

13

Amines

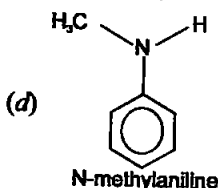
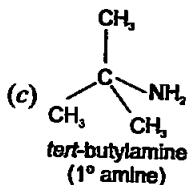
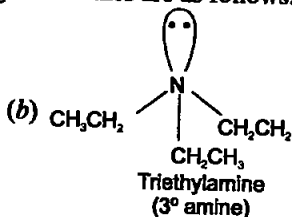
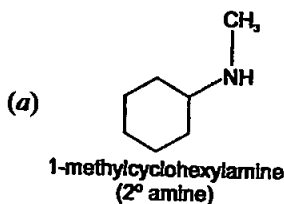
I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Which of the following is a 3° amine?

- (i) 1-methylcyclohexylamine (ii) Triethylamine
(iii) tert-butylamine (iv) N-methylaniline

Ans. (ii)

Explanation: The structure of given amines are as follows:



Hence, triethylamine is tertiary amine. The correct choice is (ii).

2. The correct IUPAC name for $\text{CH}_2=\text{CHCH}_2\text{NHCH}_3$ is

- (i) Allylmethylamine (ii) 2-amino-4-pentene
(iii) 4-aminopent-1-ene (iv) N-methylprop-2-en-1-amine

Ans. (iv)

Explanation: IUPAC name of the compound is N-methylprop-2-en-1-amine.

3. Amongst the following, the strongest base in aqueous medium is

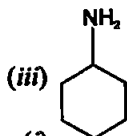
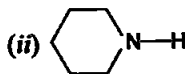
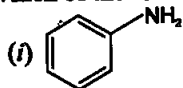
- (i) CH_3NH_2 (ii) NCCH_2NH_2
(iii) $(\text{CH}_3)_2\text{NH}$ (iv) $\text{C}_6\text{H}_5\text{NHCH}_3$

Ans. (iii)

Explanation: Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups.

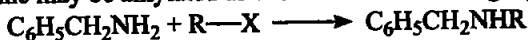
4. Which of the following is the weakest Brønsted base?



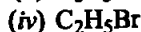
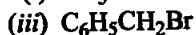
Ans. (i)

Explanation: In aniline or other arylamines, the —NH_2 group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.

5. Benzylamine may be alkylated as shown in the following equation:



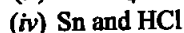
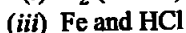
Which of the following alkylhalides is best suited for this reaction through $\text{S}_{\text{N}}1$ mechanism?



Ans. (iii)

Explanation: $\text{S}_{\text{N}}1$ reaction proceeds through the formation of carbocation since in $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ benzyl carbocation is formed which is stabilized by resonance.

6. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

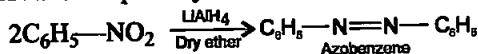


Ans. (ii)

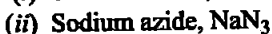
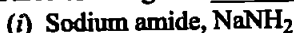
Explanation: Nitroalkanes can be easily reduced to the corresponding primary amines with LiAlH_4 .



In contrast, aromatic nitro compounds on reduction with LiAlH_4 give $\alpha = 0$ compounds and not primary amines.



7. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is _____.



- (iii) Potassium cyanide, KCN
 (iv) Potassium phthalimide, $C_6H_4(CO)_2N-K^+$

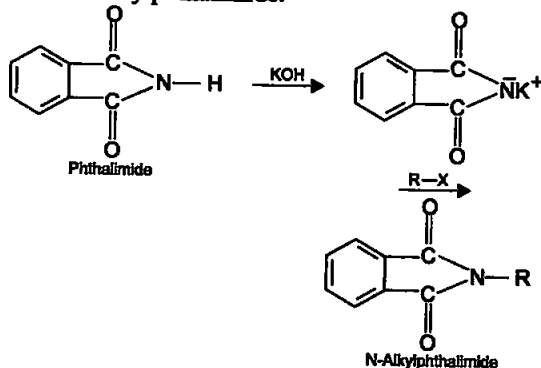
Ans. (iii)

8. The source of nitrogen in Gabriel synthesis of amines is _____.

- (i) Sodium azide, NaN_3
 (ii) Sodium nitrite, $NaNO_2$
 (iii) Potassium cyanide, KCN
 (iv) Potassium phthalimide, $C_6H_4(CO)_2N-K^+$

Ans. (iv)

Explanation: Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

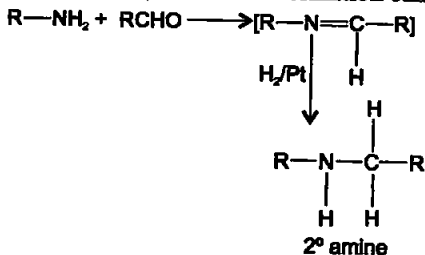


9. Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____.

- (i) $2^\circ R-Br + NH_3$
 (ii) $2^\circ R-Br + NaCN$ followed by H_2/Pt
 (iii) $1^\circ R-NH_2 + RCHO$ followed by H_2/Pt
 (iv) $1^\circ R-Br$ (2 mol) + potassium phthalimide followed by $H_3O^+/heat$

Ans. (iii)

Explanation: Chemical transformation can be shown as



While other given set of reactants give primary amine only.

(i) II < III < I

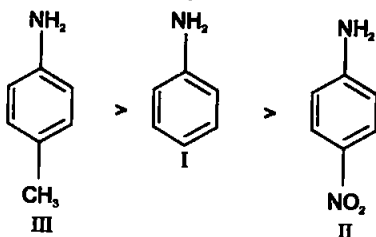
(ii) III < I < II

(iii) III < II < I

(iv) II < I < III

Ans. (iv)

Explanation: The correct increasing order of basic strength is as follows:



Greater the electron density towards ring, greater will be its basic strength. Electron withdrawing group decreases basic strength while electron donating group increases basic strength.

14. Methylamine reacts with HNO_2 to form _____.

(i) $\text{CH}_3\text{—O—N=O}$

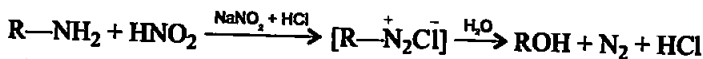
(ii) $\text{CH}_3\text{—O—CH}_3$

(iii) CH_3OH

(iv) CH_3CHO

Ans. (iii)

Explanation:



15. The gas evolved when methylamine reacts with nitrous acid is _____.

(i) NH_3

(ii) N_2

(iii) H_2

(iv) C_2H_6

Ans. (ii)

Explanation: Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohol.

16. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3 , the species which initiates the reaction is _____.

(i) NO_2

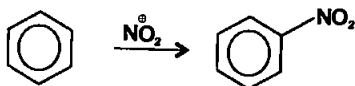
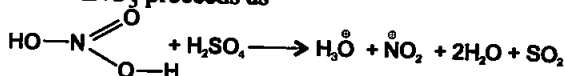
(ii) NO^+

(iii) NO_2^+

(iv) NO_2^-

Ans. (iii)

Explanation: Nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3 proceeds as



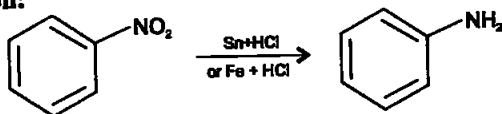
This reaction is known as electrophilic substitution reaction.

17. Reduction of aromatic nitro compounds using Fe and HCl gives _____.

- (i) aromatic oxime (ii) aromatic hydrocarbon
 (iii) aromatic primary amine (iv) aromatic amide

Ans. (iii)

Explanation:



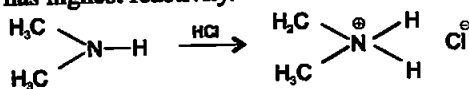
18. The most reactive amine towards dilute hydrochloric acid is _____.

- (i) $\text{CH}_3\text{—NH}_2$ (ii) $\begin{matrix} \text{H}_3\text{C} \\ \diagdown \\ \text{N} \\ \diagup \\ \text{H}_3\text{C} \end{matrix}$

- (iii) $\begin{matrix} \text{H}_3\text{C} \\ \diagdown \\ \text{N} \text{—} \text{CH}_3 \\ \diagup \\ \text{H}_3\text{C} \end{matrix}$ (iv) $\text{C}_6\text{H}_5\text{NH}_2$

Ans. (ii)

Explanation: Greater will be the strength of base, greater will be its reactivity towards dilute HCl. Hence, $(\text{CH}_3)_2\text{NH}$ has highest basic strength as it has highest reactivity.

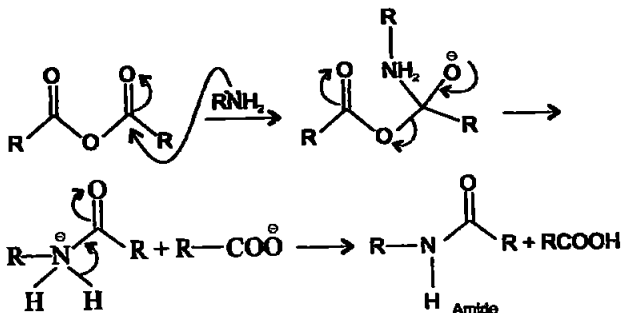


19. Acid anhydrides on reaction with primary amines give _____.

- (i) amide (ii) imide
 (iii) secondary amine (iv) imine

Ans. (i)

Explanation: Acid anhydride on reaction with primary amine produces amide as

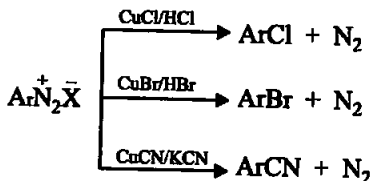


20. The reaction $\text{ArN}_2^+\text{Cl}^- \xrightarrow{\text{Cu/HCl}} \text{ArCl} + \text{N}_2 + \text{CuCl}$ is named as _____.

- (i) Sandmeyer reaction (ii) Gatterman reaction
 (iii) Claisen reaction (iv) Carbylamine reaction

Ans. (i)

Explanation:

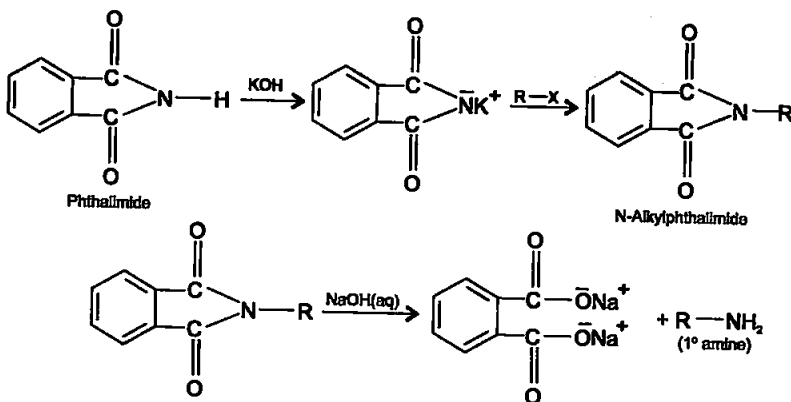


21. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is

- (i) Hoffmann Bromamide reaction
 (ii) Gabriel phthalimide synthesis
 (iii) Sandmeyer reaction
 (iv) Reaction with NH_3

Ans. (ii)

Explanation:

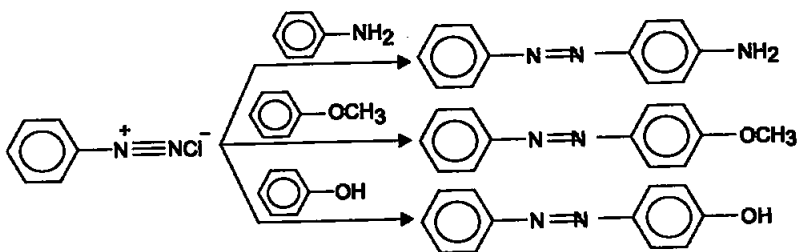


22. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride.

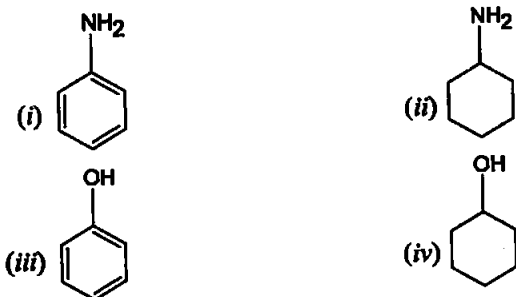
- (i) Aniline (ii) Phenol
 (iii) Anisole (iv) Nitrobenzene

Ans. (iv)

Explanation: Nitrobenzene will not undergo azo coupling reaction with benzene diazonium chloride while other three undergo diazo coupling reaction very easily. Diazonium cation is a weak E^+ and hence reacts with electron rich compounds containing electron donating group, i.e. $-\text{OH}$, $-\text{NH}_2$ and $-\text{OCH}_3$ groups and not with compounds containing electron withdrawing group, i.e., NO_2 etc.



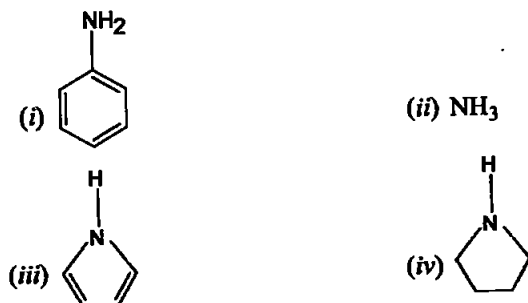
23. Which of the following compounds is the weakest Brønsted base?



Ans. (iii)

Explanation: Phenol is the weakest Brønsted base as it is the strongest acid among the four choices given above. Stronger the acid weaker is its conjugate base.

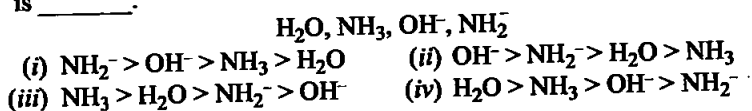
24. Among the following amines, the strongest Brønsted base is _____.



Ans. (iv)

Explanation: Pyrrolidine is strongest of two base as lone pair of nitrogen does not involved in resonance and also due to presence of two alkyl basic strength becomes high among given four compounds.

25. The correct decreasing order of basic strength of the following species is _____.



Ans. (i)

Explanation: Basic strength depends upon the electron donating capacity of the central atom, here amide is most basic due to presence of negative charge and two lone pair of electrons on nitrogen atom.

26. Which of the following should be most volatile?

- (I) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (II) $(\text{CH}_3)_3\text{N}$
 (III) $\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \diagup \\ \text{NH} \\ \diagdown \\ \text{CH}_3 \end{array}$ (IV) $\text{CH}_3\text{CH}_2\text{CH}_3$

(i) II (ii) IV (iii) I (iv) III

Ans. (ii)

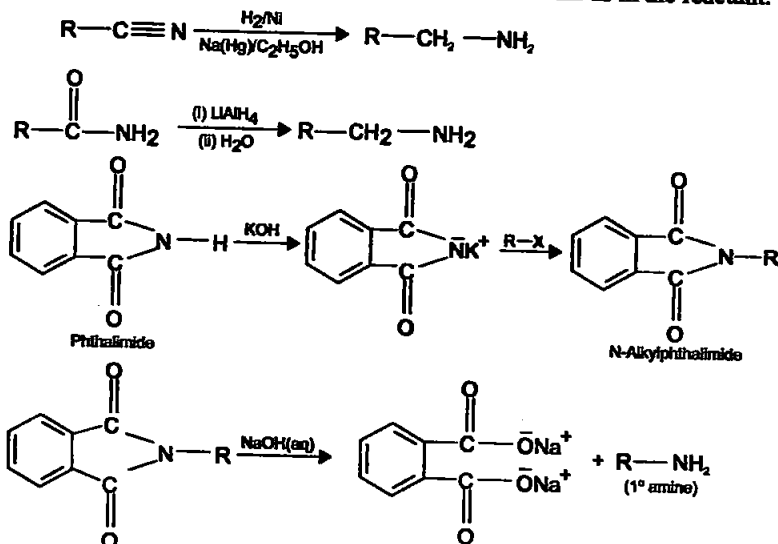
Explanation: Hydrocarbon is most volatile because of the absence of hydrogen bonding. 1°, 2°, 3° amines are less volatile because of high boiling point due to hydrogen bonding.

27. Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?

- (i) Reaction of nitrite with LiAlH_4 .
 (ii) Reaction of amide with LiAlH_4 followed by treatment with water.
 (iii) Heating alkylhalide with potassium salt of phthalimide followed by hydrolysis.
 (iv) Treatment of amide with bromine in aqueous solution of sodium hydroxide.

Ans. (iv)

Explanation: Only treatment of amide with Br_2 in aqueous solution of NaOH will give an amine with lesser number of carbon atoms than in the reactant while $\text{RCONH}_2 \xrightarrow{\text{Br}_2/\text{NaOH}} \text{RNH}_2$ all the remaining reactions given an amine with the same number of carbon atoms as in the reactant.



II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

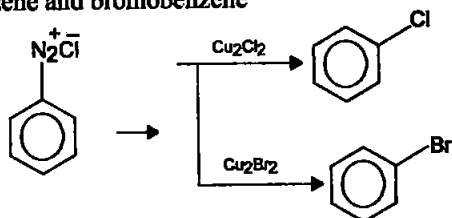
Note : In the following questions two or more options may be correct.

28. Which of the following cannot be prepared by Sandmeyer's reaction?

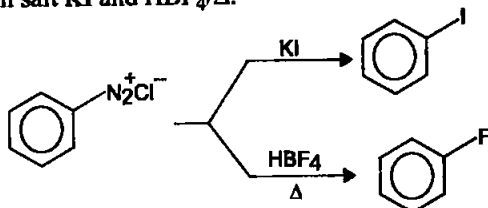
- (i) Chlorobenzene (ii) Bromobenzene
(iii) Iodobenzene (iv) Fluorobenzene

Ans. (iii) and (iv)

Explanation: Sandmeyer's reaction is used for preparation of chlorobenzene and bromobenzene



Iodobenzene and fluorobenzene can be prepared by direct reaction of diazonium salt KI and HBF_4/Δ .

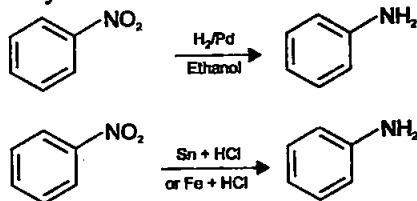


29. Reduction of nitrobenzene by which of the following reagent gives aniline?

- (i) Sn/HCl (ii) Fe/HCl
(iii) H_2 -Pd (iv) $\text{Sn}/\text{NH}_4\text{OH}$

Ans. (i), (ii) and (iii)

Explanation: Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium.



30. Which of the following species are involved in the carbylamine test?

- (i) $\text{R}-\text{NC}$ (ii) CHCl_3
(iii) COCl_2 (iv) $\text{NaNO}_2 + \text{HCl}$

Ans. (i) and (ii)

Explanation: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or

carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction.

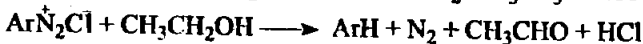


31. The reagents that can be used to convert benzenediazonium chloride to benzene are _____.

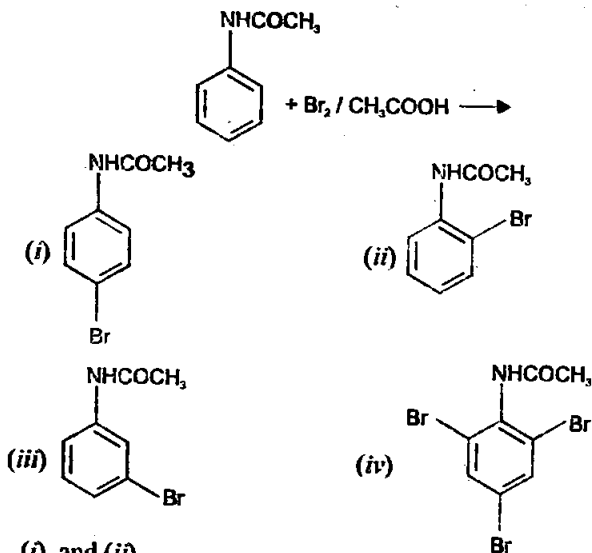
- (i) $SnCl_2/HCl$ (ii) CH_3CH_2OH
 (iii) H_3PO_2 (iv) $LiAlH_4$

Ans. (ii) and (iii)

Explanation: Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanal, respectively.

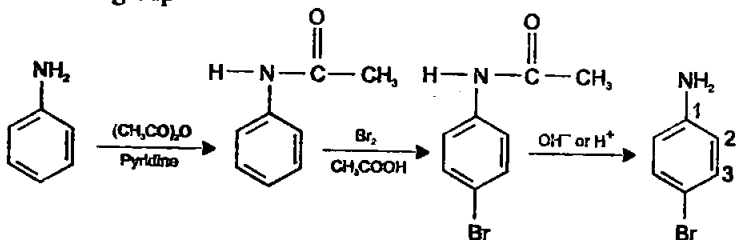


32. The product of the following reaction is _____.

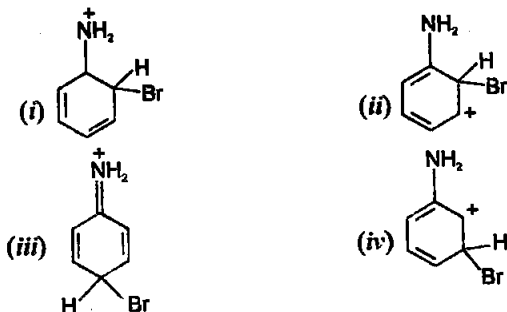


Ans. (i) and (ii)

Explanation: Activating effect of $-NHCOCH_3$ group is less than that of amino group.

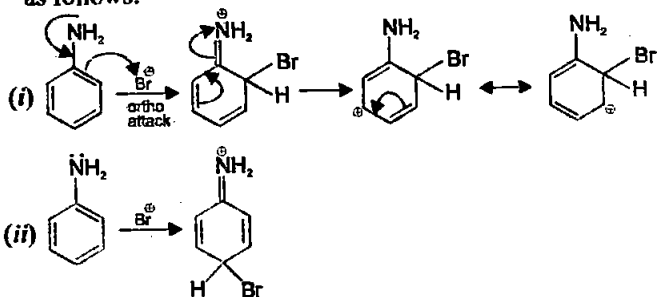


33. Arenium ion involved in the bromination of aniline is _____.



Ans. (i), (ii) and (iii)

Explanation: Arenium ion involved in the bromination of aniline are as follows:

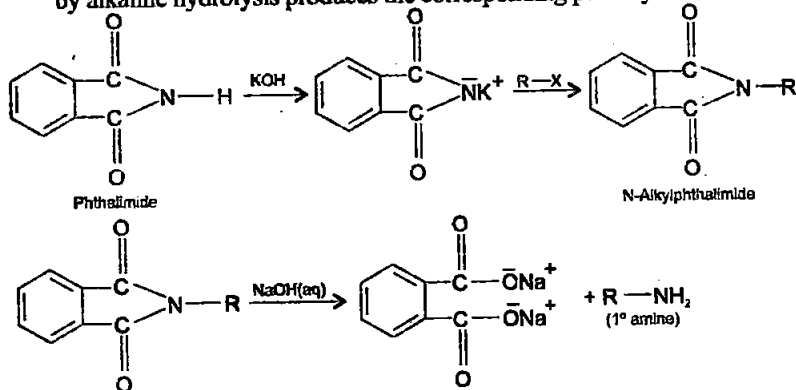


34. Which of the following amines can be prepared by Gabriel synthesis?

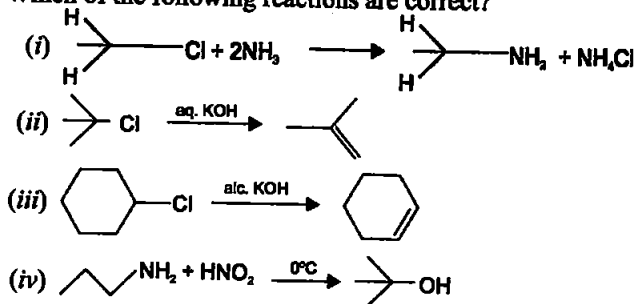
- (i) Isobutyl amine (ii) 2-Phenylethylamine
(iii) N-methylbenzylamine (iv) Aniline

Ans. (i) and (ii)

Explanation: Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.

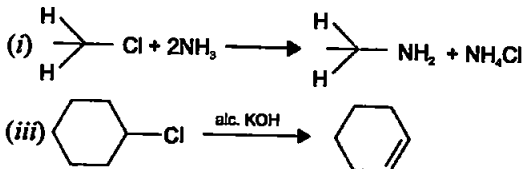


35. Which of the following reactions are correct?



Ans. (i) and (iii)

Explanation:



(i) is a nucleophilic substitution reaction.

(iii) is an elimination reaction.

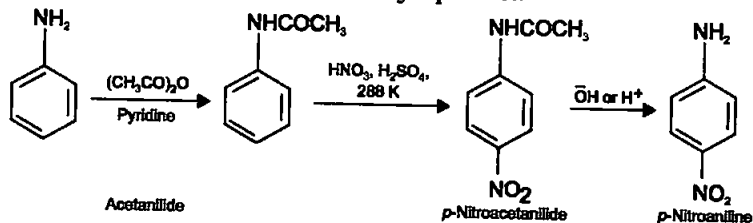
36. Under which of the following reaction conditions, aniline gives *p*-nitro derivative as the major product?

- (i) Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3 .
- (ii) Acetic anhydride/pyridine followed by conc. H_2SO_4 + conc. HNO_3 .
- (iii) Dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3 .
- (iv) Reaction with conc. HNO_3 + conc. H_2SO_4 .

Ans. (i) and (ii)

Explanation: Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is formed.

However, by protecting the $-\text{NH}_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.

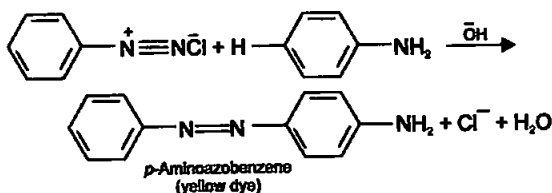


37. Which of the following reactions belong to electrophilic aromatic substitution?

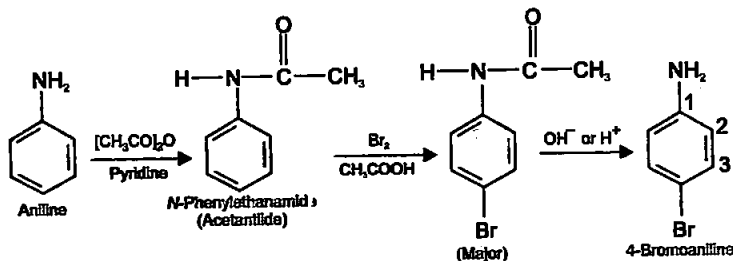
- (i) Bromination of acetanilide
- (ii) Coupling reaction of aryldiazonium salts
- (iii) Diazotisation of aniline
- (iv) Acylation of aniline

Ans. (i) and (ii)

Explanation: Benzene diazonium chloride reacts with phenol in which the phenol molecule at its *para* position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. This is an example of electrophilic substitution reaction. The reaction can be shown as:



Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline. By protecting the —NH_2 group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

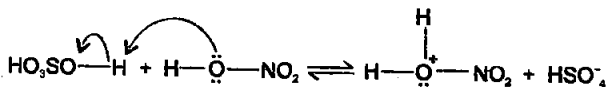


III. SHORT ANSWER TYPE

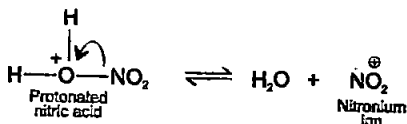
38. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

Ans. In the case of nitration, the electrophile, nitronium ion, NO_2^+ is produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

Step I

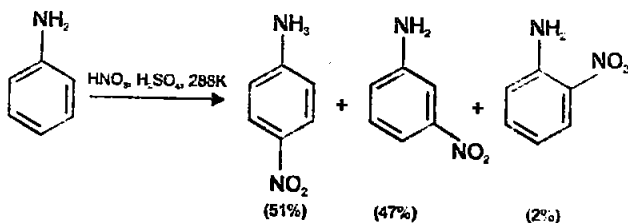


Step II

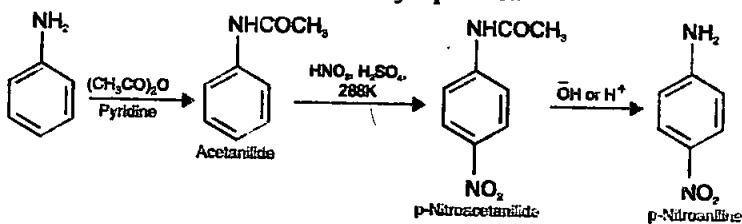


39. Why is NH_2 group of aniline acetylated before carrying out nitration?

Ans. Direct nitration of aniline yields carry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.



However by protecting the $-\text{NH}_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.

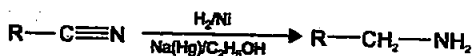


40. What is the product when $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ reacts with HNO_2 ?

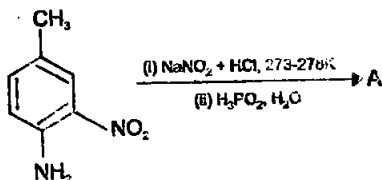
Ans. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

41. What is the best reagent to convert nitrile to primary amine?

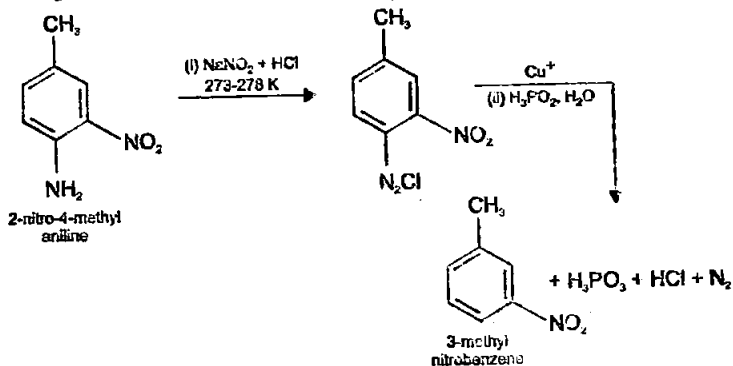
Ans. Nitriles on reduction with lithium aluminium hydride (LiAlH_4) or catalytic hydrogenation, produce primary amines.



42. Give the structure of 'A' in the following reaction.

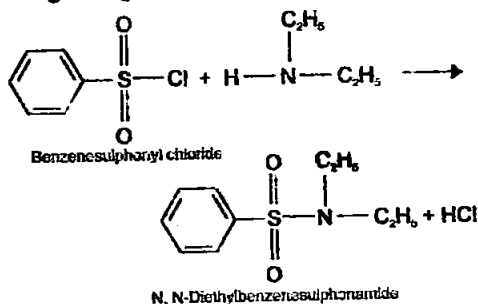


Ans. Complete conversion can be shown as



43. What is Hinsberg reagent?

Ans. Benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$), is also known as Hinsberg's reagent. It reacts with primary and secondary amines to form sulphonamides. Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$). Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N-dietylaniline reacts with Hinsberg's reagent to form N, N-dietylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.



44. Why is benzenediazonium chloride not stored and is used immediately after its preparation?

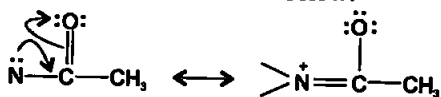
Ans. Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273–278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as diazotisation. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state.

45. Why does acetylation of —NH_2 group of aniline reduce its activating effect?

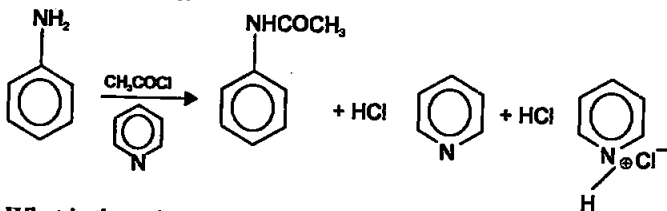
Ans. The activating effect of —NH_2 group can be controlled by protecting the —NH_2 group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:



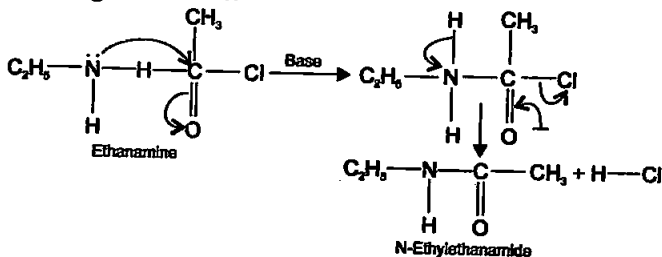
46. Explain why MeNH_2 is stronger base than MeOH ?

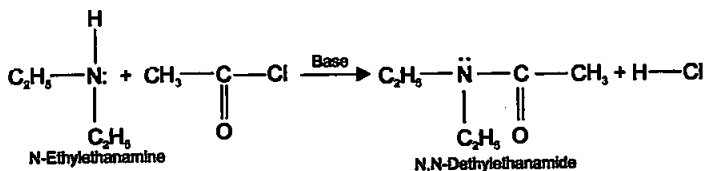
Ans. Pyridine being a base, is used to remove the side product i.e., HCl from reaction mixture.



47. What is the role of pyridine in the acylation reaction of amines?

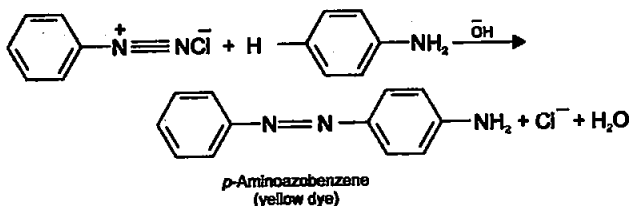
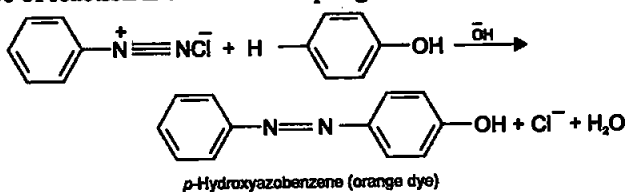
Ans. The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.





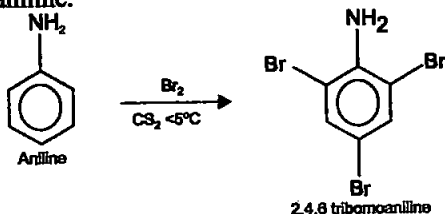
48. Under what reaction conditions (acidic/basic), the coupling reaction of aryldiazonium chloride with aniline is carried out?

Ans. The azo products obtained have an extended conjugate system having both the aromatic rings joined through the $-\text{N}=\text{N}-$ bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its *para* position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction.



49. Predict the product of reaction of aniline with bromine in non-polar solvent such as CS_2 .

Ans. Aniline on reaction with Br_2 in non-polar solvent CS_2 produces 2, 4, 6-tribromoaniline.



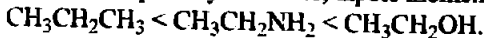
Aniline has high reactivity towards bromine as it gives the triply substituted product.

50. Arrange the following compounds in increasing order of dipole moment.



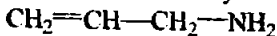
Ans. Dipole moment of amine, alcohol and hydrocarbon can be explained on the basis of bond polarity of $\text{C}-\text{H}$, $\text{N}-\text{H}$ and $\text{O}-\text{H}$ bond.

As the bond polarity increases, dipole moment increases

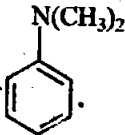


51. What is the structure and IUPAC name of the compound, allyl amine?

Ans. Structural formula of allyl amine is as follows:



prop-2-ene-1-amine



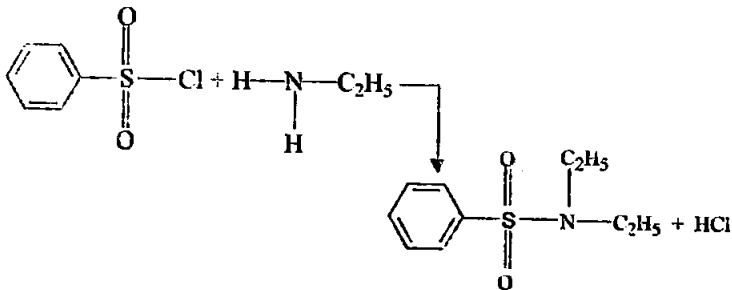
52. Write down the IUPAC name of

Ans. N,N-Dimethylaniline.

53. A compound Z with molecular formula $\text{C}_3\text{H}_9\text{N}$ reacts with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ to give a solid, insoluble in alkali. Identify Z.

Ans. Z is an aliphatic amine which gives a solid insoluble in base.

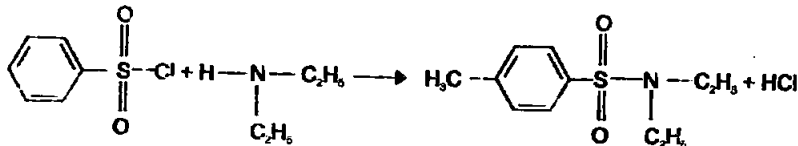
The reaction of benzenesulphonyl chloride with primary amine yields N-alkylbenzenesulphonamide.



N-Ethylbenzenesulphonamide (soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

In the reaction with secondary amine, N,N-dialkylbenzenesulphonamide is formed.

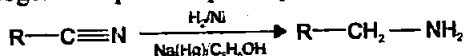


N,N-Diethylbenzenesulphonamide

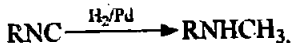
Since N,N-diethylbenzenesulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

54. A primary amine, RNH_2 can be reacted with $\text{CH}_3\text{---X}$ to get secondary amine, R---NHCH_3 but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where RNH_2 forms only 2° amine?

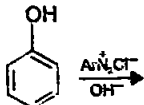
Ans. Nitriles on reduction with lithium aluminium hydride (LiAlH_4) or catalytic hydrogenation produce primary amines.



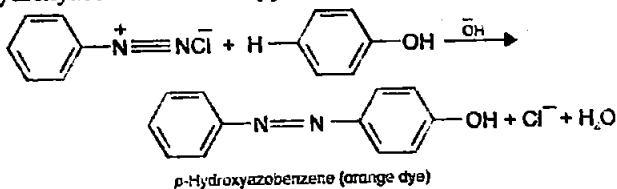
On catalytic reduction the isocyanide will give a secondary amine with one methyl group.



55. Complete the following reaction.

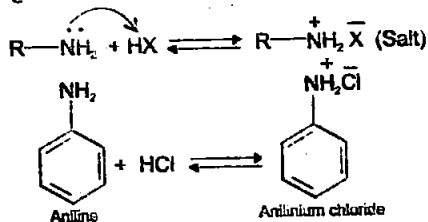


Ans. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.



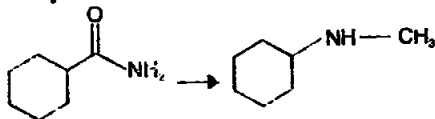
56. Why is aniline soluble in aqueous HCl?

Ans. Amines, being basic in nature, react with acids to form salts.

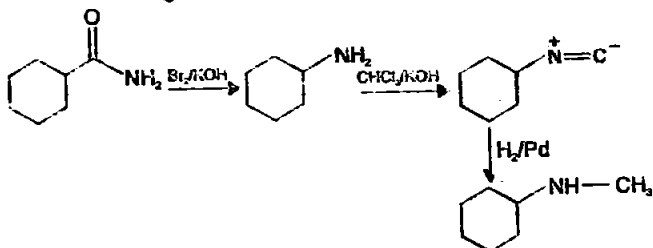


Amine salts are soluble in water.

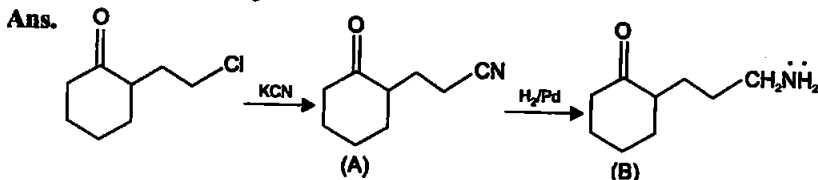
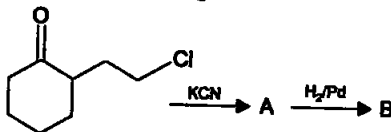
57. Suggest a route by which the following conversion can be accomplished.



Ans.



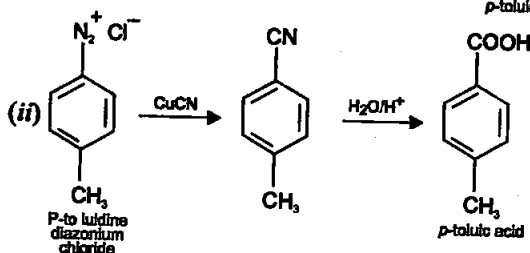
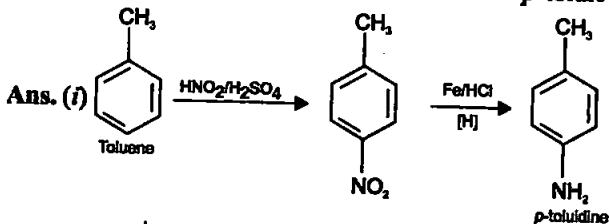
58. Identify A and B in the following reaction.



59. How will you carry out the following conversions?

(i) toluene \longrightarrow p-toluidine

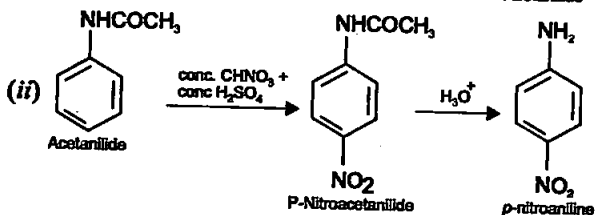
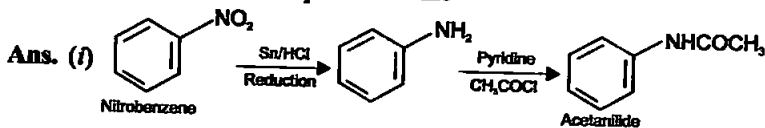
(ii) p-toluidine diazonium chloride \longrightarrow p-toluic acid



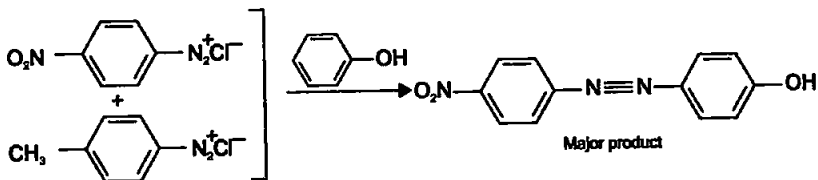
60. Write following conversions:

(i) nitrobenzene \longrightarrow acetanilide

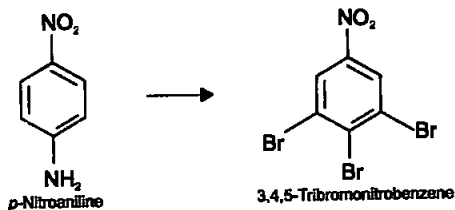
(ii) acetanilide \longrightarrow p-nitroaniline



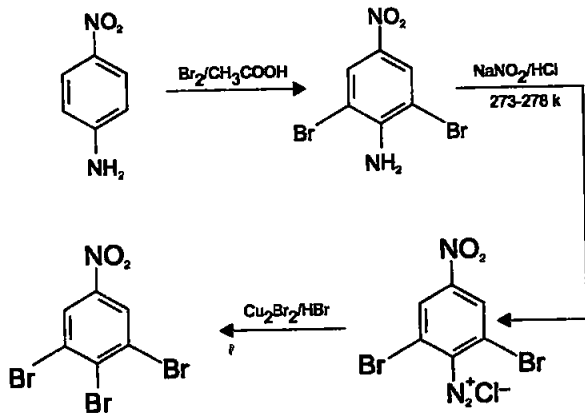
61. A solution contains 1 g mol. each of *p*-toluene diazonium chloride and *p*-nitrophenyl diazonium chloride. To this 1 g mol. of alkaline solution of phenol is added. Predict the major product. Explain your answer.
 Ans. So, nitrophenyl diazonium chloride couples preferentially with phenol.



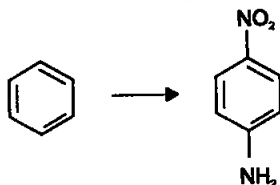
62. How will you bring out the following conversion?



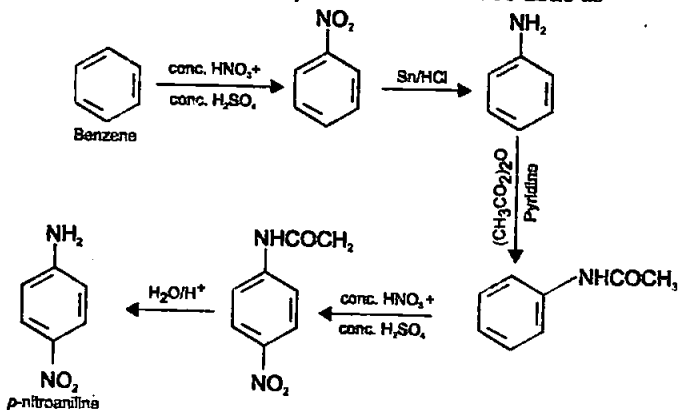
Ans. Complete conversion of above reaction can be shown as



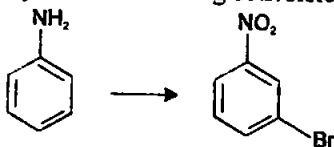
63. How will you carry out the following conversion?



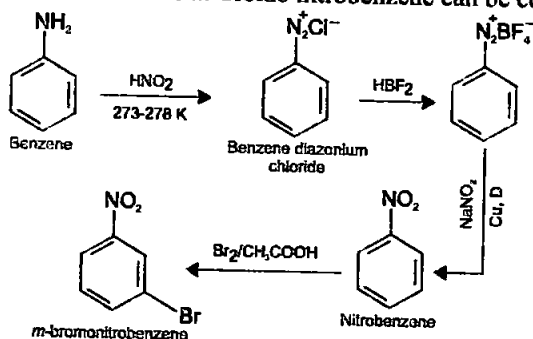
Ans. Conversion of benzene to *p*-nitroaniline can be done as



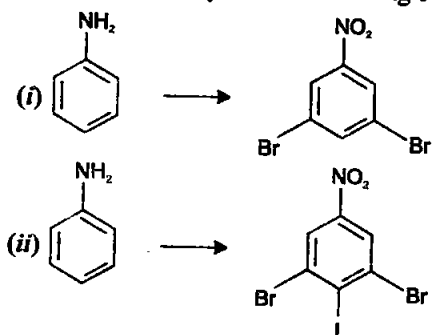
64. How will you carry out the following conversion?



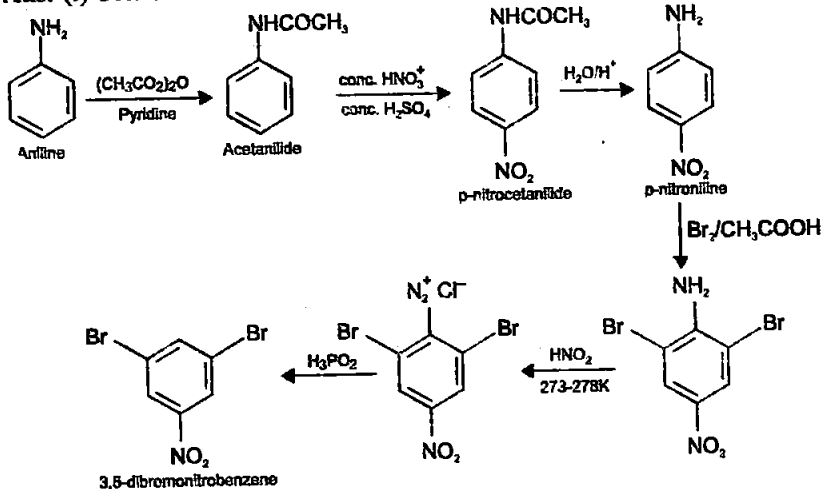
Ans. Conversion of aniline to *m*-bromo nitrobenzene can be completed as



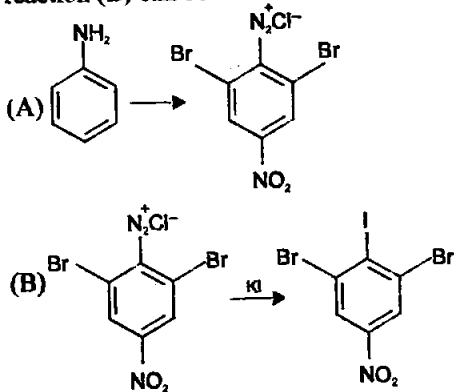
65. How will you carry out the following conversions?



Ans. (i) Conversion of aniline to 3,5-dibromonitrobenzene can be completed as



(ii) Conversion (A) given below is same as in part (i) given above after that reaction (B) can be carried out.



IV. MATCHING TYPE

Note : Match the items of Column I and Column II in the following questions.

66. Match the reactions given in Column I with the statements given in Column II.

Column I	Column II
(i) Ammonolysis	(a) Amine with lesser number of carbon atoms
(ii) Gabriel phthalimide synthesis	(b) Detection test for primary amines.

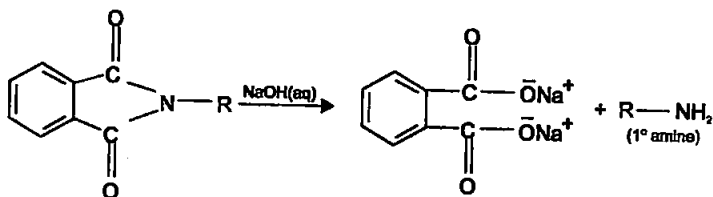
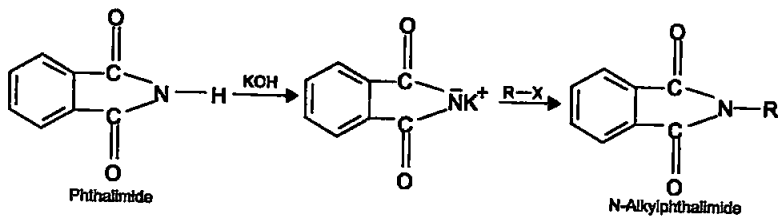
(iii) Hoffmann Bromamide reaction	(c) Reaction of phthalimide with KOH and R—X
(iv) Carbylamine reaction	(d) Reaction of alkylhalides with NH ₃

Ans. (i) → (d) (ii) → (c) (iii) → (a) (iv) → (b)

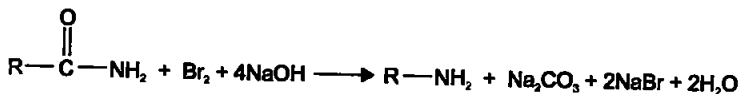
Explanation:

(i) This process of cleavage of the C—X bond by ammonia molecule is known as ammonolysis.

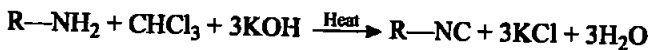
(ii) Reaction of phthalimide with KOH and R—X.



(iii) Amine with lesser number of carbon atoms



(iv) Detection test for primary amines

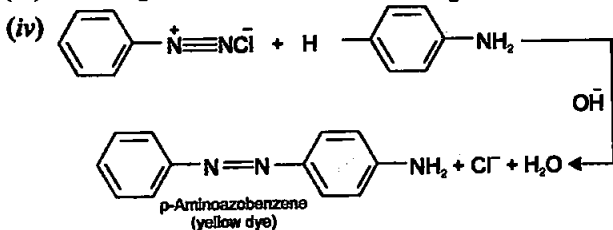
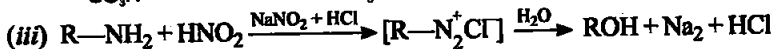
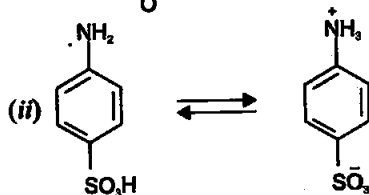
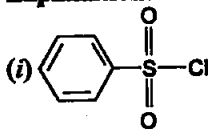


67. Match the compounds given in Column I with the items given in Column II.

Column I	Column II
(i) Benzenesulphonyl chloride	(a) Zwitter ion
(ii) Sulphanilic acid	(b) Hinsberg reagent
(iii) Alkyl diazonium salts	(c) Dyes
(iv) Aryl diazonium salts	(d) Conversion to alcohols

Ans. (i) → (b) (ii) → (a) (iii) → (d) (iv) → (c)

Explanation:



V. ASSERTION AND REASON TYPE

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

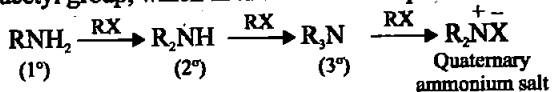
- (i) Both assertion and reason are wrong.
- (ii) Both assertion and reason are correct statements but reason is not correct explanation of assertion.
- (iii) Assertion is correct statement but reason is wrong statement.
- (iv) Both assertion and reason are correct statements and reason is correct explanation of assertion.
- (v) Assertion is wrong statement but reason is correct statement.

68. Assertion : Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

Reason : Acyl group sterically hinders the approach of further acyl groups.

Ans. (iii)

Explanation: Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or $>NH$ group by the acetyl group, which in turn leads to the production of amides.



- 69. Assertion** : Hoffmann's bromamide reaction is given by primary amines.
Reason : Primary amines are more basic than secondary amines.

Ans. (iii)

Explanation: Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.

- 70. Assertion** : N-Ethylbenzene sulphonamide is soluble in alkali.

Reason : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

Ans. (iv)

Explanation: The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

- 71. Assertion** : N, N-Diethylbenzenesulphonamide is insoluble in alkali.

Reason : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

Ans. (ii)

Explanation: Since N, N-diethylbenzenesulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

- 72. Assertion** : Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.

Reason : FeCl_2 formed gets hydrolysed to release HCl during the reaction.

Ans. (iv)

Explanation: Reduction with iron scrap and hydrochloric acid is preferred because FeCl_2 formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

- 73. Assertion** : Aromatic 1° amines can be prepared by Gabriel Phthalimide Synthesis.

Reason : Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.

Ans. (i)

Explanation: Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

74. **Assertion** : Acetanilide is less basic than aniline.

Reason : Acetylation of aniline results in decrease of electron density on nitrogen.

Ans. (iv)

Explanation: The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:



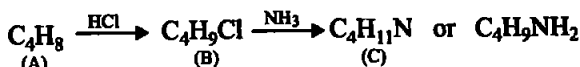
Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of $-\text{NHCOCH}_3$ group is less than that of amino group.

VI. LONG ANSWER TYPE

75. A hydrocarbon 'A', (C_4H_8) on reaction with HCl gives a compound 'B', ($\text{C}_4\text{H}_9\text{Cl}$), which on reaction with 1 mol of NH_3 gives compound 'C', ($\text{C}_4\text{H}_{11}\text{N}$). On reacting with NaNO_2 and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 mols of acetaldehyde. Identify compounds 'A' to 'D'. Explain the reactions involved.

Ans. (i) Addition of HCl to compound 'A' shows that compound 'A' is alkene. Compound 'B' is $\text{C}_4\text{H}_9\text{Cl}$.

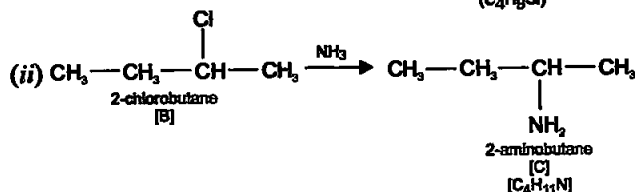
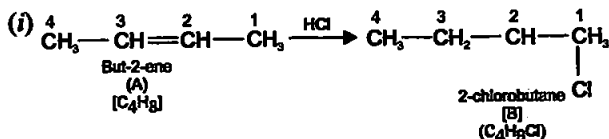
(ii) Compound 'B' reacts with NH_3 , it forms amine 'C'.

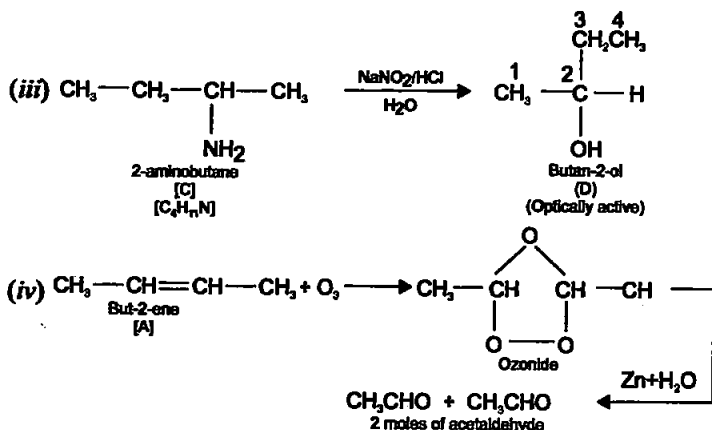


(iii) 'C' gives diazonium salt with NaNO_2/HCl , which yields an optically active alcohol. So, 'C' is aliphatic amine.

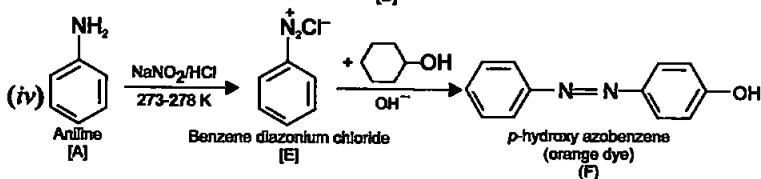
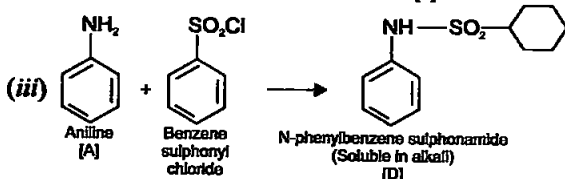
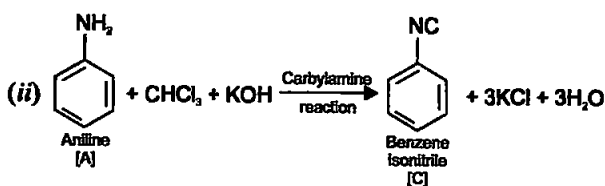
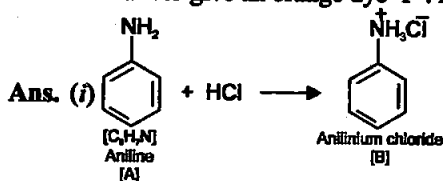
(iv) 'A' on ozonolysis produces 2 moles of CH_3CHO . So, 'A' is $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ (But-2-ene).

Reactions:

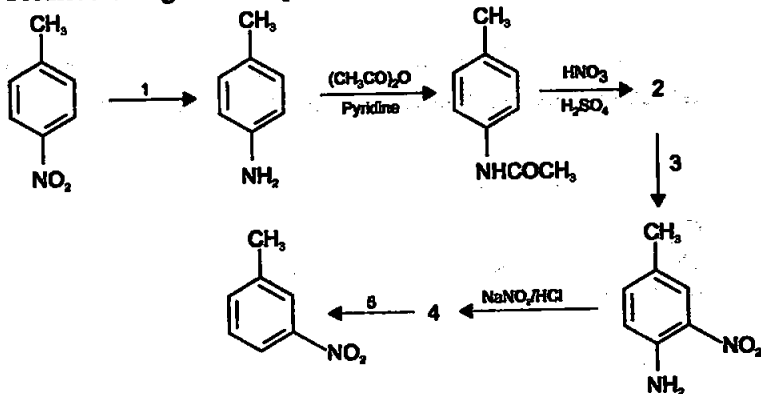




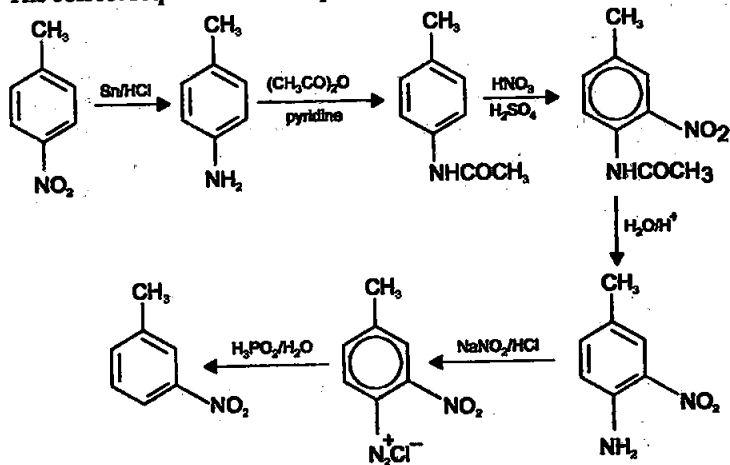
76. A colourless substance 'A' (C₆H₇N) is sparingly soluble in water and gives a water soluble compound 'B' on treating with mineral acid. On reacting with CHCl₃ and alcoholic potash 'A' produces an obnoxious smell due to the formation of compound 'C'. Reaction of 'A' with benzenesulphonyl chloride gives compound 'D' which is soluble in alkali. With NaNO₂ and HCl, 'A' forms compound 'E' which reacts with phenol in alkaline medium to give an orange dye 'F'. Identify compounds 'A' to 'F'.



77. Predict the reagent or the product in the following reaction sequence.



Ans. The correct sequence can be represented as follows including all reagents.



Hence; (i) 1 = Sn/HCl

(ii) 2 =

(iii) 3 = $\text{H}_2\text{O H}^+$

(iv) 4 =

(v) 5 = $\text{H}_3\text{PO}_2/\text{H}_2\text{O}$