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NEET SYLLABUS

Amines : Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary secondary and tertiary amines. **Cyanides and Isocyanides** (will be mentioned at relevant places) **Diazonium salt** : preparation, chemical reactions and importance in synthetic organic chemistry.

OBJECTIVES

After studying this unit, we will be able to :

- *Describe amines as derivatives of ammonia having a pyramidal structure;*
- *Classify amines as primary, secondary and tertiary;*
- *Name amines by common names and IUPAC system;*
- *Describe some of the important methods of preparation of amines;*
- *Explain the properties of amines;*
- *Distinguish between primary, secondary and tertiary amines;*
- *Describe the method of preparation of diazonium salts and their importance in the synthesis of a series of aromatic compounds including azo dyes.*

*"Learning gives creativity
Creativity leads to thinking
Thinking provides knowledge
Knowledge makes you great."*

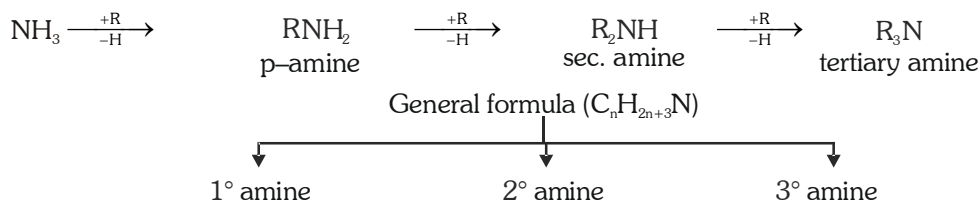
A.P.J. Abdul Kalam

NITROGEN CONTAINING COMPOUND

1.0 Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl group(s).

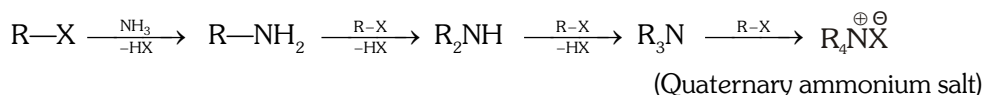
Amines are classified as primary, secondary and tertiary depending on the number of alkyl groups attached to nitrogen atom.



2.0 General methods of preparation

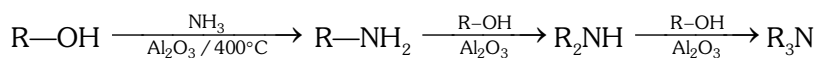
(1) Ammonolysis of alkyl halides and alcohols :

(a) **From Ammonolysis of alkyl halides [Hofmann's ammonolysis]** : When an aqueous solution of ammonia is heated with alkyl halide all the three types of amines and quaternary ammonium salt are formed.



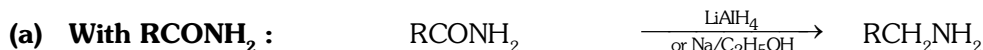
If ammonia is taken in excess, 1° amine is the main product.

(b) **Ammonolysis of alcohols** : When ROH and NH₃ are passed over Al₂O₃ or ThO₂ at 350° C all the three types of amines are formed.



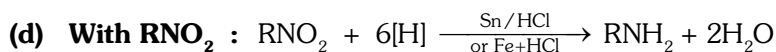
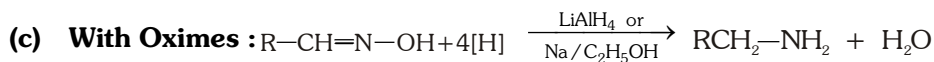
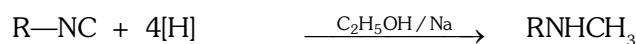
- Quaternary ammonium hydroxide is not formed.
- If excess of ammonia is used, then main product will be primary amine.

(2) By reduction :



This reaction (b) is called mendius reaction.

The reduction of alkyl isocyanides gives secondary amines.



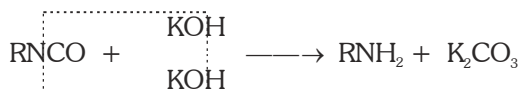
Sn/HCl is used in laboratory preparation

(3) By hydrolysis of :

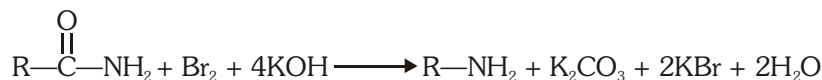
(a) **R-NC** : Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.



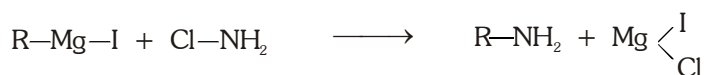
(b) **RNCO** : Alkyl isocyanate undergoes hydrolysis on heating with KOH and forms alkyl amine.



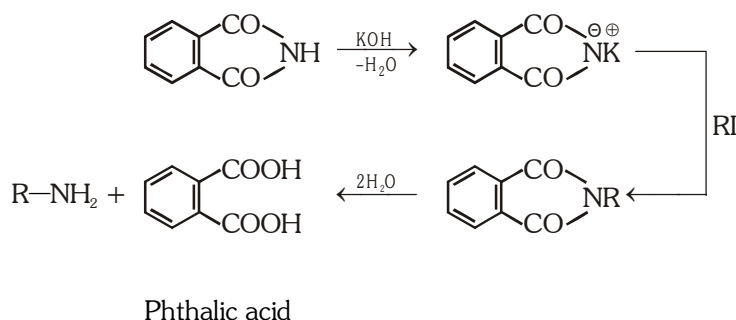
(4) **By Hofmann's bromamide reaction (Hofmann's Hypobromite reaction)** : This is a general method for the conversion of alkanamides into primary amines having one less carbon.



(5) **From Grignard reagent** : Alkyl magnesium iodide reacts with chloramine to yield alkyl amine.

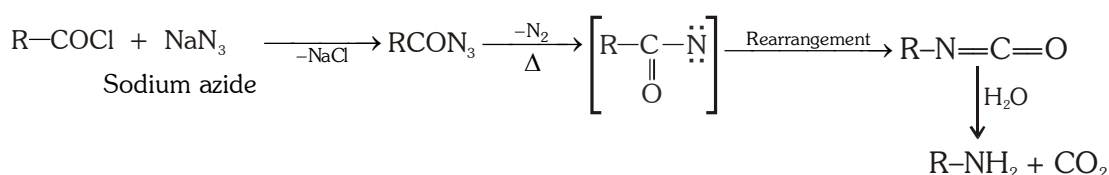


(6) **Gabriel phthalimide synthesis** : Phthalimide is first treated with KOH to obtain potassium phthalimide which is then treated with alkyl iodide. Then alkyl phthalimide on hydrolysis yields alkylamine. This method is used in the formation of pure aliphatic primary amines.

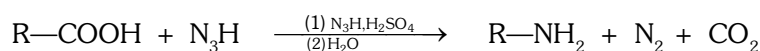


* Aniline is not formed by this reaction.

(7) **Curtius reaction** :

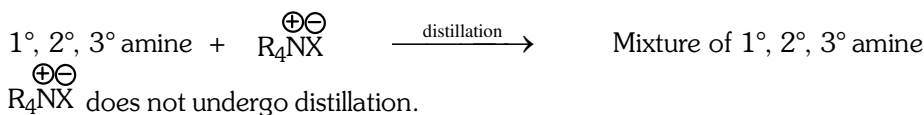


(8) **Schmidt reaction** : In presence of conc. H₂SO₄ alkanic acid reacts with hydrazoic acid (N₃H) followed by hydrolysis to yield alkylamine.



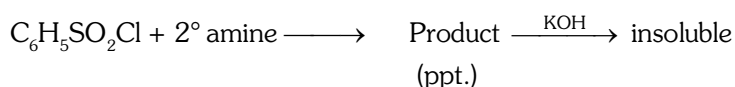
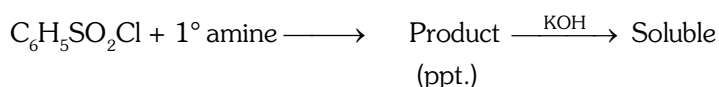
GOLDEN KEY POINTS

• Separation of 1°, 2° and 3° amines



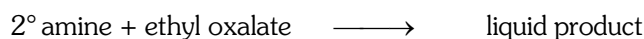
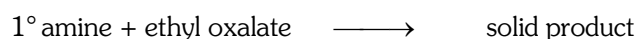
Mixture of 1°, 2°, 3° amine can be separated by following methods.

- (i) **Fractional distillation** : The mixture of amines may be separated by fractional distillation because their boiling points are quite different. It is used in industry.
- (ii) **Hinsberg method** : In this method mixture of amines is separated by using benzene sulphonyl chloride (Hinsberg's reagent).



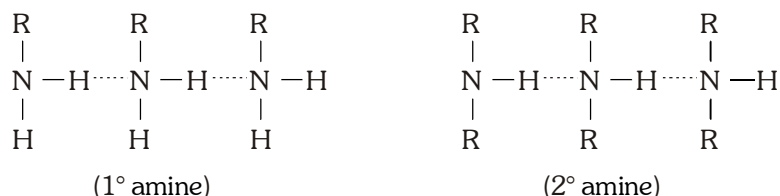
3° amine does not react with benzene sulphonyl chloride. (No ppt. formed)

- (iii) Hofmann method :** In this method mixture of amines is separated by using ethyl oxalate.



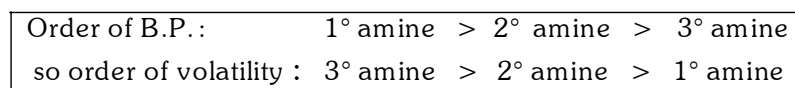
3.0 PHYSICAL PROPERTIES

- (i) CH_3NH_2 is gas and $\text{C}_2\text{H}_5\text{NH}_2$ is a volatile liquid.
- (ii) Higher amines have fishy smell.
- (iii) H – Bonding (weaker as compared to $\text{H} - \text{O} - \text{H}$).

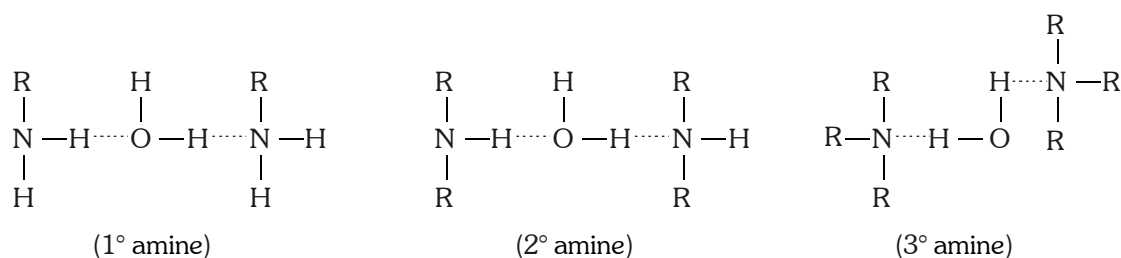


In 3° amine (due to absence of H-atom) H-bonding is not possible.

- (iv) **Boiling point :** Due to weak intermolecular H-bonding the B.P. of 1° and 2° amines are lower than those of alcohols of comparable molecular weight. The boiling point of 3° amines which form no H-bonds are near to those of alkanes of comparable molecular weight.

Boiling point $\propto$ molecular weight

- (v) **Solubility:** Low molecular weight amines are soluble in water. The water solubility of amines decreases with increasing size of alkyl group.



Order of solubility $\longrightarrow$ p- amine > s- amine > t- amine

4.0 Chemical properties

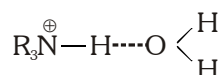
- (i) Basic character of amines is due to the presence of lone pair of electrons on the N - atom.
- (ii) Basic strength depends on electron donating tendency.
- (iii) Order of basic character in aqueous solution : $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
 $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$

GOLDEN KEY POINTS

- Tertiary amine is less basic than secondary due to following reasons :
 - (i) **Steric hindrance** : In tertiary amines (R_3N), three alkyl groups attached to N are bulkier and as such exert steric hindrance.

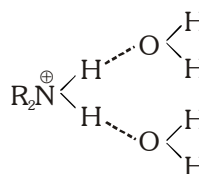
- (ii) **Decrease in hydration** :

In tertiary amine



Protonated t-amine can form H-bonding with water molecule only at one point
[less stable]

In secondary amine



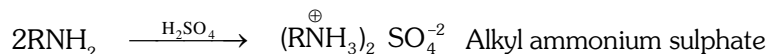
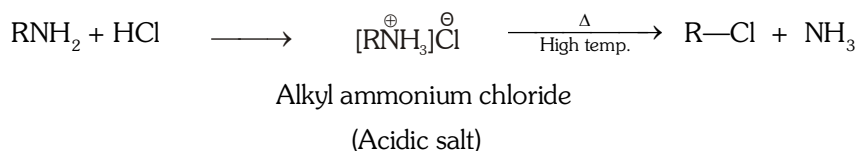
Protonated s-amine can form H-bonding with water molecules at two points
(more stable)

Conjugate acid of 3° amine are less stable as compared to 2° amine due to low hydration so less basic.

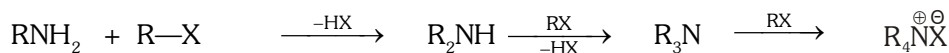
- The basic strength of aniline is less than aliphatic amines as the lone pair of electron present on N-atom interact with the delocalized π - orbital of benzene ring. Hence it is less available for protonation on N-atom.

(1) Reactions showing basic nature :

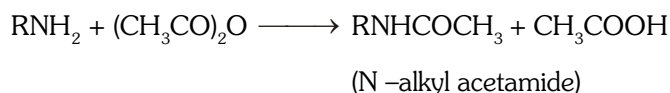
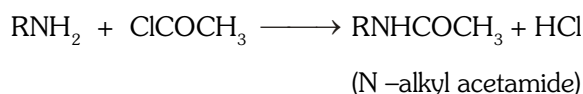
It reacts with acids to form salts.



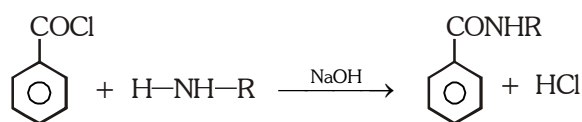
- (2) **Reaction with alkyl halides** : Alkyl amine reacts with alkyl halides and form sec., ter. amines and quaternary ammonium salt.



- (3) **Acetylation** : Acetylation takes place when alkyl amine combines with acetyl chloride or acetic anhydride.



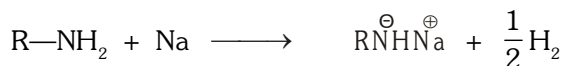
(4) Benzoylation (Schotten Baumann reaction) :



Benzoylchloride

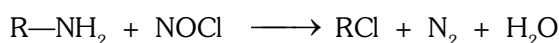
N-alkyl benzamide

(5) Acidic nature : Amines are very weak acids only 1° and 2° amines show acidic nature with active metals.

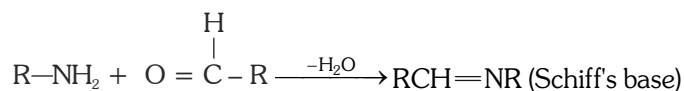


N- alkyl sodamide

(6) Reaction with Tilden reagent :

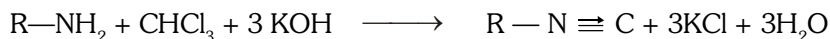


(7) Reaction with aldehydes :

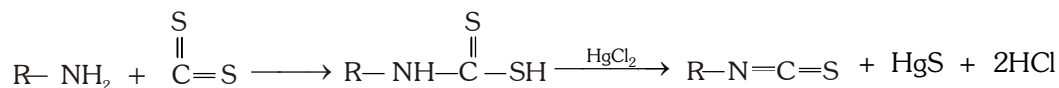


(8) Carbylamine Reaction (Isocyanide test) : When alkyl amine heated with chloroform and alc. KOH alkyl isocyanide is formed which has very bad smell.

This test is also given by aniline . This is a test for p- amines.



(9) Hofmann's mustard oil test : When alkyl amine is heated with carbon disulphide and mercuric chloride alkyl isothiocyanate is formed which has smell like mustard oil.



Alkyl isothiocyanate

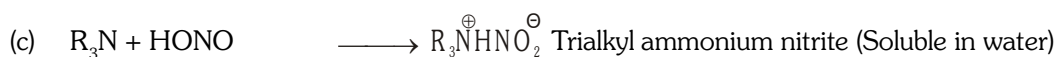


(10) Reaction with HNO₂ :

(a) Primary amines react with nitrous acid to produce nitrogen gas [seen as bubbles]

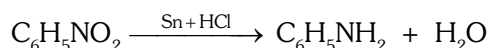
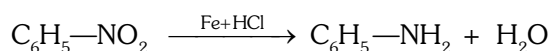
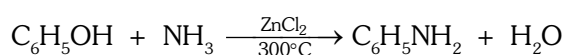
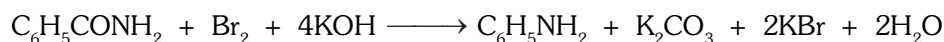
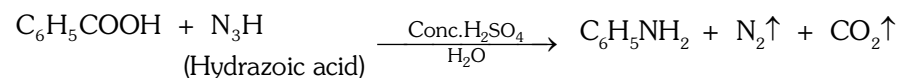
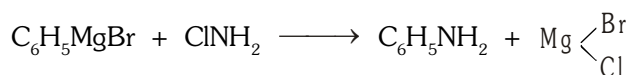


Dialkylnitroso amine (Yellow oily layer)



Points to Remember :

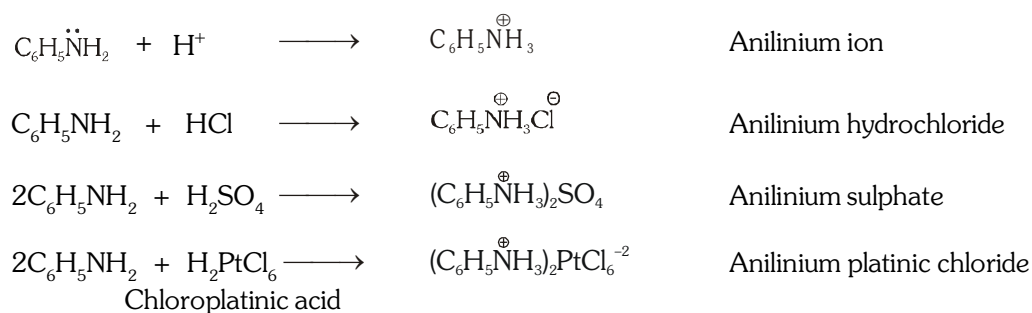
- (i) Nitrosoamines are carcinogens (Cancer causing agents)
- (ii) Amines can have chiral N-atom but cannot be resolved into enantiomeric forms because of rapid inversion of one enantiomeric form into the other.
- (iii) The Schiff's bases formed by reaction of 1° amines and aldehyde/ketones are also called anils.
- (iv) The mixture of 1°, 2°, 3° amines can be distinguished by Hofmann's test or Hinsberg's reagent or nitrous acid test.

5.0 ANILINE (C₆H₅NH₂)**5.1 General Methods of Preparation****(1) Lab method:****(2) Industrial method :****(3) From Phenol :****(4) From benzamide (Hofmann's bromamide reaction):****(5) From benzoic acid (Schmidt reaction) :****(6) From Grignard reagent :****(7) From phenyl isocyanide :****5.2 Physical Properties**

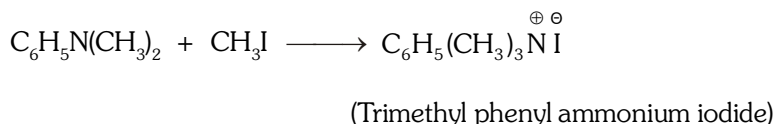
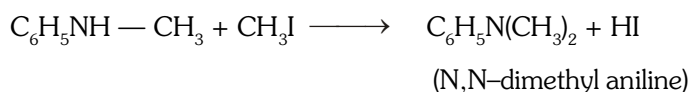
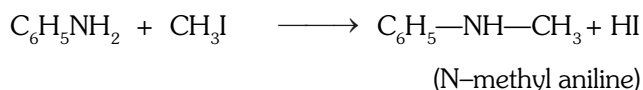
- (i) Fresh, aniline is a colourless oily liquid. On standing the colour becomes dark brown due to action of air and light.
- (ii) It's B.P. is 183°C.
- (iii) It is heavier than water.
- (iv) It has characteristic unpleasant odour. It is toxic in nature.

Reactions due to —NH₂ group

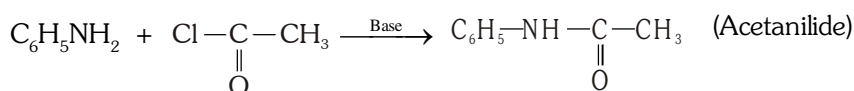
(1) Basic nature : Aniline is weak base but it forms salt with strong acids. It accepts a proton.



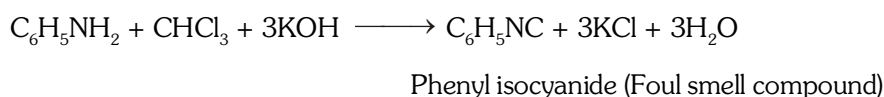
- (2) **Alkylation** : Aniline reacts with alkyl halides forming secondary, tertiary and quaternary ammonium salts depending on the concentration of alkyl halides.



- (3) **Acylation** : Aniline reacts with acid chlorides or anhydrides to form corresponding amides called anilides. [The reaction of $\text{C}_6\text{H}_5\text{NH}_2$ with benzoyl chloride is example of "**Schotten Baumann reaction**"]



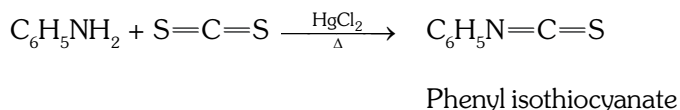
- (4) **Carbylamine reaction** :



Note : (1) Intermediate species is dichloro carbene [$:\text{CCl}_2$].

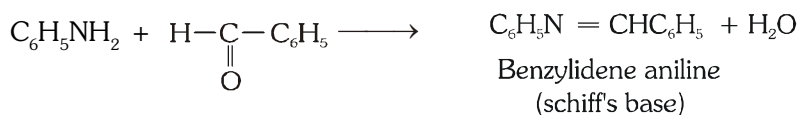
(2) This is test of aniline and other primary amine, known as **Isocyanide test**.

- (5) **Hoffmann's mustard oil reaction** : When aniline is heated with alc. CS_2 and excess of HgCl_2 phenyl isothiocyanate having a characteristic smell of mustard oil is formed.

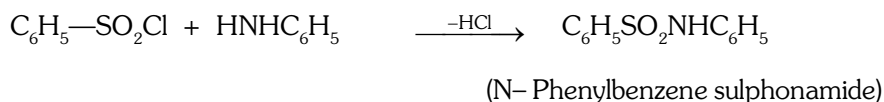


This is a test of aniline and other primary amines.

- (6) **Reaction with aldehydes** : Aniline condenses with aldehydes to form schiff's base.



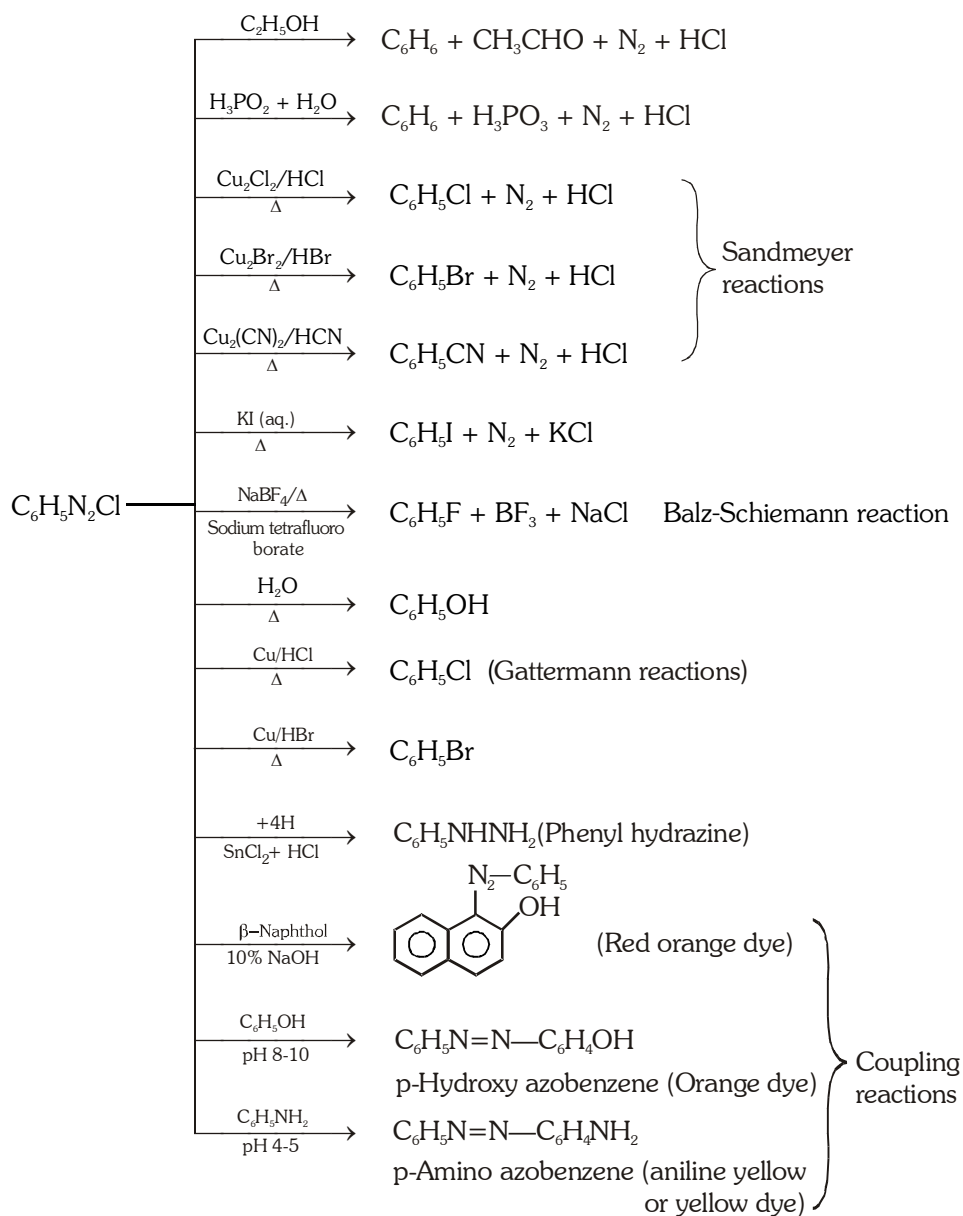
- (7) **Reaction with Hinsberg's reagent** :



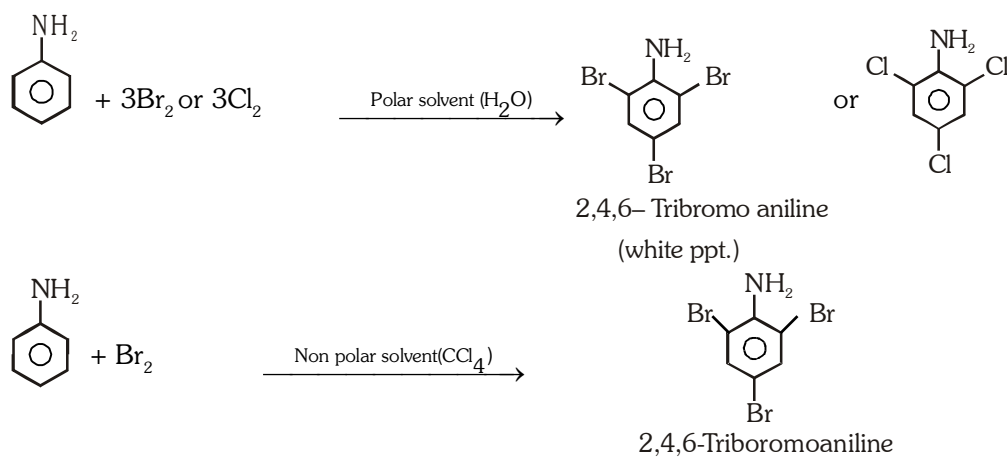
- (8) **Diazotisation** : Diazotisation is a reaction in which ice cooled solution of aniline in an inorganic acid reacts with sodium nitrite solution leading to the formation of diazonium salt.



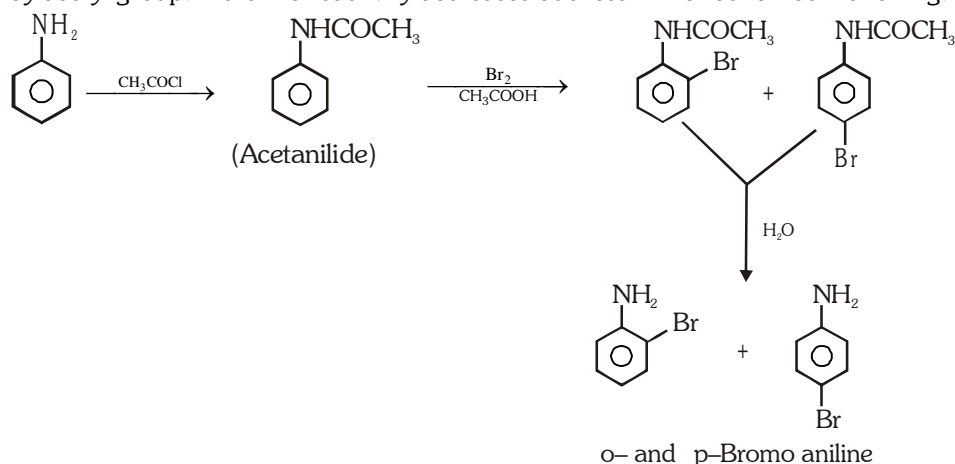
Benzene diazonium chloride is a useful synthetic reagent. It is used in the preparation of many organic compounds



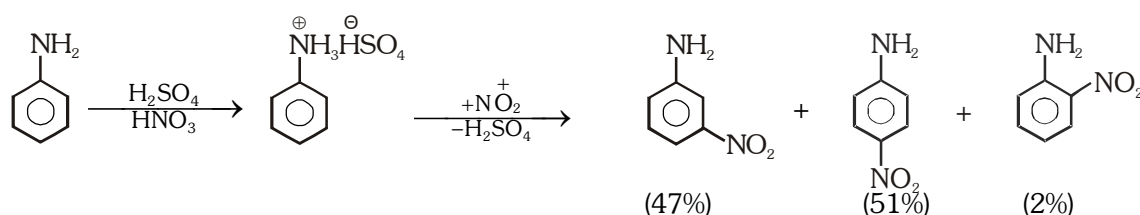
(1) Halogenation : In polar and nonpolar medium Chlorine and bromine react with aniline and form trichloro and tribromo aniline respectively.



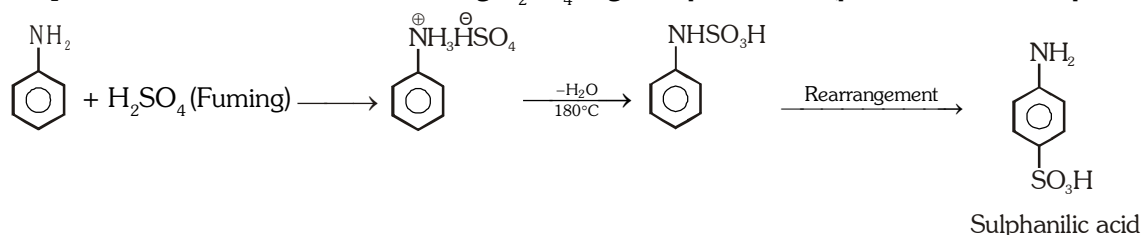
Note : However, monobromo or chloro derivative of aniline can be prepared if $-NH_2$ group is first protected by acetyl group. Here the reactivity decreases due less +M effect on benzene ring.



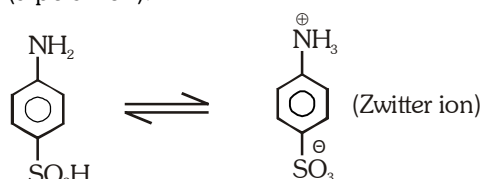
(2) Nitration :



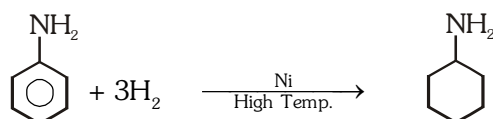
(3) Sulphonation : Aniline reacts with fuming H_2SO_4 to give sulphanilic acid. (p-Amino-benzene sulphonic acid)



- This process is called baking.
- Sulphanilic acid is an important intermediate in the manufacturing of dyes and drugs.
- The compounds in which both proton donating & proton accepting groups present are called amphotile (dipolar ion).

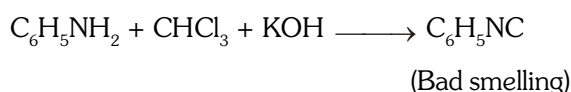


(4) Catalytic hydrogenation : Aniline undergoes hydrogenation in presence of Ni at high temp. to form cyclohexanamine.



5.3 Tests of Aniline

(i) Carbylamine test : Aniline gives carbylamine test or Isocyanide test.



(ii) Dye test : Aniline is first diazotised. On adding alkaline solution. of β -naphthol to the diazotised product a red-orange dye is formed.

(iii) On heating with bromine water, a white ppt. is formed.

BEGINNER'S BOX-1

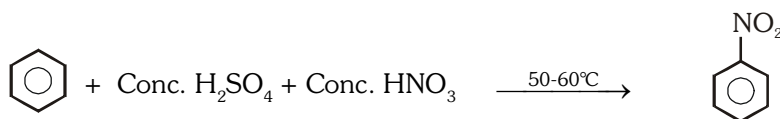
- Which one of following reaction is Schotten–Baumann reaction
 (1) Acetylation of RNH_2 (2) Acylation of RNH_2
 (3) Benzoylation of RNH_2 (4) All of them
- Which of the following pair will yield primary amine on hydrolysis
 (1) CH_3NCO , CH_3NC (2) CH_3CN , CH_3NC
 (3) $(\text{CH}_3)_2\text{NH}$, $\text{CH}_3\text{—CH=NOH}$ (4) None of the above
- Methylamine on treatment with chloroform and ethanolic caustic alkali gives foul smelling compound, the compound is
 (1) CH_3NCO (2) CH_3CNO (3) CH_3CN (4) CH_3NC

6.0 NITRO BENZENE [$\text{C}_6\text{H}_5\text{NO}_2$]

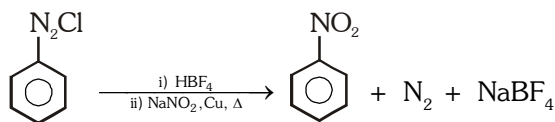
It is also called as artificial oil of bitter almonds or oil of mirbane as its odour is like that of bitter almonds.

6.1 General Methods of Preparation

(1) Lab method :



(2) From diazonium salt :



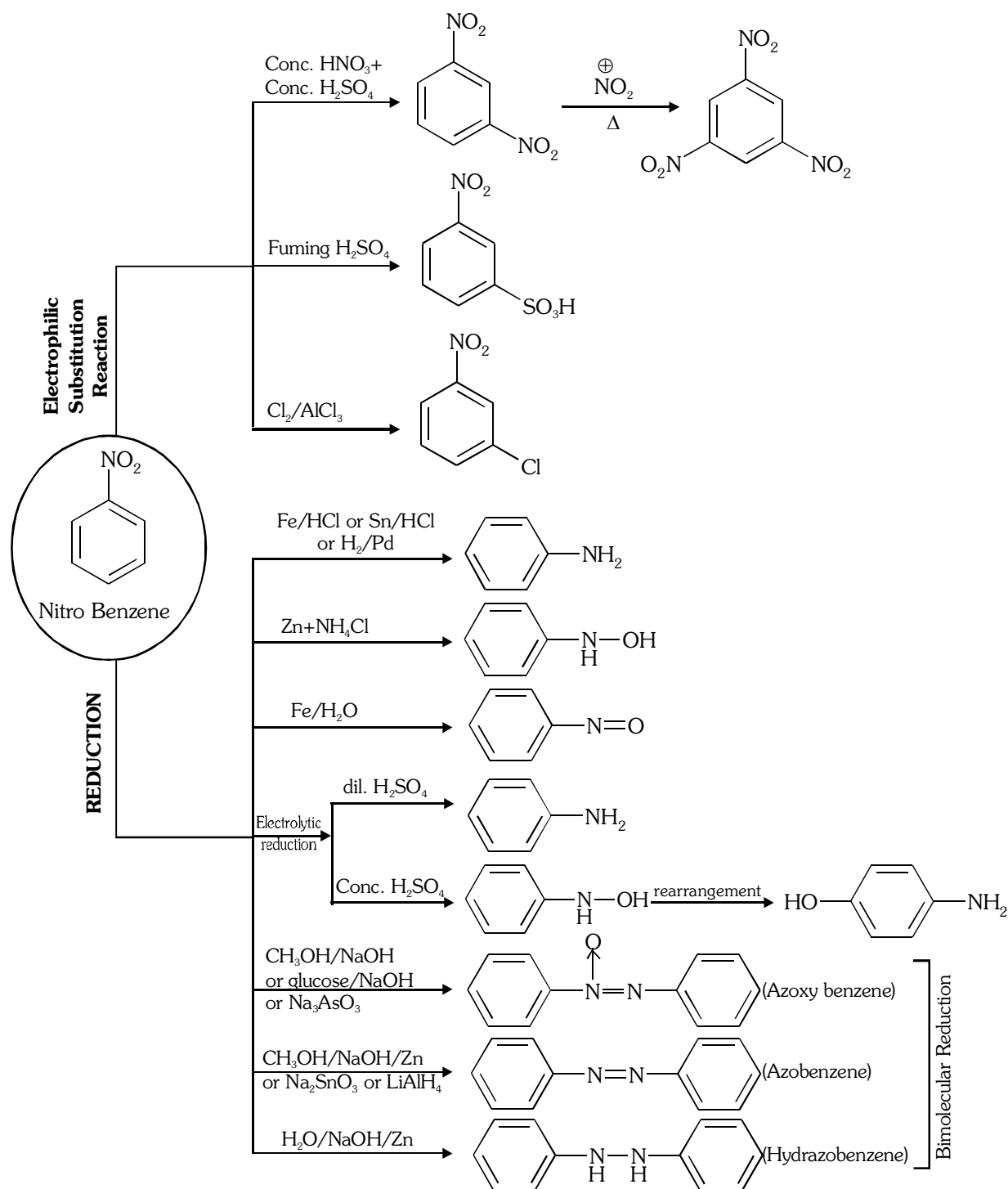
6.2 Physical Properties

- Nitro benzene is light yellow oily liquid
- It has smell of bitter almonds
- It is steam volatile. Its vapours are poisonous in nature.
- It is heavier than water
- It's B. P. is 211°C
- Smell of nitro benzene and benzaldehyde is same

6.3 Chemical Properties

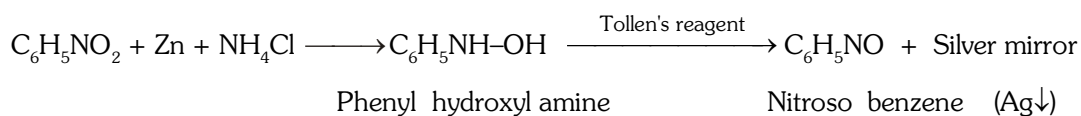
Nitrobenzene shows following chemical reactions –

- Reactions due to NO_2 group.
- Reactions due to benzene ring : (A) Electrophilic substitution (B) Nucleophilic substitution



6.4 Test of Nitrobenzene

Mullikan Barker Test : Ethanolic solution of nitrobenzene is treated with zinc dust and NH_4Cl solution. The mixture is heated and filter in a test tube containing Tollen's reagent a grey or black precipitate (Ag mirror) is formed.

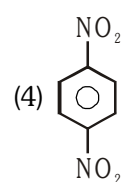
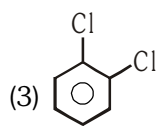
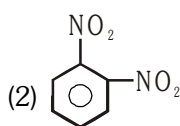
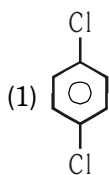


6.5 Uses

- (i) As a solvent
- (ii) In manufacture of aniline and azo dye

BEGINNER'S BOX-2

- Nitration of which of the following compound is difficult :-
 (1) Benzene (2) Nitrobenzene (3) Toluene (4) Phenol
- Nitration of nitrobenzene in presence of fuming nitric acid will generate a :-
 (1) Solid product (2) Gaseous product (3) Semi-solid product (4) Liquid product
- $C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{NaNO_2/HCl} B$; To obtain benzene from B, the suitable reagent is :
 (1) $SnCl_2 + HCl$ (2) H_3PO_2 (3) $C_2H_5N_2Cl$ (4) Methanol
- When nitrobenzene is heated with conc. HNO_3 and conc. H_2SO_4 the product would be obtained :-
 (1) T.N.T. (2) D.N.B. (3) D.D.T. (4) T.E.L.
- Which of the following has the maximum value of dipole moment ?



ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3							
	Ans.	4	1	4							

BEGINNER'S BOX-2	Que.	1	2	3	4	5					
	Ans.	2	1	2	2	2					

EXERCISE-I (Conceptual Questions)

Build Up Your Understanding

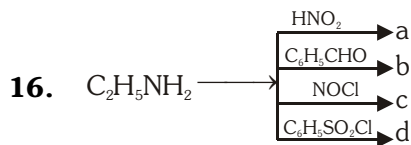
AMINE

- Among the following which one is not formed in Hoffmann degradation
 (1) RNCO (2) $\text{R}-\ddot{\text{N}}\text{H}_2$
 (3) RCONHBr (4) RNC
- $\text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow[\text{Br}_2]{\text{NaOH}} \text{A}$,
 Aqueous solution of A
 (1) Turns blue litmus to red
 (2) Turns red litmus to blue
 (3) Does not affect the litmus
 (4) Decolourise the litmus
- Ethanamine can be obtained if the following compound is heated with $[\text{KOH} + \text{Br}_2]$
 (1) Ethanamide (2) Methanamide
 (3) Propionamide (4) All the above
- $\text{CH}_3\text{CONH}_2 \xrightarrow[\text{I}]{\text{P}_2\text{O}_5} \text{A} \xrightarrow[\text{II}]{\text{Na/EtOH}} \text{B}$
 Reaction II is called
 (1) Clemensen
 (2) Stephen
 (3) Mendius
 (4) Bauveault-blank reduction
- CH_3CONH_2 , Br_2 & KOH give CH_3NH_2 as the product. The intermediates of the reaction are :-
 (a) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHBr}$ (b) $\text{CH}_3-\text{N}=\text{C}=\text{O}$
 (c) CH_3NHBr (d) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{N} \begin{matrix} \text{Br} \\ \text{Br} \end{matrix}$
 The correct answer is :-
 (1) a, b (2) a, c (3) b, d (4) c, d
- In which case alkylamine is not formed :-
 (1) $\text{R}-\text{X} + \text{NH}_3 \longrightarrow$
 (2) $\text{R}-\text{CH}=\text{NOH} + [\text{H}] \xrightarrow[\text{alc.}]{\text{Na}}$
 (3) $\text{R}-\text{CN} + \text{H}_2\text{O} \xrightarrow{\text{H}^+}$
 (4) $\text{RCONH}_2 + 4[\text{H}] \xrightarrow{\text{LiAlH}_4}$

- Tertiary amine is obtained in the reaction :-
 (1) Aniline $\xrightarrow{\text{CH}_3\text{I}} \xrightarrow{\text{CH}_3\text{I}}$
 (2) Aniline $\xrightarrow{\text{CH}_3\text{I}}$
 (3) Nitrobenzene $\xrightarrow{\text{Sn/HCl}}$
 (4) None of the above
- $\text{C}_2\text{H}_5\text{NH}_2$ cannot be prepared by the reduction of
 (1) $\text{C}_2\text{H}_5\text{NO}_2$ (2) $\text{CH}_3\text{CH}=\text{NOH}$
 (3) $\text{C}_2\text{H}_5\text{NC}$ (4) CH_3CN
- Gabriel reaction for the synthesis of amines, involves the use of
 (1) 1° amide (2) 2° amide
 (3) Imides (4) Aliphatic amide
- Gabriel phthalimide reaction is used in the synthesis of
 (1) Primary aromatic amines
 (2) Secondary amines
 (3) Primary aliphatic amines
 (4) Tertiary amines
- The reaction : $[\text{C}_2\text{H}_5\text{Br} + \text{NH}_3]$ is in fact an example of
 (1) Ammonolysis only
 (2) Nucleophilic substitution only
 (3) Ammonolysis as well as nucleophilic substitution
 (4) None
- Melting points are normally the highest for
 (1) Tertiary amides (2) Secondary amides
 (3) Primary amides (4) Amines
- Solubility of ethylamine in water is due to
 (1) Low molecular weight
 (2) Ethyl group is present in ethyl alcohol
 (3) Formation of H-bonding with water
 (4) Being a derivative of ammonia
- Which of the following compound liberates CO_2 when treated with NaHCO_3
 (1) $\text{CH}_3\text{COCH}_2\text{NH}_2$ (2) CH_3NH_2
 (3) $(\text{CH}_3)_4\text{NOH}^\oplus$ (4) $\text{CH}_3\text{NH}_3^\oplus\text{Cl}^\ominus$

15. The product obtained by the alkaline hydrolysis of $C_2H_5-N=C=O$ when treated with t-butyl magnesiumbromide, the compound obtained will be

(1) t-butylamine (2) n-butylamine
(3) Isobutane (4) n-butane



Which product is a Schiff's base :-

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

17. Acidic nature of amino group is shown by the reaction :-

(1) $R-NH_2 + NOCl \rightarrow RCl + N_2 + H_2O$
(2) $2RNH_2 + 2Na \rightarrow 2RNH.Na + H_2$
(3) $R.CH_2NH_2 + HNO_2 \rightarrow R.CH_2OH + N_2 + H_2O$
(4) $R.NH_2 + HCl \rightarrow R^+NH_3^- Cl^-$

18. The reagent used in the conversion of $C_2H_5NH_2$ to C_2H_5Cl would be

(1) SO_2Cl_2 (2) $SOCl_2$
(3) $NOCl$ (4) All

19. Hydrogen attached to nitrogen is released in the reaction

(1) $RCONH_2 + NaNH_2$
(2) $RNH_2 + Na$
(3) Both the above
(4) None of the above

20. If primary amines are treated with ketones the product is

(1) Urea (2) Guanidine
(3) Amide (4) Schiff's base

21. Reactants of reaction – I are

CH_3CONH_2 , KOH , Br_2

Reactants of reaction-II are

CH_3NH_2 , $CHCl_3$, KOH

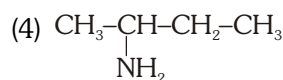
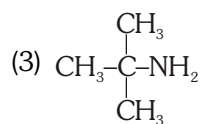
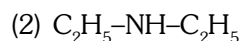
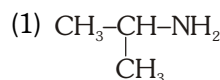
The intermediate species of reaction-I and reaction-II are respectively

(1) Carbonium ion, carbene
(2) Nitrene, carbene
(3) Carbene, nitrene
(4) Carbocation, carbanion

22. N, N-dimethyl acetamide is obtained in the reaction

(1) Acetyl chloride and methanamine
(2) Acetyl chloride and ethanamine
(3) Acetyl chloride and dimethylamine
(4) Acetyl chloride and diethylamine

23. This compound does not respond to carbylamine reaction :-



24. Blue litmus can be turned to red by the compound

(1) ROH

(2) RNH_2



25. Match List I with List II and select the correct answer using the codes given below :-

List I

[Reagent]

List II

[Used as test reagent for]

A. Ammonical $AgNO_3$

a. Primary amine

B. HIO_4

b. Aldehyde

C. Cold dil. Alkaline

c. Vicinal-OH groups

$KMnO_4$

D. Chloroform + $NaOH$

d. Double bond

Codes :

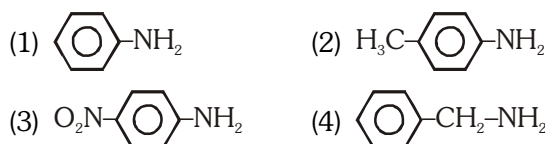
	A	B	C	D
(1)	b	c	a	d
(2)	d	b	a	c
(3)	b	c	d	a
(4)	d	c	b	a

26. Which one of the following aromatic amino compound gives alcohol with HNO_2 :-
 (1) N,N-Dimethylaniline (2) Benzylamine
 (3) N-methylaniline (4) Aniline

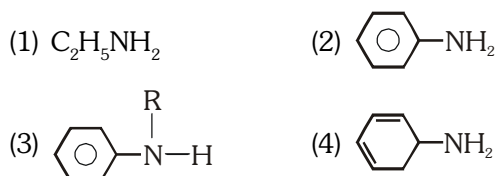
ANILINE

27. Electrolytic reduction of nitrobenzene in weakly acidic medium gives
 (1) Aniline
 (2) p-Hydroxyaniline
 (3) N-Phenylhydroxylamine
 (4) Nitrosobenzene
28. $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{Br}_2/\text{CCl}_4} ?$ The product is :-
 (1) Only o-bromoaniline
 (2) 2, 4, 6-tribromoaniline
 (3) o-and p-bromoaniline
 (4) Only p-bromoaniline
29. Before proceeding for the nitration of aminobenzene, the NH_2 group is first protected by:-
 (1) Alkylation
 (2) Acetylation
 (3) Formylation
 (4) Chloromethylation
30. Aniline is purified by :-
 (1) Azeotropic distillation
 (2) Steam distillation
 (3) distillation in presence of magnesium
 (4) Fractional distillation
31. Reaction $\text{C}_6\text{H}_5\text{NH}_2 + \text{HAuCl}_4 \longrightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+[\text{AuCl}_4]^-$ shows ... behaviour of aniline :-
 (1) Acidic (2) Neutral
 (3) Basic (4) Amphoteric
32. Aniline on treatment with bromine water yields white precipitate of :-
 (1) o-Bromoaniline
 (2) p-Bromoniline
 (3) 2, 4, 6-Tribromoaniline
 (4) m-Bromoaniline

33. Which compound does not show diazo reaction:-



34. Which of the following amines give N-nitroso derivative with NaNO_2 and HCl :-



35. Which of the following involves nitrene as an intermediate ?

- (1) Carbylamine reaction
 (2) Hofmann bromamide reaction
 (3) Reimer Tiemann reaction
 (4) Friedal crafts reaction

36. Which of the following does not reduce Tollen's reagent :-

- (1) CH_3CHO (2) HCOOH
 (3) $\text{C}_6\text{H}_5\text{NHOH}$ (4) $\text{C}_6\text{H}_5\text{NH}_2$

37. Aniline can be obtained by :-

- (1) Benzoyl chloride and ammonia
 (2) Reduction of benzamide
 (3) Phenol and ammonia in presence of ZnCl_2
 (4) Benzoic anhydride and ammonia

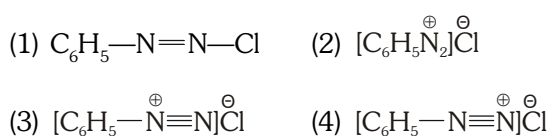
38. Aniline on direct nitration produces :-

- (1) o-Nitroaniline (2) m-Nitroaniline
 (3) p-Nitroaniline (4) All

39. Nitration of acetanilide followed by hydrolysis gives

- (1) o-Nitroaniline (2) p-Nitroaniline
 (3) o- & p-Nitroaniline (4) o-Nitroanilinium ion

40. $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[0-5^\circ\text{C}]{\text{NaNO}_2/\text{HCl}} \text{A}$, Which is the incorrect structure of the product 'A' :-



41. Chloroform and ethanolic KOH is used as a reagent in the following reaction :-

- Hoffmann carbylamine reaction
- Hoffmann degradation reaction
- Reimer-Tiemann reaction
- Hoffmann mustard oil reaction

Code is :-

- Only for a
- Only for a and b
- Only for b and d
- Only for a and c

42. Acetanilide when treated with bromine in acetic acid mainly gives :-

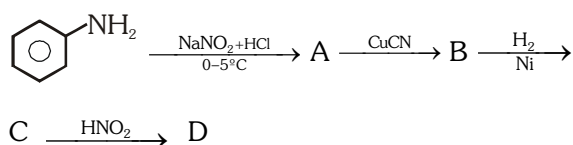
- o-Bromoacetanilide
- N-Bromoacetanilide
- p-Bromoacetanilide
- m-Bromoacetanilide

43. Aromatic nitriles (ArCN) are not prepared by reaction

- $\text{ArX} + \text{KCN}$
- $\text{ArN}_2^+ + \text{CuCN}$
- $\text{ArCONH}_2 + \text{P}_2\text{O}_5$
- $\text{ArCONH}_2 + \text{SOCl}_2$

NITRO GROUP, CYANIDE & ISOCYANIDE

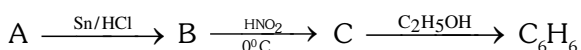
44. Aniline in a set of reactions yielded end product D



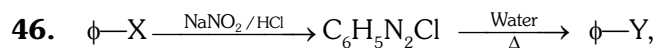
The structure of the product D would be

- $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- $\text{C}_6\text{H}_5\text{NHOH}$
- $\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_3$

45. In the reaction sequence identify the functional group present in A, B, C :-



- NO_2 , NH_2 , $\text{N}=\text{N}$
- NO_2 , NH_2 , OH
- $-\text{OH}$, $-\text{NH}_2$, $-\text{NO}$
- $-\text{NH}_2$, $-\text{NO}_2$, $-\text{N}=\text{N}-$



In the above sequence X and Y are :-

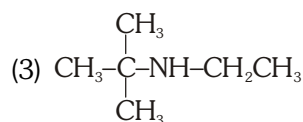
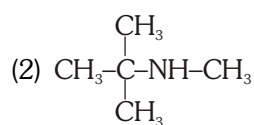
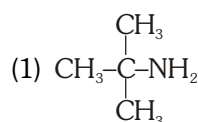
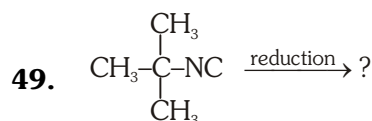
- o-, p- and m-directing
- o-, p- and o-, p-directing
- m and m directing
- m and o, p directing

47. Which of the following compound gives an explosive on decarboxylation :-

- 2,4,6-Trinitrobenzoic acid
- 2,4-Dinitrobenzoic acid
- o-Aminobenzoic acid
- o-Hydroxybenzoic acid

48. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was:-

- Methylisocyanate
- Methylamine
- Ammonia
- Phosgene



(4) None

50. Reaction of RCN with sodium and alcohol leads to the formation of :-

- RCONH_2
- $\text{RCOO}^-\text{NH}_4^+$
- RCH_2NH_2
- $\text{R}(\text{CH}_2)_3\text{NH}_2$

51. $C_6H_5NO_2 \xrightarrow{SnCl_2/HCl} A \xrightarrow[0^\circ C]{NaNO_2/HCl} B$; In the

above sequence Benzene from B, is suitably obtained by using :-

- (1) Ethanol
- (2) H_3PO_2
- (3) Both the above
- (4) Methanol

52. Which reagent is used to get iodo benzene from benzene diazonium acid sulphate $[C_6H_5N_2HSO_4]$:

- (1) $CuBr, \Delta$
- (2) Cu powder + HI
- (3) KI, Δ
- (4) None

53. Which of the following is used as a solvent in the Friedel-Crafts reaction :-

- (1) Toluene
- (2) Nitrobenzene
- (3) Benzene
- (4) Aniline

54. Match list I with II and choose the correct answer from the codes given below :-

List I

List II

- | | |
|---------------------|---|
| (A) Aniline | a. Used in making azo dyes |
| (B) Nitrobenzene | b. Sulpha drug |
| (C) Sulphanilamide | c. Solvent in the Friedel Crafts reaction |
| (D) Trinitrotoluene | d. Used as explosive |

Code is :-

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

55. In the Sandmeyer's reaction, $-N=N-X$ group of diazonium salt is replaced by :-

- (1) Halide group
- (2) Nitro group
- (3) $-OH$ group
- (4) $-NHNH_2$ group

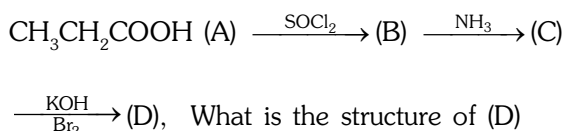
EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	2	3	3	1	3	1	3	3	3	3	3	3	4	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	2	3	3	4	2	3	2	4	3	2	1	2	2	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	3	4	3	2	4	3	4	3	1	4	3	1	1	1
Que.	46	47	48	49	50	51	52	53	54	55					
Ans.	2	1	1	2	3	3	3	2	1	1					

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2006**

1. In a set of reactions propionic acid yielded a compound (D) ;



- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (2) $\text{CH}_3\text{CH}_2\text{CONH}_2$
 (3) $\text{CH}_3\text{CH}_2\text{NHCH}_3$ (4) $\text{CH}_3\text{CH}_2\text{NH}_2$

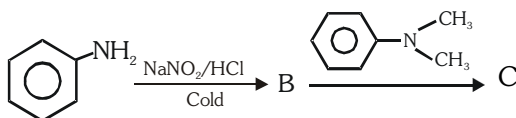
AIPMT 2007

2. Which one of the following on reduction with LiAlH_4 yields a secondary amine

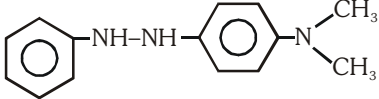
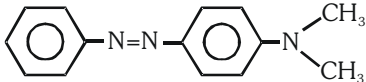
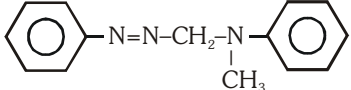
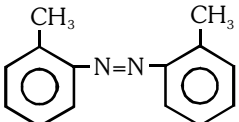
- (1) Methyl isocyanide
 (2) Acetamide
 (3) Methyl cyanide
 (4) Nitro ethane

AIPMT 2008

3. In a reaction of aniline a coloured product C was obtained.

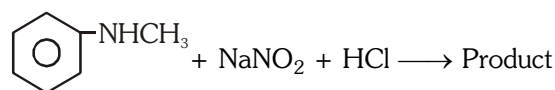


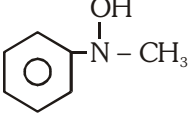
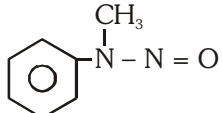
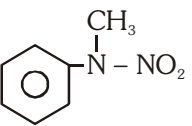
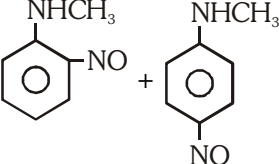
The structure C would be :

- (1) 
 (2) 
 (3) 
 (4) 

AIPMT 2009

4. Predict the product :



- (1)  (2) 
 (3)  (4) 

AIPMT 2010

5. Which of the following statements about primary amines is 'False' ?

- (1) Alkyl amines are stronger bases than ammonia
 (2) Alkyl amines are stronger bases than aryl amines
 (3) Alkyl amines react with nitrous acid to produce alcohols
 (4) Aryl amines react with nitrous acid to produce phenols

6. Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine ?

- (1) PCl_5 (2) NaOH/Br_2
 (3) Sodalime (4) Hot conc. H_2SO_4

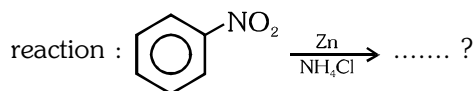
AIIMS 2010

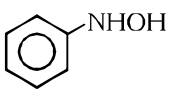
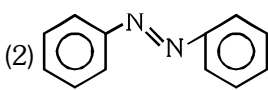
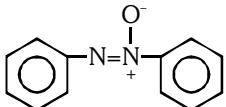
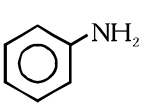
7. Which of the following gives a soluble complex on reaction with benzene sulphonyl chloride (which of the following compounds after reacting with benzene sulphonyl chloride is soluble in alkali solution) :-

- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
 (2) $\text{CH}_3\text{CH}_2\text{NHCH}_3$
 (3) $\text{CH}_3\text{CH}_2\text{OH}$
 (4) $(\text{CH}_3)_3\text{N}$

AIPMT Pre. 2011

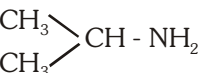
8. What is the product obtained in the following



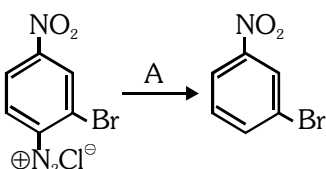
- (1)  (2) 
 (3)  (4) 

AIPMT Mains 2012

9. An organic compound C_3H_9N (A), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A):

- (1) $CH_3 - N - CH_3$ (2) $CH_3CH_2CH_2 - NH_2$
 (3)  (4) $CH_3CH_2 - NH - CH_3$

NEET UG 2013

10. In the reaction  A is

- (1) H^+/H_2O (2) $HgSO_4/H_2SO_4$
 (3) Cu_2Cl_2 (4) H_3PO_2 and H_2O

11. Nitrobenzene on reaction with conc. HNO_3/H_2SO_4 at $80-100^\circ C$ forms which one of the following products ?

- (1) 1, 2, 4-Trinitrobenzene
 (2) 1, 2-Dinitrobenzene
 (3) 1, 3-Dinitrobenzene
 (4) 1, 4-Dinitrobenzene

AIIMS 2013

12. Reaction of aniline with HNO_2 followed by treatment of dilute acid gives :-

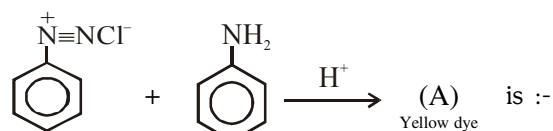
- (1) C_6H_5NHOH (2) C_6H_5OH
 (3) $C_6H_5NHNH_2$ (4) C_6H_6

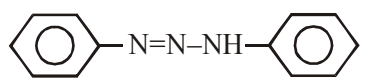
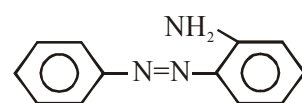
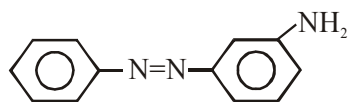
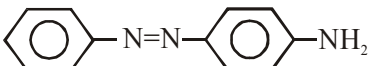
13. Which of the following will give carbylamine test?

- (1) CH_3NH_2 (2) CH_3NHCH_3
 (3) $(CH_3)_3N$ (4) CH_3CONH_2

AIPMT 2014

14. In the following reaction, the product (A)



- (1) 
 (2) 
 (3) 
 (4) 

15. Which of the following will be most stable diazonium salt $RN_2^+X^-$?

- (1) $CH_3N_2^+X^-$ (2) $C_6H_5N_2^+X^-$
 (3) $CH_3CH_2N_2^+X^-$ (4) $C_6H_5CH_2N_2^+X^-$

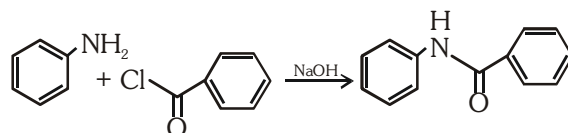
AIPMT 2015

16. The electrolytic reduction of nitrobenzene in strongly acidic medium produces :-

- (1) Azoxybenzene (2) Azobenzene
 (3) Aniline (4) p-Aminophenol

RE-AIPMT 2015

17. The following reaction



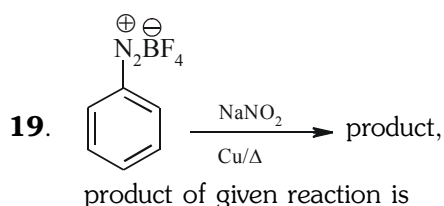
is known by the name :

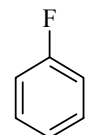
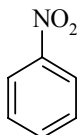
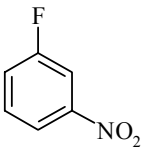
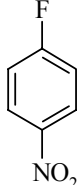
- (1) Acetylation reaction
 (2) Schotten-Baumann reaction
 (3) Friedel-Craft's reaction
 (4) Perkin's reaction

18. Method by which Aniline cannot be prepared is :-

- (1) reduction of nitrobenzene with H_2/Pd in ethanol
- (2) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution
- (3) hydrolysis of phenylisocyanide with acidic solution
- (4) degradation of benzamide with bromine in alkaline solution

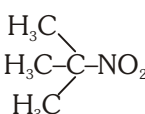
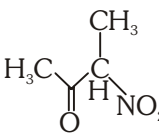
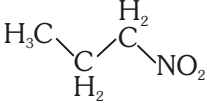
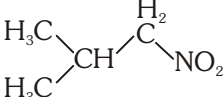
AIIMS 2015



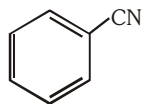
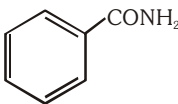
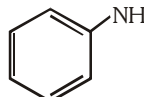
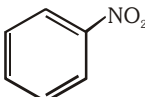
- (1) 
- (2) 
- (3) 
- (4) 

NEET-II 2016

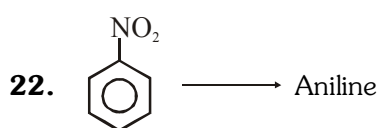
20. Which one of the following nitro-compounds does not react with nitrous acid ?

- (1) 
- (2) 
- (3) 
- (4) 

21. A given nitrogen-containing aromatic compound (A) reacts with Sn/HCl , followed by HNO_2 to give an unstable compound (B). (B), on treatment with phenol, forms a beautiful coloured compound (C) with the molecular formula $C_{12}H_{10}N_2O$. The structure of compound (A) is :-

- (1) 
- (2) 
- (3) 
- (4) 

AIIMS 2016



Aniline will not be prepared in presence of :-

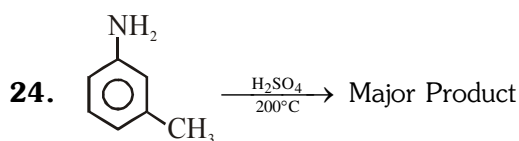
- (1) $Sn + HCl$
- (2) $Fe + HCl$
- (3) $Zn + NH_4Cl$
- (4) H_2/Pd

NEET(UG) 2017

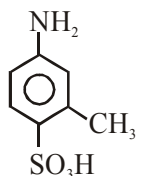
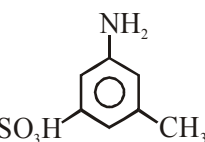
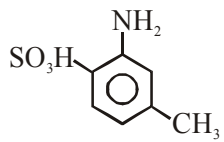
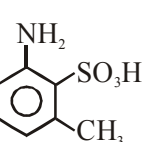
23. Which of the following reactions is appropriate for converting acetamide to methanamine ?

- (1) Hoffmann hypobromamide reaction
- (2) Stephens reaction
- (3) Gabriels phthalimide synthesis
- (4) Carbylamine reaction

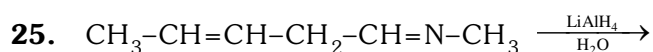
AIIMS 2017



Major product of this reaction is :-

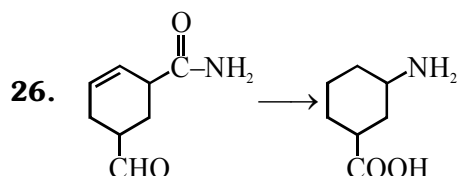
- (1) 
- (2) 
- (3) 
- (4) 

AIIMS 2018



product.

- (1) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$
- (2) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$
- (3) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{N}-\text{CH}_3$
- (4) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{N}-\text{CH}_3$



Select the correct sequence of reagents for the above conversion.

- (1) H_2 -Pd/c ; Br_2/KOH , Tollen's Reagent
- (2) Tollen's Reagent, Br_2/KOH , H_2 -Pd-c
- (3) Br_2/KOH , Tollen's Reagent, Br_2/KOH
- (4) H_2 -Pd-c, Tollen's Reagent, Br_2/KOH

27. Which of the following is incorrect statement regarding diazo salt :-

- (1) On reaction with $\text{C}_2\text{H}_5\text{OH}$, it form benzene
- (2) on reaction with HCN/CuCN it forms 
- (3) It gives nitrobenzene with NaNO_2
- (4) It gives iodobenzene with KI/Δ

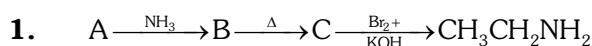
EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	1	2	2	4	2	1	1	3	4	3	2	1	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27			
Ans.	4	2	2	2	1	4	3	1	1	1	2	3			

EXERCISE-III (Analytical Questions)

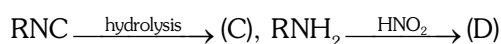
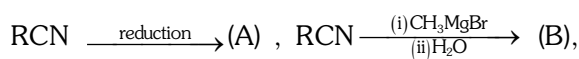
Check Your Understanding



A is :-

- (1) CH_3COOH
- (2) $CH_3CH_2CH_2COOH$
- (3) $CH_3-\underset{\text{CH}_3}{\text{CH}}-COOH$
- (4) CH_3CH_2COOH

2. The correct set of the products obtained in the following reactions

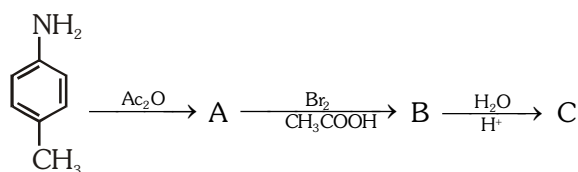


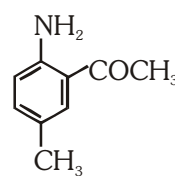
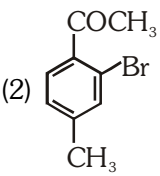
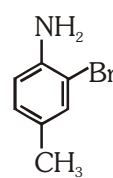
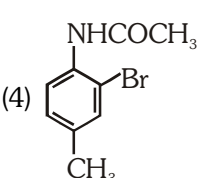
The answer is

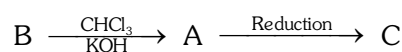
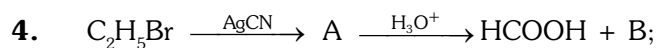
A B C D

- (1) 2°Amine Methyl ketone 1°Amine Alcohol
- (2) 1°Amine Methyl ketone 1°Amine Alcohol
- (3) 2°Amine Methyl ketone 2°Amine Acid
- (4) 1°Amine Methyl ketone 2°Amine Aldehyde

3. The final product C, obtained in this reaction would be

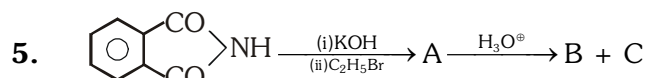


- (1) 
- (2) 
- (3) 
- (4) 



A, B, C respectively in the above sequence are

- (1) Ethane amine, methane nitrile and diethyl amine
- (2) Carbyl amino ethane, ethane amine and primary amine
- (3) Ethyl isocyanide, ethyl amine and methyl isocyanate
- (4) Carbylamino ethane, ethanamine and ethyl methyl amine



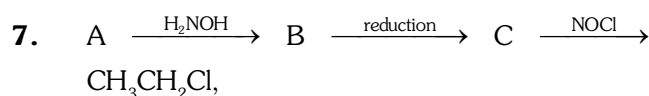
B and C in the above sequence are

- (1) Benzoic acid + aniline
- (2) Phthalic acid + ethylamine
- (3) Phthalic acid + aniline
- (4) Benzoic acid + ethylamine

6. The end-product in the reaction sequence would be :



- (1) Ethyl cyanide
- (2) Ethyl amine
- (3) Methyl amine
- (4) Acetamide



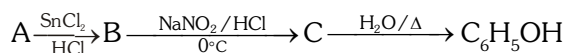
A and C in the above sequence respectively are:-

- (1) Methanal, Methylamine
- (2) Acetone, ethanamine
- (3) Ethanal, dimethylamine
- (4) Acetaldehyde, ethylamine

8. A compound of mol. wt. 180 gm is acetylated to give a compound of mol. wt. 390. The number of amino groups in the compound are :-

- (1) 2
- (2) 4
- (3) 5
- (4) 6

9. In the reaction sequence A, B and C are :-



- (1) Benzene, nitrobenzene, aniline
- (2) Nitrobenzene, aniline and azo-compound
- (3) Nitrobenzene, benzene, aniline
- (4) Benzene, amino compound, aniline

10. Which one of the following tests can be used to identify primary amino group in a given organic compound

- (1) Iodoform test
- (2) Victor Meyer's test
- (3) Carbylamine reaction
- (4) Libermann's reaction

11. At 0°C temperature reaction of aniline with HNO_2 and subsequent treatment with alkaline β -naphthol solution produces a precipitate whose colour would be :-

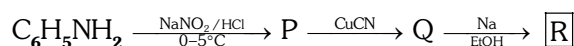
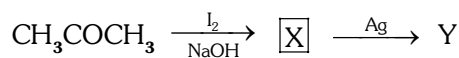
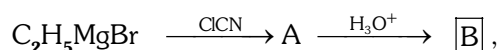
- (1) Black
- (2) Purple
- (3) White
- (4) Orange

12. $\text{CH}_3\text{Cl} \xrightarrow{\text{KCN}} \xrightarrow{+4\text{H}} \text{A} \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{Ethanol} + ?$

Apart from ethanol as the main product, the other products would be

- (1) $\text{H}_2\text{C}=\text{CH}_2$
- (2) $\text{CH}_3\text{CH}_2\text{-ONO}$
- (3) $\text{CH}_3\text{CH}_2\text{-Cl}$
- (4) All the above

13. Identify B, X and R respectively in the following sequence of reactions



- (1) $\text{C}_2\text{H}_5\text{COOH}$, CHI_3 , $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- (2) $\text{C}_2\text{H}_5\text{COOH}$, CH_3I , $\text{C}_6\text{H}_5\text{COOH}$
- (3) $\text{C}_2\text{H}_5\text{CH}_2\text{NH}_2$, CH_3I , $\text{C}_6\text{H}_5\text{COOH}$
- (4) $\text{C}_2\text{H}_5\text{COOH}$, $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{CONH}_2$

14. Using Fe/HCl , which one of the following reaction is possible [Here $\phi = \text{C}_6\text{H}_5$]

- (1) $\phi\text{-NO}_2 \rightarrow \phi\text{-NH-NH-}\phi$
- (2) $\phi\text{-NO}_2 \rightarrow \phi\text{-NH}_2$
- (3) $\phi\text{-NO}_2 \rightarrow \phi\text{-NHOH}$
- (4) $\phi\text{-NO}_2 \rightarrow \phi\text{-N=N-}\phi$

15. An aromatic compound A on treatment with $\text{Zn}/\text{NH}_4\text{Cl}$, and subsequent filtration in ammonical silver nitrate solution gives a black precipitate. Hence compound A bears the group :-

- (1) -COOH
- (2) -NO_2
- (3) -CHO
- (4) -NH_2

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	2	3	4	2	2	4	3	2	3	4	4	1	2	2

EXERCISE-IV (Assertion & Reason)

Target AIIMS

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

1. **Assertion :-** Boiling point of trimethyl amine is higher than that of n-propyl amine.

Reason :- H-bonding is stronger in tertiary amines.

- (1) A (2) B (3) C (4) D

2. **Assertion :-** $\text{H}-\text{C}-\text{N}-\text{CH}_3$ and $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 \end{array}$

$\text{CH}_3-\text{C}-\text{NH}-\text{CH}_3$ are metamers.

Reason :- There is adjustment of $-\text{CH}_2-$ group in the molecule.

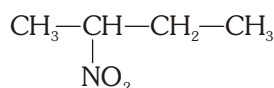
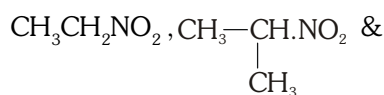
- (1) A (2) B (3) C (4) D

3. **Assertion :-** Pyrole is alicyclic compound.

Reason :- It is aliphatic in nature and has cyclic chain.

- (1) A (2) B (3) C (4) D

4. **Assertion :-** The following compound are given below –



all three compounds are soluble in NaOH.

Reason :- All above compound have lower boiling than CH_3NO_2 .

- (1) A (2) B (3) C (4) D

5. **Assertion :-** Acetonitrile is another name of ethanenitrile.

Reason :- α -H atom of acetonitrile exhibit acidic character.

- (1) A (2) B (3) C (4) D

6. **Assertion :-** Benzene diazonium chloride on reaction with ethanol gives benzene.

Reason :- Ethanol is good oxidising agent.

- (1) A (2) B (3) C (4) D

7. **Assertion :-** Diazonium salt is prepared at low temperature.

Reason :- Diazonium salt is hydrolysed to give phenol.

- (1) A (2) B (3) C (4) D

8. **Assertion :-** Carbylamine reaction involves reaction between 1° amine and chloroform in basic medium to give isocyanide.

Reason :- Methylene ($:\text{CH}_2$) carbene is formed as a reaction intermediate.

- (1) A (2) B (3) C (4) D

9. **Assertion :-** Suitable method for preparation of primary amine is when haloalkane is treated with excess of NH_3 .

Reason :- In this reaction primary, secondary, tertiary amines are formed.

- (1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9
Ans.	4	4	4	3	2	3	1	3	3