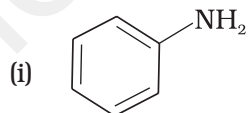
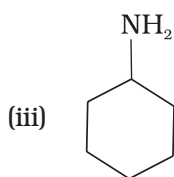


Unit 13 AMINES

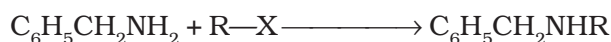
I. Multiple Choice Questions (Type-I)

- Which of the following is a 3° amine?
 - 1-methylcyclohexylamine
 - Triethylamine
 - tert*-butylamine
 - N-methylaniline
- The correct IUPAC name for $\text{CH}_2=\text{CHCH}_2\text{NHCH}_3$ is
 - Allylmethylamine
 - 2-amino-4-pentene
 - 4-aminopent-1-ene
 - N-methylprop-2-en-1-amine
- Amongst the following, the strongest base in aqueous medium is _____.
 - CH_3NH_2
 - NCCH_2NH_2
 - $(\text{CH}_3)_2\text{NH}$
 - $\text{C}_6\text{H}_5\text{NHCH}_3$
- Which of the following is the weakest Brønsted base?





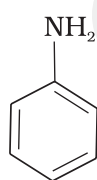
5. Benzylamine may be alkylated as shown in the following equation :



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

- (i) CH_3Br
 - (ii) $\text{C}_6\text{H}_5\text{Br}$
 - (iii) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$
 - (iv) $\text{C}_2\text{H}_5\text{Br}$
6. Which of the following reagents would **not** be a good choice for reducing an aryl nitro compound to an amine?
- (i) H_2 (excess)/Pt
 - (ii) LiAlH_4 in ether
 - (iii) Fe and HCl
 - (iv) Sn and HCl
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 _____.
- (i) Sodium amide, NaNH_2
 - (ii) Sodium azide, NaN_3
 - (iii) Potassium cyanide, KCN
 - (iv) Potassium phthalimide, $\text{C}_6\text{H}_4(\text{CO})_2\text{N}^-\text{K}^+$
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, $\text{C}_6\text{H}_4(\text{CO})_2\text{N}^-\text{K}^+$
9. Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____.
- (i) $2^\circ \text{R}-\text{Br} + \text{NH}_3$
 - (ii) $2^\circ \text{R}-\text{Br} + \text{NaCN}$ followed by H_2/Pt

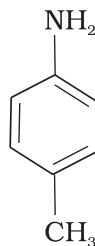
- (iii) $1^\circ \text{R}-\text{NH}_2 + \text{RCHO}$ followed by H_2/Pt
 (iv) $1^\circ \text{R}-\text{Br}$ (2 mol) + potassium phthalimide followed by $\text{H}_3\text{O}^+/\text{heat}$
10. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is ____.
- (i) excess H_2
 (ii) Br_2 in aqueous NaOH
 (iii) iodine in the presence of red phosphorus
 (iv) LiAlH_4 in ether
11. The best reagent for converting, 2-phenylpropanamide into 1-phenylethanamine is ____.
- (i) excess H_2/Pt
 (ii) NaOH/Br_2
 (iii) $\text{NaBH}_4/\text{methanol}$
 (iv) $\text{LiAlH}_4/\text{ether}$
12. Hoffmann Bromamide Degradation reaction is shown by ____.
- (i) ArNH_2
 (ii) ArCONH_2
 (iii) ArNO_2
 (iv) ArCH_2NH_2
13. The correct increasing order of basic strength for the following compounds is ____.



(I)



(II)



(III)

- (i) $\text{II} < \text{III} < \text{I}$
 (ii) $\text{III} < \text{I} < \text{II}$
 (iii) $\text{III} < \text{II} < \text{I}$
 (iv) $\text{II} < \text{I} < \text{III}$
14. Methylamine reacts with HNO_2 to form ____.
- (i) $\text{CH}_3-\text{O}-\text{N}=\text{O}$
 (ii) $\text{CH}_3-\text{O}-\text{CH}_3$

- (iii) CH_3OH
- (iv) CH_3CHO

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

- (i) NH_3
- (ii) N_2
- (iii) H_2
- (iv) C_2H_6

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 _____.

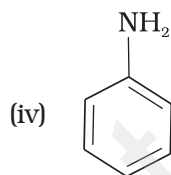
- (i) NO_2
- (ii) NO^+
- (iii) NO_2^+
- (iv) NO_2^-

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

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

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

- (i) $\text{CH}_3\text{—NH}_2$
- (ii) $\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \text{—NH}$
- (iii) $\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \text{—N—CH}_3$



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

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

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

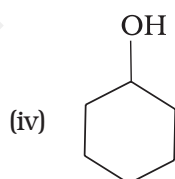
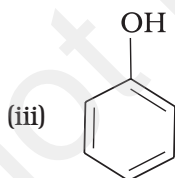
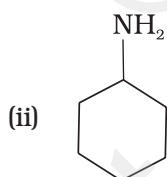
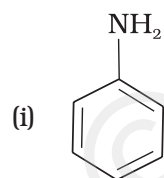
21. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is

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

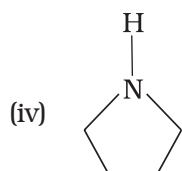
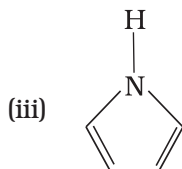
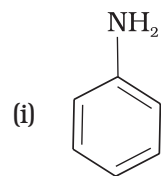
22. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride.

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

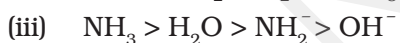
23. Which of the following compounds is the weakest Brönsted base?



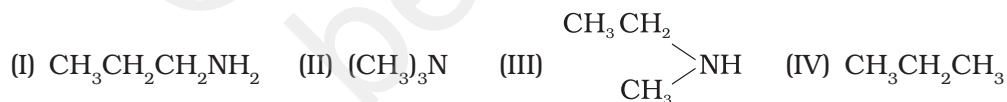
24. Among the following amines, the strongest Brönsted base is _____.



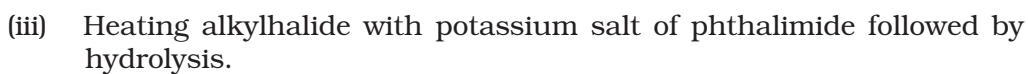
25. The correct decreasing order of basic strength of the following species is _____.



26. Which of the following should be most volatile?



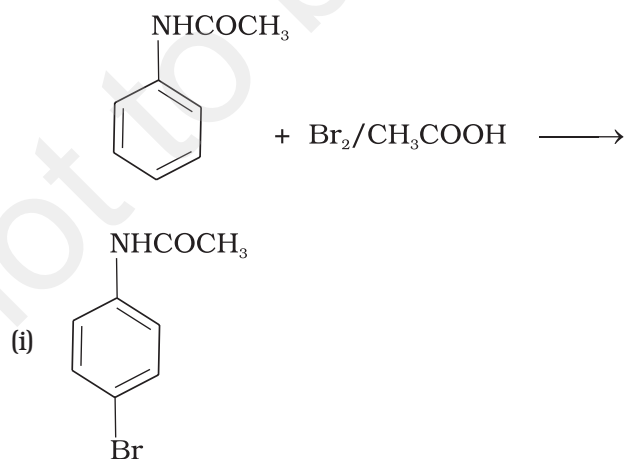
27. Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?

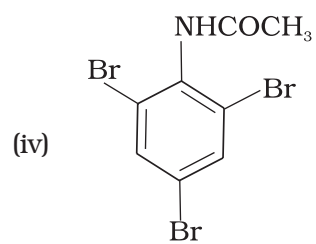
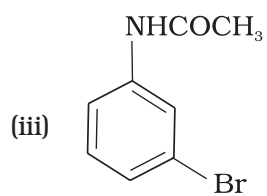
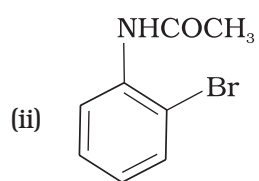


II. Multiple Choice Questions (Type-II)

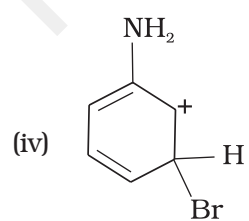
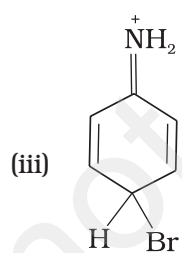
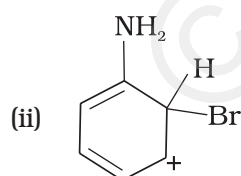
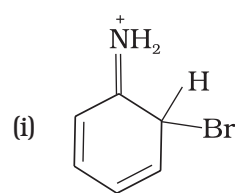
Note : In the following questions two or more options may be correct.

28. Which of the following cannot be prepared by Sandmeyer's reaction?
- (i) Chlorobenzene
 - (ii) Bromobenzene
 - (iii) Iodobenzene
 - (iv) Fluorobenzene
29. Reduction of nitrobenzene by which of the following reagent gives aniline?
- (i) Sn/HCl
 - (ii) Fe/HCl
 - (iii) $\text{H}_2\text{-Pd}$
 - (iv) $\text{Sn/NH}_4\text{OH}$
30. Which of the following species are involved in the carbylamine test?
- (i) R-NC
 - (ii) CHCl_3
 - (iii) COCl_2
 - (iv) $\text{NaNO}_2 + \text{HCl}$
31. The reagents that can be used to convert benzenediazonium chloride to benzene are _____.
- (i) SnCl_2/HCl
 - (ii) $\text{CH}_3\text{CH}_2\text{OH}$
 - (iii) H_3PO_2
 - (iv) LiAlH_4
32. The product of the following reaction is _____.





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



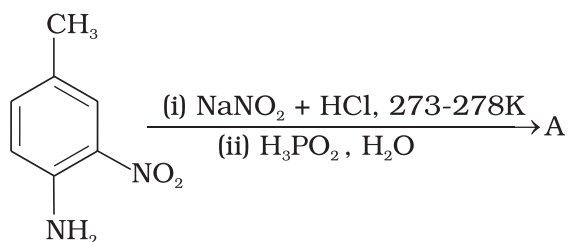
34. Which of the following amines can be prepared by Gabriel synthesis.
- Isobutyl amine
 - 2-Phenylethylamine
 - N-methylbenzylamine
 - Aniline
35. Which of the following reactions are correct?
- $$\begin{array}{c} \text{H} \\ | \\ \text{---C---Cl} \\ | \\ \text{H} \end{array} + 2\text{NH}_3 \longrightarrow \begin{array}{c} \text{H} \\ | \\ \text{---C---NH}_2 \\ | \\ \text{H} \end{array} + \text{NH}_4\text{Cl}$$
 - $$\begin{array}{c} \text{---C---Cl} \\ | \\ \text{---C---} \end{array} \xrightarrow{\text{aq. KOH}} \begin{array}{c} \text{---C---} \\ | \\ \text{---C---} \end{array}$$
 - $$\text{Cyclohexyl-Cl} \xrightarrow{\text{alc. KOH}} \text{Cyclohexene}$$
 - $$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{HNO}_2 \xrightarrow{0^\circ\text{C}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$$
36. Under which of the following reaction conditions, aniline gives *p*-nitro derivative as the major product?
- Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3 .
 - Acetic anhydride/pyridine followed by conc. H_2SO_4 + conc. HNO_3 .
 - Dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3 .
 - Reaction with conc. HNO_3 + conc. H_2SO_4 .
37. Which of the following reactions belong to electrophilic aromatic substitution?
- Bromination of acetanilide
 - Coupling reaction of aryl diazonium salts
 - Diazotisation of aniline
 - Acylation of aniline

III. Short Answer Type

38. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?
39. Why is NH_2 group of aniline acetylated before carrying out nitration?
40. What is the product when $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ reacts with HNO_2 ?

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

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



43. What is Hinsberg reagent?

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

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

46. Explain why MeNH_2 is stronger base than MeOH ?

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

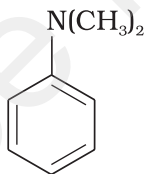
48. Under what reaction conditions (acidic/basic), the coupling reaction of aryl diazonium chloride with aniline is carried out?

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

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



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

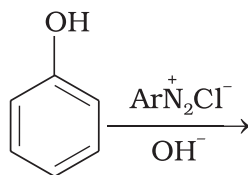


52. Write down the IUPAC name of

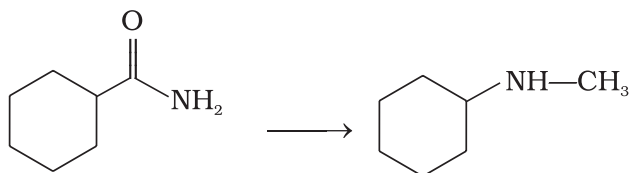
53. A compound Z with molecular formula $\text{C}_3\text{H}_9\text{N}$ reacts with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ to give a solid, insoluble in alkali. Identify Z.

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?

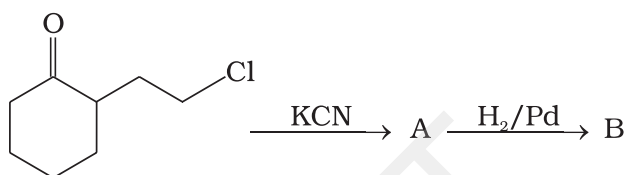
55. Complete the following reaction.



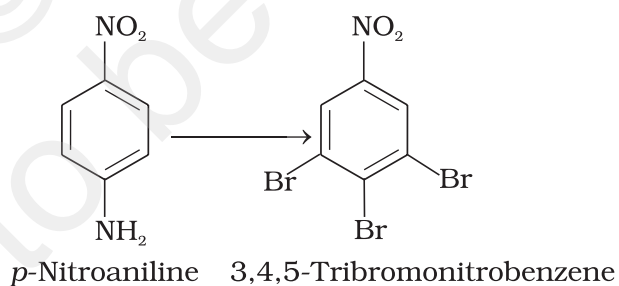
56. Why is aniline soluble in aqueous HCl?
57. Suggest a route by which the following conversion can be accomplished.



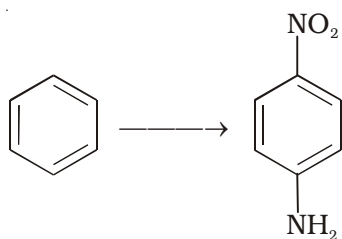
58. Identify A and B in the following reaction.



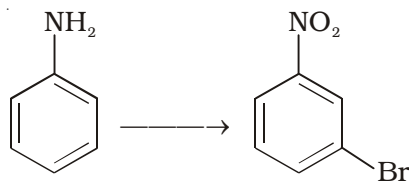
59. How will you carry out the following conversions?
- toluene $\longrightarrow$ *p*-toluidine
 - p*-toluidine diazonium chloride $\longrightarrow$ *p*-toluic acid
60. Write following conversions:
- nitrobenzene $\longrightarrow$ acetanilide
 - acetanilide $\longrightarrow$ *p*-nitroaniline
61. A solution 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.
62. How will you bring out the following conversion?



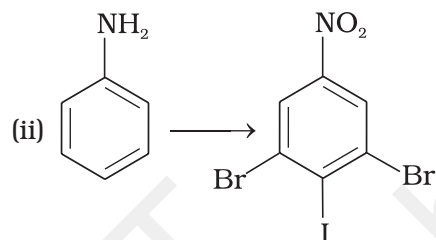
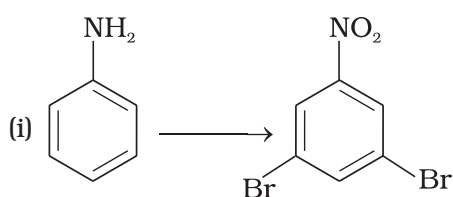
63. How will you carry out the following conversion?



64. How will you carry out the following conversion?



65. How will you carry out the following conversions?



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

- (i) Ammonolysis
- (ii) Gabriel phthalimide synthesis
- (iii) Hoffmann Bromamide reaction
- (iv) Carbylamine reaction

Column II

- (a) Amine with lesser number of carbon atoms
- (b) Detection test for primary amines.
- (c) Reaction of phthalimide with KOH and R—X
- (d) Reaction of alkylhalides with NH_3

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

Column I

- (i) Benzene sulphonyl chloride
- (ii) Sulphanilic acid
- (iii) Alkyl diazonium salts
- (iv) Aryl diazonium salts

Column II

- (a) Zwitter ion
- (b) Hinsberg reagent
- (c) Dyes
- (d) Conversion to alcohols

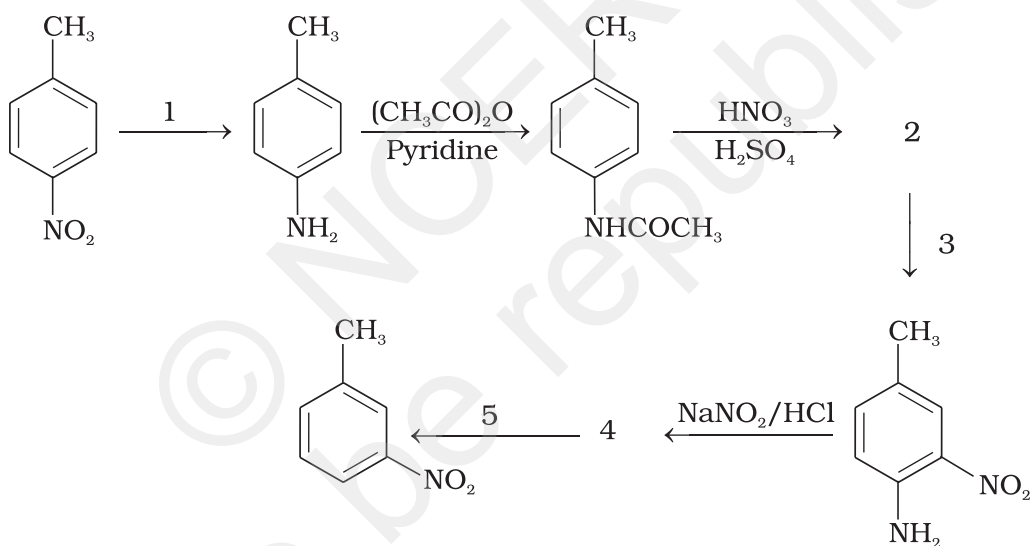
V. Assertion and Reason Type

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.
- 69. Assertion :** Hoffmann's bromamide reaction is given by primary amines.
- Reason :** Primary amines are more basic than secondary amines.
- 70. Assertion :** N-Ethylbenzene sulphonamide is soluble in alkali.
- Reason :** Hydrogen attached to nitrogen in sulphonamide is strongly acidic.
- 71. Assertion :** N, N-Diethylbenzene sulphonamide is insoluble in alkali.
- Reason :** Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.
- 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.
- 73. Assertion :** Aromatic 1° amines can be prepared by Gabriel Phthalimide Synthesis.
- Reason :** Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.
- 74. Assertion :** Acetanilide is less basic than aniline.
- Reason :** Acetylation of aniline results in decrease of electron density on nitrogen.

VI. Long Answer Type

75. A hydrocarbon 'A', (C_4H_8) on reaction with HCl gives a compound 'B', (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound 'C', ($C_4H_{11}N$). 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.
76. A colourless substance 'A' (C_6H_7N) is sparingly soluble in water and gives a water soluble compound 'B' on treating with mineral acid. On reacting with $CHCl_3$ 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 $NaNO_2$ 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.



ANSWERS

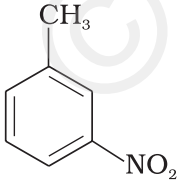
I. Multiple Choice Questions (Type-I)

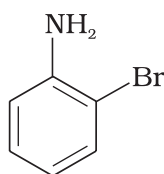
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|----------|-----------|-----------|-----------|-----------|----------|
| 1. (ii) | 2. (iv) | 3. (iii) | 4. (i) | 5. (iii) | 6. (ii) |
| 7. (iii) | 8. (iv) | 9. (iii) | 10. (iv) | 11. (ii) | 12. (ii) |
| 13. (iv) | 14. (iii) | 15. (ii) | 16. (iii) | 17. (iii) | 18. (ii) |
| 19. (i) | 20. (ii) | 21. (ii) | 22. (iv) | 23. (iii) | 24. (iv) |
| 25. (i) | 26. (ii) | 27. (iii) | | | |

II. Multiple Choice Questions (Type-II)

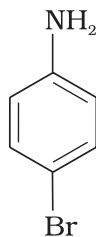
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|-----------------|----------------------|---------------|-----------------|
| 28. (iii), (iv) | 29. (i), (ii), (iii) | 30. (i), (ii) | 31. (ii), (iii) |
| 32. (i), (ii) | 33. (i), (ii), (iii) | 34. (i), (ii) | 35. (i), (iii) |
| 36. (i), (ii) | 37. (i), (ii) | | |

III. Short Answer Type

38. HNO_3 acts as a base in the nitrating mixture and provides the electrophile, NO_2^+ .
39. See NCERT textbook for Class XII.
40. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
41. Reduction of nitriles with sodium/alcohol or LiAlH_4 gives primary amine.
42. 
43. Benzene sulphonylchloride.
44. Benzene diazonium chloride is very unstable.
45. See NCERT textbook for Class XII.
46. Nitrogen is less electronegative than oxygen therefore lone pair of electrons on nitrogen is readily available for donation. Hence, MeNH_2 is more basic than MeOH .
47. Pyridine and other bases are used to remove the side product i.e. HCl from the reaction mixture.
48. Reaction is done in mild basic conditions.
49. A mixture of 2-bromoaniline and 4-bromoaniline is formed.

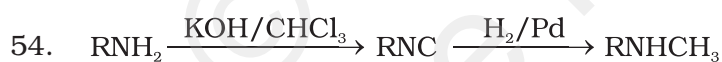
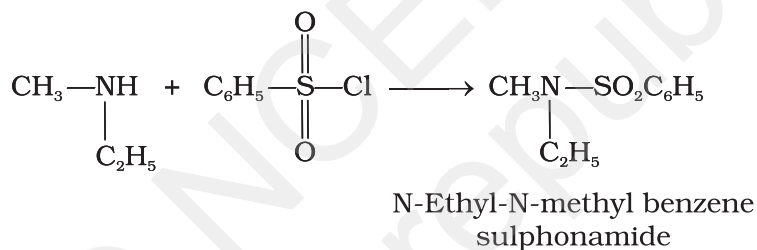


(2-Bromoaniline)



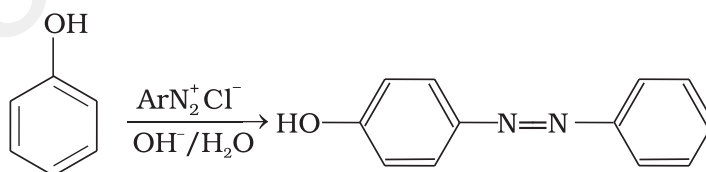
(4-Bromoaniline)

50. $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{CH}_2\text{NH}_2 < \text{CH}_3\text{CH}_2\text{OH}$
51. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_2$, prop-2-en-1-amine
52. N, N-Dimethylbenzenamine
53. Z is an aliphatic amine which gives a solid insoluble in base. This implies that reaction with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ must give a product without any replaceable hydrogen attached to nitrogen. In other words, the amine must be a secondary amine. i.e. Z is ethylmethylamine.

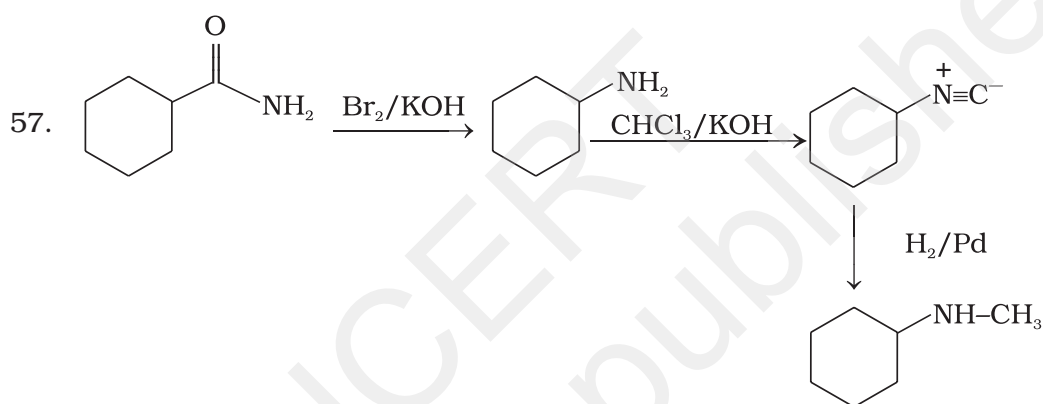
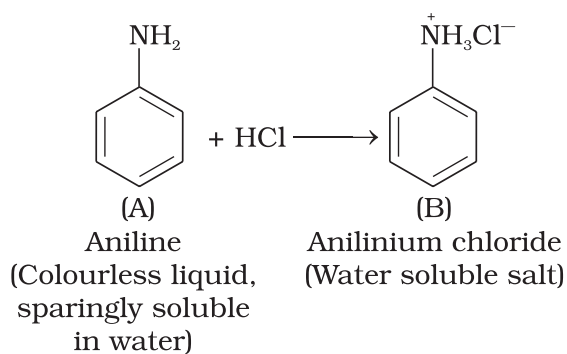


Carbylamine reaction is shown by 1° amine only which results in the replacement of two hydrogen atoms attached to nitrogen atom of NH_2 group by one carbon atom. On catalytic reduction the isocyanide will give a secondary amine with one methyl group.

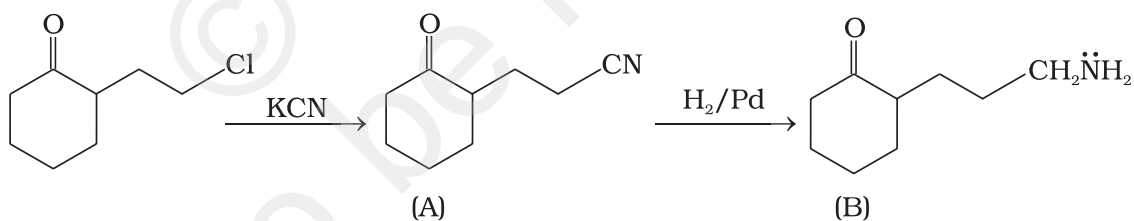
55. The reaction exhibits azo-coupling of phenols. In mild alkaline conditions phenol moiety participates in the azo-coupling and para position of phenol is occupied.



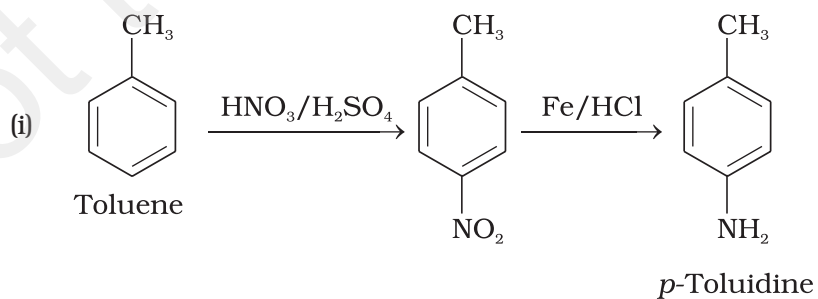
56. Aniline forms the salt anilinium chloride which is water soluble.

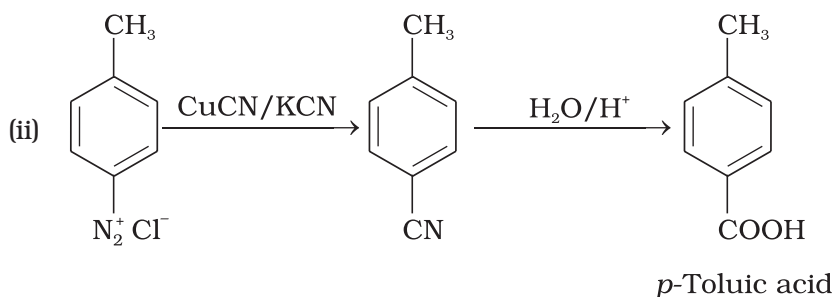


58.

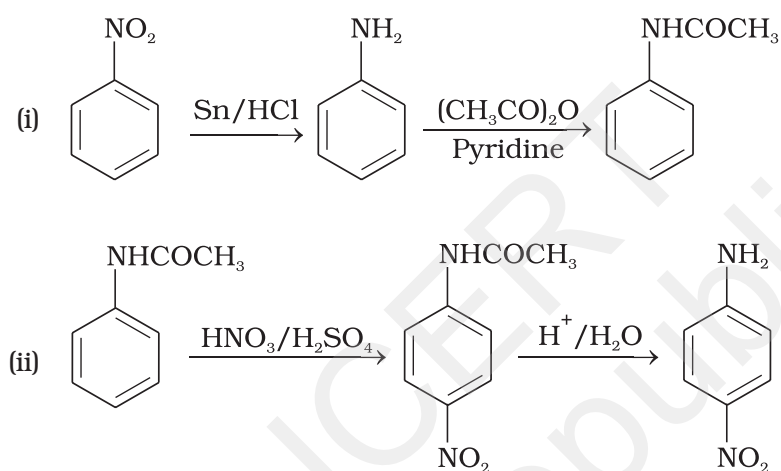


59.

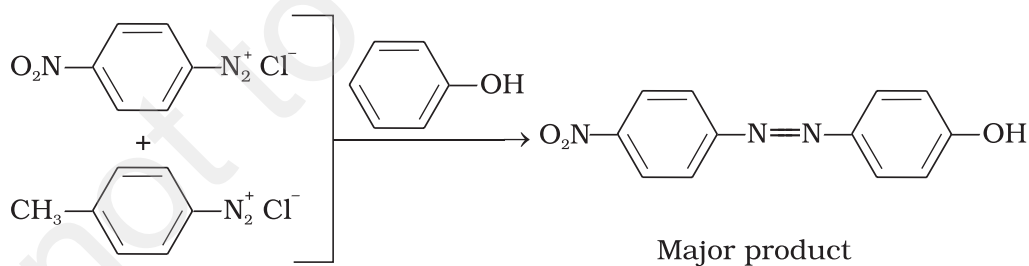




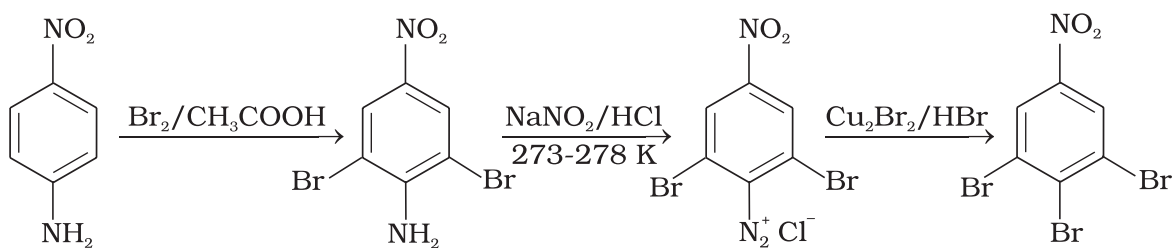
60.



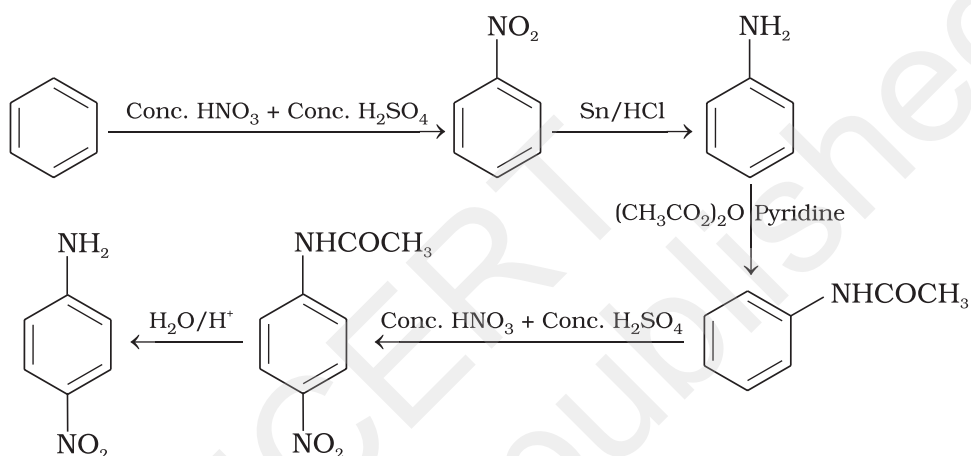
61. This reaction is an example of electrophilic aromatic substitution. In alkaline medium, phenol generates phenoxide ion which is more electron rich than phenol and hence more reactive for electrophilic attack. The electrophile in this reaction is aryldiazonium cation. Stronger the electrophile faster is the reaction. *p*-Nitrophenyldiazonium cation is a stronger electrophile than *p*-toluene diazonium cation. Therefore, it couples preferentially with phenol.



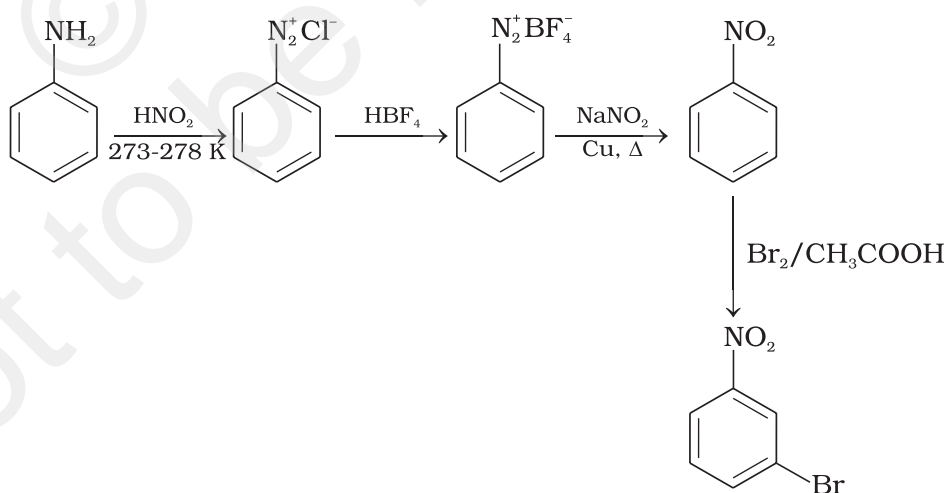
62.



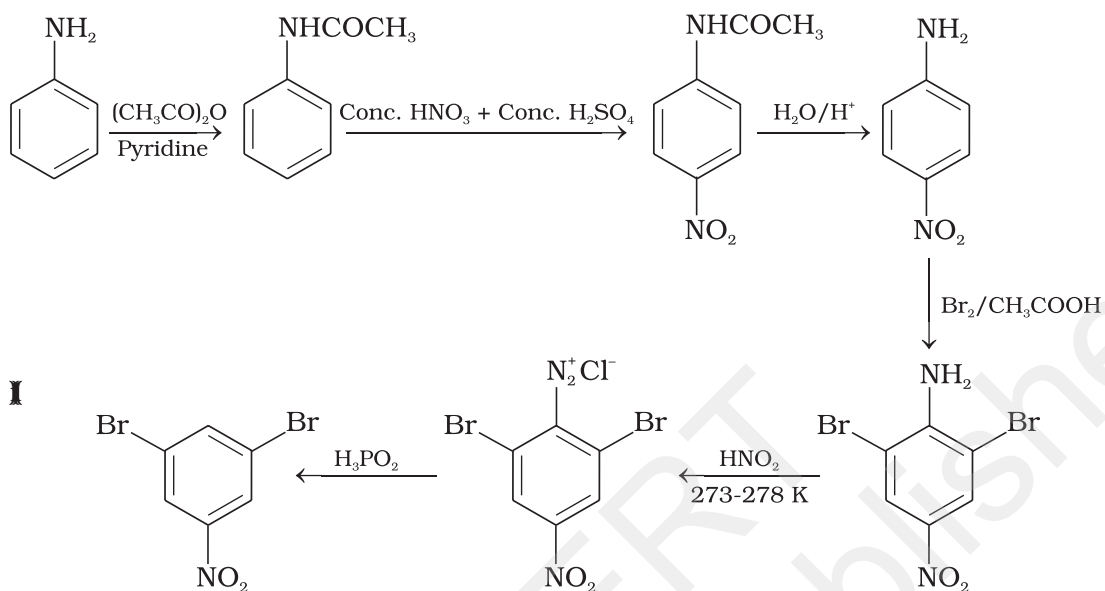
63.



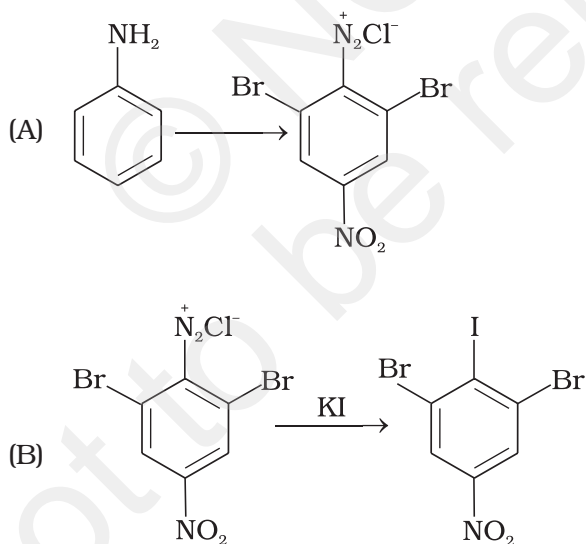
64.



65. (i)



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



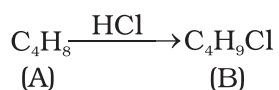
IV. Matching Type

- | | | | |
|---------------------------|------------------------|-------------------------|------------------------|
| 66. (i) $\rightarrow$ (d) | (ii) $\rightarrow$ (c) | (iii) $\rightarrow$ (a) | (iv) $\rightarrow$ (b) |
| 67. (i) $\rightarrow$ (b) | (ii) $\rightarrow$ (a) | (iii) $\rightarrow$ (d) | (iv) $\rightarrow$ (c) |

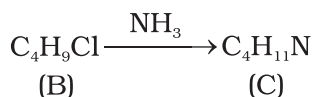
V. Assertion and Reason Type

- | | | | | | | |
|-----------|-----------|----------|----------|----------|---------|----------|
| 68. (iii) | 69. (iii) | 70. (iv) | 71. (ii) | 72. (iv) | 73. (i) | 74. (iv) |
|-----------|-----------|----------|----------|----------|---------|----------|

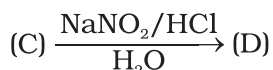
VI. Long Answer Type



Addition of HCl has occurred on 'A'. This implies 'A' is an alkene.



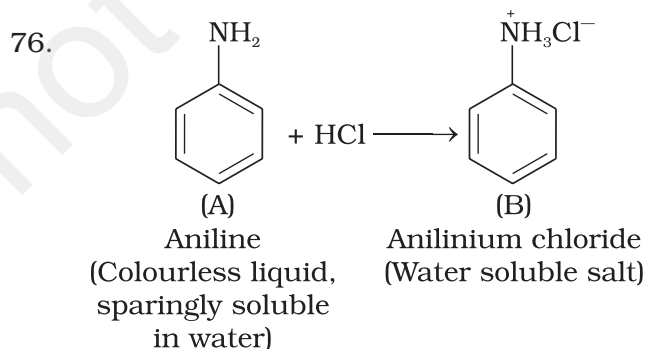
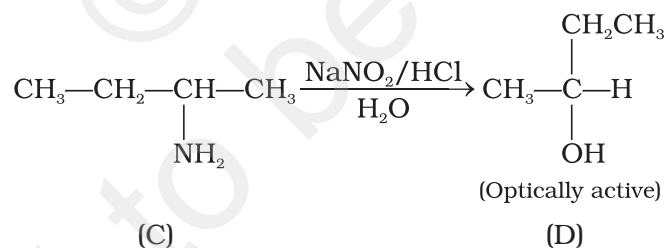
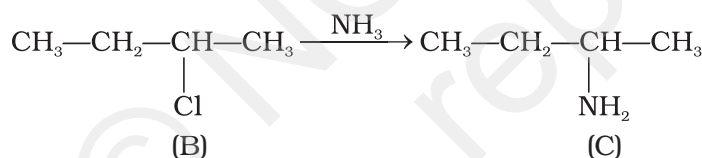
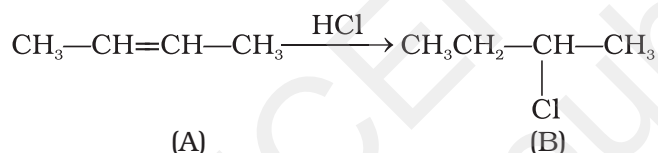
Cl in compound 'B' is substituted by NH_2 to give 'C'.

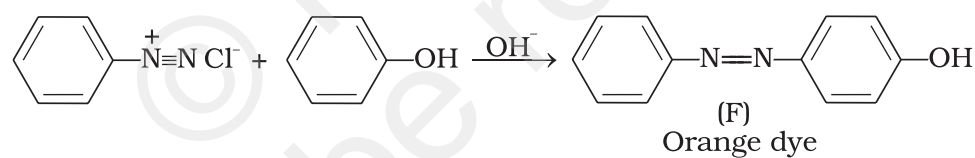
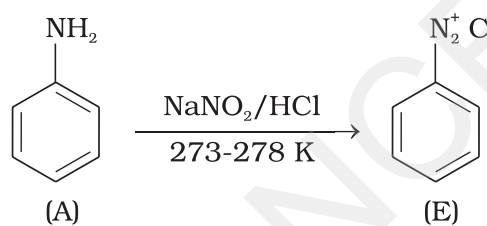
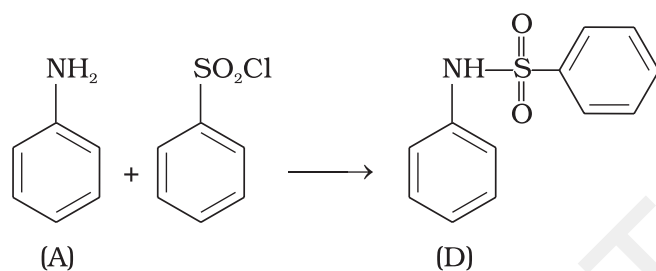
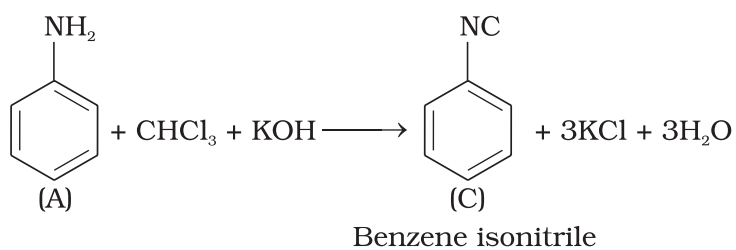


'C' gives a diazonium salt with NaNO_2/HCl that liberates N_2 to give optically active alcohol. This means that 'C' is an aliphatic amine. Number of carbon atoms in amine is same as in compound 'A'.

Since products of ozonolysis of compound 'A' are $\text{CH}_3-\text{CH}=\text{O}$ and $\text{O}=\text{CH}-\text{CH}_3$. The compound 'A' is $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$

On the basis of structure of 'A' reactions can be explained as follows :

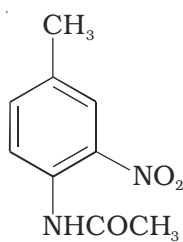




77.

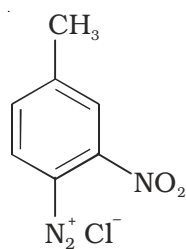
1. Sn-HCl

2.



3. H₂O/H⁺

4.



5. H₃PO₂/H₂O