortho-para* directing in nature and *para* product is predominating.

9



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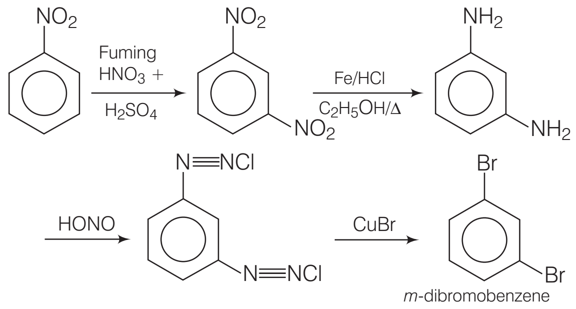

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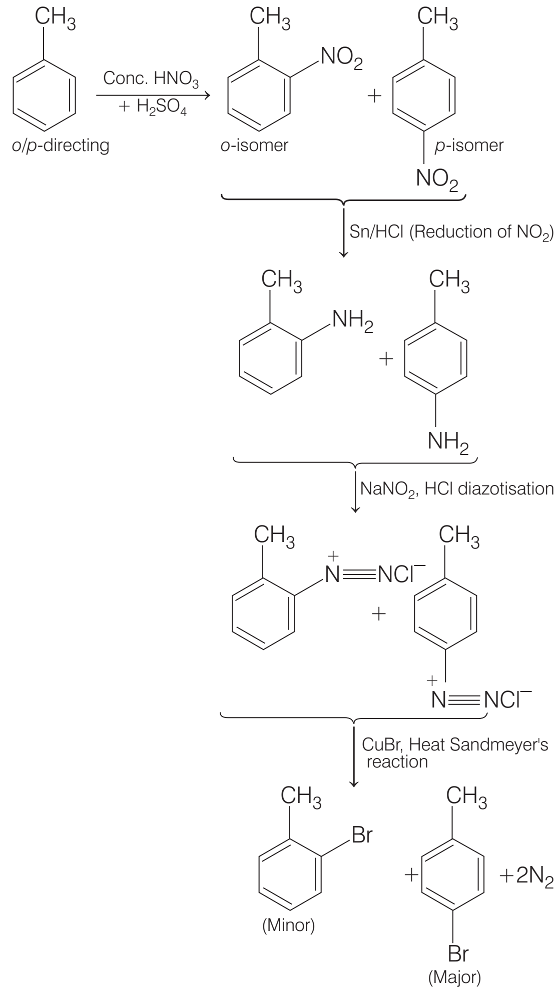
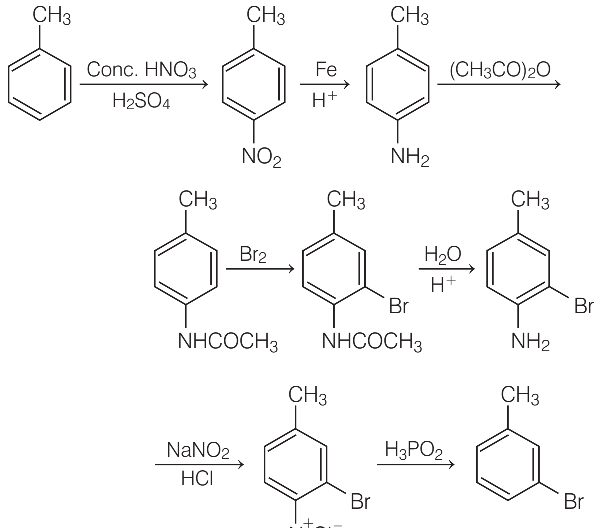


o- and *p*-bromotoluenes

12



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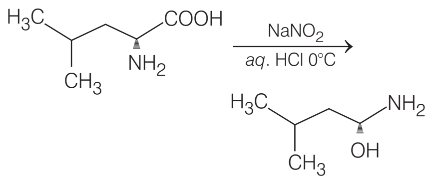

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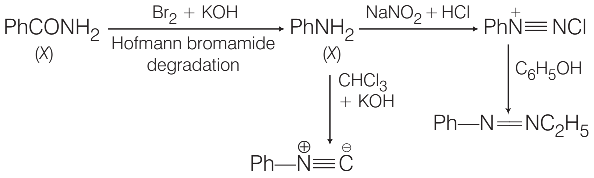

15 CH_3NC (carbylamino methane) when subjected to reduction with Zn-Hg/HCl forms N-methyl methanamine

$$CH_3 — NC \xrightarrow[HCl]{Zn\text{-}Hg/} CH_3NHCH_3$$

16 Electron releasing groups increase the basic strength of amines whereas, electron withdrawing groups decrease it. Therefore, III > II > I > IV, since in $NHCOCH_3$, —NH group is placed between two electron withdrawing groups.