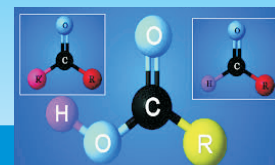


6

ORGANIC CHEMISTRY

AMINES

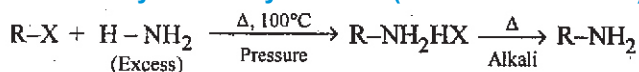
by Dr. M.K. JAIN (HOD- CHEMISTRY)



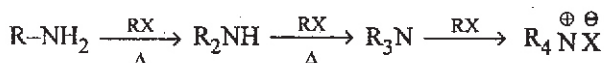
AMINES

Preparation

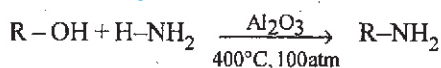
1. Ammonolysis of alkyl halides (Hofmann's Method) :



On taking the alkyl halides in excess, the primary amines gets further alkylated to form 2° & 3° amines and finally quaternary ammonium salt.



2. Ammonolysis of alkanols :



3. Reduction

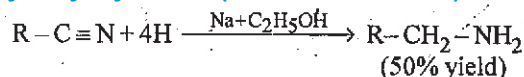
(i) By nitroalkanes :



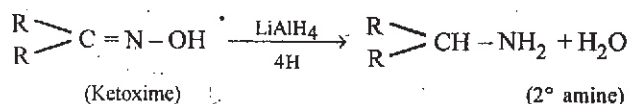
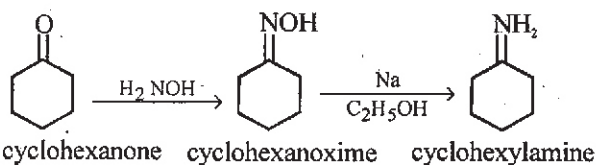
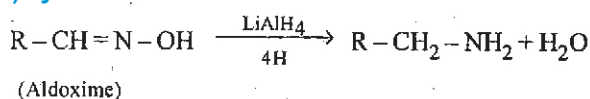
The following reductants can be used

- (a) Metal + Acid (b) $LiAlH_4$ or $NaBH_4$
(c) Raney nickel + H_2 , etc

(ii) By Alkyl cyanides (Mendius Reaction) :

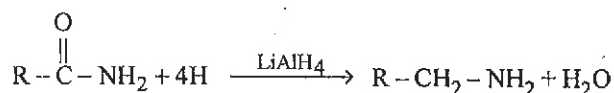


(iii) By Oximes :

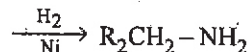
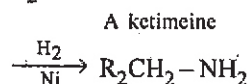
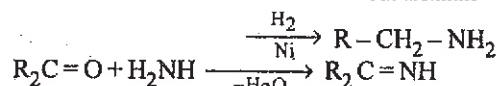
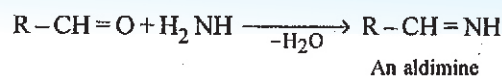


Reductants, which can be used are $Na + C_2H_5OH$; $LiAlH_4$; $NaBH_4$; Ni/H_2

(iv) By Acid Amides :

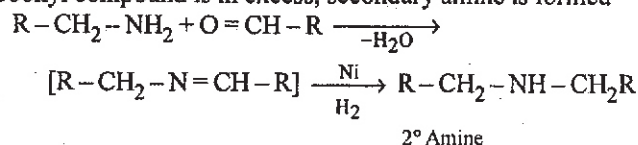


v. By Reductive Amination of carbonyl compounds?



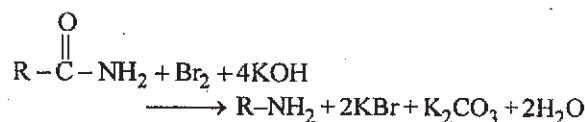
Note:

If carbonyl compound is in excess, secondary amine is formed

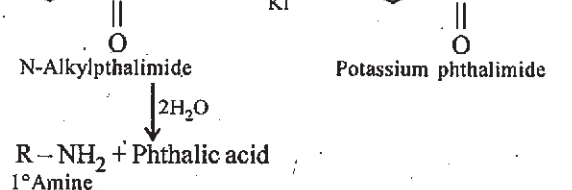
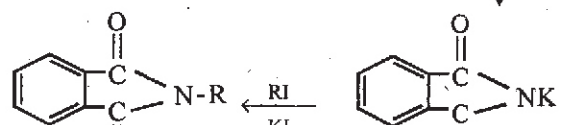
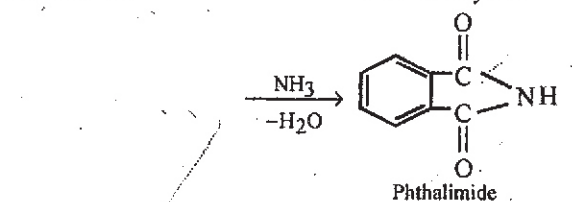
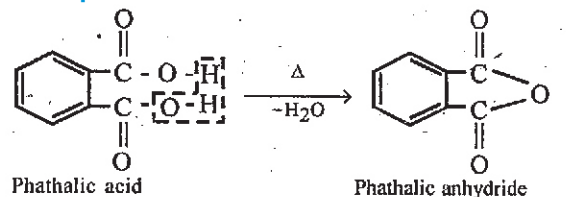


4. By Hydrolysis :

(i) Hofmann's Bromamide reaction :

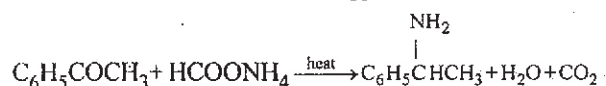
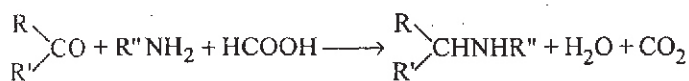
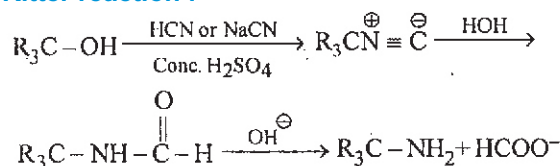
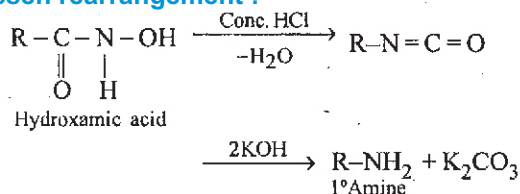
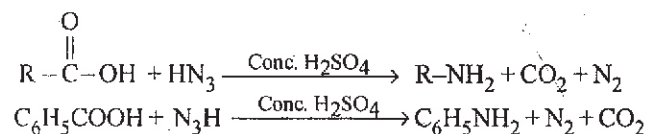
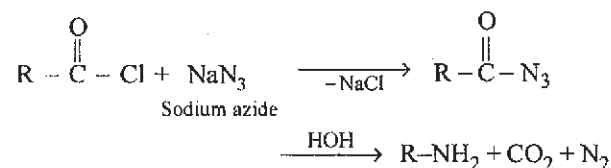


(ii) Gabriel phthalimide reaction :



**Note :**

The reaction is best used for the preparation of pure 1° Amines.

(iii) Alkyl isocyanides :**(iv) Alkyl Isocyanates (Wurtz Method) :****(v) Leuckart reaction :****(vi) Ritter reaction :****(vii) Lossen rearrangement :****(viii) Schmit reaction :****(ix) Curtius reaction :****Physical Properties****(i) Solubility :**

$$\text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

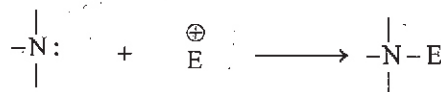
- (ii) Boiling point** b.p. of alcohols & carboxylic acids > b.p. of amines > b.p. of alkanes
and, b.p. of 1° amine > 2° amine > 3° amine

Explanation :

- (i) Primary and secondary amines form inter molecular H-bonds, while tertiary amines do not form inter-molecular H-bonds. As a result, 1° & 2° amines show high B.P. than 3° amines.
- (ii) H-bonding in amines is through nitrogen atoms while in alcohols and carboxylic acids, it is through oxygen atoms and nitrogen is less electronegative than oxygen. So H-bonding in amines is weaker than that in carboxylic acids and alcohols.

Chemical Properties**(i) Basic nature of amines :** Basic nature arises due to presence

of lone pair of e^- s on the N-atom, which can be shared with an electron deficient species (an electrophile).



Nucleophile Electrophile

Basic strength of amines depends on combined effect of two factors :

- (a) +I effect : Base strength $\propto$ +I effect
(b) Steric hindrance :

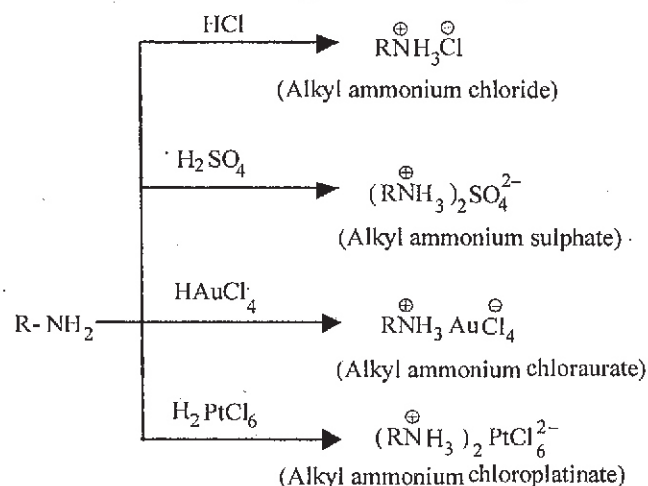
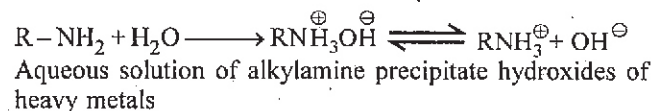
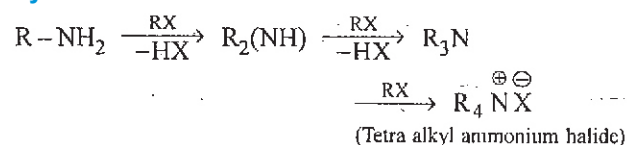
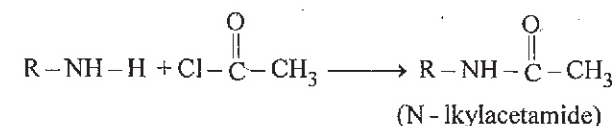
$$\text{Base strength} \propto \frac{1}{\text{Steric hindrance}}$$

Since both the factors work in opposite direction, the factor which is more predominant is more effective in deciding the base strength of amines.

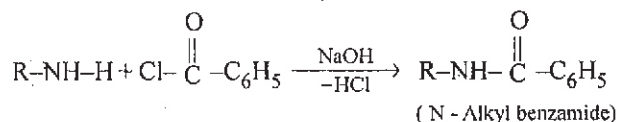
Order of basic character of amines is :

- (i) $R=CH_3$: $R_2NH > RNH_2 > R_3N > NH_3$
(ii) $R=C_2H_5$: $R_2NH > RNH_2 > NH_3 > R_3N$
(iii) $R=(CH_3)_2CH$: $R-NH_2 > NH_3 > R_2NH > R_3N$
(iv) $R=(CH_3)_3C$: $NH_3 > RNH_2 > R_2NH > R_3N$

Salts are formed on reacting amines with strong acids

**(ii) Reaction with water :** Give alkaline solution in water.**(iii) Alkylation :****(iv) Acetylation :**

(v) Benzoylation : (Schotten-Baumann reaction)



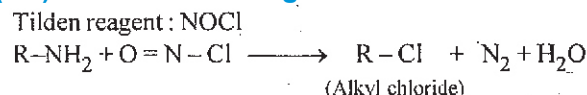
(vi) Acidic behaviour :



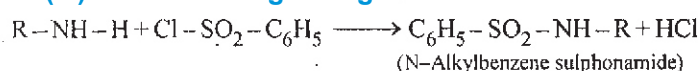
(vii) With Grignard's reagent :



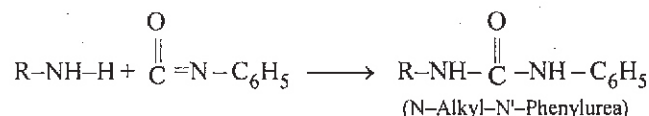
(viii) With Tilden's reagent :



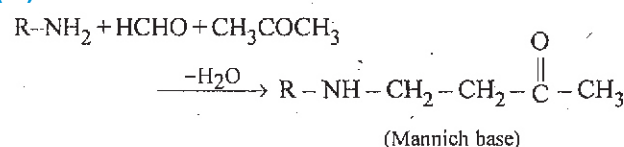
(ix) With Hinsberg's reagent :



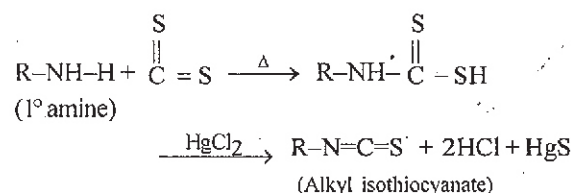
(x) With Phenyl isocyanate :



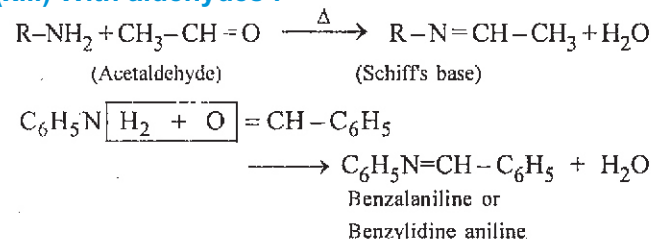
(xi) Mannich reaction :



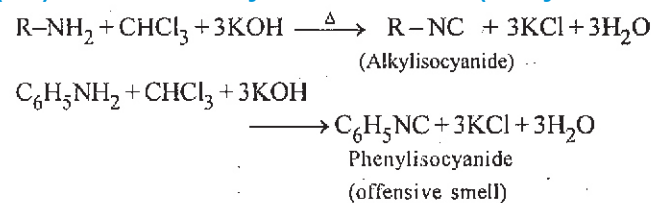
(Xii) Hofmann's Mustard oil reaction (HMO reaction)



(xiii) With aldehydes :

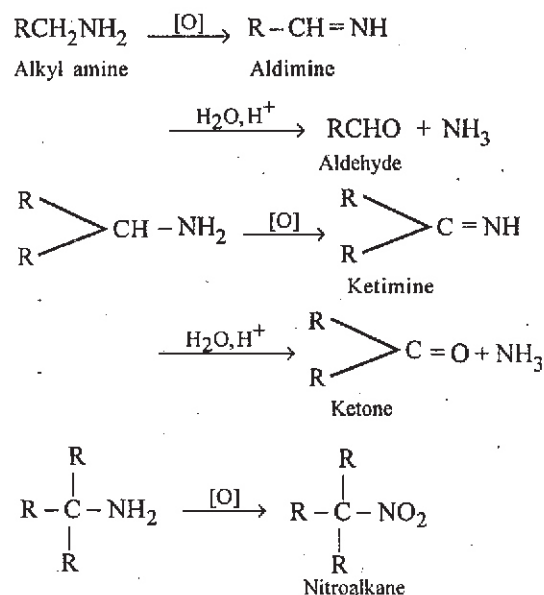


(xiv) Hofmann carbylamine reaction (Isocyanide test) :

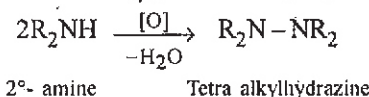


(xv) Oxidation

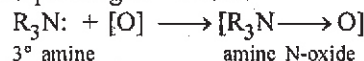
(a) Primary amines : Primary aliphatic amines on oxidation with KMnO_4 followed by hydrolysis give aldehydes, ketones and nitroalkanes.



(b) Secondary amines : Secondary aliphatic amines on oxidation with KMnO_4 give tetra alkyl hydrazine.



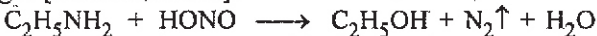
(c) Tertiary amines : Tertiary amines are not oxidised by KMnO_4 but are oxidised by Caro's acid or ozone or H_2O_2 to corresponding N-oxides.



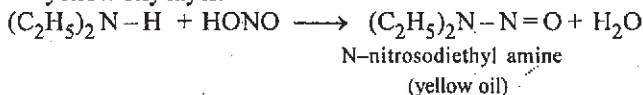
(xvi) Distinction between 1°, 2° and 3° amines :

(a) Reaction with HNO_2 :

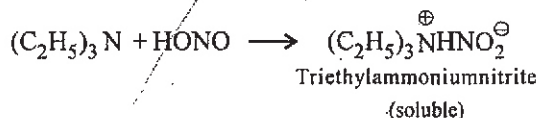
(a) Primary amines react with nitrous acid to produce nitrogen gas [seen as bubbles]:



(b) Secondary amines react with nitrous acid to produce a yellow oily layer.

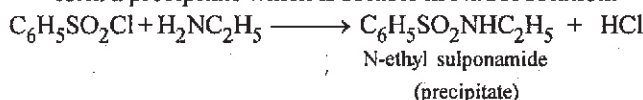


(c) Tertiary amines react with nitrous acid to form soluble nitrite:

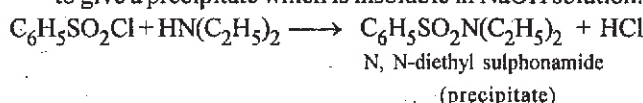


(b) Reaction with benzene sulphonyl chloride :

(a) Primary amines react with benzenesulphonyl chloride to form a precipitate which is soluble in NaOH solution.



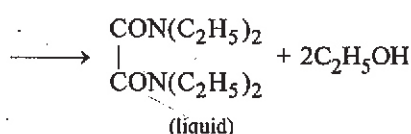
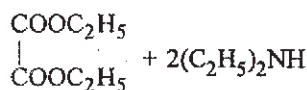
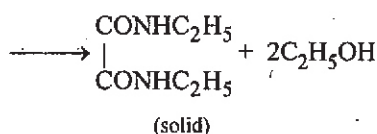
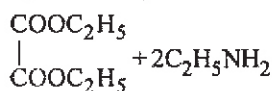
(b) Secondary amines react with benzene sulphonyl chloride to give a precipitate which is insoluble in NaOH solution.



(c) Tertiary amines do not react with benzenesulphonyl chloride as they do not possess replaceable hydrogen.

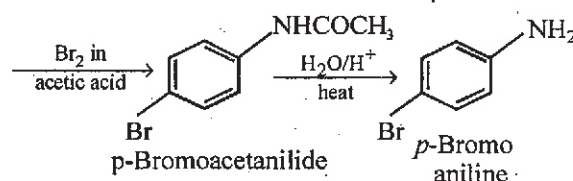
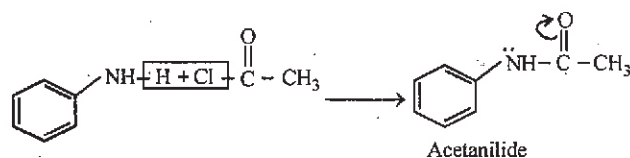
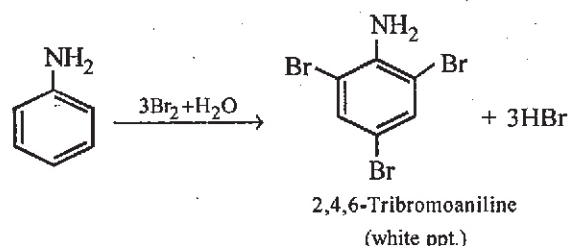
(c) Reaction with diethyloxalate (Hofmann's method)

Primary amines react to form solid crystalline oxamide. Secondary amines react to give oily dialkyl oxamic ester. Tertiary amines do not react as they do not contain a replaceable H atom.



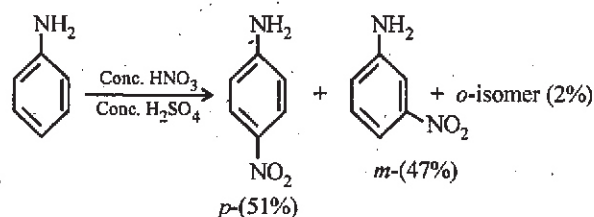
Diethyl oxalate + tertiary amine $\longrightarrow$ No reaction.

(ii) Halogenation :

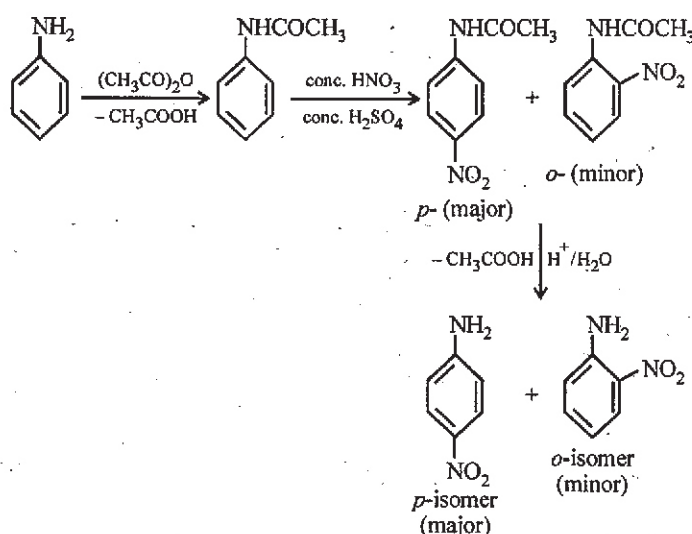


Electron attracting group ($>\text{C}=\text{O}$) present in acetanilide decreases availability of lone pair on nitrogen atom and hence decreases electron density on benzene ring of aniline.

(iii) Nitration : Under controlled conditions, nitration of aniline gives a mixture of *p*- and *m*-nitro aniline in approx 1:1 ratio.



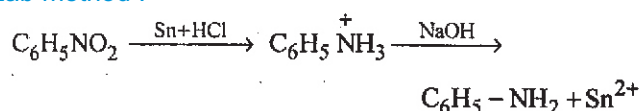
Under strongly acidic conditions, most of aniline is converted into anilinium ion and since $-\text{NH}_3^+$ is a *m*-directing group, thus an unexpected large amount of *m*-nitroaniline is obtained. To avoid this, the amino group is first protected by acetylation and the acetyl group is finally removed by hydrolysis to give a mixture of *o*- and *p*-nitroaniline i.e.,



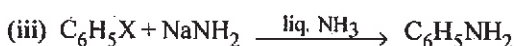
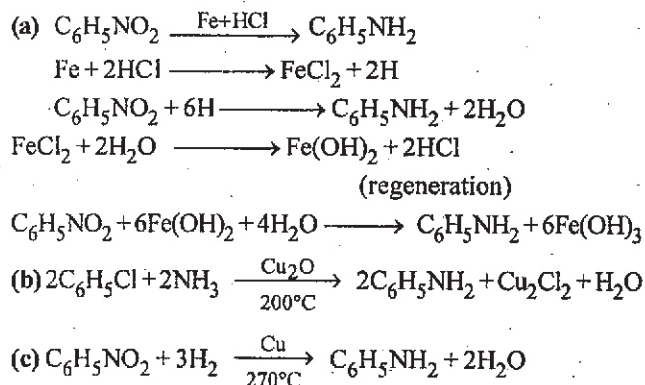
ANILINE

Methods of Preparation

(i) Lab method :

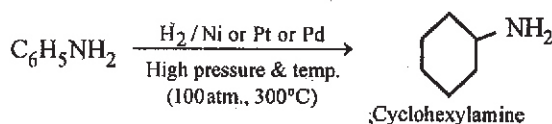


(ii) Industrial method :



Reactions

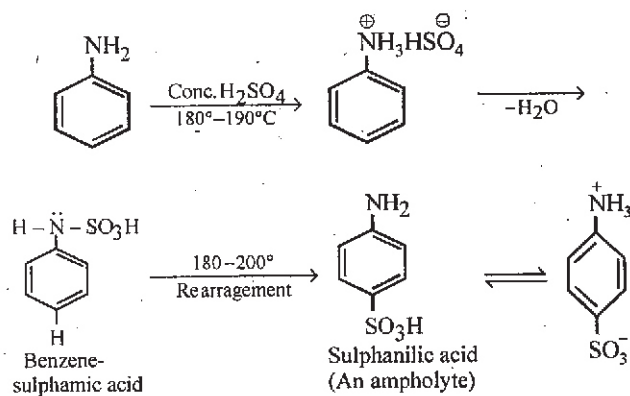
(i) Catalytic hydrogenation :



 Note :

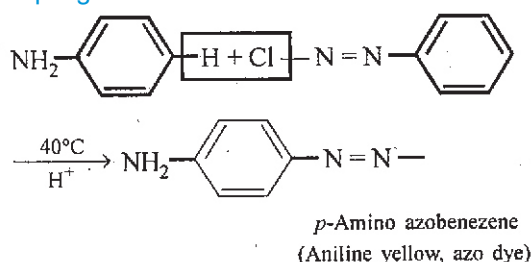
Hybridisation state changes from sp^2 to sp^3 .

(iv) Sulphonation :

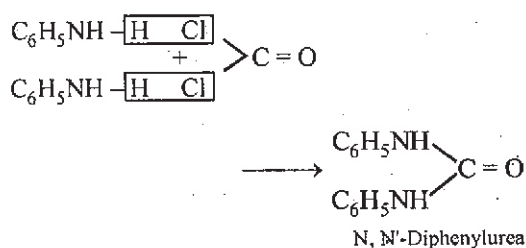
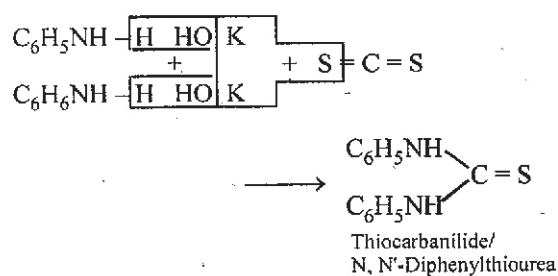


[used in the preparation of sulpha drugs]

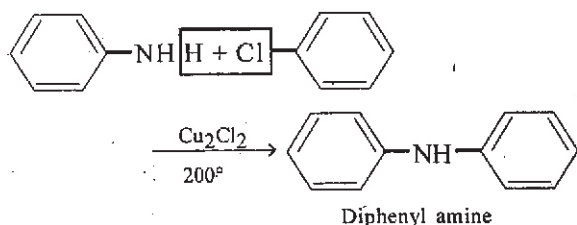
(v) Coupling reaction :



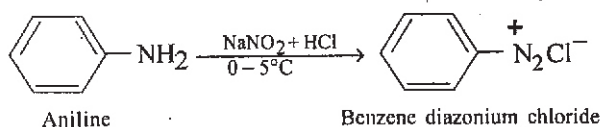
(vi) Reaction with phosgene :

(vii) Reaction with CS₂ + Solid KOH :

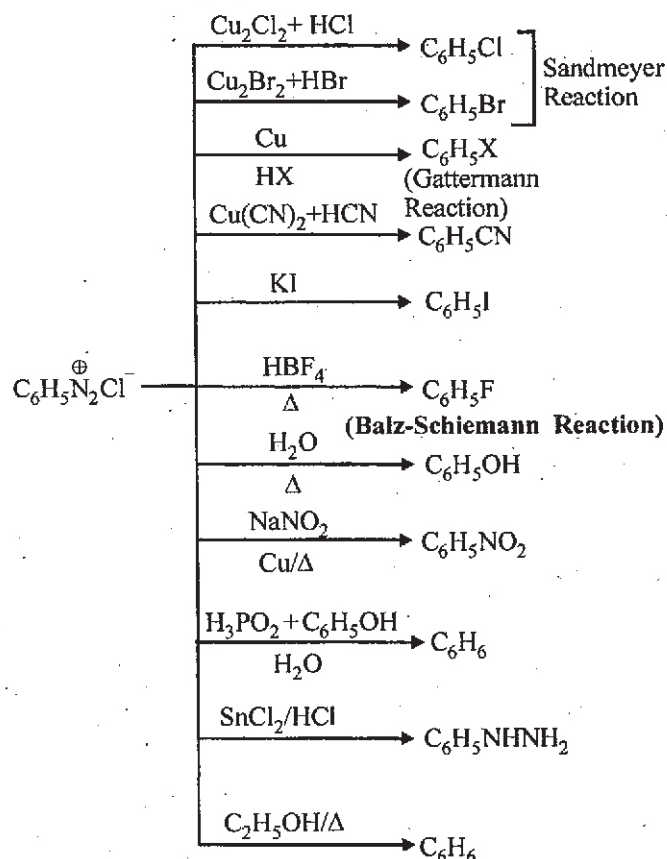
(viii) Arylation :



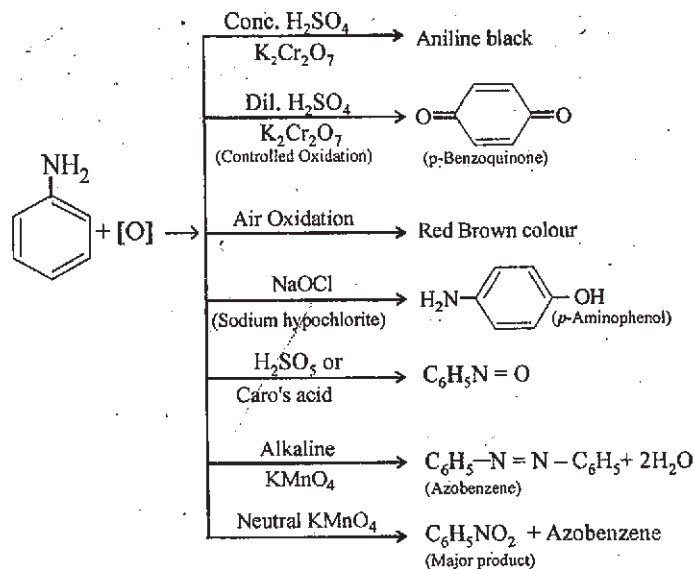
(ix) Diazotization :



Benzene diazonium chloride is extremely useful synthetically. It is used in the preparation of many organic compounds.



(x) Oxidation :



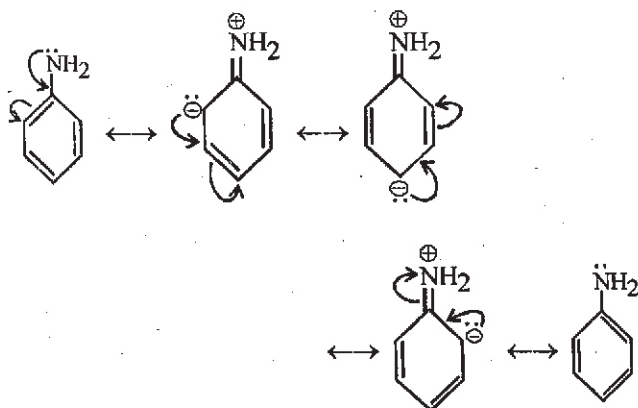
Test for Aniline :

- Isocyanide test : $\text{C}_6\text{H}_5\text{NC}$ (pungent odour) is formed on treating Aniline with $\text{CHCl}_3 + \text{KOH}$
- Bromine water test : White ppt. (2,4,6-Tribromoaniline) is formed on reaction of Aniline with bromine water.
- Aqueous NaOCl test : A violet colour instantly appears, which rapidly fades.
- Dye test : A bright red orange azo dye is formed on reaction of benzene diazonium chloride with 10% NaOH solution of β -Naphthol.

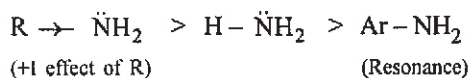
Uses :

- In manufacturing dyes.
- As a rocket fuel
- In manufacture of explosives, plastics, medicines, etc.

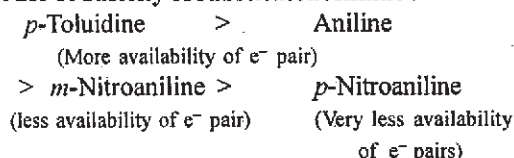
Resonance in Aniline and related points



- The group ($-\ddot{\text{N}}\text{H}_2$) present in aniline shows +M effect i.e. it increases electron density in benzene ring by giving lone pair of e^- s.
- $-\ddot{\text{N}}\text{H}_2$ is an ortho (o -) and para (p -) directing group because it increases e^- density on o - and p -positions, due to which the attacking electrophile comes at o - and p - position.
- Aniline is a weaker base as compared to aliphatic amines because availability of e^- s on N-atom is less due to resonance. So order of basicity.



4. Order of basicity of substituted Aniline :

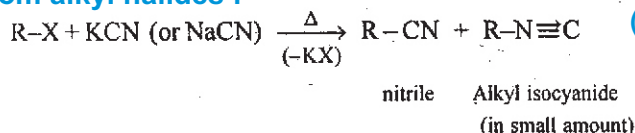


Electron donating groups increase the basic strength while electron withdrawing groups decrease the basic strength.

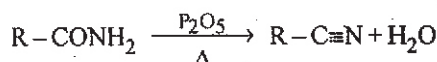
CYANIDES AND ISOCYANIDES

Preparation

(i) From alkyl halides :



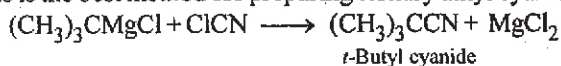
(ii) From acid amides :



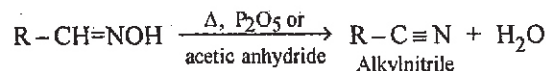
(iii) From Grignard reagent :



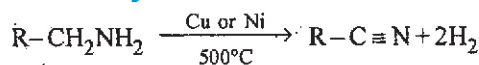
This is the best method for preparing tertiary alkyl cyanides.



(iv) By the dehydration of aldoximes :



(v) From Primary amines :

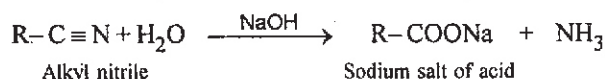
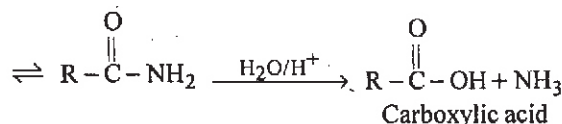
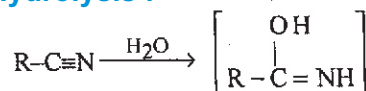


Physical Properties

- Alkyl cyanides are sweet smelling, fairly stable liquids.
- Lower alkyl cyanides are soluble in water as they can form H-bonds with water, but solubility diminishes with rise in molecular mass. They are readily miscible with organic solvents.
- They are poisonous but less than HCN.

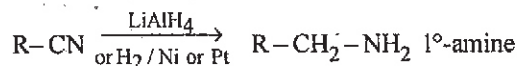
Chemical Properties

(i) Hydrolysis :

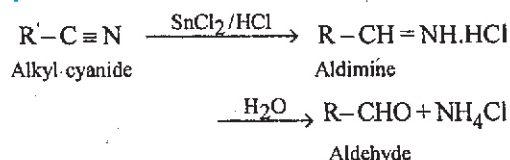


(ii) Reduction :

(a) With LiAlH_4 or H_2/Ni , RCN gives 1° -amine

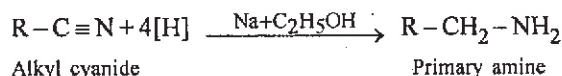


(b) Stephen's reaction :

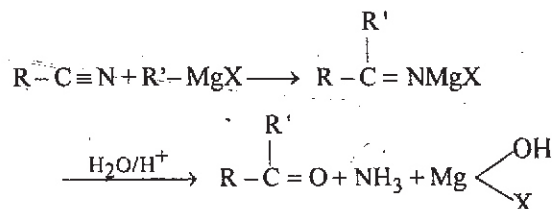


(c) Mendius reaction

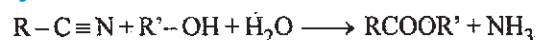
It involves reduction of RCN with Na and alcohol.



(iii) Reaction with Grignard reagent : Ketones are obtained.



(iv) Ethanolysis :

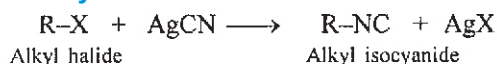


Alkyl cyanides are important intermediates in the laboratory for preparation of organic compounds such as amides, amines, acids, ester, etc.

ISOCYANIDES

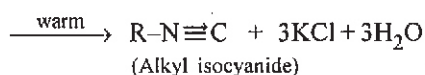
Preparation

(i) From alkyl halides :

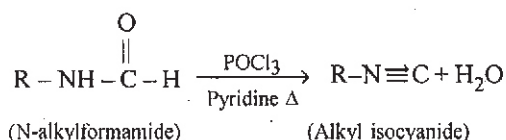


(ii) From primary amines (carbylamine reaction) :

By heating primary amine with chloroform and alc. KOH.
 $\text{R-NH}_2 + \text{CHCl}_3 + 3\text{KOH}$



(iii) From N-alkylformamide :

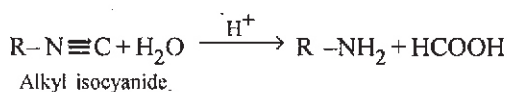


Physical Properties

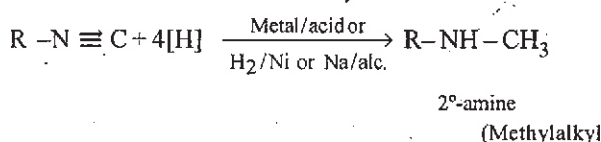
- (i) Alkyl isocyanides are colourless, most unpleasant smelling liquids with lower b.p. than the isomeric alkyl cyanides.
- (ii) They are not very soluble in water because the nitrogen atom does not have a lone pair of electrons for H-bond formation with H_2O molecules.
- (iii) Isocyanides are much more poisonous than isomeric cyanides.

Chemical Properties

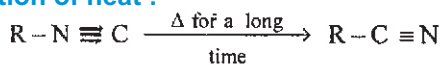
(i) **Hydrolysis** : These are hydrolysed by dil. acids (not by alkalis) to give primary amines and formic acid.



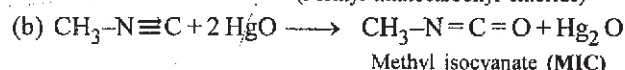
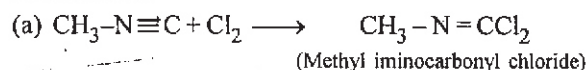
(ii) **Reduction** : Alkyl isocyanides are reduced to secondary amines either by dissolving metals or by catalytic reduction.



(iii) Action of heat :

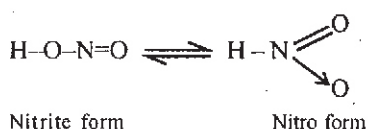


(iv) **Addition reactions** : Alkyl isocyanides give addition reactions due to the presence of unshared electron pairs on carbon atom.

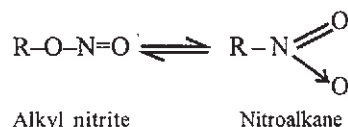


ALKYL NITRITES AND NITROALKANES

Nitrous acid exists in two tautomeric forms :

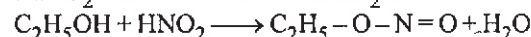


Thus, nitrous acid gives two types of alkyl derivatives.

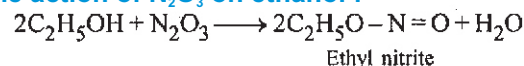
ETHYL NITRITE ($\text{C}_2\text{H}_5\text{-O-N=O}$)

1. Preparation

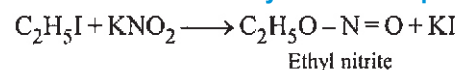
(i) **By adding conc. HCl or sulphuric acid to an aqueous solution of sodium nitrite and ethyl alcohol.**



(ii) **By the action of N_2O_3 on ethanol :**



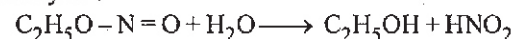
(iii) **By the reaction between ethyl iodide and potassium nitrite.**



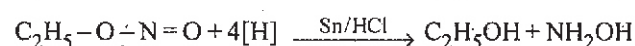
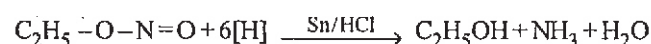
2. Properties

(i) Ethyl nitrite is a gas at ordinary temperature.

(ii) Hydrolysis :



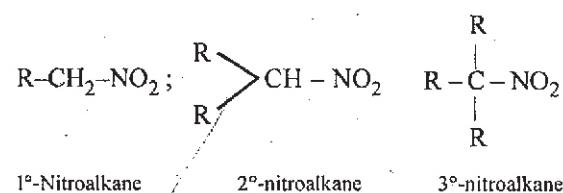
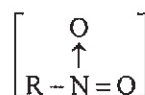
(iii) Reduction :



3. Uses

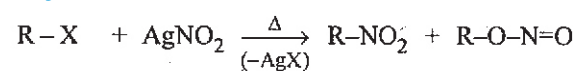
It dilates blood vessels and lowers blood pressure, so it is used in medicine for the treatment of asthma and heart diseases.

NITRO ALKANE



Preparation

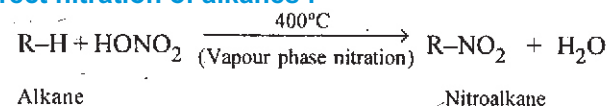
(i) **From alkyl halides :**



Alkyl halide Nitro alkane Alkyl nitrite
(a small amount)

A mixture of nitroalkane and alkyl nitrite can be separated by fractional distillation.

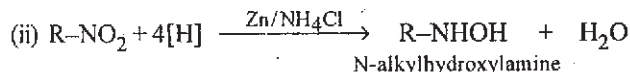
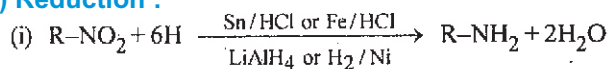
(ii) **By direct nitration of alkanes :**



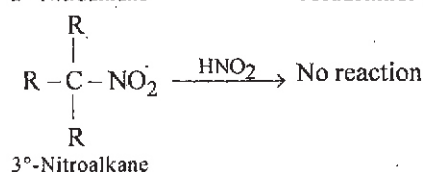
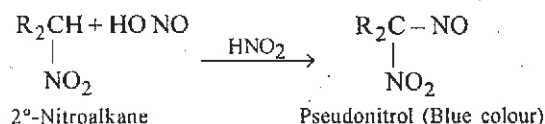
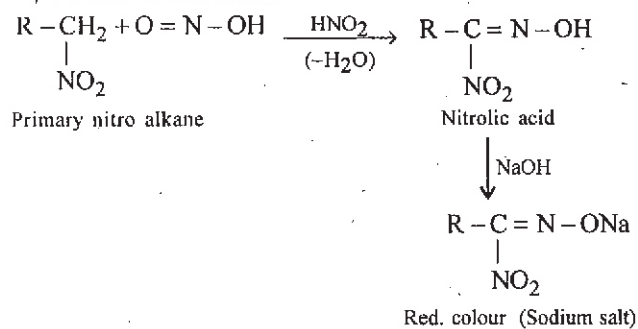
Properties

(i) Nitroalkanes are colourless, pleasant smelling liquids. They have much higher b.p. than isomeric alkyl nitrites. They are sparingly soluble in water, but soluble in organic solvents.

(ii) Reduction :

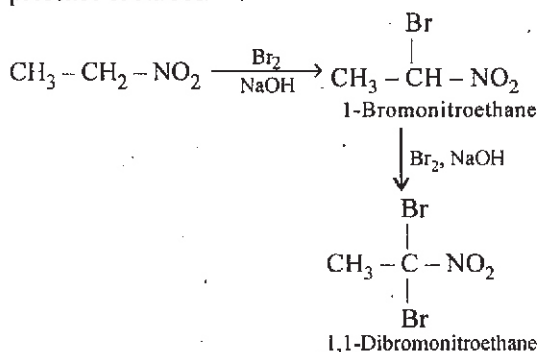


(iii) Action of nitrous acid : Different products are formed from 1°, 2° and 3°-nitroalkanes.



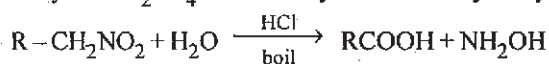
This reaction can be used to distinguish between 1°, 2°, and 3°-nitroalkanes.

(iv) Halogenation : Primary and secondary nitroalkanes are readily halogenated at α-position by treatment with Cl₂ or Br₂ in the presence of NaOH.

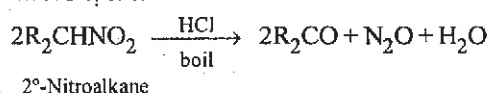


(v) Hydrolysis :

1°-nitroalkanes are hydrolysed by boiling hydrochloric acid or by 85% H₂SO₄ to a carboxylic acid and hydroxylamine.



2°-nitroalkanes on hydrolysis with boiling HCl give ketones and nitrous oxide.



3°-nitroalkanes are generally unaffected by HCl.

Uses

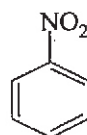
Nitroalkanes are used :

- (i) as powerful explosives.
- (ii) as solvent for cellulose acetate, synthetic rubber, etc.
- (iii) for preparing amines, hydroxyl amines, etc.

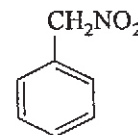
NITROBENZENE

Aromatic nitro compound are of two types.

- (a) Those compounds, in which nitro group is attached directly to the benzene ring e.g. nitro benzene.
- (b) Those compounds, in which nitro group is attached to a side chain.



(I)
(nitro benzene)

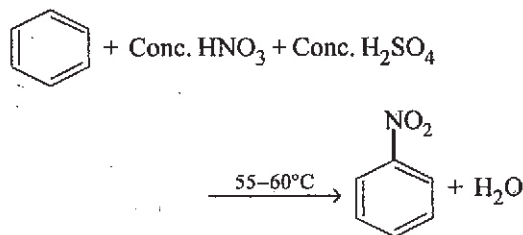


(II)
(phenyl nitromethane)

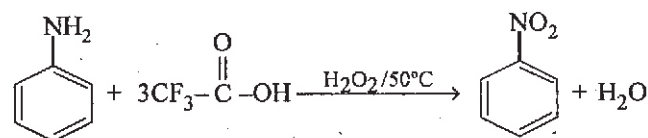
Nitrobenzene is also called as 'oil of mirbane' or 'artificial oil of bitter almond's.

METHODS OF PREPARATION

(i) By Nitration of Benzene (Laboratory Method)



(ii) By Oxidation of Aniline :



Physical properties

- (1) Pale yellow, poisonous, volatile oily liquid.
- (2) Heavier than water, very sparingly soluble in water, but miscible with organic solvents like alcohol, ether, benzene, etc.
- (3) B.P. = 211°C

Chemical reactions

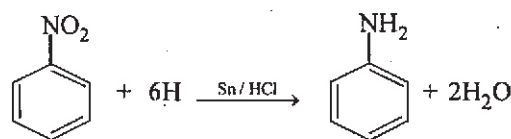
(1) Reactions due to Nitro group

Reduction of nitrobenzene takes place due to nitro (–NO₂) group.

(a) Reduction in acidic medium :

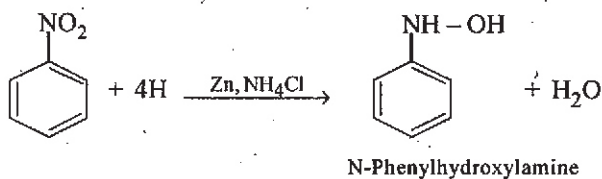
Acidic medium = Zn + HCl,

Zn + CH₃COOH; Fe + HCl; Sn + HCl, etc.



(b) Neutral medium :

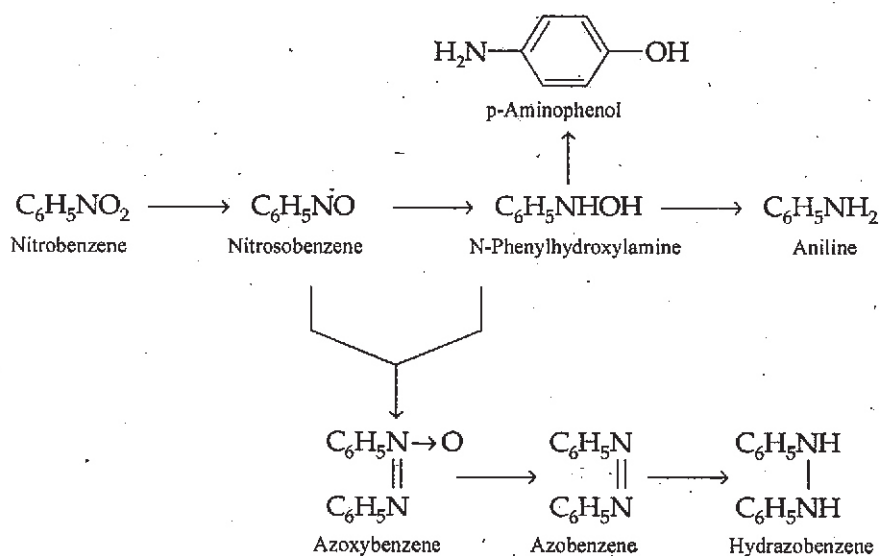
Neutral medium = $\text{Zn} + \text{NH}_4\text{Cl}$, $\text{Zn} + \text{CaCl}_2$,
 $\text{Zn} + \text{CH}_3\text{COONa}$; $\text{Al} - \text{Hg} + \text{NH}_4\text{Cl}$, etc.



(c) Alkaline medium :

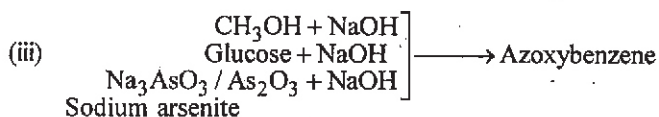
Alkaline medium : $\text{Zn} + \text{NaOH}$; $\text{CH}_3\text{OH} + \text{NaOH}$; $\text{Sn} + \text{NaOH}$; Glucose + NaOH ; $\text{SnCl}_2 + \text{NaOH}$; $\text{As}_2\text{O}_3 + \text{NaOH}$

Nitrosobenzene and N-phenylhydroxylamine are formed, which interact to form dinuclear products like azoxybenzene, azobenzene and finally hydrazobenzene.

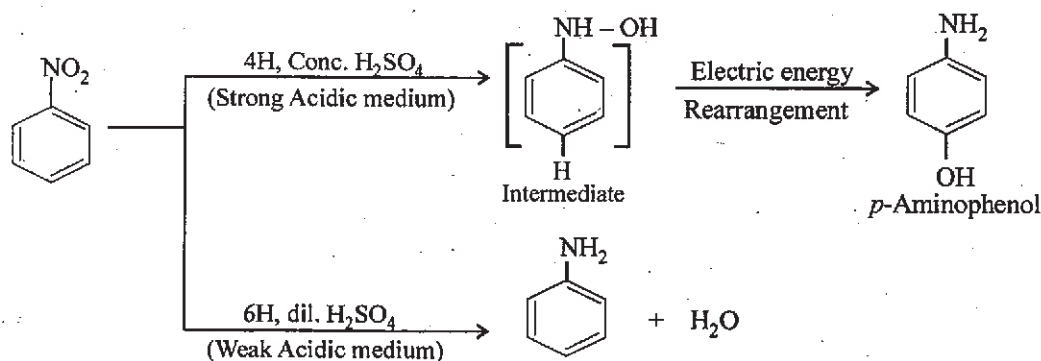


Each of the above product can be isolated depending upon the nature of the reducing agent. Following are the important products along with the corresponding reducing agent.

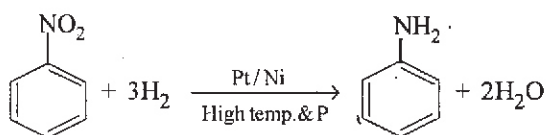
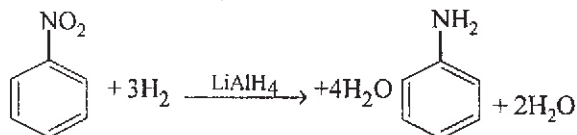
- (i) $\text{Na}_2\text{ZnO}_2 / \text{Zn} + \text{NaOH} \longrightarrow \text{Hydrazobenzene or N, N - Diphenyl hydrazine}$
 (Sodium zincate)
- (ii) $\text{Na}_2\text{SnO}_2 / \text{Sn} + \text{NaOH} \longrightarrow \text{Azobenzene}$
 (Sodium stannate)



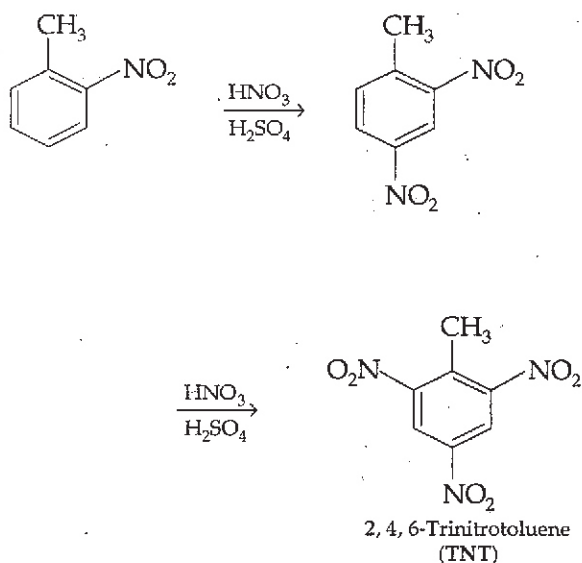
(d) Electrolytic reduction :



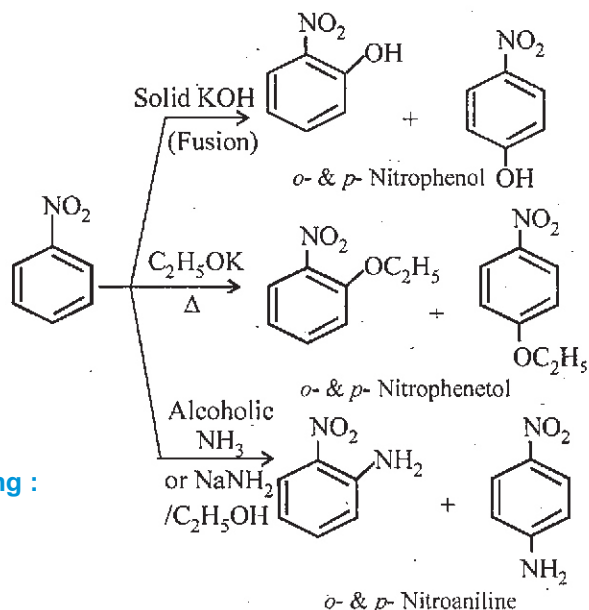
(c) Catalytic reaction :

(f) Reduction by Lithium aluminium hydride (LiAlH_4) :

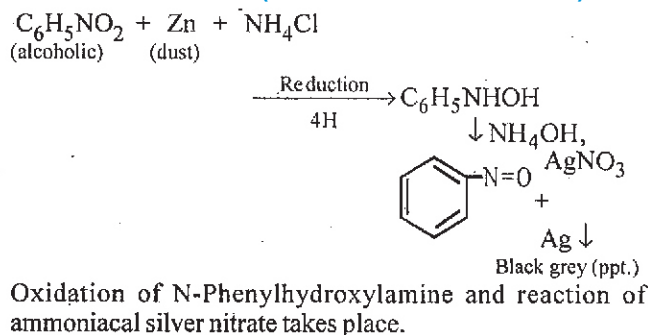
(2) Electrophilic substitution reaction due to benzene ring :



(3) Nucleophilic substitution reactions :



Test of Nitrobenzene : (Mulliken and Barker test)



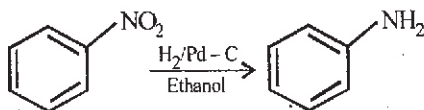
Uses

- (i) As an industrial solvent
- (ii) Used as an intermediate in the production of an explosive 1, 3, 5-Trinitrobenzene (T.N.B.)
- (iii) In the preparation of shoe polish, floorpolishes, etc.
- (iv) In manufacturing of aniline.

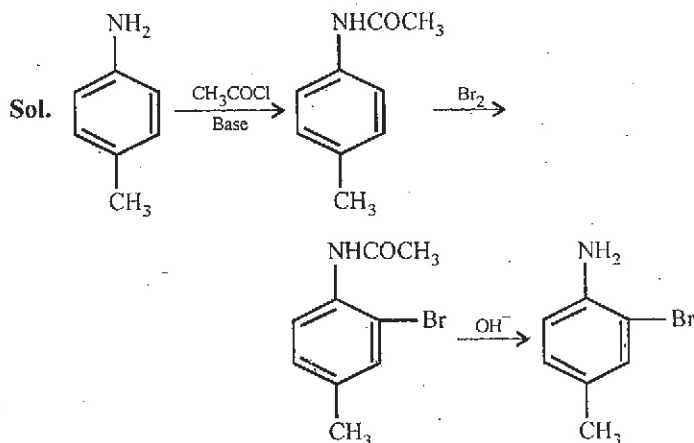
MISCELLANEOUS SOLVED EXAMPLES

Example 1 : How is nitrobenzene converted to aniline under neutral conditions?

Sol. By catalytic hydrogenation using Pd/C catalyst in ethanol.



Example 2 : How will you convert p-toluidine to 2-bromo-4-methylaniline?





- Acetamide and ethylamine can be distinguished by reacting with
 - aqueous HCl and heat
 - aqueous NaOH and heat
 - acidified KMnO_4
 - bromine water.
- Which of the following reagents will convert *p*-methylbenzenediazonium chloride into *p*-cresol?
 - Cu powder
 - H_2O
 - H_3PO_2
 - $\text{C}_6\text{H}_5\text{OH}$
- Benzamide on reaction with POCl_3 gives
 - aniline
 - chlorobenzene
 - benzylamine
 - benzonitrile
- Which of the following will produce isopropyl amine –
 - $(\text{CH}_3)_2\text{CO} \xrightarrow{\text{NH}_2\text{OH}} \text{X} \xrightarrow{\text{LiAlH}_4}$
 - $\text{CH}_3 - \text{CH}_2 - \text{CHO} \xrightarrow[\text{heat}]{\text{NH}_3} \text{X} \xrightarrow{\text{LiAlH}_4}$
 - $(\text{CH}_3)_2\text{CH} - \text{OH} + \text{PCl}_5 \longrightarrow \text{X} \xrightarrow{\text{NH}_3}$
 - $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \xrightarrow{\text{heat}}$
 - I, II
 - II, III
 - I, III
 - IV only
- $$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} = \text{N} - \text{OH} \\ \diagup \\ \text{R}' \end{array} \xrightarrow{\text{H}^+} [\text{X}], \text{ the product and name of this reaction is -}$$
 - $\text{R} - \text{C}(=\text{O}) - \text{NHR}'$; Pinnacole rearrangement
 - $\text{R}' - \text{C}(=\text{O}) - \text{NHR}$; Fries rearrangement
 - $\text{R} - \text{C}(=\text{O}) - \text{NHR}'$; Beckmann's rearrangement
 - $\text{R} - \text{C}(=\text{O}) - \text{NHR}'$, Allylic rearrangement
- $\text{R} - \text{NH}_2 + \text{CH}_3\text{COCl} \xrightarrow{(\text{excess})} \text{A}$
The product (A) will be –
 - RNHCOCH_3
 - $\text{RN}(\text{COCH}_3)_2$
 - $\text{RN}^+(\text{COCH}_3)_3\text{Cl}^-$
 - $\text{R} - \text{CONH}_2$
- Carbylamine reaction is used for the detection of
 - aliphatic 2° amines
 - aliphatic 1° amines
 - aromatic 1° amines
 - Both (b) and (c)
- Identify Z in the following sequence of reactions –

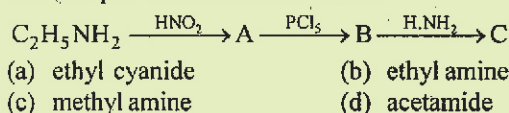
$$\text{CH}_3 - \text{COONH}_4 \xrightarrow{\Delta} \text{X} \xrightarrow{\text{P}_2\text{O}_5} \text{Y} \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{Z}$$
 - $\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{NH}_2$
 - $\text{CH}_3 - \text{CN}$
 - $(\text{CH}_3\text{CO})_2\text{O}$
 - $\text{CH}_3 - \text{COOH}$
- Ethylamine can be prepared by the action of bromine, caustic potash and :
 - acetamide
 - propionamide
 - formamide
 - methyl cyanide
- The number of primary amines of formula $\text{C}_4\text{H}_{11}\text{N}$ is :
 - 1
 - 3
 - 4
 - 2
- p*-Chloroaniline and anilinium hydrogen chloride can be distinguished by :
 - Sandmeyer reaction
 - Carbylamine reaction
 - Hinsberg's reaction
 - AgNO_3
- The conversion of acetophenone to acetanilide is best accomplished by using :
 - Beckmann rearrangement
 - Curtius rearrangement
 - Lossen rearrangement
 - Hofmann rearrangement
- High basicity of Me_2NH relative to Me_3N is attributed to :
 - effect of solvent
 - inductive effect of Me
 - shape of Me_2NH
 - shape of Me_3N
- In the following sequence of reactions, the compound C formed would be

$$\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \text{CH}_3 \xrightarrow[\text{H}_2\text{O}]{\text{HNO}_2} \text{A} \xrightarrow{[\text{O}]} \text{B} \xrightarrow[\text{H}^+/\text{H}_2\text{O}]{\text{CH}_3\text{MgI}} \text{C}$$
 - 1,1-dimethyl ethanol
 - butanol-1
 - butanol-2
 - 2-methyl-propanol-1
- Ethylamine reacts with HNO_2 giving :
 - $\text{C}_2\text{H}_5\text{OH}$
 - $\text{C}_2\text{H}_5\text{NO}_2$
 - NH_3
 - C_2H_6
- Primary amines react with benzaldehyde to form:
 - diazonium salts
 - azo dyes
 - anilides
 - schiff's base
- In the reaction sequence

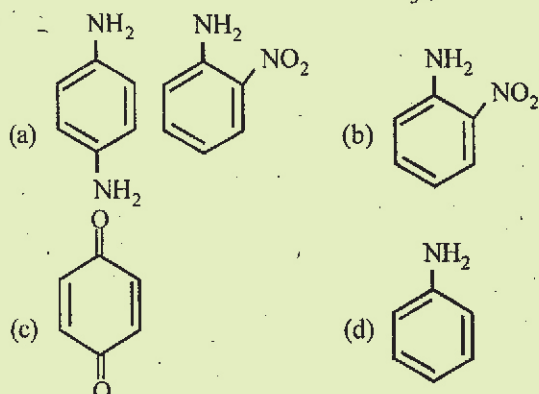
$$\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[0^\circ\text{C}]{\text{NaNO}_2, \text{HCl}} \text{A} \xrightarrow{\text{CuCN}} \text{B} \xrightarrow{\text{LiAlH}_4} \text{C}$$
 the product 'C' is:
 - benzonitrile
 - benzaldehyde
 - benzoic acid
 - benzylamine
- The end product (Y) in the reaction sequence

$$\text{CH}_3\text{CONH}_2 \xrightarrow[\Delta]{\text{P}_2\text{O}_5} \text{X} \xrightarrow{\text{Sn}/\text{HCl}} \text{Y}$$
 is :
 - ethane nitrile
 - acetic acid
 - ethanamine
 - chloroethane

19. The end product of the reactions is



20. Aniline when treated with conc. HNO_3 gives



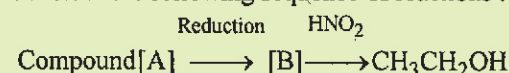
21. The correct order of basicity in amines

- (i) $\text{C}_2\text{H}_5\text{NH}_2$ (ii) CH_3NH_2
(iii) $(\text{CH}_3)_2\text{NH}$ (iv) $(\text{CH}_3)_3\text{N}$
(a) (i) < (iv) < (ii) < (iii) (b) (iv) < (ii) < (iii) < (i)
(c) (i) < (ii) < (iii) < (iv) (d) (ii) < (iii) < (iv) < (i)

22. Which is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl ?

- (a) Acetic acid (b) Acetamide
(c) Methyl cyanide (d) Acetic anhydrides

23. Consider the following sequence of reactions :



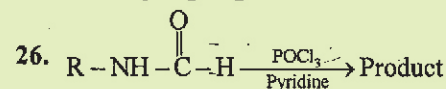
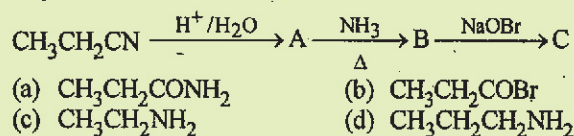
The compound [A] is

- (a) $\text{CH}_3\text{CH}_2\text{CN}$ (b) CH_3NO_2
(c) CH_3NC (d) CH_3CN

24. An isocyanide is prepared by

- (a) Friedel-Crafts reaction (b) Perkin reaction
(c) Carbylamine reaction (d) Wurtz reaction

25. What will be the final product in the following reaction sequence –



In the given reaction what will be the product

- (a) $\text{R}-\text{N}=\text{C}=\text{O}$ (b) $\text{R}-\text{N}^+\equiv\text{C}^-$
(c) $\text{R}-\text{C}\equiv\text{N}$ (d) None of these.

27. Hydrolysis of phenyl isocyanide forms

- (a) Benzoic acid (b) Formic acid
(c) Acetic acid (d) None of these

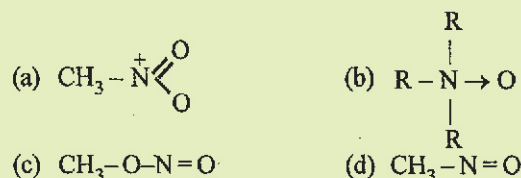
28. $\text{CH}_3-\text{CH}_2\text{C}\equiv\text{N} \xrightarrow{\text{X}} \text{CH}_3\text{CH}_2\text{CHO}$. The compound X is

- (a) $\text{SnCl}_2/\text{HCl}/\text{H}_2\text{O}$, boil (b) $\text{H}_2/\text{Pd}-\text{BaSO}_4$
(c) $\text{LiAlH}_4/\text{ether}$ (d) $\text{NaBH}_4/\text{ether}/\text{H}_3\text{O}^+$

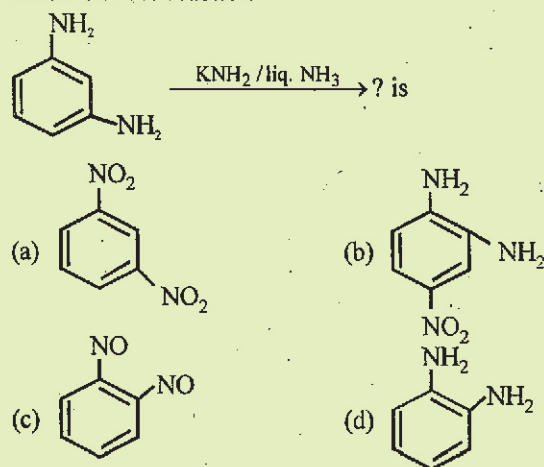
29. Acetanilide on nitration followed by alkaline hydrolysis mainly gives –

- (a) o-Nitroaniline (b) p-Nitroaniline
(c) m-Nitroaniline (d) 2,4,6-Trinitroaniline

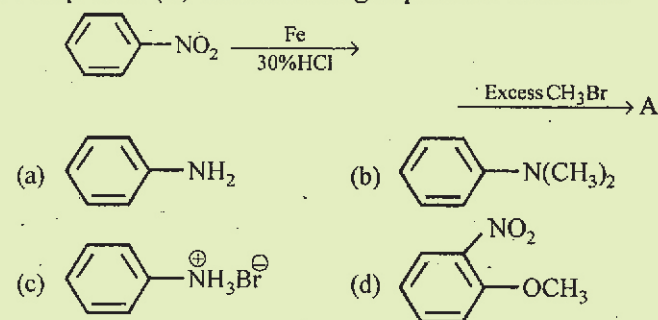
30. Identify the compounds which has a nitro group in it.



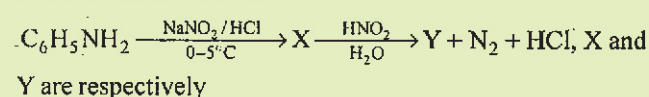
31. Product of the reaction



32. End product (A) of the following sequence of reaction is :



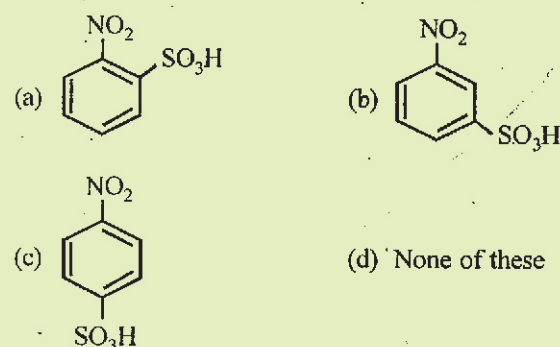
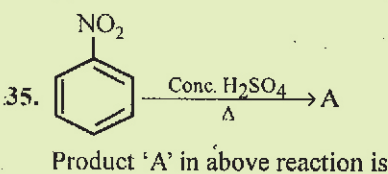
33. In the series of reaction



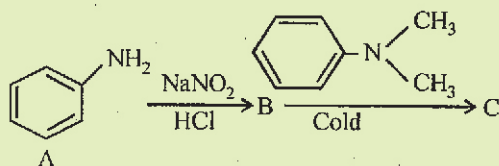
- (a) $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$
(b) $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$
(c) $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, $\text{C}_6\text{H}_5\text{NO}_2$
(d) $\text{C}_6\text{H}_5\text{NO}_2$, C_6H_6

34. What is formed, when nitrobenzene is reduced using zinc and alkali

- (a) Phenol (b) Aniline
(c) Nitrosobenzene (d) Hydrazobenzene



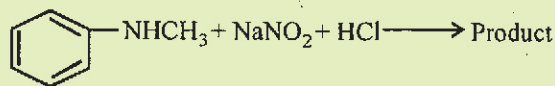
36. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine?
 (a) Methyl isocyanide (b) Acetamide
 (c) Methyl cyanide (d) Nitroethane
37. In a reaction of aniline a coloured product C was obtained.



The structure of C would be :

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

38. Predict the product:



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

39. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 in the mixture, nitric acid acts as a/an :
 (a) acid (b) base
 (c) catalyst (d) reducing agent

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

- (a) $\text{NaOH} - \text{Br}_2$ (b) Sodalime
 (c) Hot conc. H_2SO_4 (d) PCl_5

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

- (a) Alkyl amines are stronger bases than aryl amines
 (b) Alkyl amines react with nitrous acid to produce alcohols
 (c) Aryl amines react with nitrous acid to produce phenols
 (d) Alkyl amines are stronger bases than ammonia

42. Match the compounds given in List - I with their characteristic reactions given in List - II. Select the correct option.

List - I
Compounds

- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
 (2) $\text{CH}_3\text{C} \equiv \text{CH}$
 (3) $\text{CH}_3\text{CH}_2\text{COOCH}_3$
 (4) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

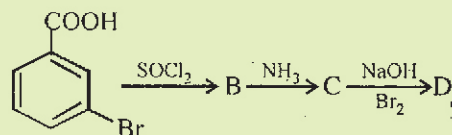
List - II
Reactions

- (i) alkaline hydrolysis
 (ii) with KOH (alcohol) and CHCl_3 produces bad smell
 (iii) gives white ppt. with ammonical AgNO_3
 (iv) with Lucas reagent cloudiness appears after 5 minutes

Options :

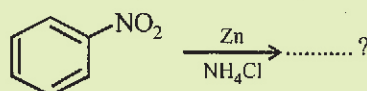
- (1) (2) (3) (4)
 (a) (iv) (ii) (iii) (i)
 (b) (ii) (i) (iv) (iii)
 (c) (iii) (ii) (i) (iv)
 (d) (ii) (iii) (i) (iv)

43. In a set of reactions *m*-bromobenzoic acid gave a product D. Identify the product D.

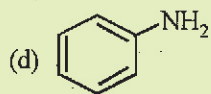
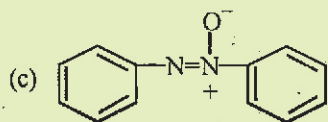


- (a)
- (b)
- (c)
- (d)

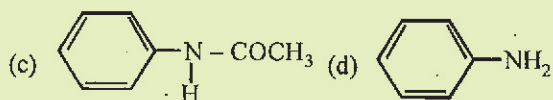
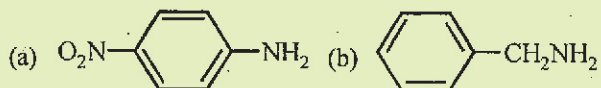
44. What is the product obtained in the following reaction :



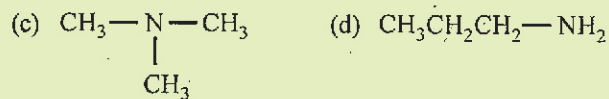
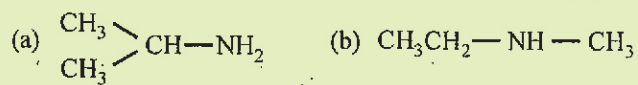
- (a)
- (b)



45. Which of the following compounds is most basic?

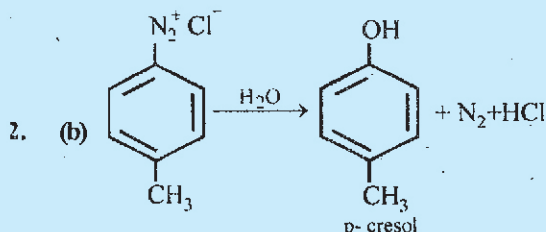
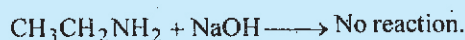
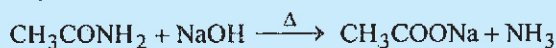


46. An organic compound (C_3H_9N) (A), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A).

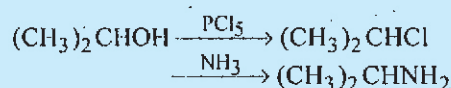
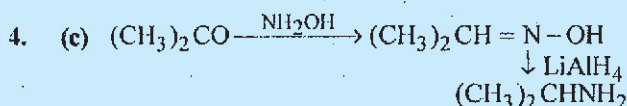
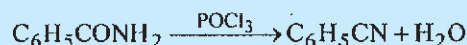


SOLUTION

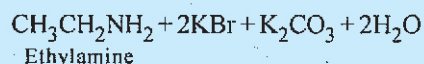
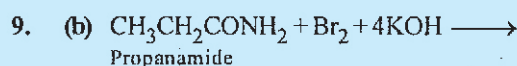
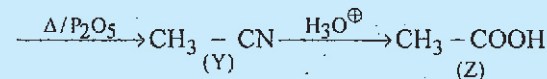
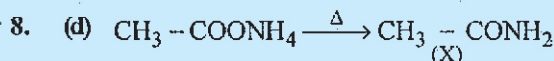
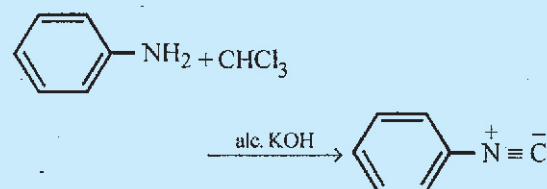
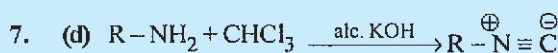
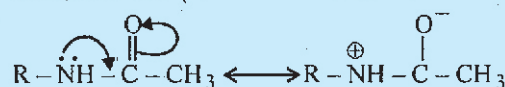
1. (b) Acetamide and ethylamine can be distinguished by heating with NaOH solution. Acetamide evolves NH_3 but ethylamine does not.



3. (d) POCl_3 is a dehydrating agent. Hence

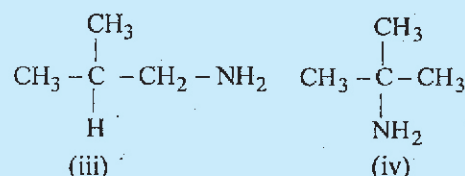
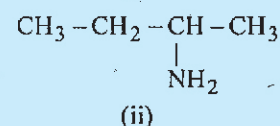
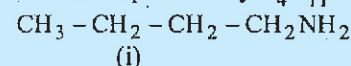


5. (c) Beckmann rearrangement is used to form N-alkyl amide.
 6. (a) Acylation occurs in one step only because lone pair of nitrogen is delocalized with acyl group.

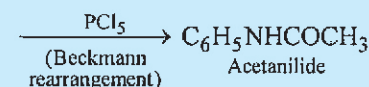
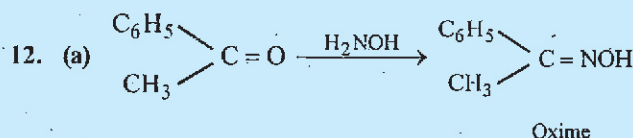


This is Hofmann bromamide reaction in which amide is converted into amine having one carbon atom less than amide.

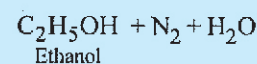
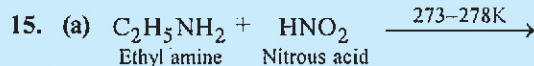
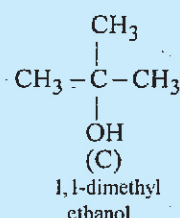
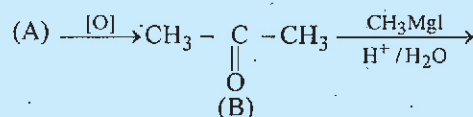
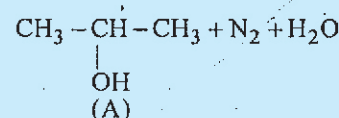
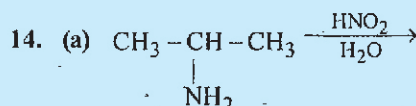
10. (c) 1° amines have $-\text{NH}_2$ group in their structure. 4 primary amines are possible by $\text{C}_4\text{H}_{11}\text{N}$.



11. (d) *p*-Chloroaniline and anilinium hydrogen chloride can be distinguished by AgNO_3 . Anilinium hydrogen chloride will give white ppt of AgCl on reaction with AgNO_3 but *p*-chloroaniline will not react with it because Cl is directly attached to benzene nucleus.

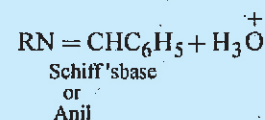
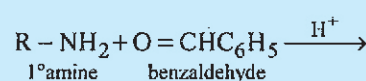


13. (a) Secondary amines are more basic than tertiary amines due to stabilisation of 2° amine by hydrogen bonding with solvent molecule.

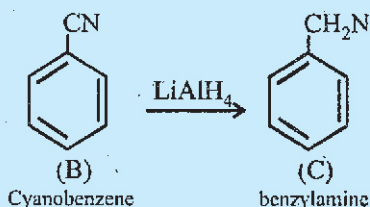
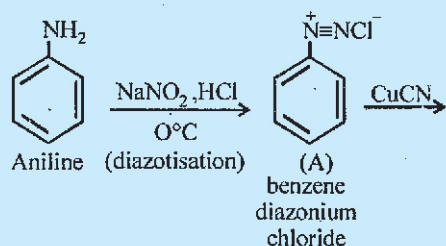


NOTE: This reaction is used as a test for aliphatic amines since no other class of amines liberates N_2 gas on treatment with HNO_2 .

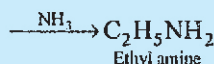
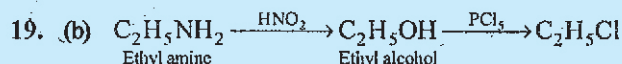
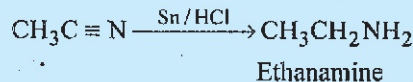
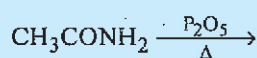
16. (d) Primary amines react with benzaldehyde in presence of a trace of an acid as catalyst to form Schiff's base or Anil



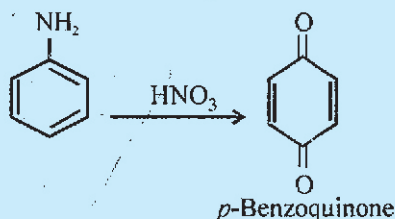
17. (d)



18. (c) Completing the given reaction we get

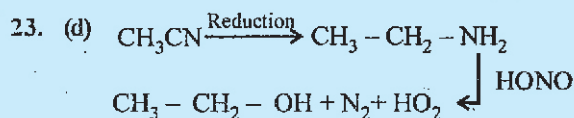
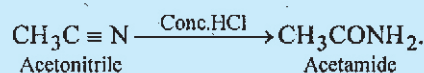


20. (c)

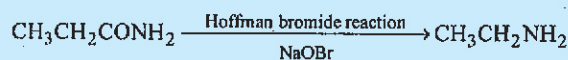
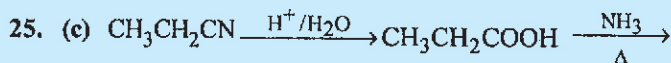
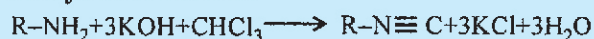


21. (b) $(\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$

22. (b) Methyl cyanide on treatment with conc. HCl give acetamide.



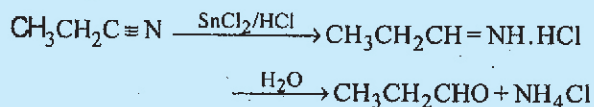
24. (c) Carbylamine reaction :



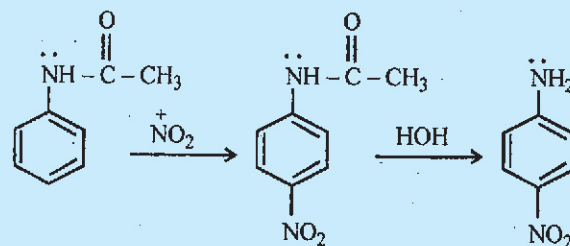
26. (b) N-alkyl formamides when dehydrated with POCl_3 in presence of pyridine give isocyanides.

27. (b) Hydrolysis of phenyl isocyanide forms formic acid.

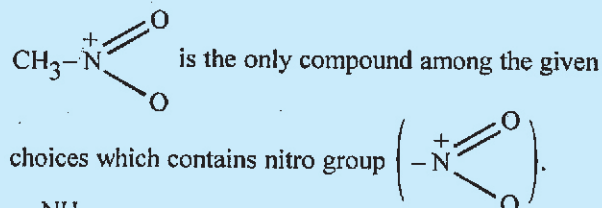
28. (a) It is Stephen's reaction.



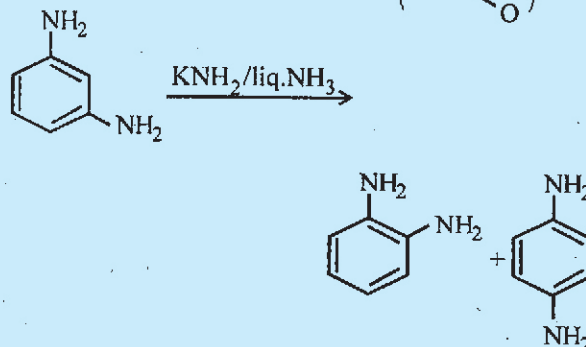
29. (b)



30. (a)

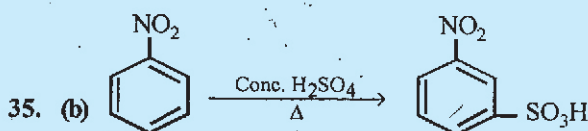
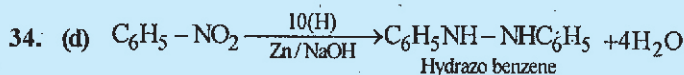
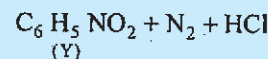
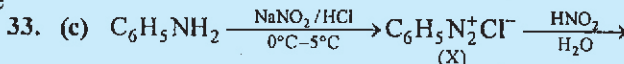
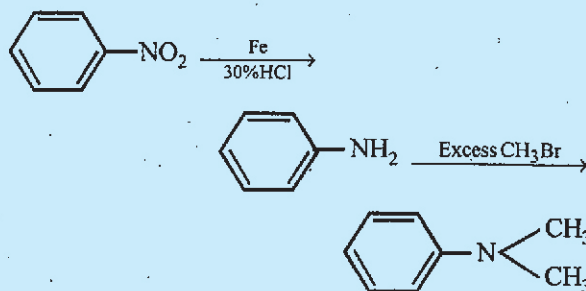


31. (d)

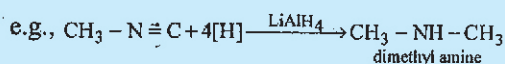


It is an example of nucleophilic aromatic substitution. It proceeds via the formation of an intermediate benzyne.

32. (b) Completing the given reaction

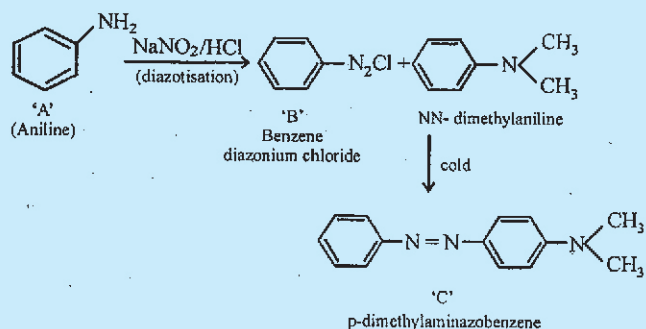


36. (a) Reduction of alkyl isocyanides in presence of LiAlH_4 yields secondary amines containing methyl as one of the alkyl group.

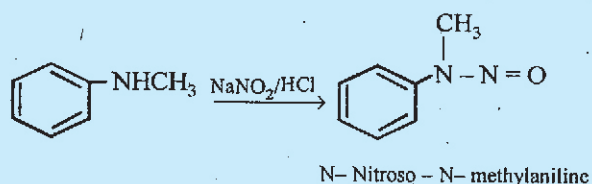


whereas, alkyl cyanides give 1° amine on reduction.

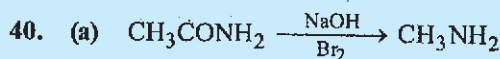
37. (d) The reaction can be completed as follows:



38. (d) Secondary amine with ($\text{NaNO}_2 + \text{HCl}$) gives a nitroso product



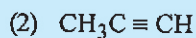
39. (b) $\text{HONO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-$
 Nitric acid acts as a base by accepting a proton.



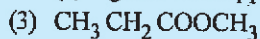
(Hofmann bromamide reaction)

41. (c) Aryl amines do not produce phenol on treatment with nitrous acid

42. (d) (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
 (ii) with KOH (alcohol) and CHCl_3 produces bad smell



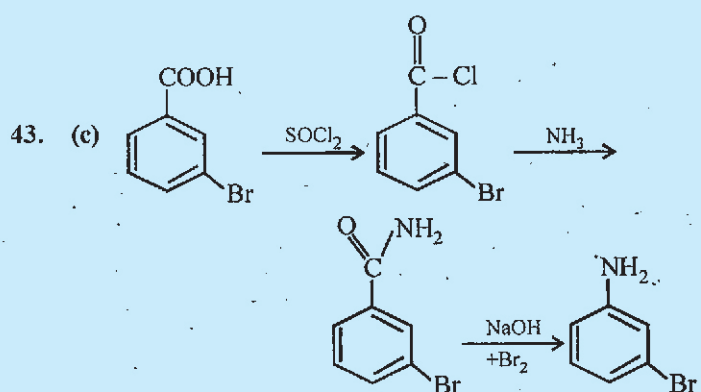
(ii) gives white ppt with ammonical AgNO_3



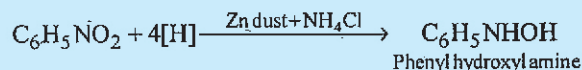
(i) alkaline hydrolysis



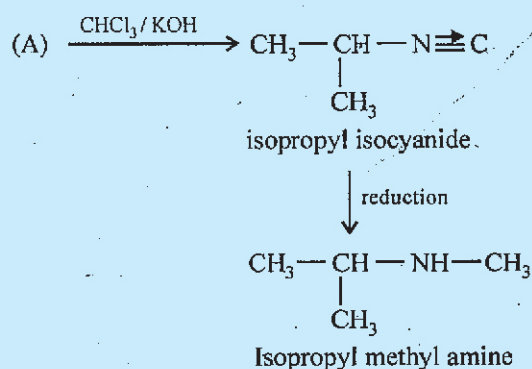
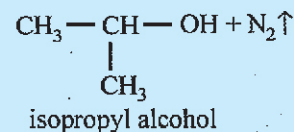
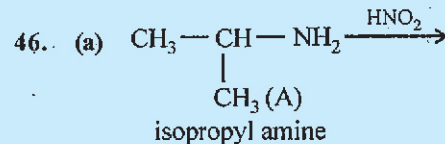
(iv) with Lucas reagent cloudiness appears after 5 minutes

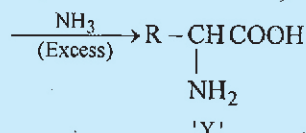
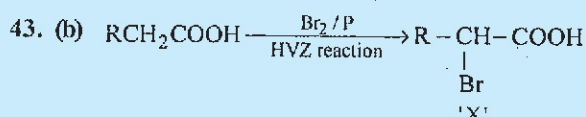
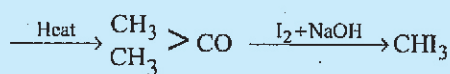
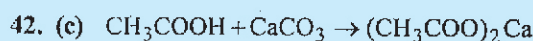
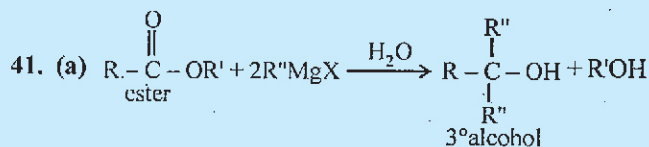
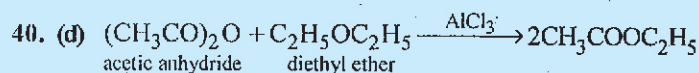
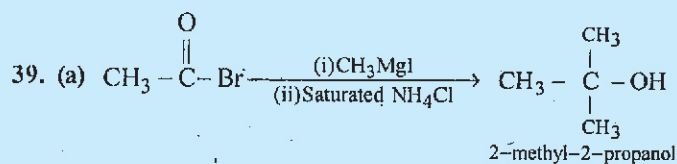


44. (a) When nitro compound is reduced with a neutral reducing agent (Zn dust + NH_4Cl) the corresponding hydroxyl amine is formed

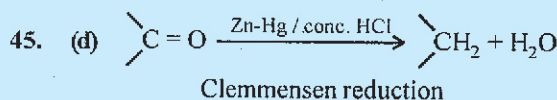
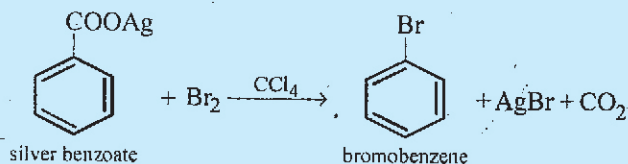


45. (b) compound is most basic due to localized lone pair of electron on nitrogen atom while other compounds have delocalized lone pair of electron.

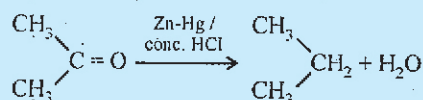




44. (c) This is Hunsdiecker's reaction.

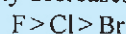


e.g.

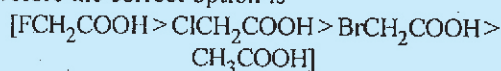


46. (c) Electron withdrawing substituent (like halogen, $-\text{NO}_2$, C_6H_5 etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.

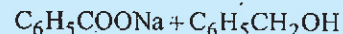
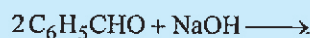
Electronegativity decreases in order



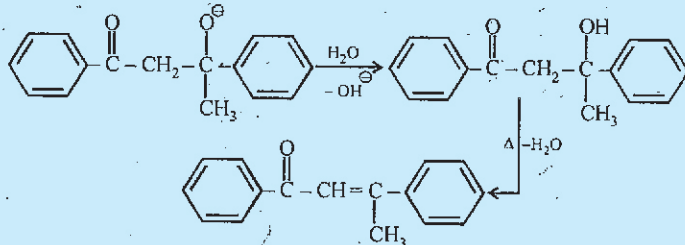
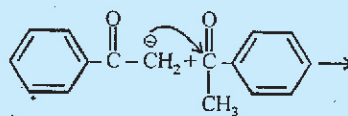
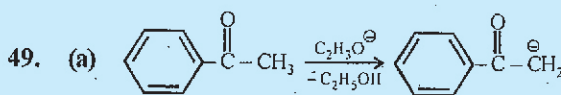
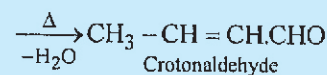
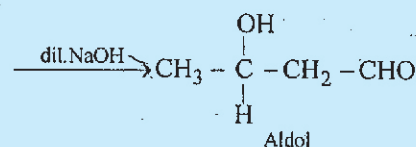
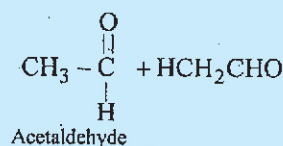
and hence $-I$ effect also decreases in the same order, therefore the correct option is



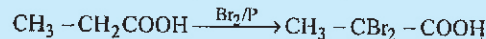
47. (a) Aldehydes containing no α -hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e., self oxidation-reduction known as cannizzaro's reaction.



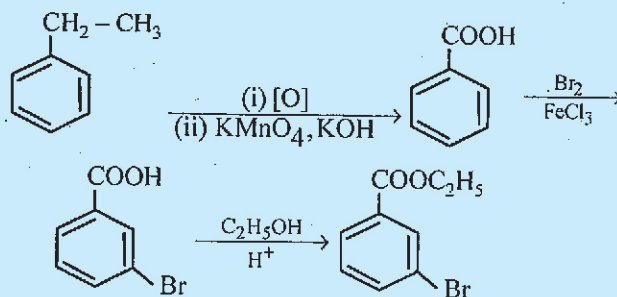
48. (a) Aldehydes and ketones having at least one α -hydrogen atom in presence of dilute alkali give β -hydroxy aldehyde or β -hydroxy ketone

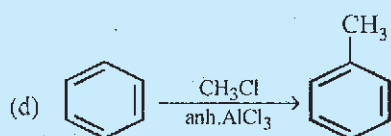
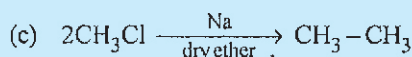
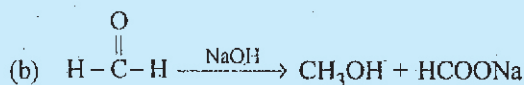
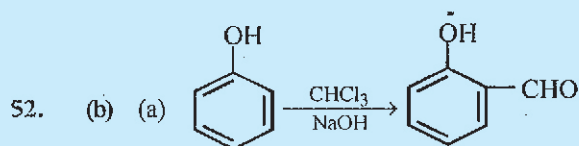


50. (c) This reaction is an example of Hell-Volhard Zelinsky reaction. In this reaction acids containing α -H on treatment with X_2/P give di-halo substituted acid.



51. (d)



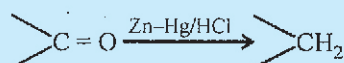


Note that new C-C bond is formed in a, c and d.

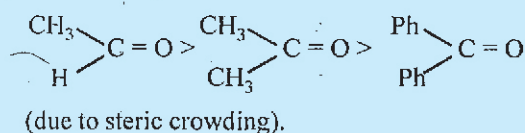
53. (d) Among the given compounds only CH_3OH does not give iodoform reaction.

54. (d) The intermediate is carbocation which is destabilised by C=O group in the first three cases. In (d), α -hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the C=O group.

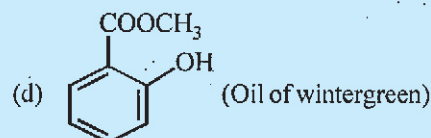
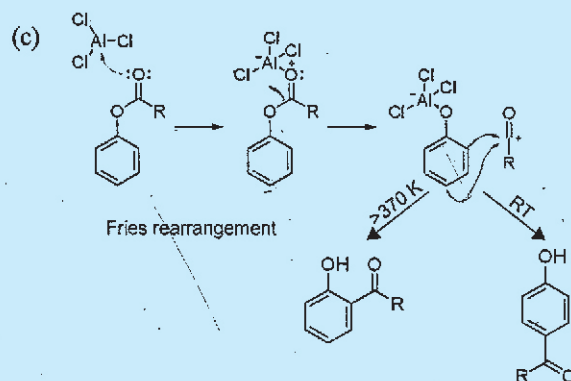
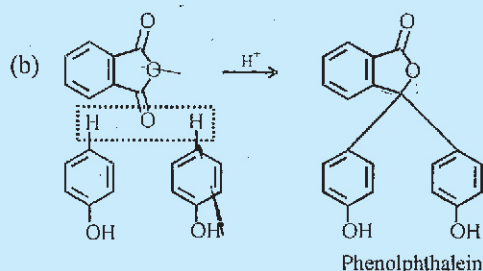
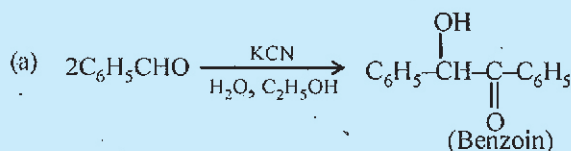
55. (b) Clemmensen reduction is



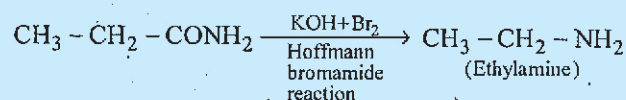
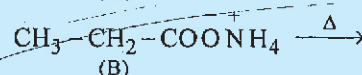
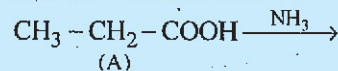
56. (d) The reactivity of the carbonyl group toward the nucleophilic addition reactions depend upon the magnitude of the positive charge on the carbonyl carbon atom (electronic factor) and also on the crowding around the carbonyl carbon atom in the transition state (steric factor). Both these factors predict the following order



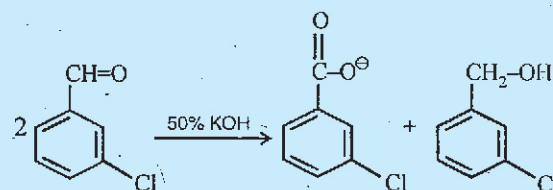
57. (d)



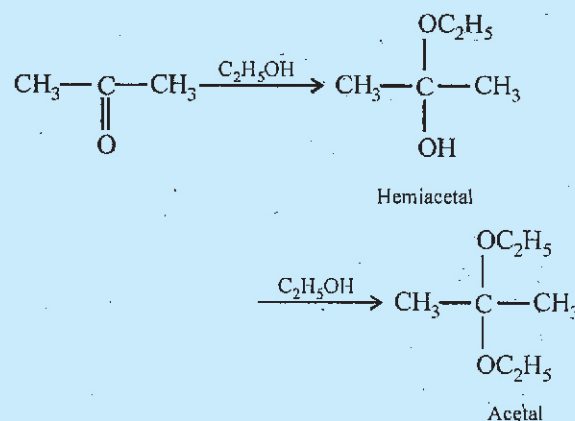
58. (d) Since, C when heated with Br_2 in presence of KOH produces ethylamine, hence it must be propanamide and hence the organic compound (A) will be propanoic acid. The reactions follows.



59. (c) Cannizzaro reaction - when an aldehyde containing α -H undergo reaction in presence of 50% KOH. It disproportionates to form a molecule of carboxylic acid and a molecule of alcohol.



60. (d) Anhydrous alcohols add to the carbonyl group of aldehydes in the presence of anhydrous hydrogen chloride to form acetals via hemiacetals.

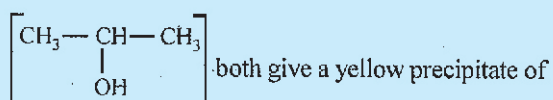
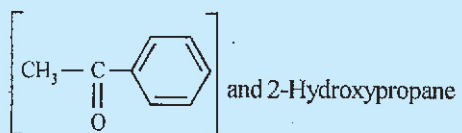


61. (a) $\text{CF}_3\text{COOH} > \text{CCl}_3\text{COOH} > \text{HCOOH} > \text{CH}_3\text{COOH}$ (K_a order)

The halogenated acids are much stronger acids than the parent acid and more over the acidity among the halogenated acid is increased almost proportionately with the increase in electronegativity of the halogen present. Further formic acid having no alkyl group is more acidic than acetic acid.

62. (d) $\text{R}-\text{CH}=\text{O} + \text{H}_2\text{N}-\text{NH}_2 \rightarrow \text{R}-\text{CH}=\text{N}-\text{NH}_2$
Such reactions take place in slightly acidic medium and involve nucleophilic addition of the ammonia derivative.

63. (b) It is iodoform reaction. Acetophenone



CHI_3 (iodoform) with iodine and alkali.