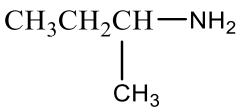
Chapter – Amines

Short Answer Question **2 Mark**

1. **Write IUPAC names of the following:**

(i) 

Ans. The IUPAC name of the given compound is 2 – Butylamine.

(ii) $CH_3NHCH(CH_3)_2$

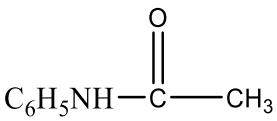
Ans. The IUPAC name of the given compound is N-Methyl-2-methylethanamine

(iii) $(CH_3)_3N$

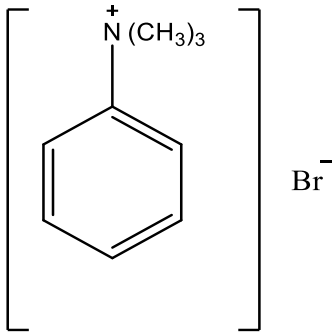
Ans. The IUPAC name of the given compound is trimethylamine.

(iv) $C_6H_5NHCH_3$

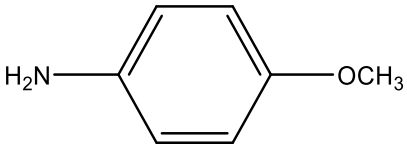
Ans. The IUPAC name of the given compound is N-methyl aniline.

(v) 

Ans. The IUPAC name of this compound is N-Phenylacetamide

(vi) 

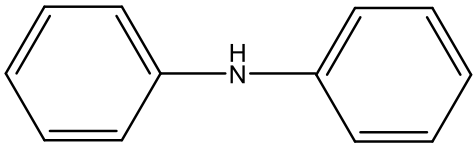
Ans. The IUPAC name of this compound is Trimethylphenylammonium bromide

(vii) 

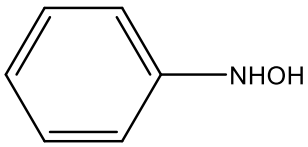
Ans. The IUPAC name of this compound is 4-Methoxyaniline.

(viii) $H_2N(CH_2)_6NH_2$

Ans. The IUPAC name of the given compound is Hexane-1,6-diamine.

(ix) 

Ans. The IUPAC name of this compound is diphenylamine or N-Phenylaniline.

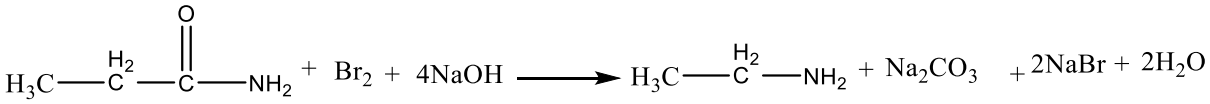
(x) 

Ans. The IUPAC name of this compound is N-Hydroxyaniline.

2. Giving an example of each, describe the following reactions:

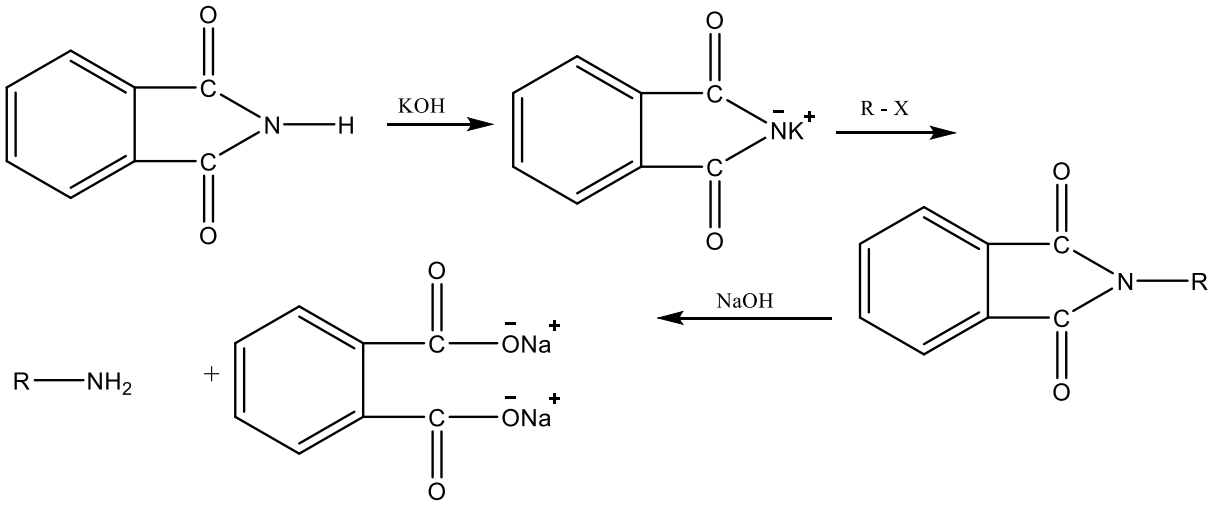
(i) Hoffman bromamide reaction

Ans. The reaction can be shown as:



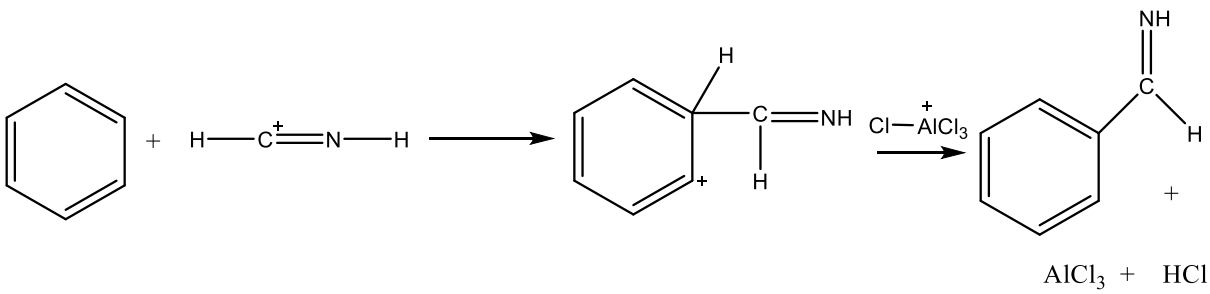
(ii) Gabriel phthanlimide synthesis

Ans. The reaction can be shown as a conversion of phthalimide to primary amine:



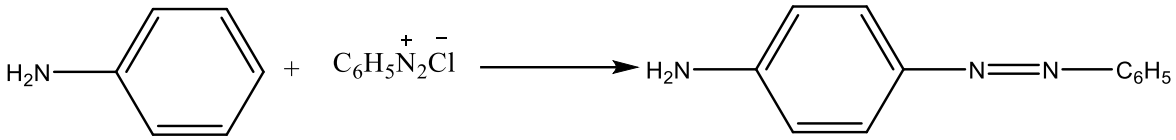
(iii) Gatterman reaction

Ans. Gatterman reaction between benzene to benzaldimine is shown as:



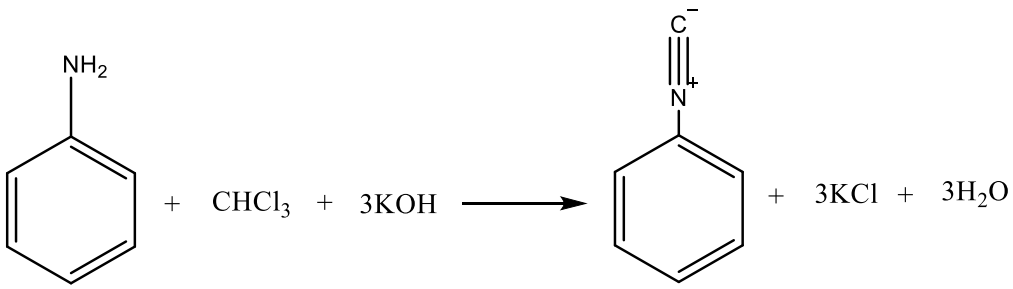
(iv) Coupling reaction

Ans. The coupling reaction for the conversion of aniline to azo dye is shown as:



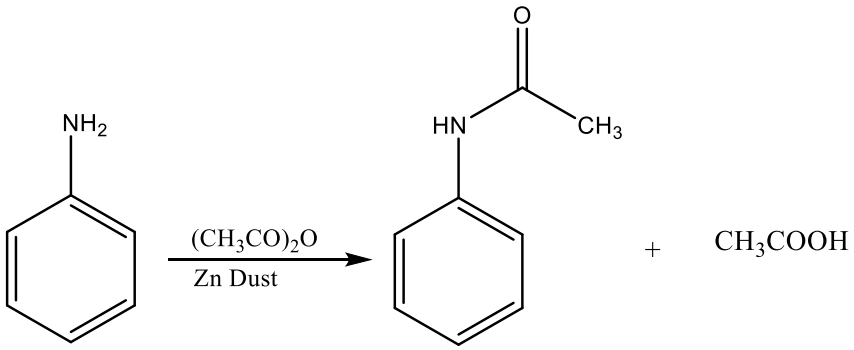
(v) Carbylamine reaction

Ans. The carbylamines reaction is given as a conversion of aniline to phenylisocyanide as:



(vi) Acetylation of aniline

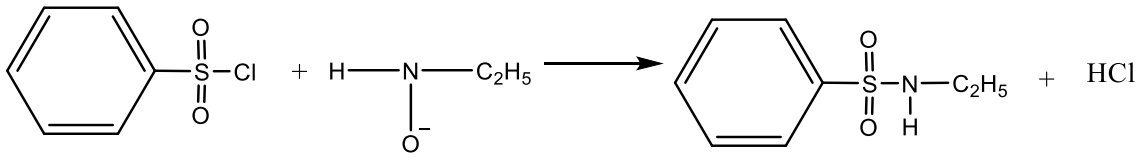
Ans. Acetanilide is synthesized after the acetylation of aniline:



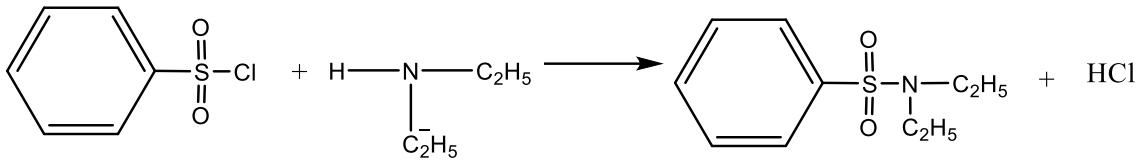
3. Describe the Hinsberg's test for identification of primary, secondary and tertiary amines. Also write the chemical equations of the reactions involved.

Ans. Hinsberg test: Benzenesulphonyl chloride $(C_6H_5SO_2Cl)$, commonly known as Hinsberg's reagent, forms sulphonamides when it interacts with primary and secondary amines.

(i) For primary amines: N-ethylbenzenesulphonyl amide is produced by reacting benzenesulphonyl chloride with primary amine. Because of the strong electron withdrawing sulphonyl group, the hydrogen linked to nitrogen in sulphonamide is highly acidic. As a result, it is alkali soluble.



(ii) For secondary amines: N,N-diethylbenzenesulphonamide is produced in the reaction with secondary amine. It is not acidic and hence insoluble in alkali because N, N-diethylbenzene sulphonamide has no hydrogen atom linked to the nitrogen atom.



(iii) For tertiary amines: Benzenesulphonyl chloride does not react with tertiary amines. This characteristic of amines reacting differently with benzenesulphonyl chloride is used to distinguish primary, secondary, and tertiary amines, as well as to separate a mixture of amines.

4. Arrange the following in the increasing order of given property indicated

(i) $C_2H_5NH_2$ **,** $(C_2H_5)_2NH$ **,** $(C_2H_5)_3N$ **and** NH_3 **, (Basic strength in aqueous solution).**

Ans. The increasing order of basic strength in aqueous solution is:

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

(ii) $C_2H_5NH_2$ **,** $(C_2H_5)_2NH$ **,** $(C_2H_5)_3N$ **and** NH_3 **, (Basic strength in gaseous phase).**

Ans. The increasing order of basic strength in gaseous phase is:

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

(iii) Aniline, p-toluidine, p-nitroaniline. (Basic strength).

Ans. The increasing order of basic strength of the compounds is given as:

p-nitroaniline < Aniline < p-toluidine

(iv) C_2H_5OH **,** $(CH_3)_2HN$ **,** $C_2H_5NH_2$ **(Boiling point)**

Ans. The increasing order of boiling points of the compounds given is:

$$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$$

5. Identify A and B in the following reactions:

(i) $CH_3CH_2Cl + NH_3(\text{Excess}) \xrightarrow[OH^-]{373\ K} A$

Ans. The given equation can be completed as:

$$CH_3CH_2Cl + NH_3(\text{Excess}) \xrightarrow[OH^-]{373\ K} CH_3CH_2NH_2 + HCl$$

(ii) $CH_3CH_2Cl\ (\text{excess}) + NH_3 \xrightarrow[OH^-]{373\ K}$

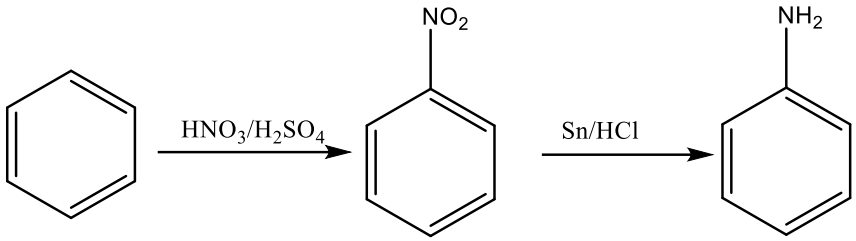
Ans. The given equation can be completed as:

$$CH_3CH_2Cl\ (\text{excess}) + NH_3 \xrightarrow[OH^-]{373\ K} (C_2H_5)_4N^+Cl^-$$

6. How will you bring about the following conversions?

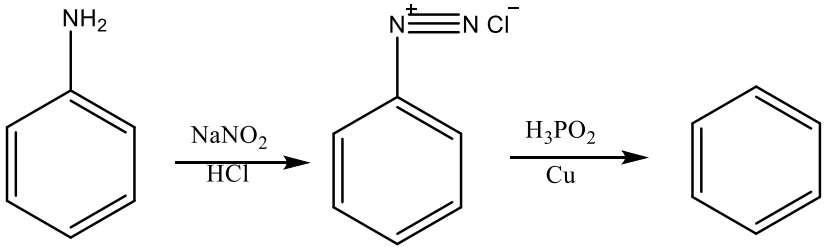
(i) Benzene to Aniline

Ans. The conversion of benzene to aniline is as followed:



(ii) Aniline to benzene

Ans. The conversion of aniline to benzene is as followed:



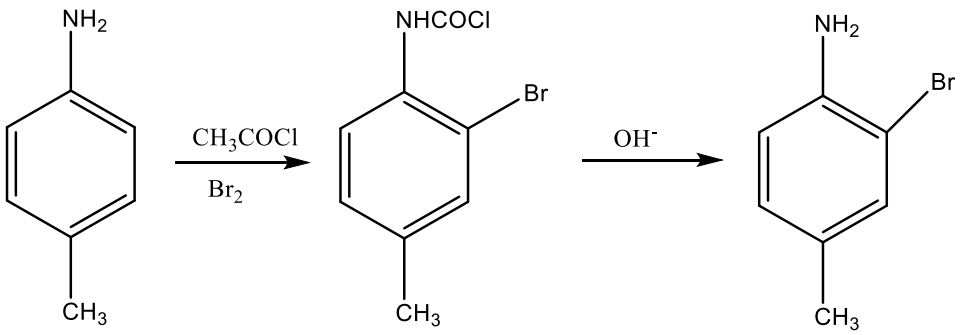
(iii) Ethanoic acid to ethanamine

Ans. The conversion of ethanoic acid to ethanamine is as followed:

$$CH_3COOH \xrightarrow{NH_3} CH_3COO^-NH_4^+ \xrightarrow[\Delta]{} CH_3CONH_2 \xrightarrow{LiAlH_4} CH_3CH_2NH_2$$

(iv) p-toluidine to 2-bromo-4-methylaniline

Ans. The conversion of p-toluidine to 2-bromo-4-methylaniline is as followed:



(v) Methylbromide to ethanamine

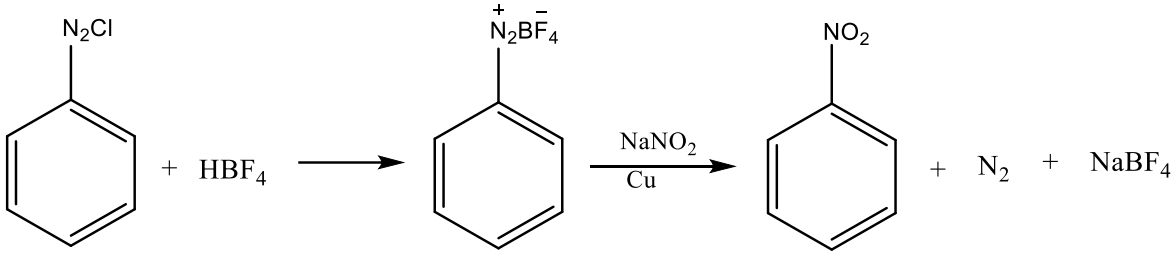
Ans. The conversion of methylbromide to ethanamine is as followed:

$$CH_3Br + KCN \rightarrow CH_3CN + KBr$$

$$CH_3CN + 4[H] \xrightarrow[\text{Alc.}]{\text{Na}} CH_3CH_2NH_2$$

(vi) Benzenediazonium chloride to nitrobenzene

Ans. The conversion of benzenediazonium chloride to nitrobenzene is as followed:



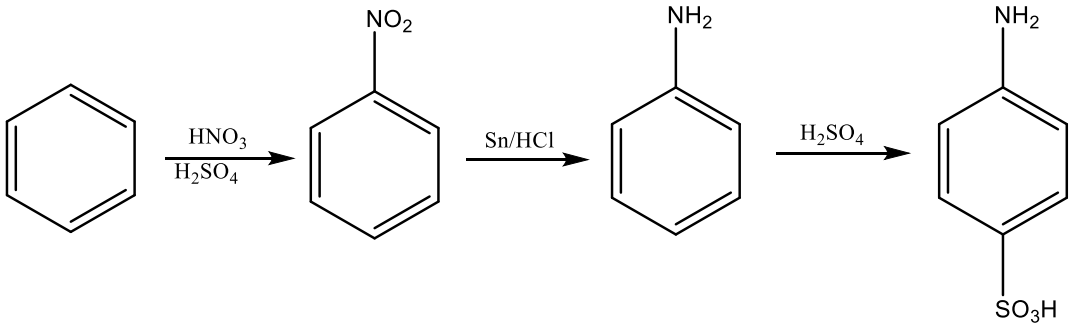
(vii) Ethylamine to methylamine

Ans. The conversion of ethylamine to methylamine is as followed:

$$CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{[O]} CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$$

(viii) Benzene to sulphanilic acid

Ans. The conversion of benzene to sulphanilic acid is as followed:

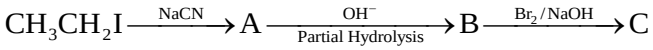


(ix) Hexanenitrile to 1-aminopentane

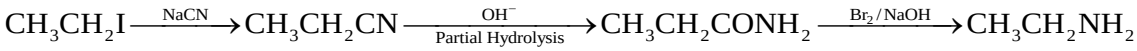
Ans. The conversion of hexanenitrile to 1-aminopentane is as followed:

$$C_5H_{11}CN \xrightarrow{H^+/H_2O} C_5H_{11}COOH \xrightarrow{SOCl_2} C_5H_{11}COCl \xrightarrow[\text{Excess}]{NH_3} C_5H_{11}CONH_2 \xrightarrow{Br_2/KOH} C_5H_{11}NH_2$$

7. Write the products formed in the following sequence of reactions:

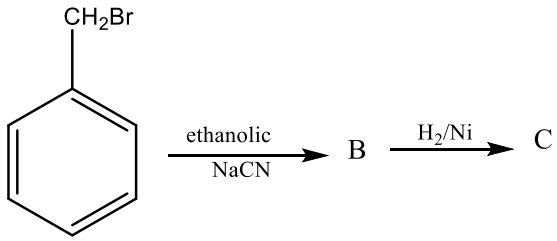


Ans. The products formed are:

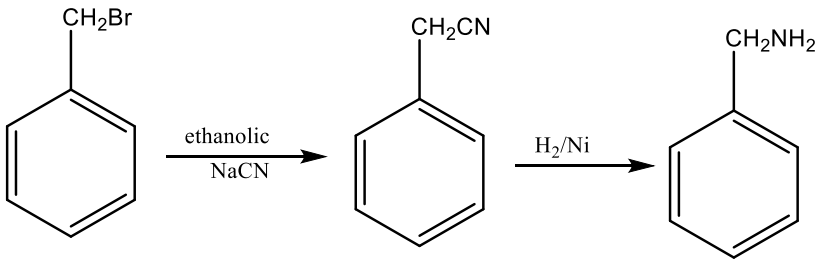


8. Identify the missing reagent/product in the following reactions:

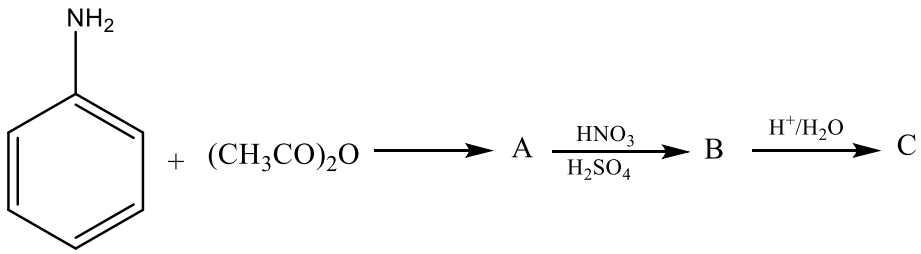
(i)



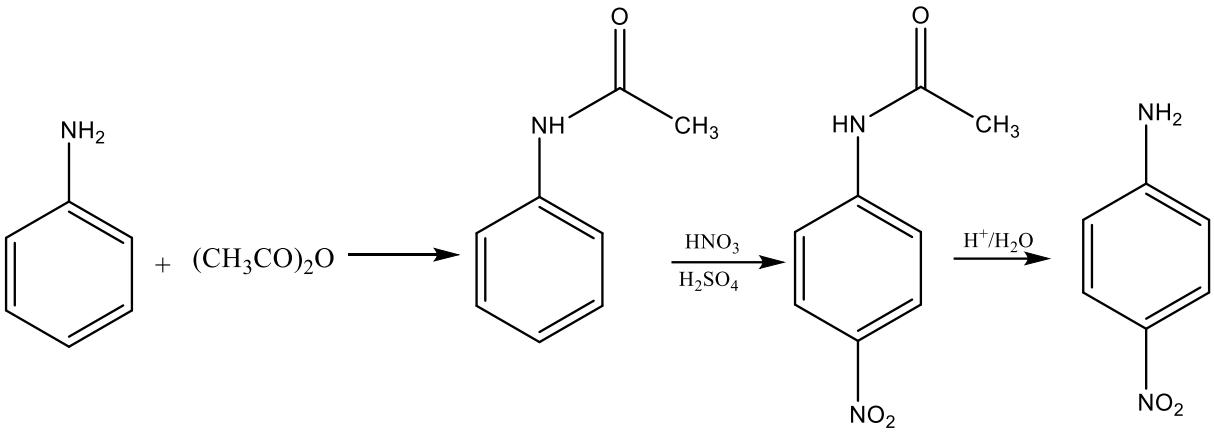
Ans. The missing reagents/products are:



(ii)



Ans. The missing reagents/products are:



(iii) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B$

Ans. The missing reagents/products are:

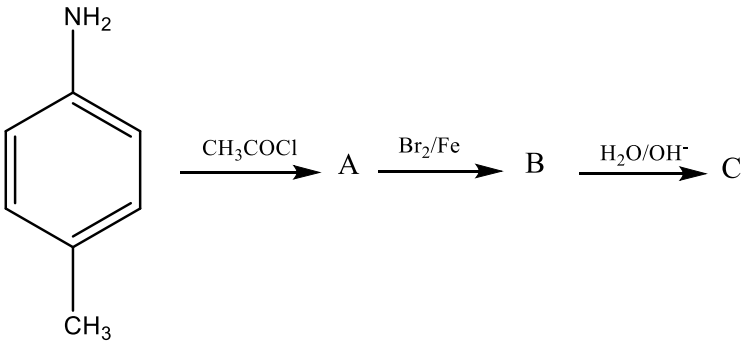
$C_6H_5N_2^+Cl^- \xrightarrow{CuCN} C_6H_5CN \xrightarrow{H_2O/H^+} C_6H_5COOH$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{H_2SO_4} B \xrightarrow[\Delta]{} C$

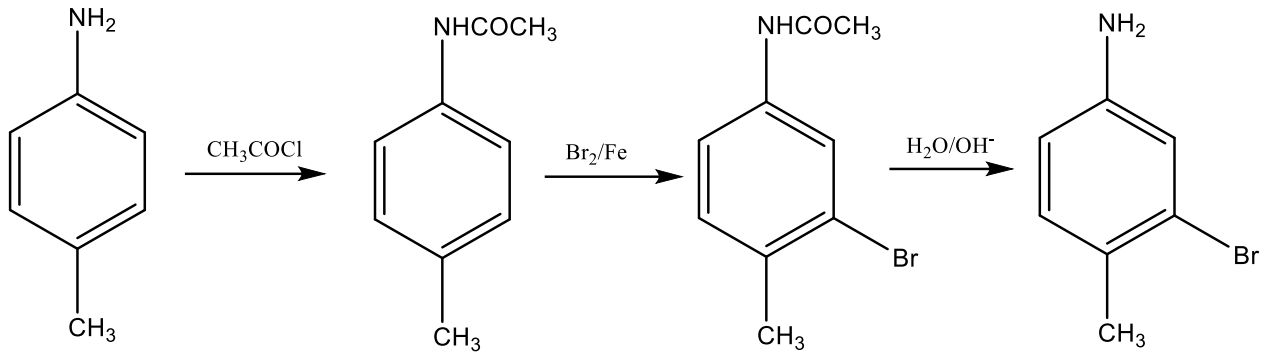
Ans. The missing reagents/products are:

$C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2 \xrightarrow{H_2SO_4} C_6H_5N^+H_3HSO_4^- \xrightarrow[\Delta]{} C_6H_5NH_2SO_3H$

(v)



Ans. The missing reagents/products are:



9. Give one chemical test to distinguish between the following pairs of compounds:

(i) Methylamine and dimethylamine

Ans. Methylamine and dimethylamine can be distinguished by carbylamines test:

Carbylamine test: Aliphatic and aromatic primary amines create foul-smelling isocyanides or carbylamines when heated with chloroform and ethanolic potassium hydroxide. The Carbylamine test is positive for methylamine (an aliphatic primary amine), but not for dimethylamine.

$$CH_3\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3\text{-}NC + 3KCl + 3H_2$$

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(ii) Secondary and tertiary amines

Ans. Allowing secondary and tertiary amines to react with Hinsberg's reagent distinguishes them (Benzenesulphonyl chloride, $C_6H_5SO_2Cl$). Secondary amines react with Hinsberg's reagent to produce an alkali-insoluble product. N, Ndiethylamine, for example, interacts with Hinsberg's reagent to produce N, Ndiethylbenzenesulphonamide, which is insoluble in alkali. Hinsberg's reagent, on the other hand, does not react with tertiary amines.

(iii) Ethylamine and aniline

Ans. The azo-dye test can differentiate between ethylamine and aniline. A reaction of aromatic amines with HNO_2 ($NaNO_2$ + dil. HCl) at 0-5°C produces a dye, the produced dye then undergoes a reaction with an alkaline solution of 2-naphthol. The colour of the dye is generally yellow, red, or orange. Under comparable conditions, aliphatic amines produce a rapid effervescence (due to the development of N_2 gas).

(iv) Aniline and benzylamine

Ans. The reactions of aniline and benzylamine with nitrous acid, which is made in situ from a mineral acid and sodium nitrite, differentiate them. With the development of nitrogen gas, benzylamine interacts with nitrous acid to create an unstable diazonium salt, which then yields alcohol.

$$C_6H_5CH_2-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [C_6H_5CH_2-N_2^+Cl^-] \xrightarrow{H_2O} C_6H_5CH_2-OH + HCl + N_2$$

Aniline, on the other hand, forms a stable diazonium salt when it interacts with HNO_2 at a low temperature. As a result, no nitrogen gas is produced.

$$C_6H_5NH_2 \xrightarrow[273\,K-278\,K]{NaNO_2-HCl} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

(v) Methylamine and methanol

Ans. Methylamine gives the carbylamine test, in which a primary amine when heated with chloroform and potassium hydroxide produces a foul smelling isocyanides. Whereas, ethanol does not give positive carbylamine test.

(vi) Methylamine and N, N-dimethylamine

Ans. N,N-dimethylamine is a secondary amine and methylamine is a primary amine and the only test used to distinguish between a primary and a secondary amine is the carbylamines test.

Aliphatic and aromatic primary amines create foul-smelling isocyanides or carbylamines when heated with chloroform and ethanolic potassium hydroxide. The Carbylamine test is positive for methylamine (an aliphatic primary amine), but not for N,N-dimethylamine.

(vii) Ethanol and ethanamine

Ans. Test for ethanol: After heating, ethanol produces turbidity when treated with Lucas reagent (anhy. $ZnCl_2$ and conc. HCl).

Test for ethanamine: Ethanamine when treated with HNO_2 and mixture of $NaNO_2$ and dilute HCl gives brisk effervescence as nitrogen gas is evolved in the process.

10.Explain why

(i) The $C-N-C$ bond angle in trimethyl amine is 108°

Ans. The bond angle of $C-N-C$ is 108° due to the repulsion between the bulky methyl groups on both the sides of the nitrogen atoms.

(ii) The quaternary ammonium salts having four different alkyl groups are optically active.

Ans. There is no rapid inversion in quaternary ammonium compounds because nitrogen atoms do not have a lone pair of electrons. The optical activity of the nitrogen atom is due to its sigma bonding to four alkyl groups.

(iii) Alkylamines are more basic than ammonia.

Ans. The alkyl group (R) pulls electrons towards nitrogen in alkyl amine due to its electron-releasing nature, making the unshared electron pair more available for sharing with the acid's proton. Therefore, alkyl amines shows more basic nature than ammonia.

(iv) Aniline cannot be prepared by Gabriel phthalimide synthesis.

Ans. Because aryl halides cannot undergo nucleophilic substitution with the anion produced by phthalimide, Gabriel phthalimide synthesis technique cannot produce aniline.

(v) Garbriel phthalimide synthesis is preferably used for synthesising primary amines.

Ans. This process is used to make primary amines from primary alkyl halides. Because secondary and tertiary amines are not generated during this synthesis, only pure primary amines are produced, which is why this reaction is favoured for primary amine production. N-Alkyl Phthalimide is formed as a result of this reaction.

(vi) Ethylamine is soluble in water but aniline is not.

Ans. When ethylamine is mixed with water, it creates intermolecular hydrogen bonds. However, due to the presence of a large hydrophobic $-C_6H_5$ group, aniline does not form hydrogen bond with water to a great amount. As a result, aniline is water insoluble.

(vii) Amines are soluble in dilute HCl **.**

Ans. The amines become charged when they receive an H^+ ion from the acid, allowing them to form (strong) ion-dipole interactions with water molecules. It basically turns into a salt and dissolves in the same way that table salt does in a glass of water.

(viii) Amines have lower boiling point than alcohols of comparable molecular masses.

Ans. Because nitrogen is less electronegative than oxygen, amines have lower boiling points than alcohols. As a result, the $N-H$ bond is less polar than the $O-H$ bond, and the hydrogen bond between amines and alcohols is weaker.

(ix) 1° amines have higher boiling points than 2° amines which in turn, are higher boiling than 3° amines.

Ans. Because primary amines have replacement hydrogen atoms that are accessible for hydrogen bonding, they have a higher boiling point than tertiary amines. The boiling point of tertiary amine rises due to hydrogen bonding because more heat is required to break these hydrogen bonds.

(x) The pK_b **value of benzeneamine is 9.33 while that of ammonia is 4.75.**

Ans. The pK_b value of benzylamine is more than ammonia because ammonia is more basic than benzyl amine. Higher pK_b value indicates lower basicity.

(xi) Aniline does not undergo Friedel-Crafts reaction.

Ans. Because the reagent $AlCl_3$ (the Lewis acid employed as a catalyst in Friedel crafts reactions) is electron deficient, it functions as a Lewis base and does not undergo Friedel craft reactions. It attacks the lone pair of nitrogen in aniline, forming an insoluble complex that precipitates out, stopping the process. That is why aniline does not undergo Friedal-Crafts reaction.

(xii) Aniline readily forms 2, 4, 6-tribromoaniline on reaction with bromine water.

Ans. Because of the nitrogen atom and the low $+I$ impact of hydrogen, aniline is a strongly activating group. This results in a highly dense electron cloud in benzene, resulting in a strong reaction with Br water, yielding 2, 4, 6-Tribromoaniline.

(xiii) Sulphanilic acid is insoluble in water.

Ans. Because it cannot establish hydrogen bonds with water molecules, sulphanilic acid is insoluble in both water and acid. However, it is soluble in aqueous mineral acids such as HF , HCl , and HNO_3 because mineral acids may form hydrogen bonds with them.

(xiv) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

Ans. In water, methylamine interacts with ferric chloride to form ferric hydroxide. Methylamine is more basic than water due to the $+I$ action of the $-CH_3$ group. As a result, methylamine creates OH^- ions in water by absorbing H^+ ions from the environment. Methyl amine is a base that produces hydroxide ions when it dissolves in water.

(xv) Diazonium salt of aromatic amines are more stable than the diazonium salts of aliphatic amines.

Ans. The positive charge on the benzene ring disperses due to resonance. The diazonium ion's stability is due to this resonance. As a result, aromatic amine diazonium salts are more stable than aliphatic amine diazonium salts.

(xvi) Although amino group is o, p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

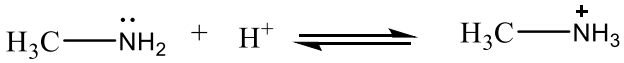
Ans. Nitration takes place in an acidic environment. Aniline is protonated to yield anilinium ion in an acidic media (which is meta-directing).

11. Why do amines act as nucleophiles? Give example of a reaction in which methylamine acts as a nucleophile.

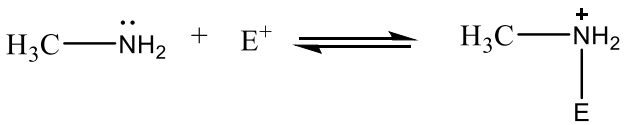
Ans. Nucleophiles are aliphatic amines. This is owing to the fact that nitrogen has a lone pair of electrons. Aromatic amines are nucleophiles but not nucleophiles. This is due to the fact that the lone pair of electrons on nitrogen in aromatic amines is in resonance with the benzene ring and hence unavailable to nucleophile attack.

Methyl amine acts as a nucleophile in the following reaction:

When the lone pair on methyl amine reacts with the hydrogen ion, then it acts as a base:



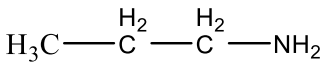
When the lone pair on methyl amine reacts with any other atom other than the hydrogen , then it acts as a nucleophile:



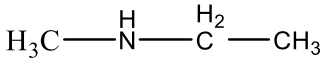
12. Three isomeric amines A, B and C have the molecular formula C_3H_9N . Compound A on reaction with benzene sulphonyl chloride forms a product which is soluble in NaOH . Compound B on reaction with benzene sulphonyl chloride forms a product which is insoluble in NaOH and compound C does not react with benzene sulphonyl chloride. Identify A, B and C.

Ans. The test shown is the hinsberg test for the detection of primary, secondary and tertiary amines:

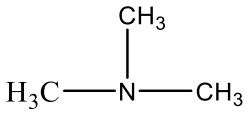
Compound A is a primary amine because it forms a compound soluble in sodium hydroxide after the reaction with benzene sulphonyl chloride, compound A is propyl amine or propan-1-amine.



Compound B is a secondary amine because it forms a compound insoluble in sodium hydroxide after the reaction with benzene sulphonyl chloride, compound B is N-methylethaneamine.



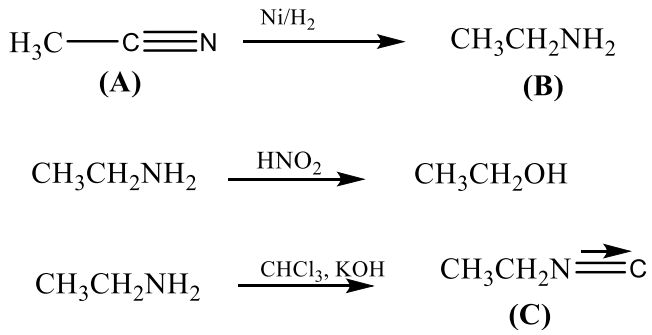
Compound C is a tertiary amine because it does not react with benzene sulphonyl chloride and hence does not give a hinsberg test, compound C is trimethylamine or N,N-dimethylmethaneamine.



13. An organic compound A (C_2H_3N) is used as a solvent of choice for many organic reactions because it is not reactive in mild acidic and basic conditions. Compound A on treatment with Ni/H_2 forms B. When B is treated with nitrous acid at 273 K, ethanol is obtained. When B is

warmed with chloroform and $NaOH$, a foul smelling compound C formed. Identify A, B and C.

Ans. The compound A is methyl cyanide which on undergoing reduction with Ni/H_2 forms compound B which is ethanamine. Ethanamine when reacted with nitrous acid produces ethanol and when ethanamine is warmed with chloroform and sodium or potassium hydroxide it produces a foul smelling compound C which is ethyl isocyanide. The reactions are given below:



14.An organic compound [A] $C_3H_6O_2$ on reaction with ammonia followed by heating yield B. Compound B on reaction with Br_2 and alc. $NaOH$ gives compound C (C_2H_7N) . Compound C forms a foul smelling compound D on reaction with chloroform and $NaOH$. Identify A, B, C, D and the write the equations of reactions involved.

Ans. Compound A is propionic acid which on reaction with ammonia and after heating yields compound B which is propanamide. Compound B which is propanamide on reaction with bromine and alcoholic sodium hydroxide yields compound C which is ethylamine. Ethylamine on reaction with chloroform and sodium hydroxide gives a foul smelling compound D which is ethyl isocyanide.

The reaction is given as:

$$CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2COO^-NH_4^+ \xrightarrow[\Delta]{} CH_3CH_2CONH_2 \xrightarrow{NaOH/Br_2} CH_3CH_2NH_2 \xrightarrow{CHCl_3/NaOH} CH_3CH_2N{=}C$$