

## ANSWERS

## Section-A

1. Determination of the empirical formula of A:

ELEMENT	C	H	N
Mass per 100 gms.	61.01	15.25	23.73
No. Of moles	$\frac{61.01}{12} = 5.08$	$\frac{15.25}{1} = 15.25$	$\frac{23.73}{14} = 1.69$
Simplest ratio	$\frac{5.08}{1.69} = 3$	$\frac{15.25}{1.69} = 9$	1

Empirical formula of A is  $C_3H_9N$ .

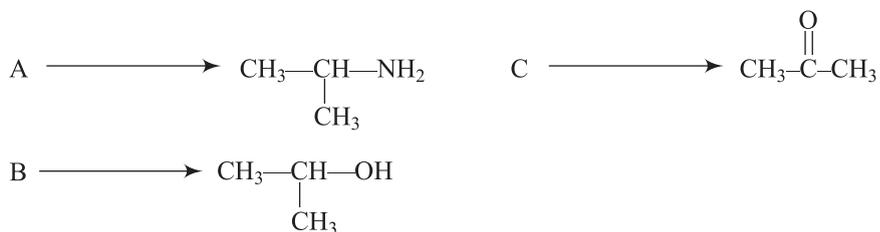
Determination of the molecular formula of B:

ELEMENT	C	H	N
Mass per 100 gms.	60.00	13.33	26.67
No. Of moles	$\frac{60.00}{12} = 5.00$	$\frac{13.33}{1} = 13.33$	$\frac{26.67}{16} = 1.67$
Simplest ratio	$\frac{5.00}{1.67} = 3.0$	$\frac{13.33}{1.67} = 8$	1

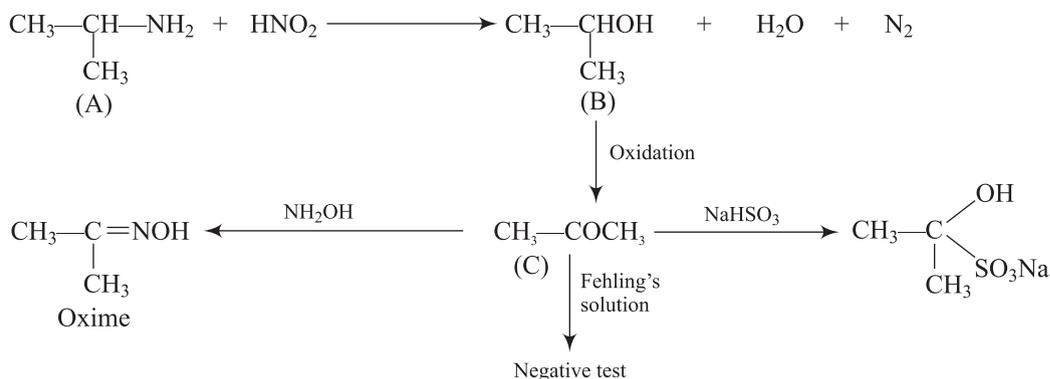
Empirical formula of B is  $C_3H_8O$ .Molecular mass of B is  $2 \times VD = 2 \times 30 = 60$ Hence, the molecular formula of B is also  $C_3H_8O$ .Reaction of A with  $HNO_2$  does not change the number of carbon atoms. Hence, the molecular formula of A is also  $C_3H_9N$ .A liberates  $N_2$  gas with  $HNO_2$  indicates the presence of  $-NH_2$  group ( $1^\circ$  amine) and  $HNO_2$  converts  $-NH_2$  group into  $-OH$ .Compound B may be a primary alcohol,  $CH_3CH_2CH_2OH$  or secondary alcohol,  $CH_3-\underset{\text{CH}_3}{\text{CHOH}}$ 

Primary alcohol on oxidation gives aldehyde but secondary alcohol forms ketone. As compound C gives Fehling solution test confirms that C is a ketone and hence B is a secondary alcohol.

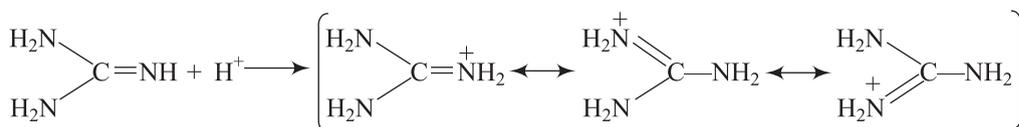
The structure of A, B and C respectively are:



The reactions involved are:



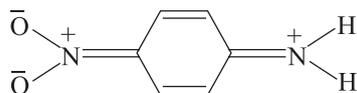
2. (a) Guanidine contains two different nitrogen,  $-\text{NH}_2$  group has  $\text{sp}^3$  N-atom while  $=\text{NH}$  group has  $\text{sp}^2$  N-atom. N of NH group is less basic than N of  $\text{NH}_2$  group but still protonation of imino N leads to a symmetrical resonance stabilised cation.



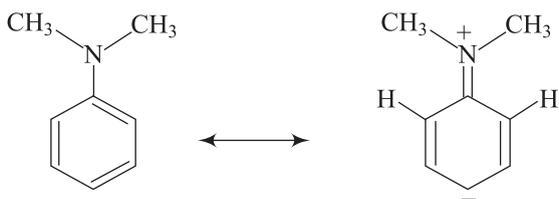
These three resonating structures are equivalent and contributes more for the larger delocalization energy and stability of the carbon.

This results in the enhanced basicity of guanidine. Guanidine is probably the strongest organic N base known.

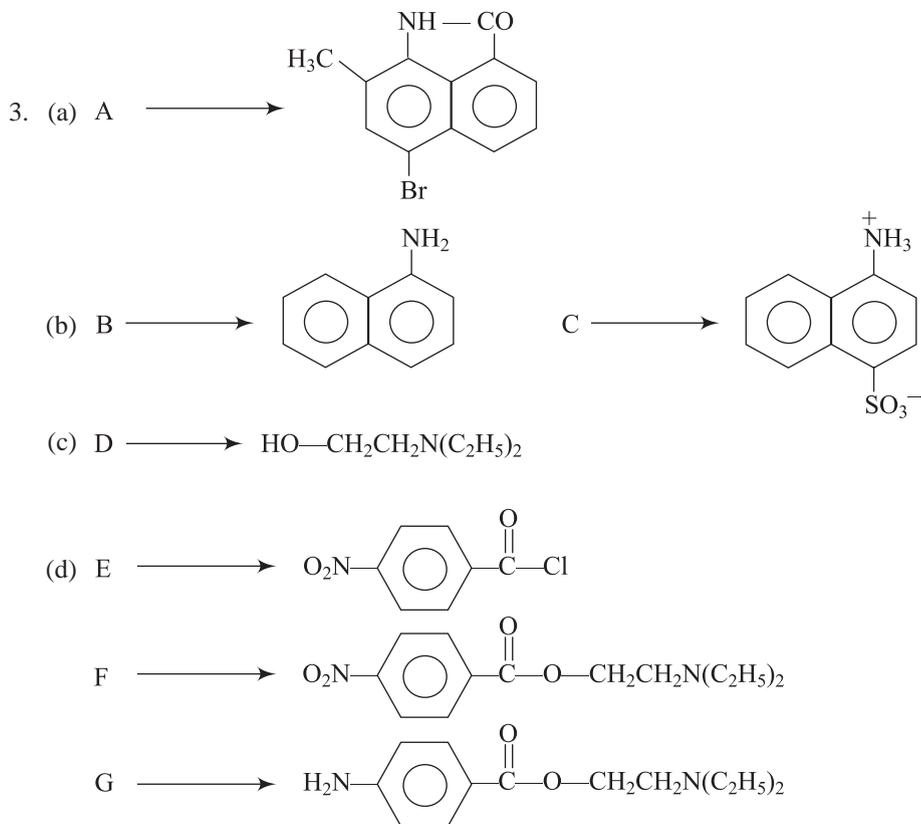
- (b)   $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$  is much weaker base than aniline because  $\text{NO}_2$  is electron withdrawing mainly by extended  $\pi$  bonding from the ortho and para position ( $-\text{R}$  effect).



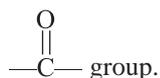
- (c) By using the lone pair present into resonance with the benzene ring, the N atom becomes coplanar with the ring and its ortho bonds in N,N-dimethyl aniline.



But due to the presence of bulky substituents in the ortho 2, 6 positions sterically hinder the attainment of coplanarity (it means difficult sterically for lone pair on N-atom to participate into resonance with the benzene ring). As a result, the lone pair on N-atom is more available. Hence, N,N-2, 6-tetramethyl aniline is a stronger base than N,N-dimethyl aniline.



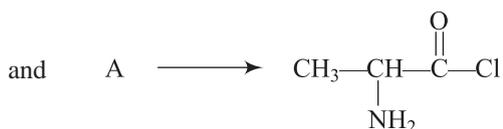
4. Compound A undergoes reaction with ammonia with the loss of Cl indicates that Cl is directly bonded to



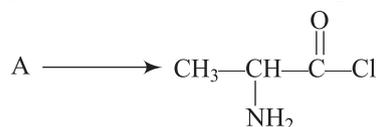
The compound A must contain  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{Cl} \end{array}$  group.

The compound C undergoes hydrolysis with HNO<sub>2</sub> which involves the replacement of —NH<sub>2</sub> group by —OH. This gives compound D. The compound D gives a positive iodoform test indicates the presence

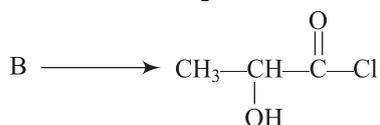
of  $\begin{array}{c} \text{OH} \\ | \\ \text{CH}_3-\text{CH} \end{array}$  group. Hence, the structures of D, C and A respectively are:



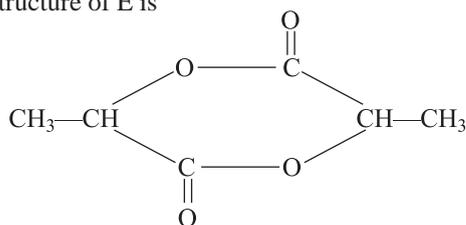
The compound A also reacts with  $\text{HNO}_2$  indicates the presence of  $-\text{NH}_2$  group. The structure of A is



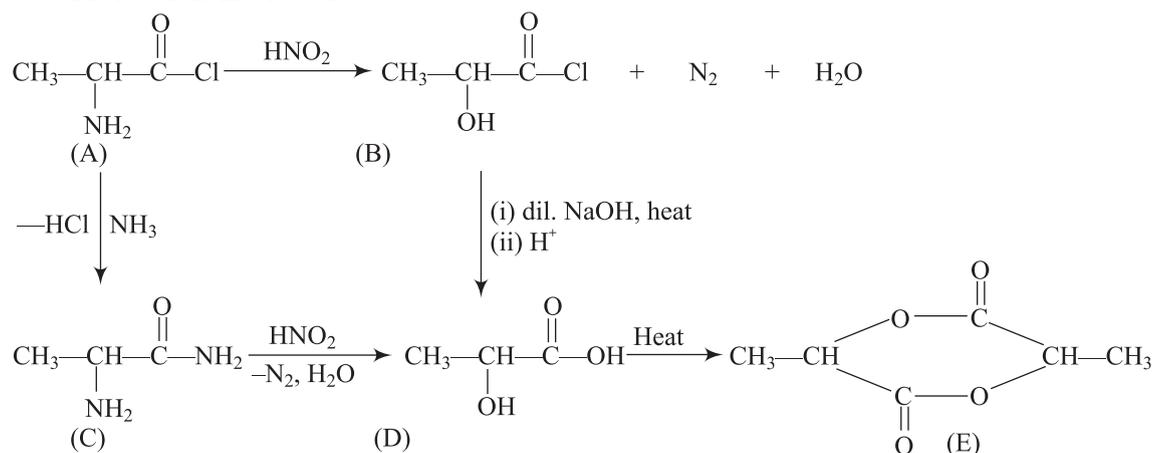
and the reaction with  $\text{HNO}_2$  results in the formation of  $\alpha$ -hydroxy acid chloride. The structure of B is



The compound D is an  $\alpha$ -hydroxy acid which on heating undergo intermolecular esterification to form E. The structure of E is



The reactions involved are:



5. Derivation of the molecular formula of A.

ELEMENT	C	H	O	N
Mass percent	69.42	5.78	13.23	11.57
Moles	$\frac{69.42}{12} = 5.785$	$\frac{5.78}{1} = 5.78$	$\frac{13.23}{16}$	$\frac{11.57}{14} = 0.826$
Simplest ratio	$\frac{5.785}{0.827} = 7.00$	$\frac{5.78}{0.826} = 7.00$	1	1

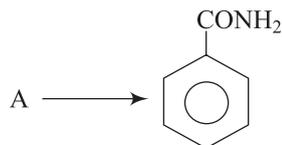
Empirical formula is  $\text{C}_7\text{H}_7\text{ON}$ .

Empirical formula weight is  $121 \text{ g mol}^{-1}$ .

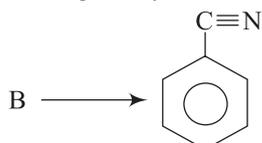
Molecular weight is also  $121 \text{ g mol}^{-1}$ . Hence, molecular formula is same as the empirical formula i.e.  $\text{C}_7\text{H}_7\text{ON}$ .

As compound A gives pungent vapors of  $\text{NH}_3$  with  $\text{KOH}$  indicates the presence of amide group ( $-\text{CONH}_2$ ).

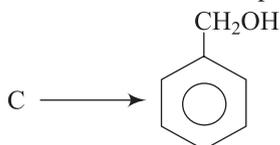
The compound A has a structure:



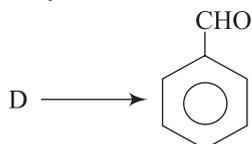
A on dehydration with  $\text{P}_4\text{O}_{10}$  to form B ( $\text{C}_7\text{H}_7\text{N}$ ) also confirms the presence of amide group. Amide on dehydration gives cyanides. The structure of compound B is



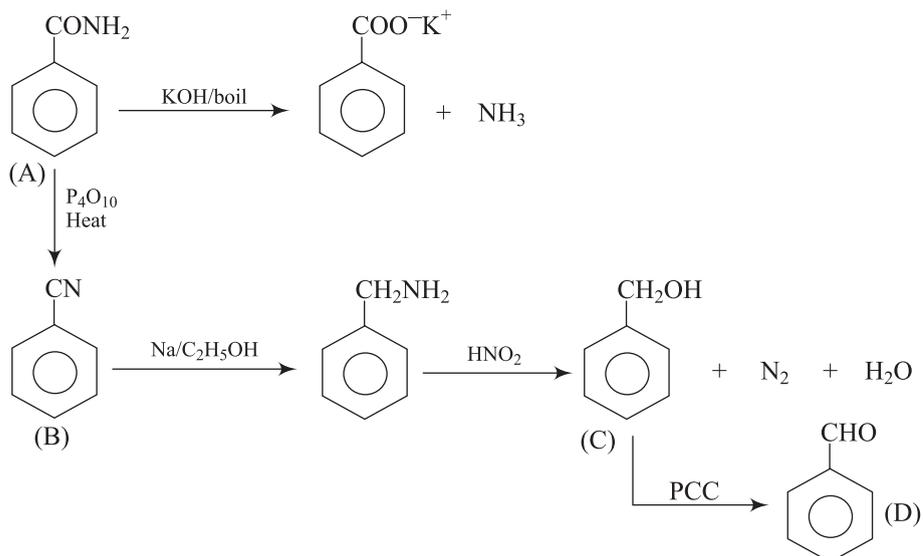
B on reduction with  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$  (Mendius reaction) followed by  $\text{HNO}_2$  converts  $-\text{C}\equiv\text{N}$  group into  $-\text{CH}_2\text{OH}$ . The structure of compound C is



C is a primary alcohol which on mild oxidation with  $\text{PCC}$  gives benzaldehyde. D has the structure



The reactions involved are:





group.

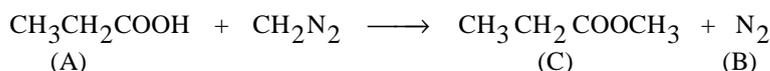
Suppose the formula of a Compound A is R—COOH, then



The molecular formula of acid A is  $C_2H_5COOH$  and its structure will be

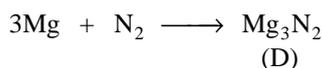


and the gas B is  $N_2$

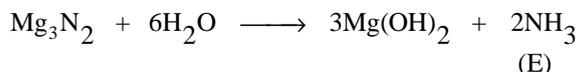


The compound C is  $CH_3CH_2COOCH_3$

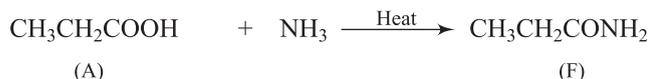
The  $N_2$  combines with Mg to form white solid magnesium nitride.



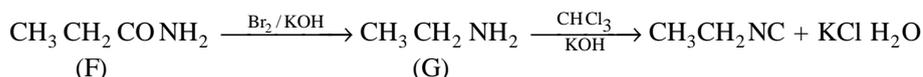
The compound D on hydrolysis gives a pungent vapours of  $NH_3$  (compound E)



The compound A reacts with  $NH_3$  to give acid amide F



The compound G is  $CH_3CH_2NH_2$  which gives a foul smelling compound  $CH_3CH_2NC$  with  $CHCl_3$  and caustic potash.

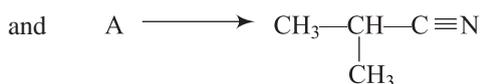
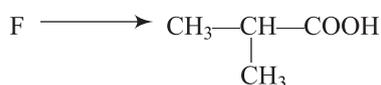
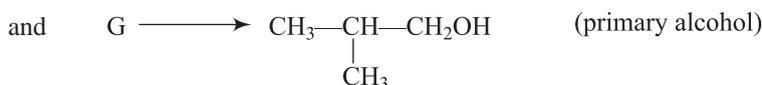
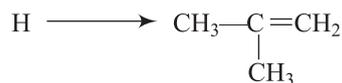


8. As compound A on reduction with  $LiAlH_4$  gives a basic compound B, A must be a nitrile.

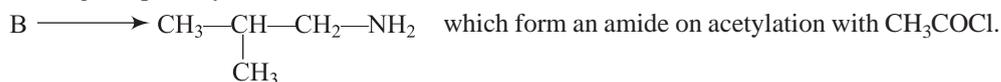


A on hydrolysis gives an acid F which on reduction gives primary alcohol, G, R—COOH.

Alcohol on heating with  $H_3PO_4$  gives an alkene. This alkene gives only acetone on oxidation. Hence, the alkene H must be 2-methyl propene.

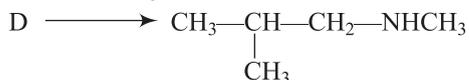


A on reduction gives primary amine, B

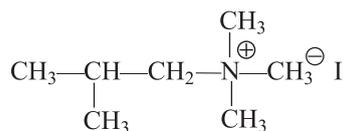


The structure of compound C is  $C \longrightarrow \text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{NHCOCH}_3$

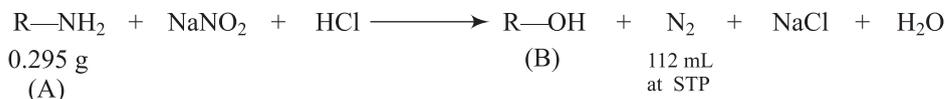
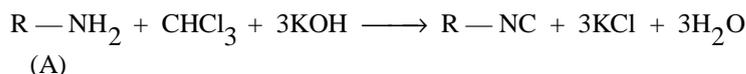
B on reaction with  $\text{CH}_3\text{I}$  gives N-methyl alkanamine, D



D on reaction with excess  $\text{CH}_3\text{I}$  gives quaternary ammonium salt, E. The structure of E is



9. As compound A gives foul smelling compound with  $\text{CHCl}_3/\text{KOH}$  indicates the presence of  $-\text{NH}_2$  group (primary amine). The compound A liberates colourless, odourless gas with  $\text{NaNO}_2$  and ice-cold  $\text{HCl}$  confirms that  $-\text{NH}_2$  group is bonded to an alkyl group and not benzene ring. Suppose the compound A is  $\text{R}-\text{NH}_2$ , then



Number of moles of  $\text{R}-\text{NH}_2 = \text{number of moles of } \text{N}_2$

$$\frac{0.295}{M} = \frac{112}{22400} = \frac{1}{200}$$

where M is the molar mass of  $\text{R}-\text{NH}_2$

$$\therefore M = 0.295 \times 200 = 59 \text{ g mol}^{-1}$$

Out of 59 g, 16 g is the mass of  $-\text{NH}_2$  group.

Therefore, the mass of the alkyl group is 43 and the alkyl group is  $\text{C}_3\text{H}_7-$

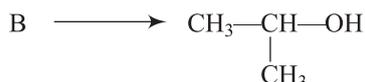
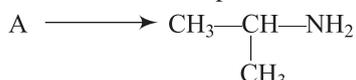
Compound A is  $\text{C}_3\text{H}_7-\text{NH}_2$  and

Compound B is  $\text{C}_3\text{H}_7-\text{OH}$

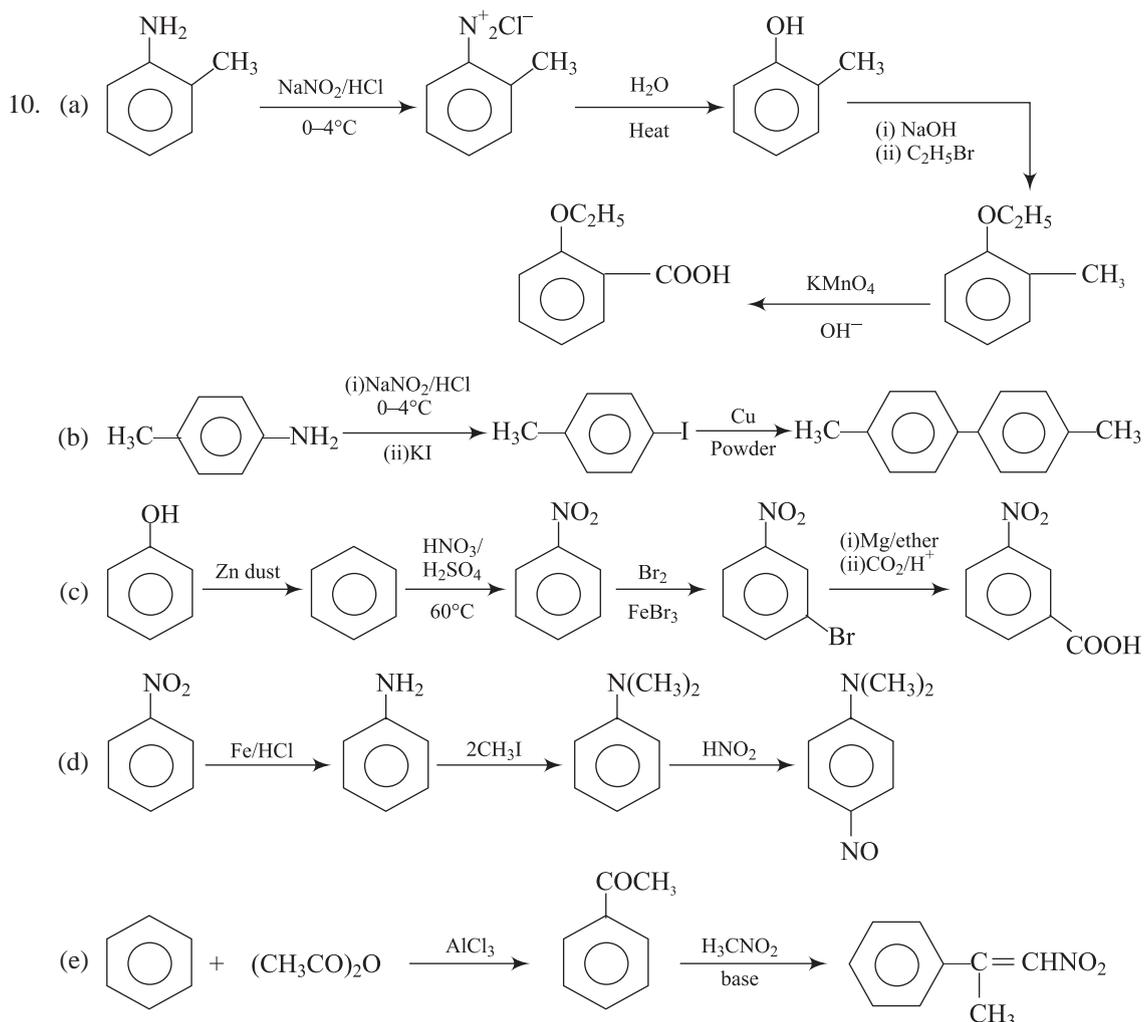
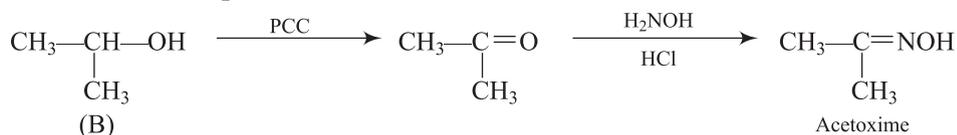
But the alkaline solution of B gives yellow precipitate with iodine confirms the presence of  $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-$

group.

Hence, the structures of compounds A and B are



## Conversion of compound B into acetoxime.

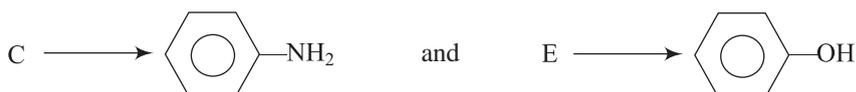


11. As compound A splits into two compounds C (as its sulphate) and B (an acid with two —COOH group). The compound A must contain an amide group.

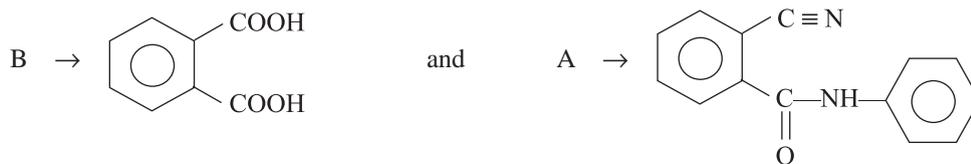
Both B and C contains benzene ring.

The structure of C contains NH<sub>2</sub> group directly bonded to the benzene ring as it undergoes diazotisation.

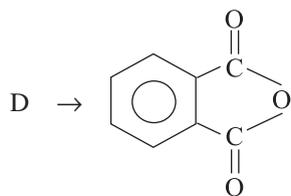
The structure of C is



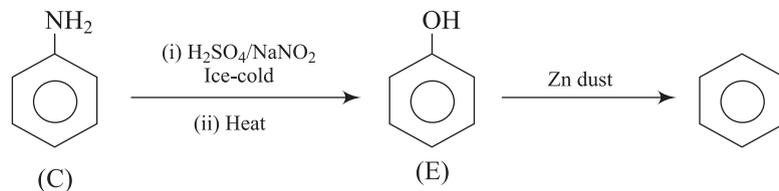
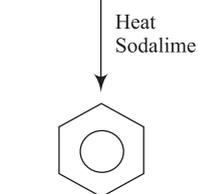
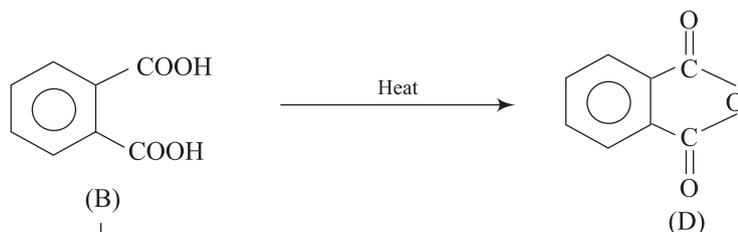
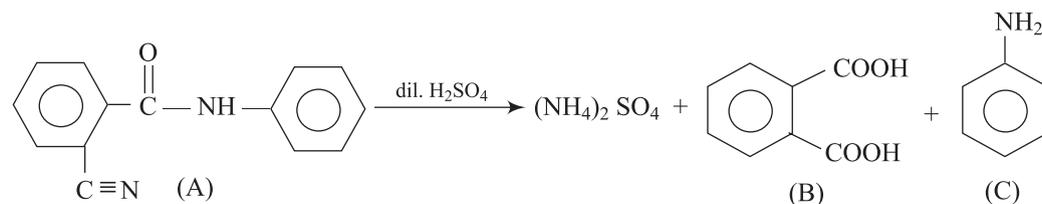
The compound B must contain two  $\text{—COOH}$  groups at ortho position as this on heating gives anhydride. Out of two  $\text{—COOH}$  groups, one is derived from amide and the other must be coming from  $\text{—C}\equiv\text{N}$ . The structure of B is



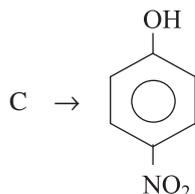
The compound D is anhydride



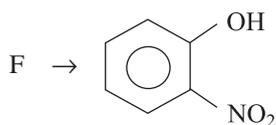
The reactions involved are:



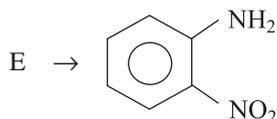
12. The compound C gives a colour with neutral  $\text{FeCl}_3$  and is a phenolic compound. It is non-volatile in steam and gives two monobromo products means, the compound C is a para-nitrophenol and its structure is



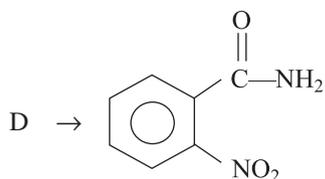
The compound F is also a nitrophenol but as it is steam volatile, F is an ortho-nitrophenol. F is steam volatile due to intramolecular hydrogen bonding. The structure of F is



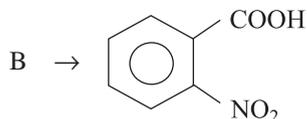
The compound E must contain  $\text{NH}_2$  group directly bonded to benzene as it undergoes diazotisation. The structure of compound E is



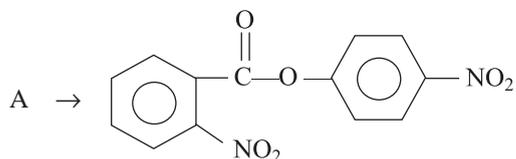
D is an amide as it gives positive Hofmann bromamide reaction. The structure of compound D is



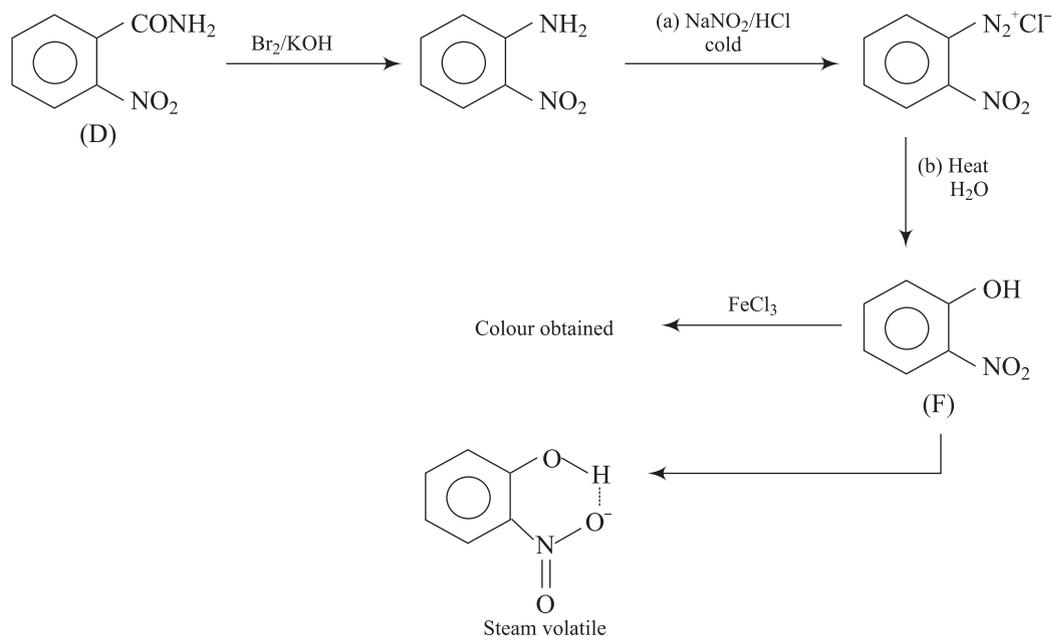
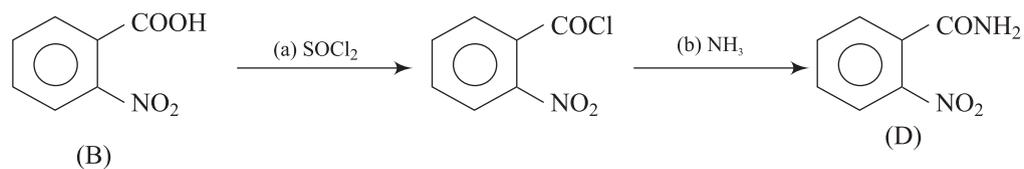
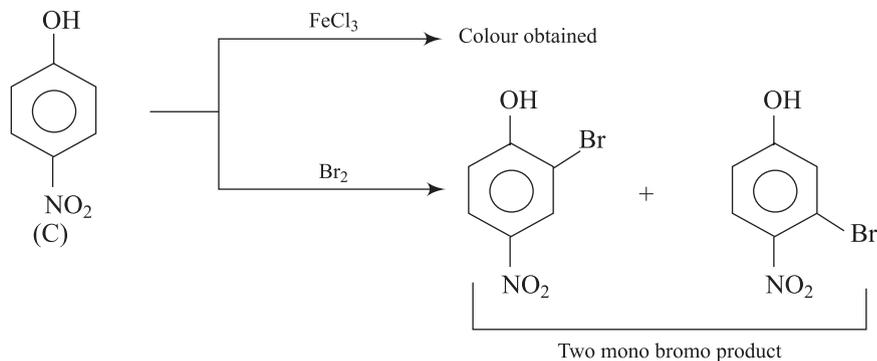
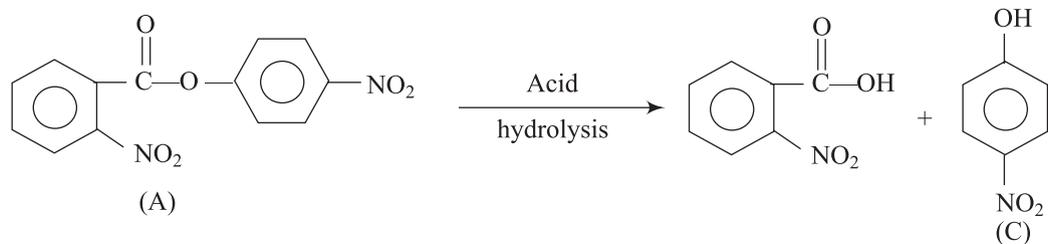
B must be an acid. Its structure is



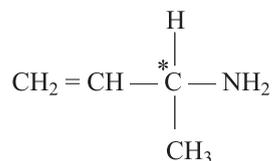
As we know the structure of B and C, A must be an ester which on hydrolysis splits into an acid and a compound with OH group. The structure of A is



The reactions involved are:



13. (a) The structure of R is



(b) S  $\rightarrow$   $\text{CH}_3\text{CH}_2 - \text{N} \equiv \text{C}$

T  $\rightarrow$   $\text{CH}_3\text{CH}_2\text{NH}_2$

(c) W  $\rightarrow$   $\text{CH}_3\text{COOH}$

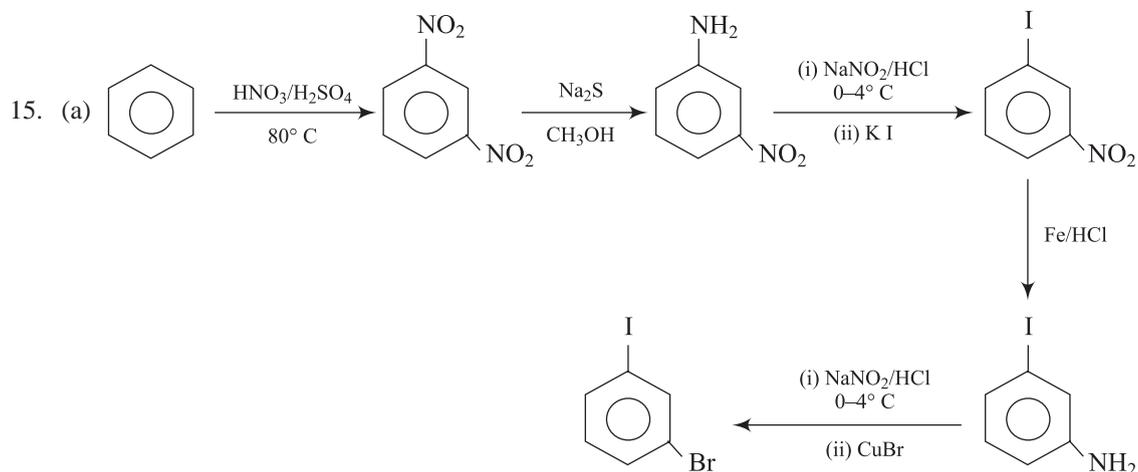
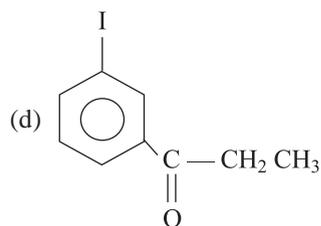
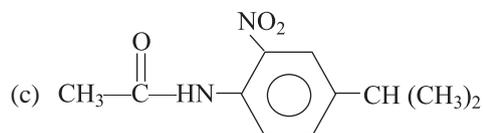
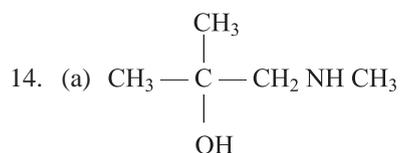
U  $\rightarrow$   $\text{HCOOH}$

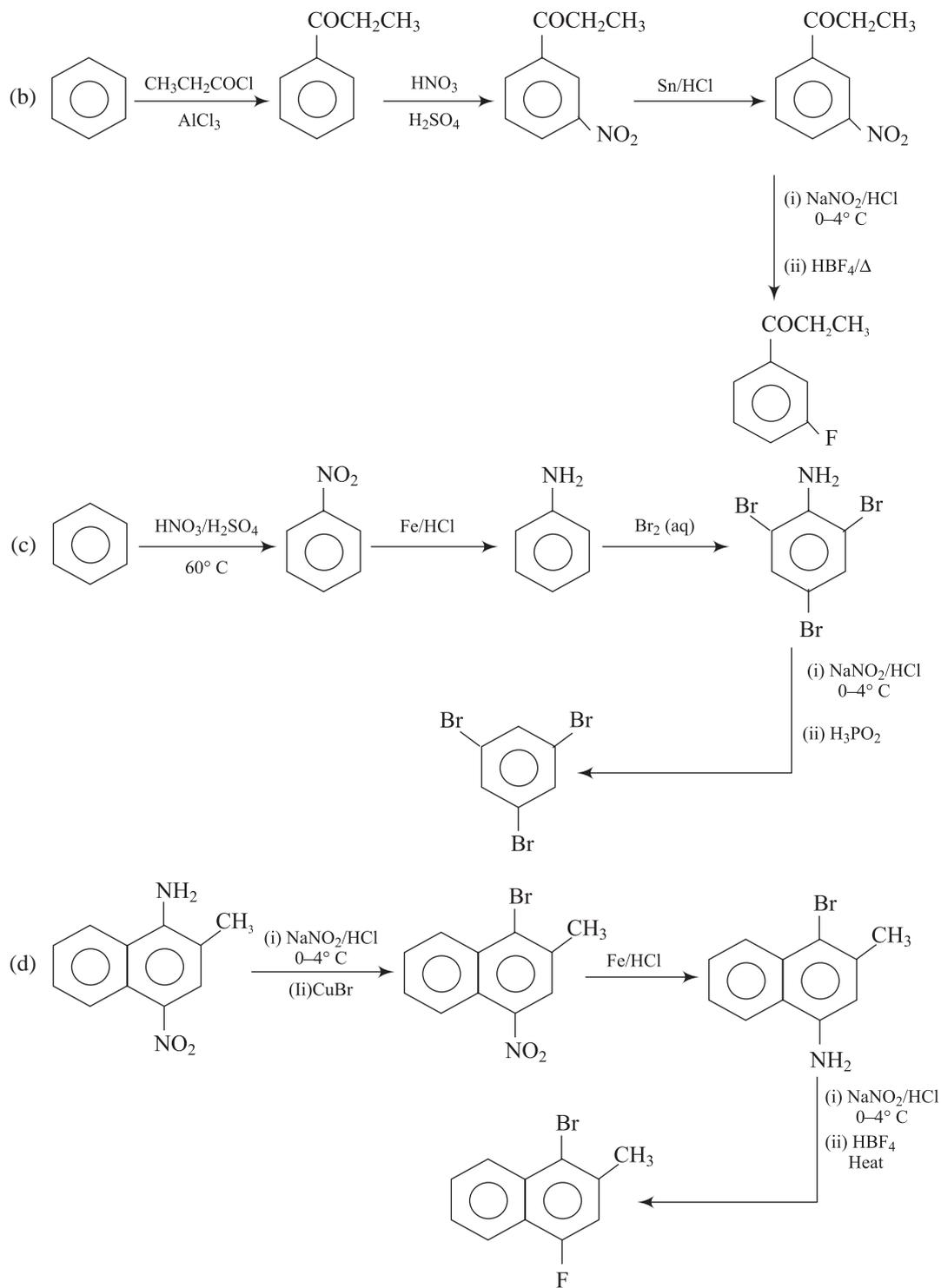
V  $\rightarrow$   $\text{CH}_3 - \text{CH}_2\text{OH}$

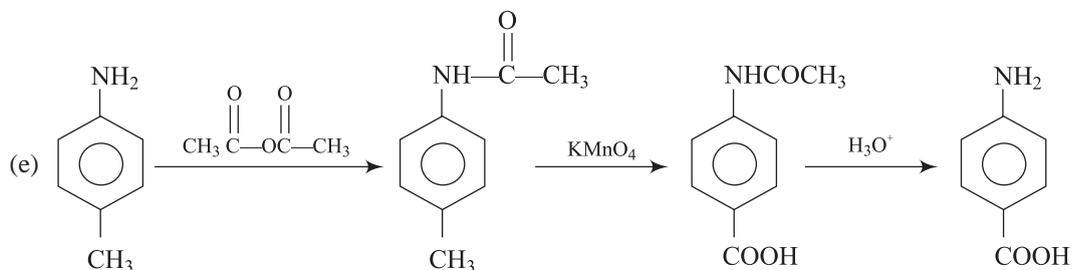
Y  $\rightarrow$   $\text{CH}_3\overset{\text{O}}{\underset{\text{CH}_3}{\text{C}}} = \text{NOH}$

X  $\rightarrow$   $\text{CH}_3\text{COCH}_3$

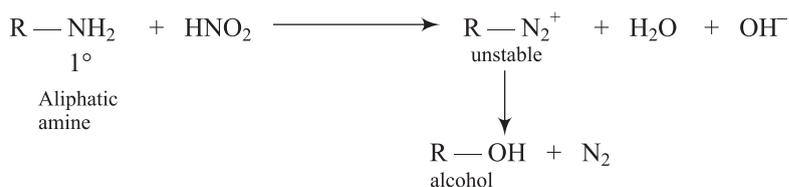
Z  $\rightarrow$   $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{NHCH}_3$



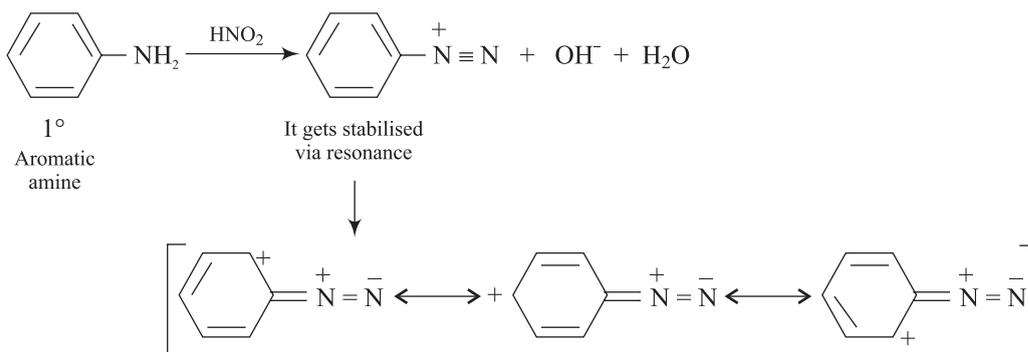




16. (a) Both primary aliphatic and aromatic amines form diazonium salt on reaction with nitrous acid. But due to the absence of resonance, primary aliphatic amines diazonium salt decomposes to give alcohol and evolved nitrogen gas.



While aromatic primary amine forms a resonance stabilised diazonium salt, as a result, nitrogen gas is not evolved.



Hence, primary aromatic amine does not form alcohol.

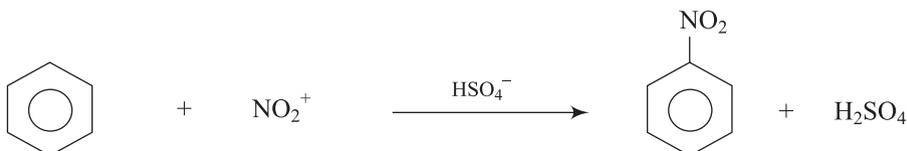
- (b) The self-ionization of  $\text{HNO}_3$  is very slow. To speed up the formation of nitronium ion, we add  $\text{H}_2\text{SO}_4$ . The sulphuric acid is so strong an acid that it transfers a proton to nitric acid.



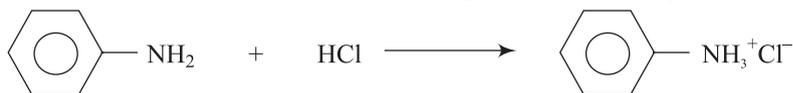
The protonated nitric acid then undergoes a spontaneous heterolysis to form the nitronium ion,  $\text{NO}_2^+$



This nitronium ion then acts as the electrophilic reagent with which the benzene reacts.

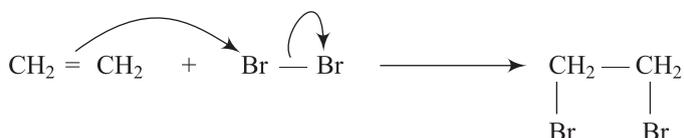


- (c) Phenyl amine being basic in nature dissolves in dilute HCl solution to a much greater extent than it dissolves in water. With hydrochloric acid, phenylamine forms phenylamine hydrogen chloride.



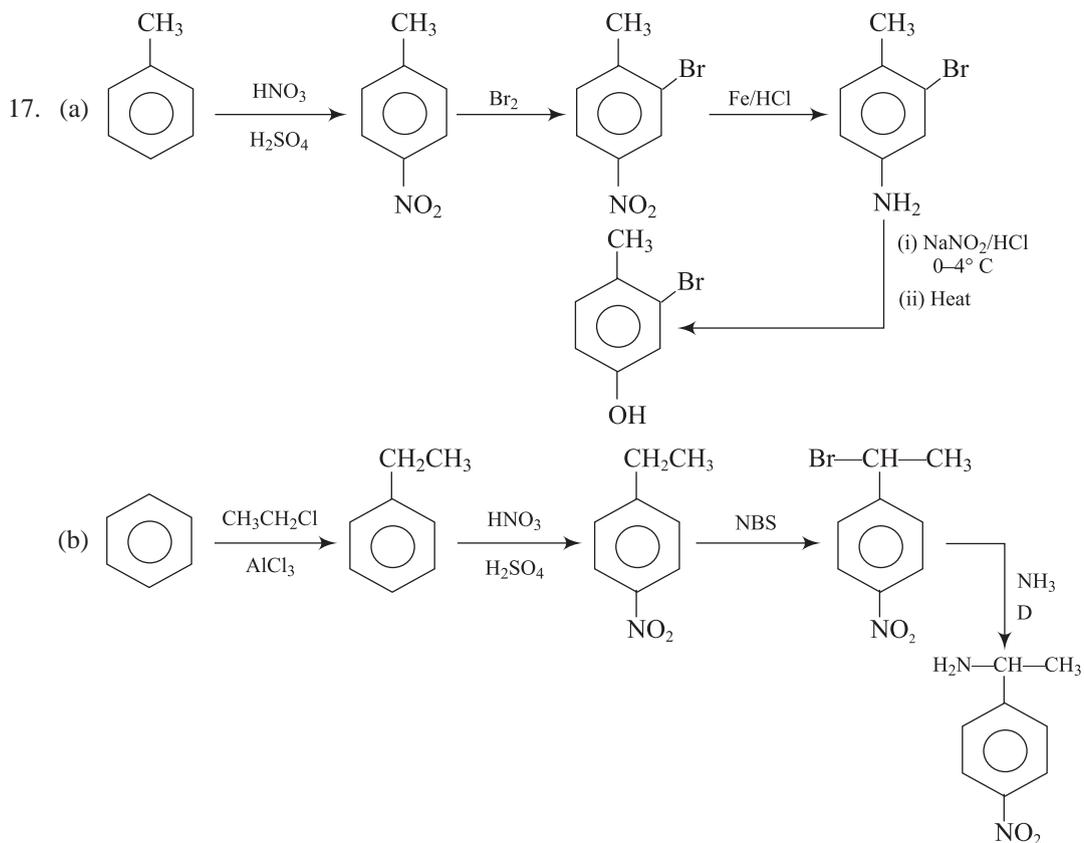
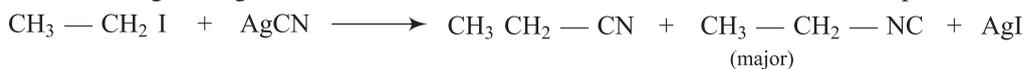
Anilinium chloride

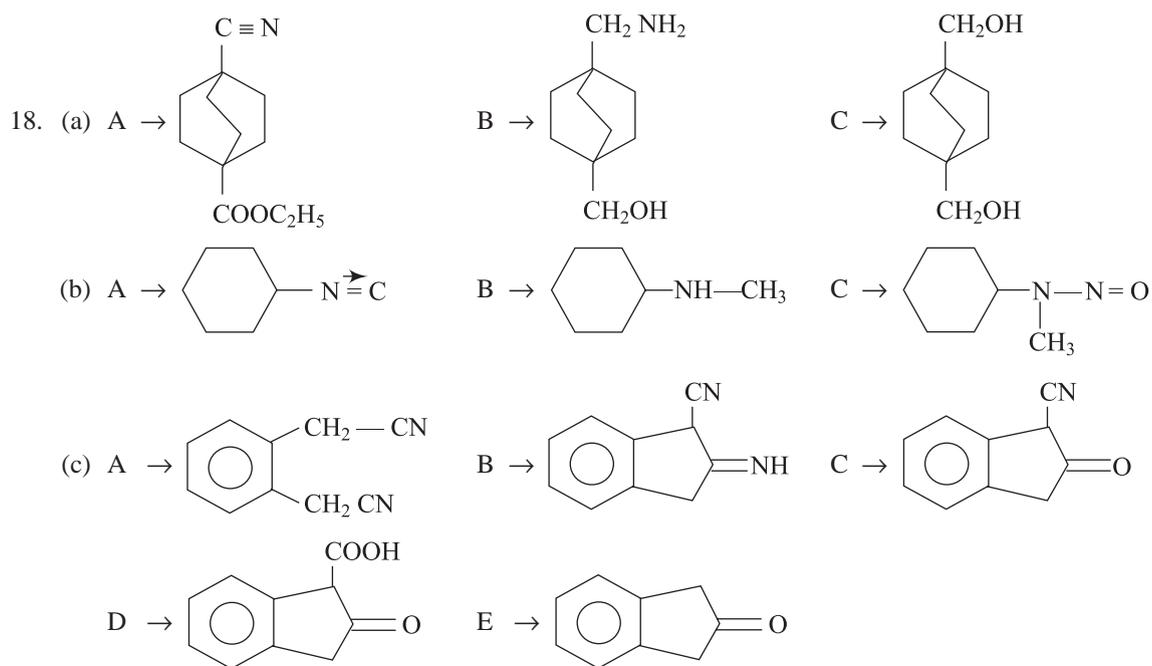
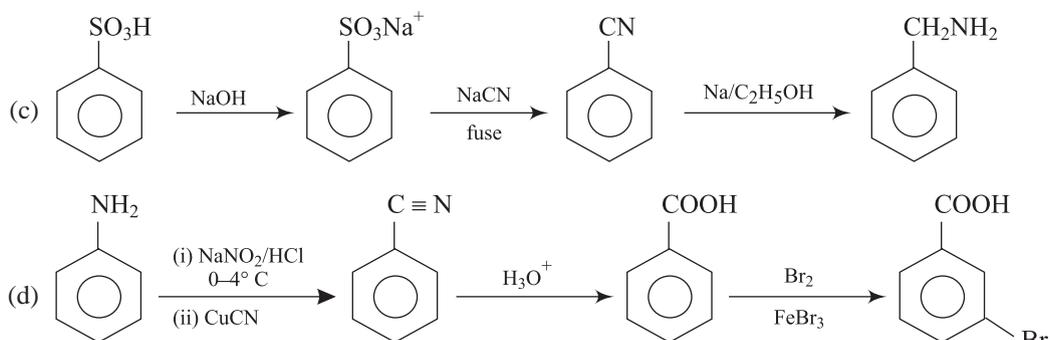
- (d) Addition of  $\text{Br}_2$  to ethene is an electrophilic addition reaction.



In propenenitrile, the carbon-carbon double bond is in conjugation with  $\text{C} \equiv \text{N}$ . Moreover the CN group is strongly electron-withdrawing and the electron density in carbon-carbon double bond decreases. The reactivity towards electrophilic addition decreases. Hence, the bromination of propenenitrile proceeds slowly.

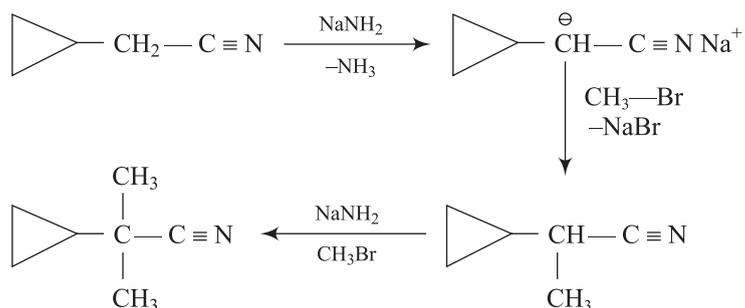
- (e) The reaction of iodoethane and silver cyanide is an example of a nucleophilic substitution reaction. Being an ambident nucleophile, the CN group can bind to the alkyl group either through carbon atom or through nitrogen atom and this results in the formation of two isomeric compounds.

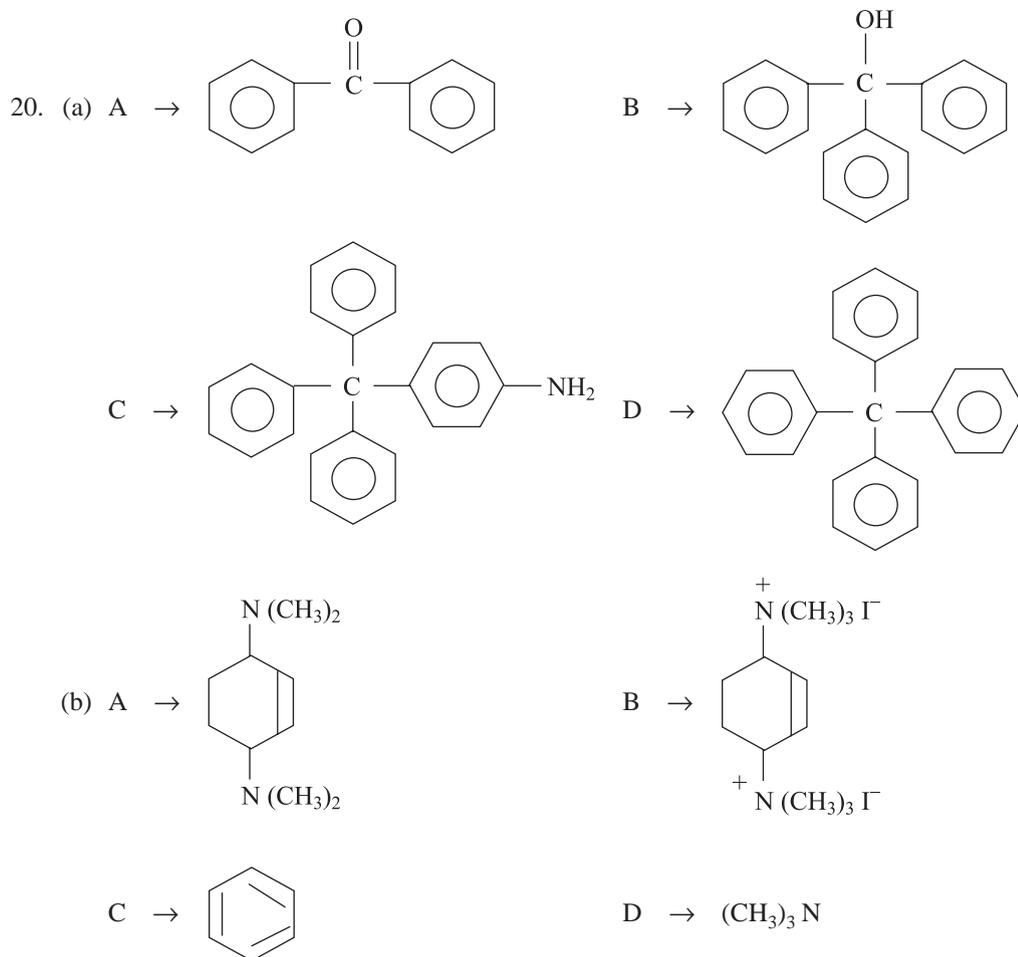




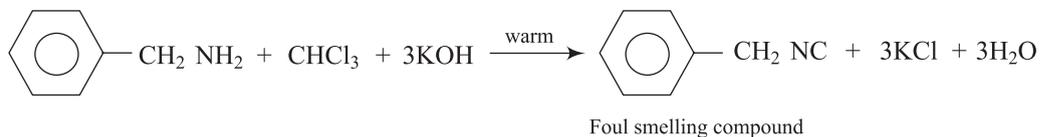
19.  $\text{NaNH}_2$  is a very strong base and the  $\alpha$ -hydrogen of  is highly acidic.

Step (1)



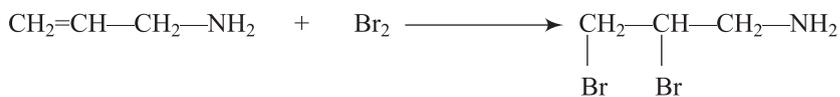


21. (a) By carbylamine reaction, (I) will give positive test

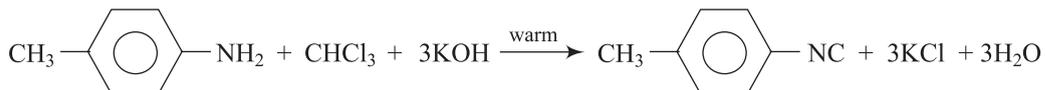


Compound (II) will not give carbylamine test.

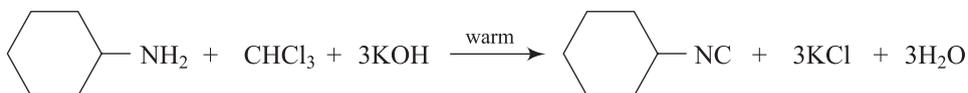
(b) By bromine water test, (I) will decolourize bromine water. The compound (II) will not



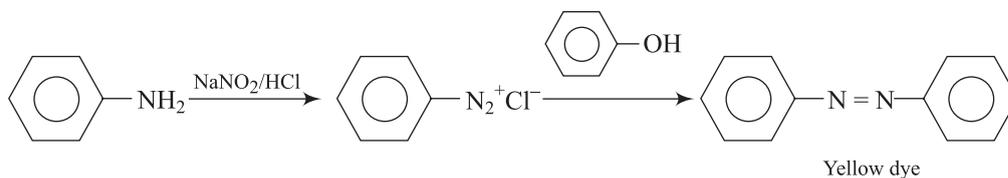
(c) By carbylamine reaction, (I) will give positive test while (II) will not give.



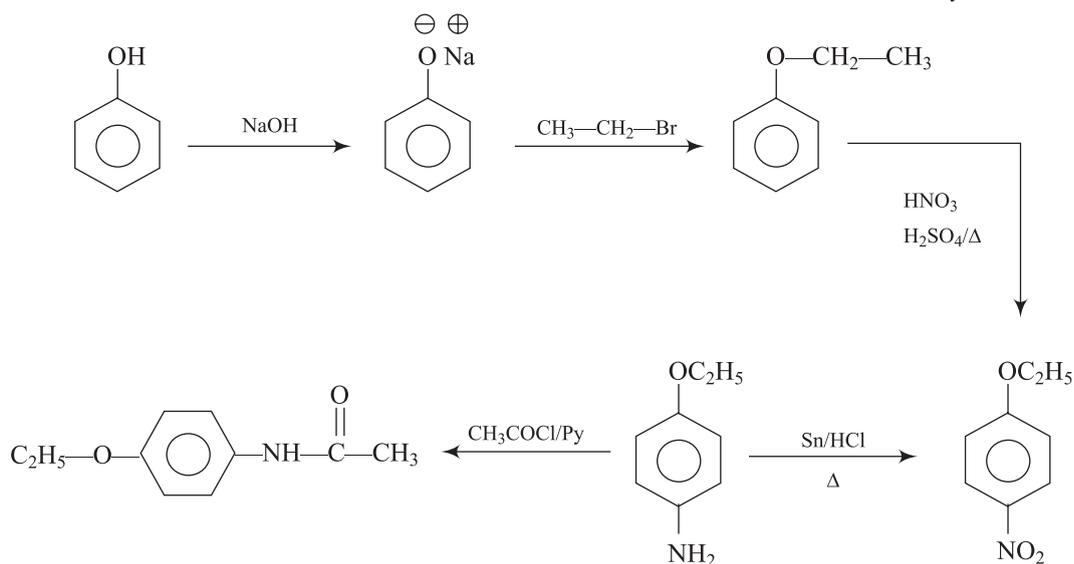
(d) By using carbylamine reaction, (I) will give positive test



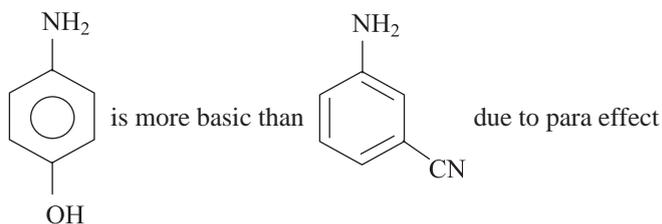
(e) By using nitrous acid followed by reaction with phenol (dye test), (II) will give yellow dye. (I) will evolve  $\text{N}_2$  gas.



22.



23. (a)



(b)  $\text{C}_6\text{H}_5\text{—NH—CH}_2\text{—CH}_3$  is more basic than  $\text{C}_6\text{H}_5\text{—NH—COCH}_3$  because  $\text{C}_2\text{H}_5$  is +I gp and  $\text{—COCH}_3$  is -I gp.

(c)  $\text{C}_6\text{H}_5\text{—CH}_2\text{—NH}_2$  is aliphatic primary amine whereas  $\text{C}_6\text{H}_5\text{—NH}_2$  is aromatic primary amine hence  $\text{C}_6\text{H}_5\text{—CH}_2\text{—NH}_2$  will be more basic than  $\text{C}_6\text{H}_5\text{—NH}_2$ .

(d) Cyclohexyl-NH<sub>2</sub> is aliphatic amine whereas  $\text{C}_6\text{H}_5\text{NH}_2$  is aromatic amine hence (I) will be more basic than (II).

(e) I is more basic than II, nitrogen is  $\text{sp}^3$  hybridised whereas in II, nitrogen atom is  $\text{sp}^2$  hybridised.

