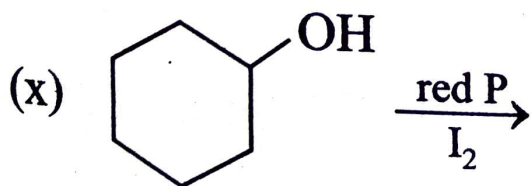
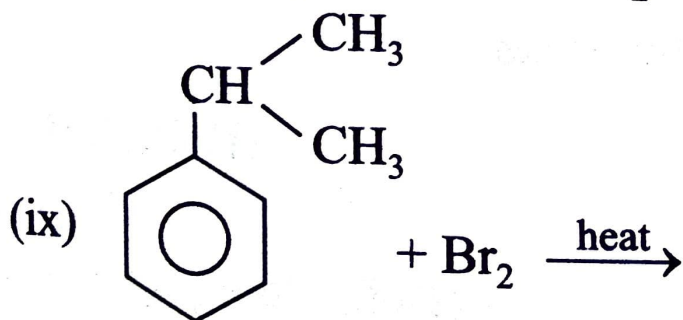
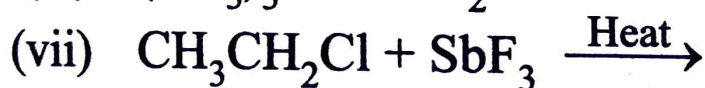
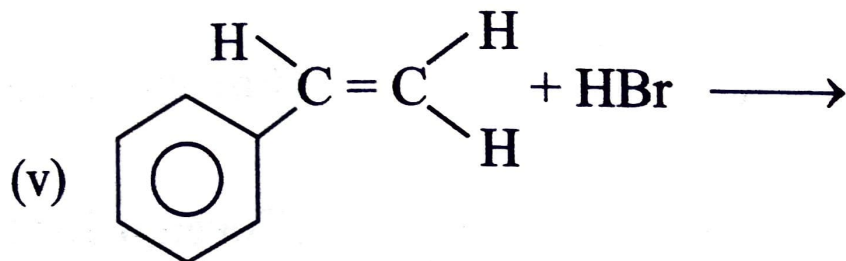
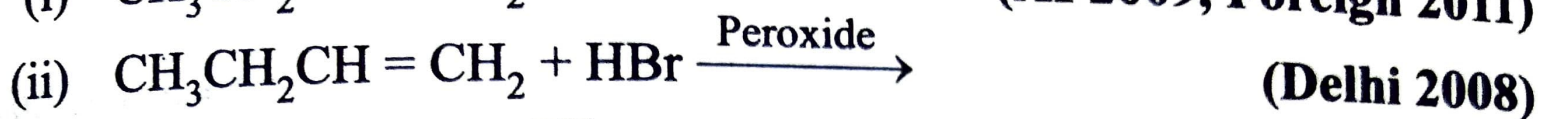
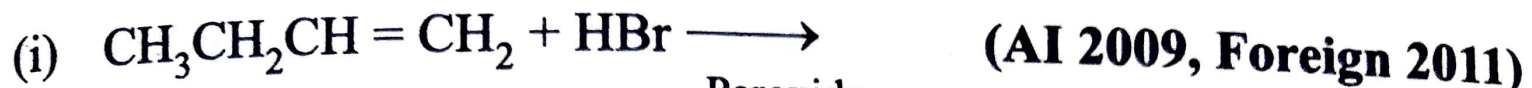
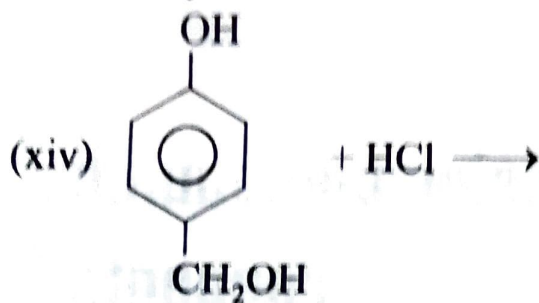
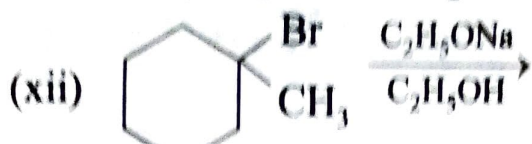
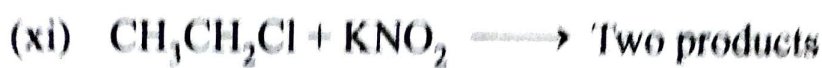


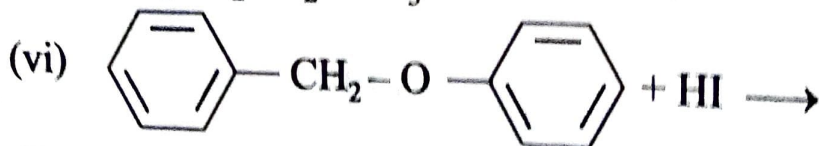
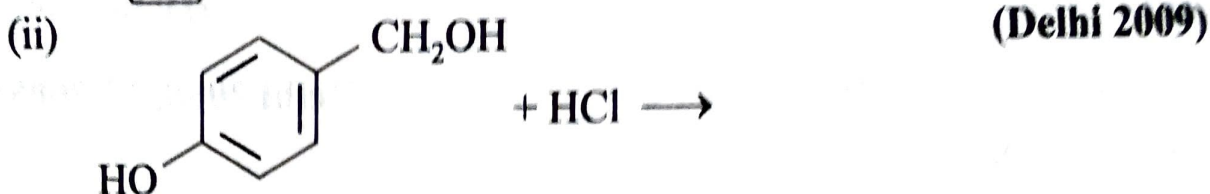
Q1. Complete the following :

(A) Hydrocarbons and halogen derivatives.

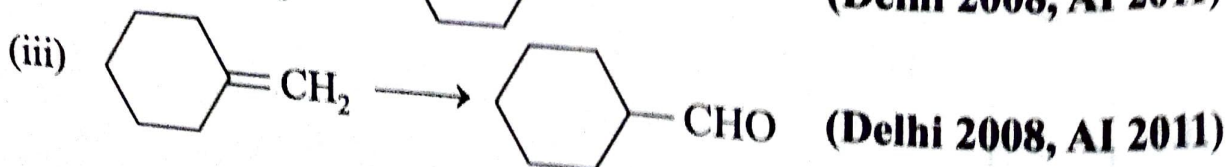


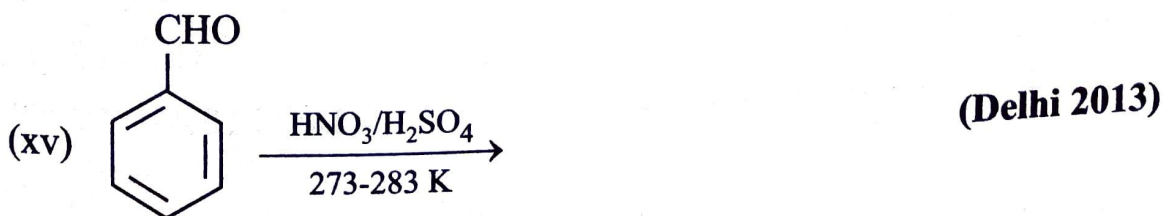
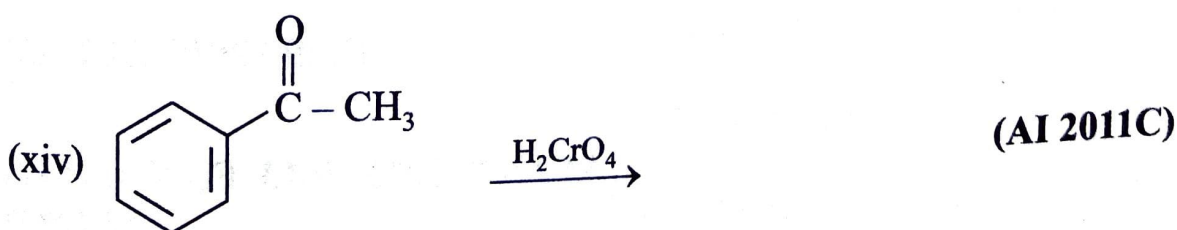
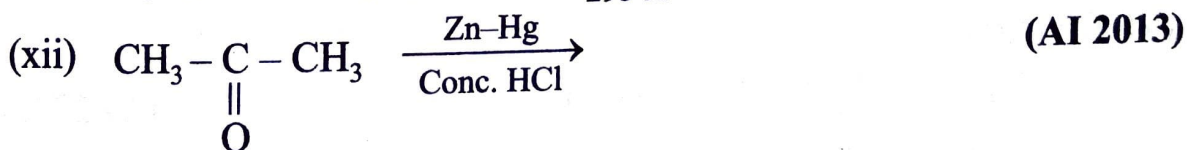
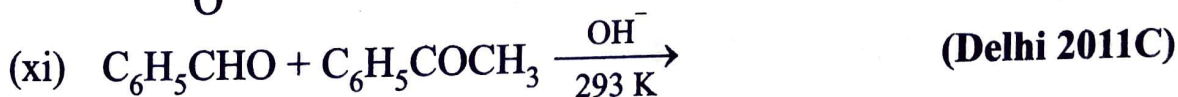
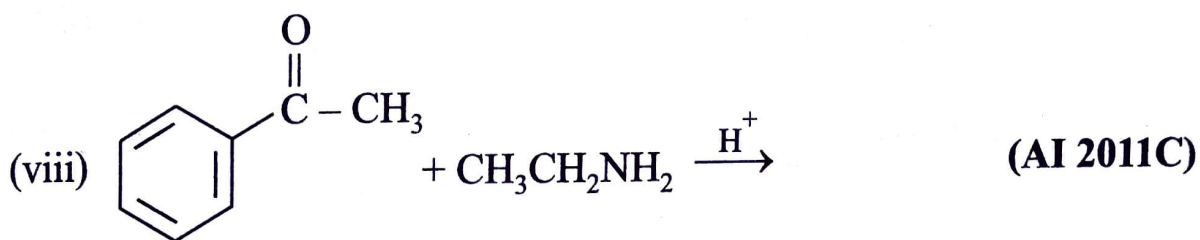
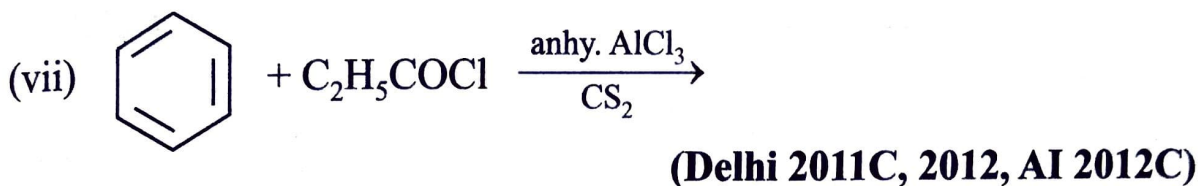
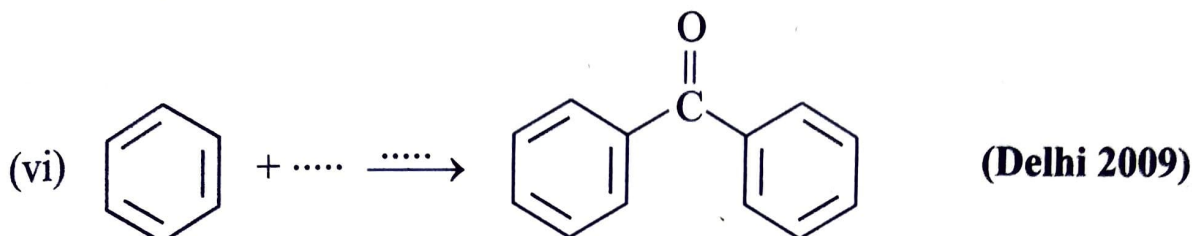
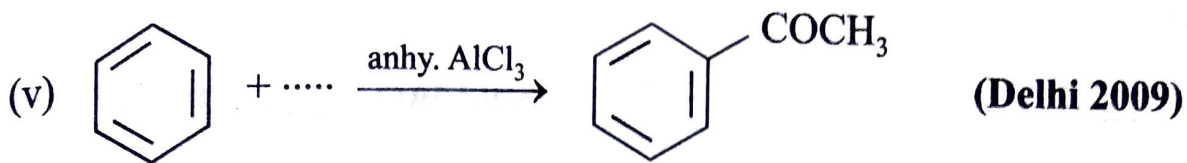


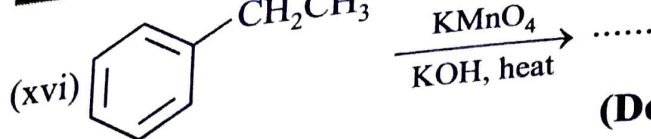
(B) Alcohols, phenols and ethers.



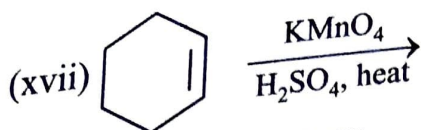
(C) Aldehydes, ketones and carboxylic acids.



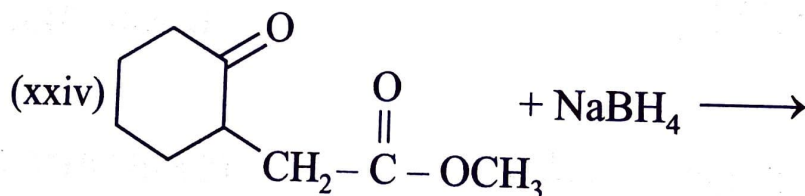
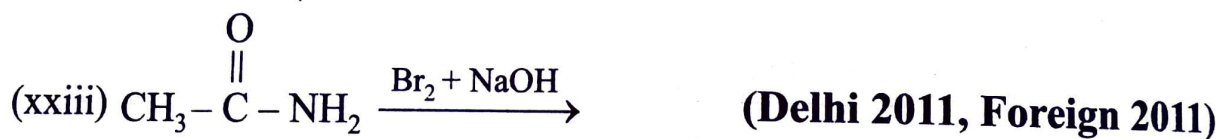
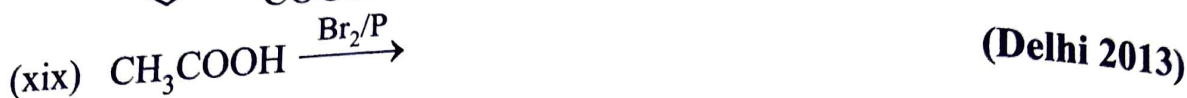
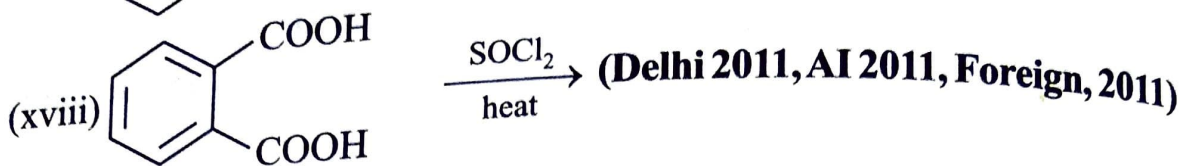




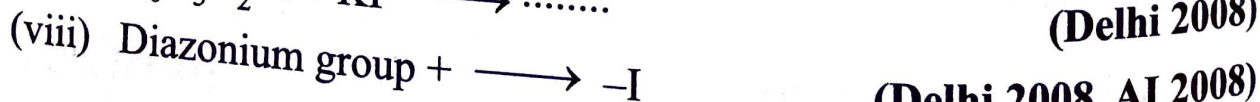
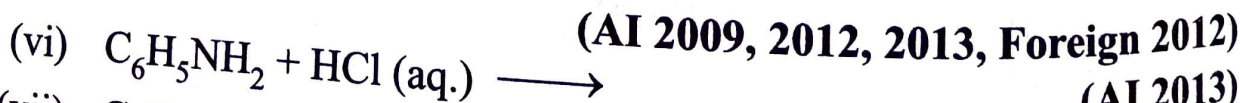
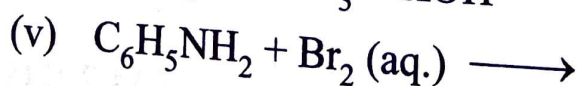
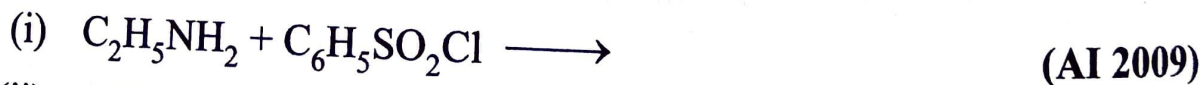
(Delhi 2008, 2011, Foreign 2011)



(AI 2011C)



(D) Amines.



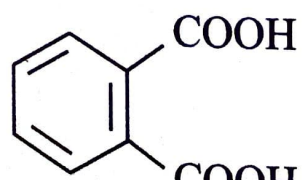
(Delhi 2008, AI 2008)

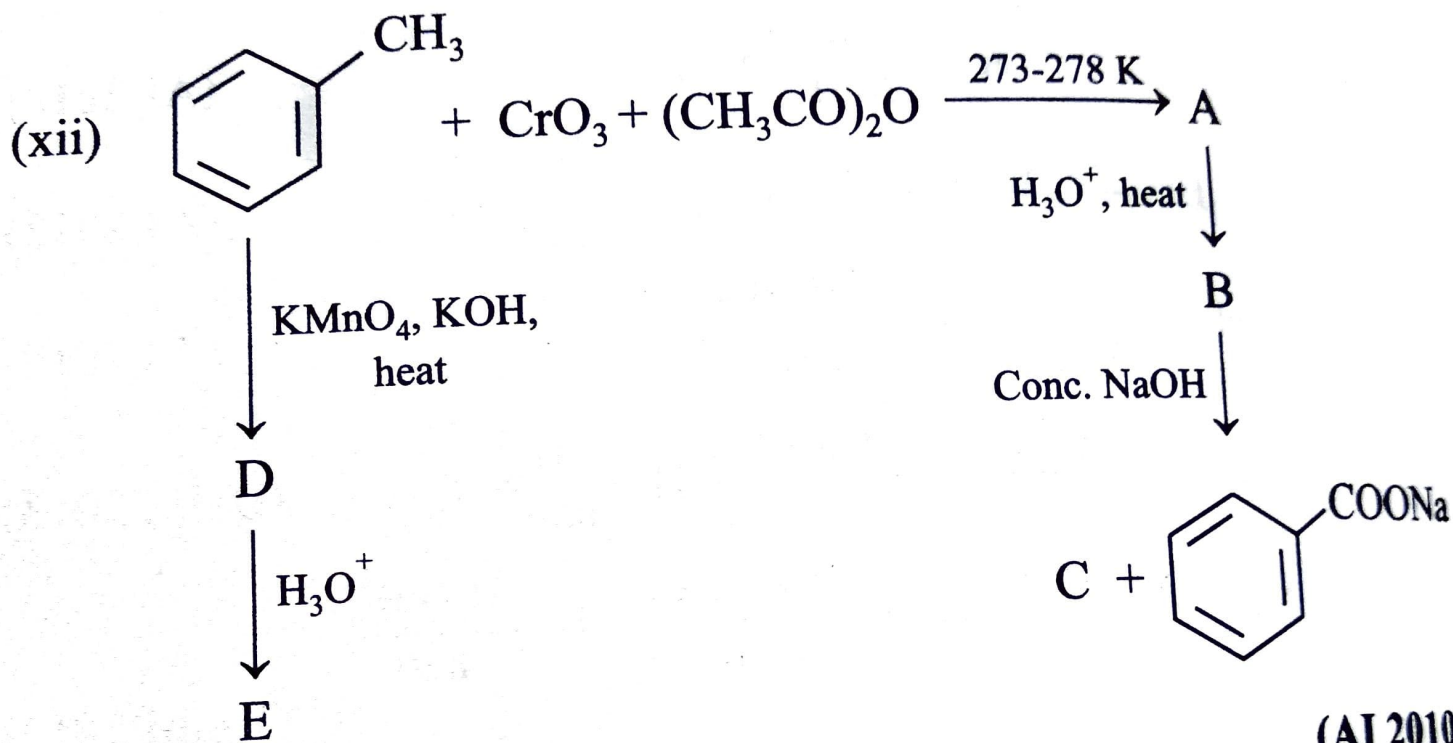
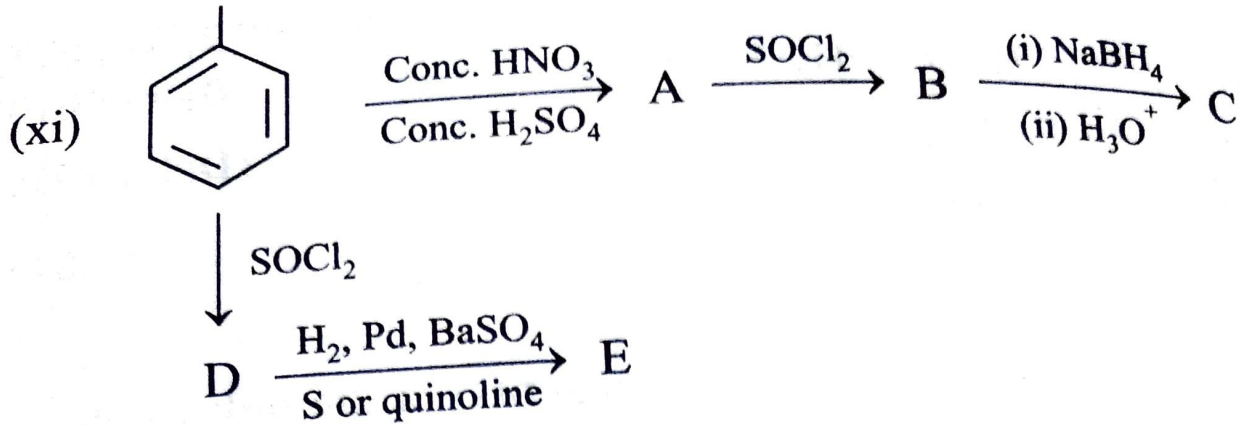
- (ix) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$ (AI 2009, 2012, Foreign 2012, AI 2013)
(Delhi 2010)
- (x) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$ (Delhi 2010)
- (xi) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$ (Delhi 2010)
- (xii) $C_6H_5N_2^+Cl^- \xrightarrow[\text{room temp.}]{H_2O}$ (AI 2013)

Q2. Identify the missing compounds (reagents) in the following:

- (i) $C_2H_5Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{\text{Reduction}} B$ (AI 2010)
- (ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^\circ C]{HNO_2} C$ (AI 2013)
- (iii) $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} A \xrightarrow[OH^-]{C_6H_5NH_2} B$ (AI 2010)
- (iv) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\text{heat}]{NH_3} C$ (Delhi 2013)
- (v) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273 K]{NaNO_2 + HCl} B \xrightarrow[\text{heat}]{H_2O/H^+} C$ (Delhi 2013)
- (vi) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow[\text{alc. KOH}]{CHCl_3} C$ (AI 2013)
- (vii) $CH_3CHO \xrightarrow[(ii) H_2O]{(i) C_2H_5MgCl} A \xrightarrow{\text{Conc. } H_2SO_4} B \xrightarrow[\text{peroxide}]{HBr} C$ (Delhi 2011C)
- (viii) $A \xrightarrow{[O]} B \xrightarrow{Ca(OH)_2} C \xrightarrow[(-CaCO_3)]{\text{Distill}} D \xrightarrow{LiAlH_4} E \xrightarrow{HBr}$

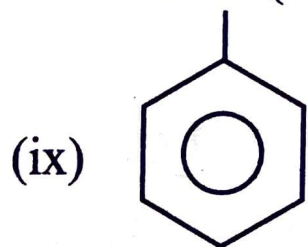
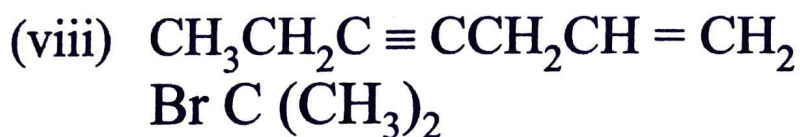
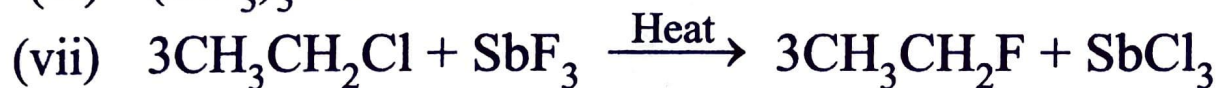
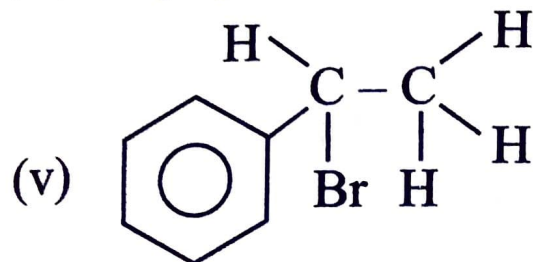
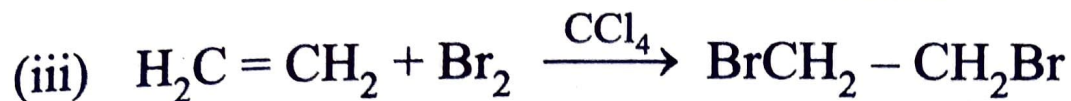
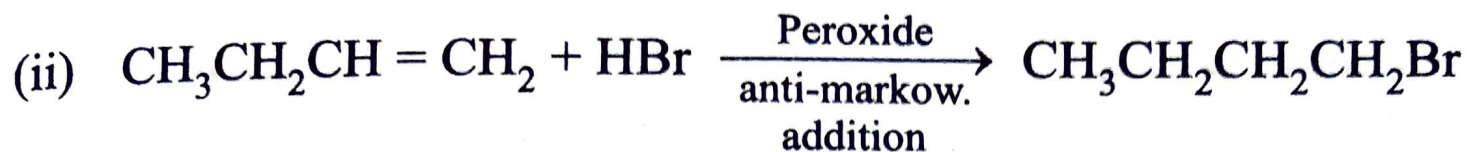
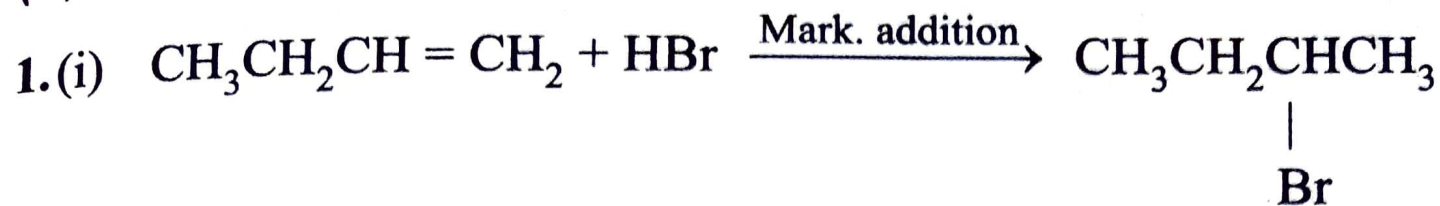
$$\begin{array}{c} CH_3 - CH - CH_3 \\ | \\ Br \end{array}$$
 (AI 2008C)
- (ix) $CH_3CH_2COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2/KOH} B \xrightarrow{HONO} C \xrightarrow{O}$

$$CH_3COOH \xrightarrow[(ii) \text{distill}]{(i) Ca(OH)_2} D \xrightarrow{LiAlH_4} E$$
 (AI 2009C)
- (x)  + $NH_3 \rightleftharpoons A \xrightarrow{\text{Heat}} B \xrightarrow[\text{strong heating}]{\text{strong heating}} C$ (AI 2011C)



(AI 2010C)

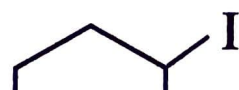
(A) Hydrocarbons and halogen derivatives.



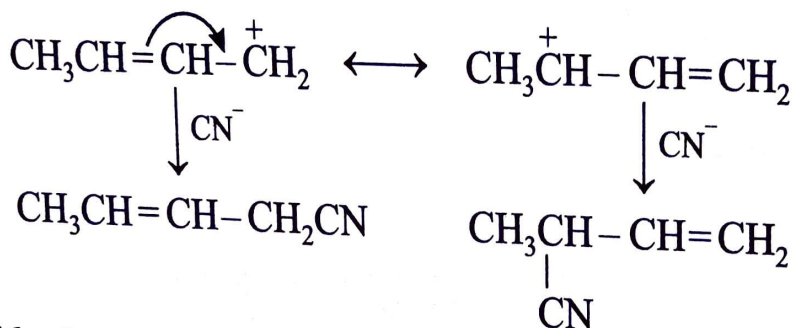
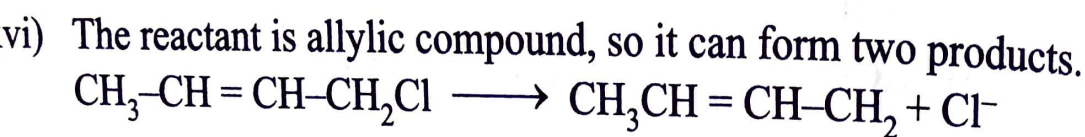
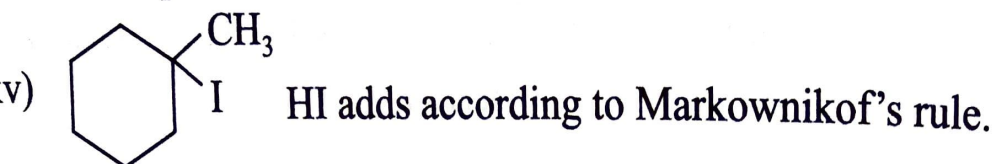
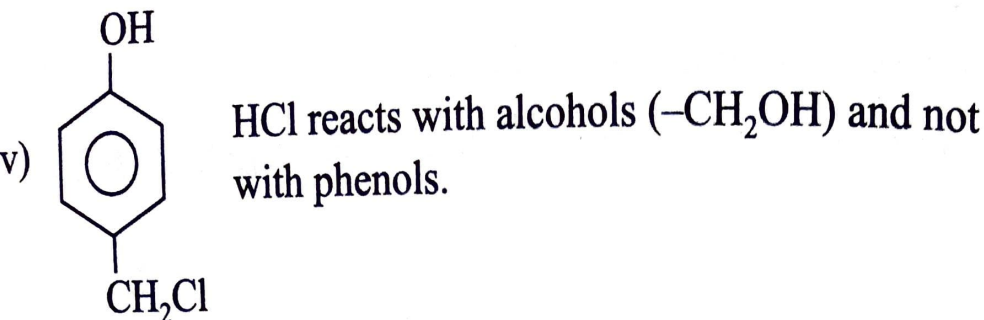
(Bromination takes place at α -position.)



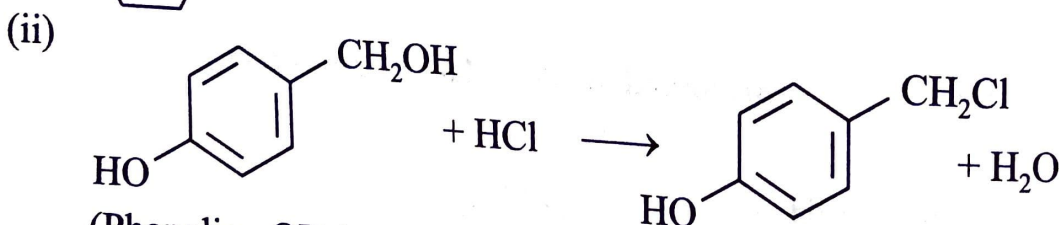
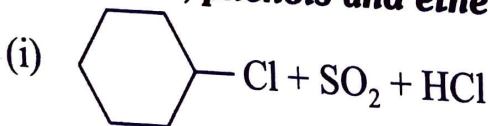
red P



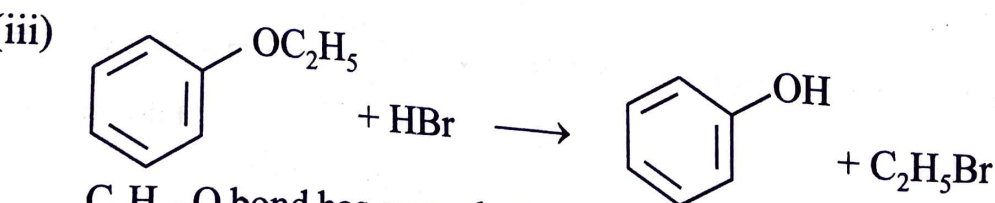
In presence of heat and light, allylic bromination takes place, while in dark bromine adds on double bond to form dibromoderivative.



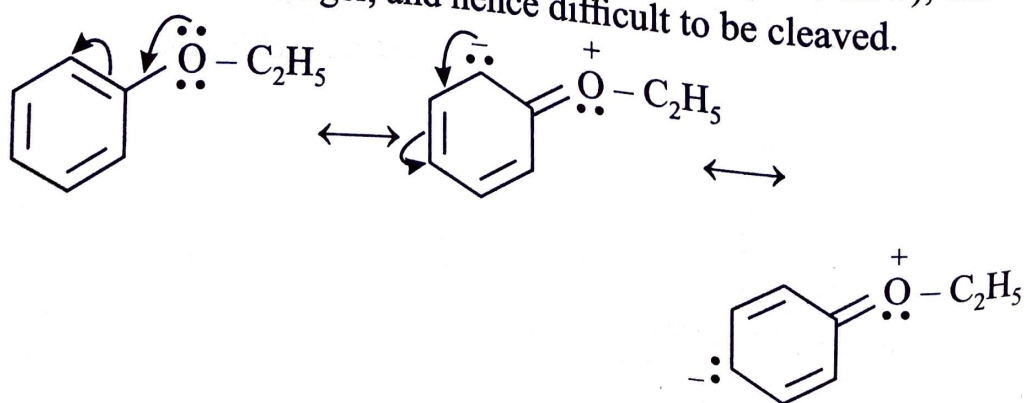
B) Alcohols, phenols and ethers.



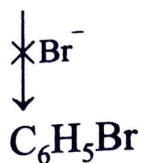
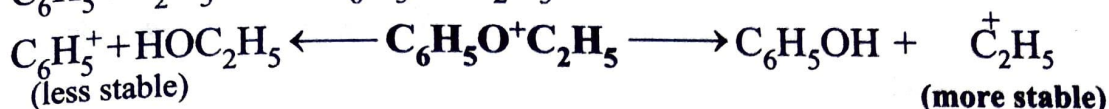
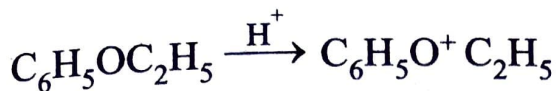
(Phenolic $-\text{OH}$ is not easily replaced, hence does not react with HCl)



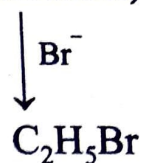
$\text{C}_6\text{H}_5-\text{O}$ bond has some double bond character (see below), thus it is shorter and stronger, and hence difficult to be cleaved.



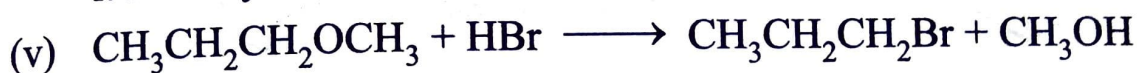
Moreover, $C_2H_5^+$ is more stable than $C_6H_5^+$.



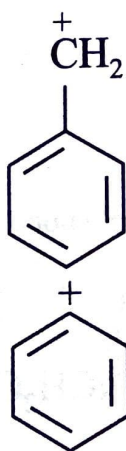
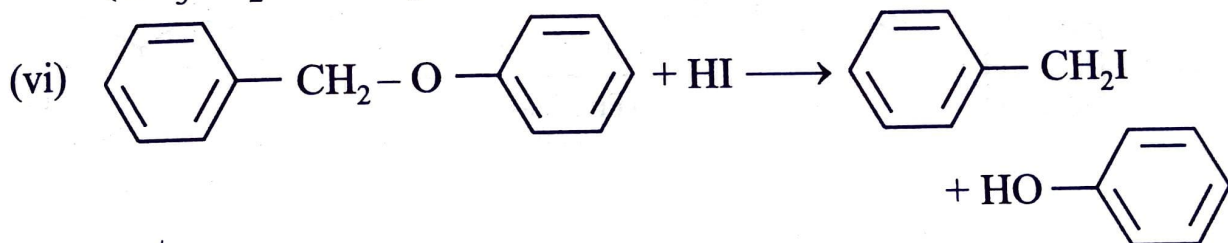
(not formed)



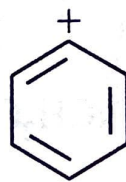
$(CH_3)_3C^+$ (a 3° carbocation) is more stable than the $C_2H_5^+$, hence it is easily formed.



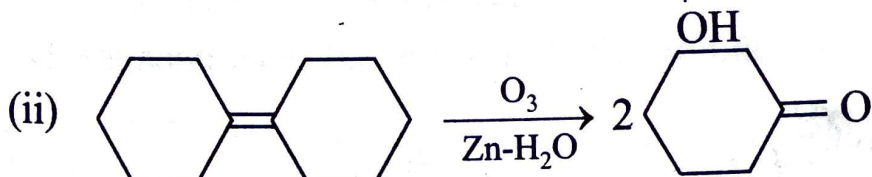
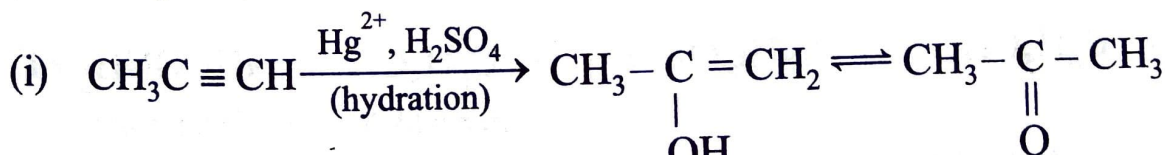
$CH_3CH_2\overset{+}{C}H_2$ is more stable than CH_3^+ due to inductive effect ($CH_3CH_2 \rightarrow CH_2^+$) as well as hyperconjugation.



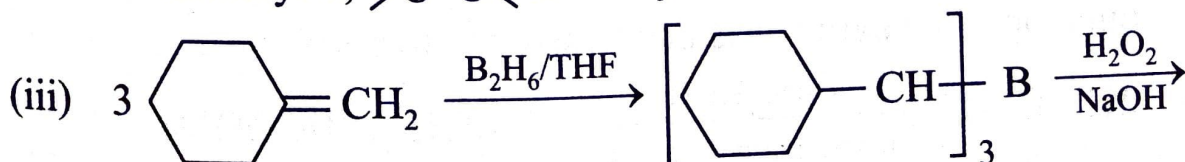
(benzyl carbocation) is more stable due to resonance than

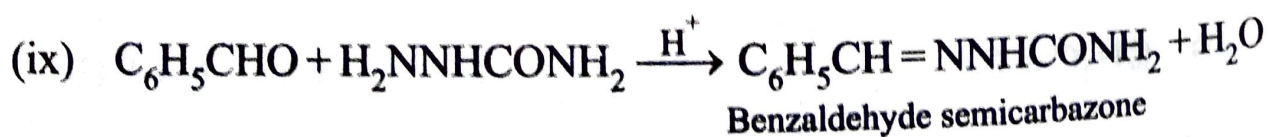
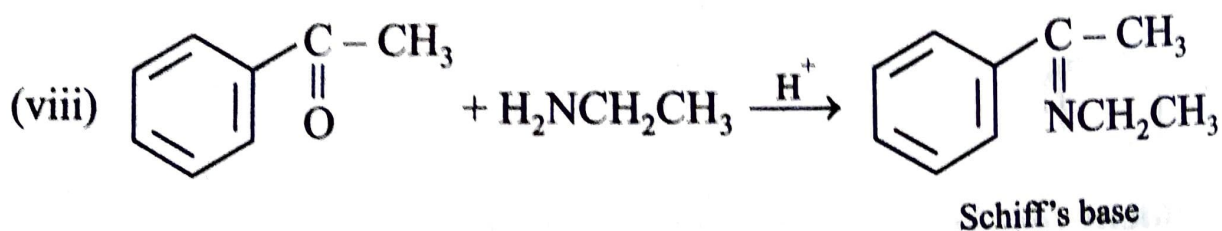
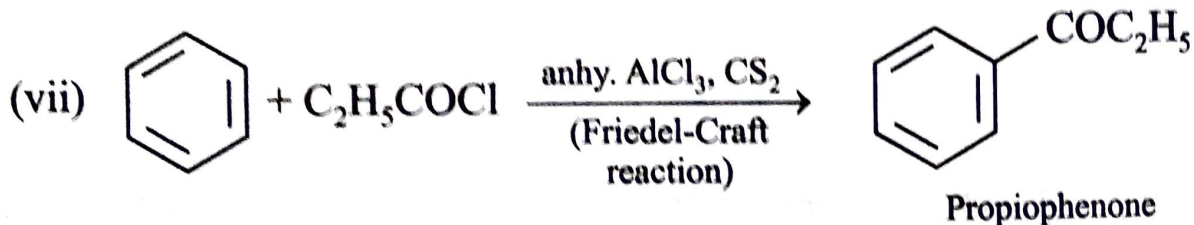
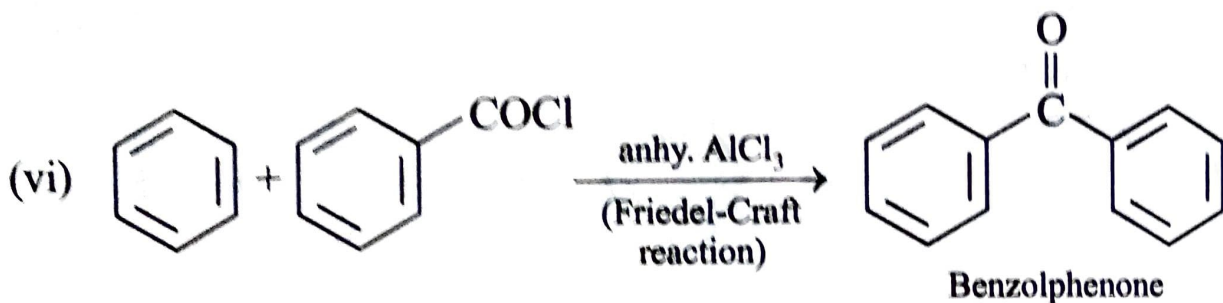
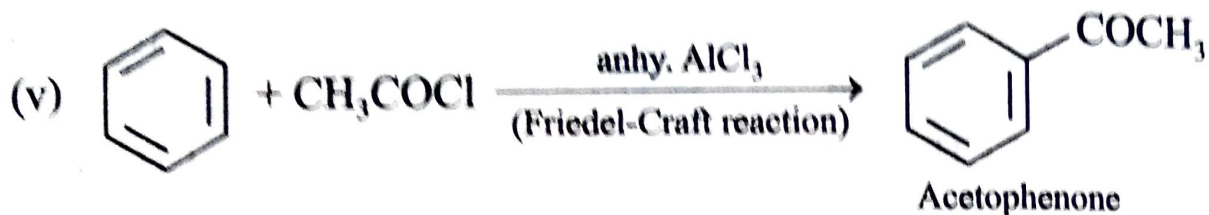
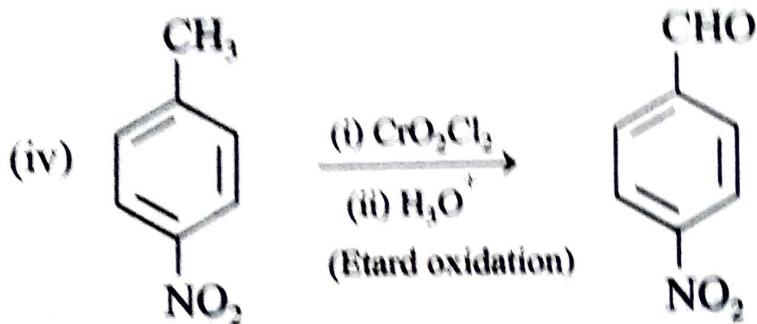


(C) Aldehydes, ketones and carboxylic acids.

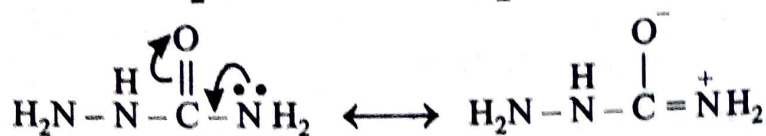


In ozonolysis, $>C=C<$ is always cleaved to $>C=O + O=C<$.

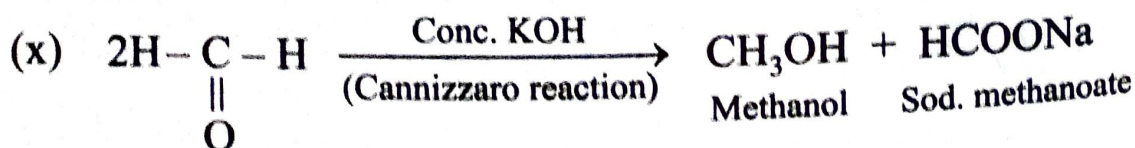


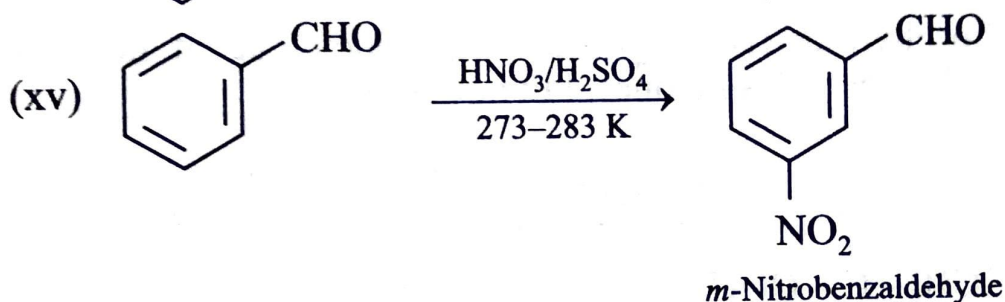
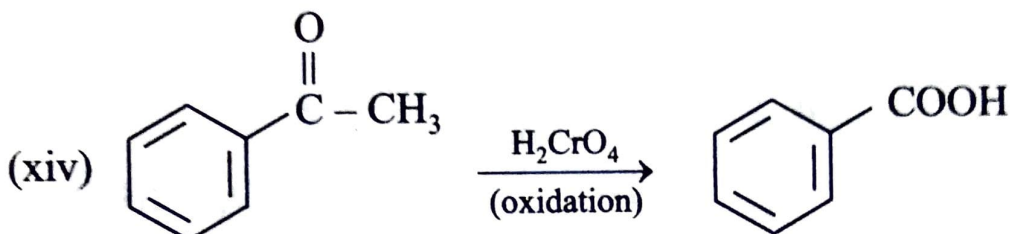
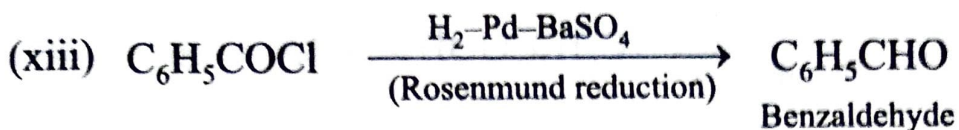
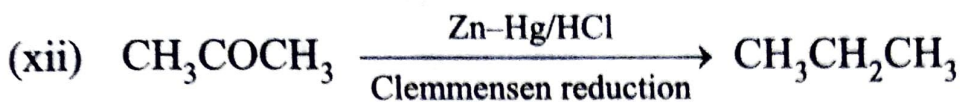
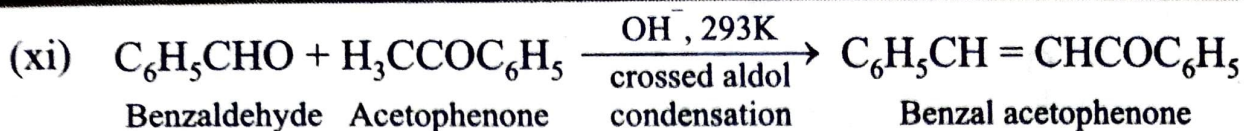


Note that the $-\text{NH}_2$ end of $-\text{CONH}_2$ does not react because its

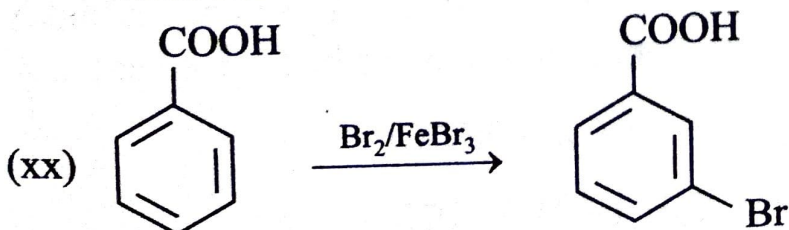
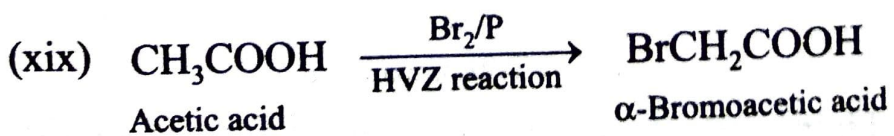
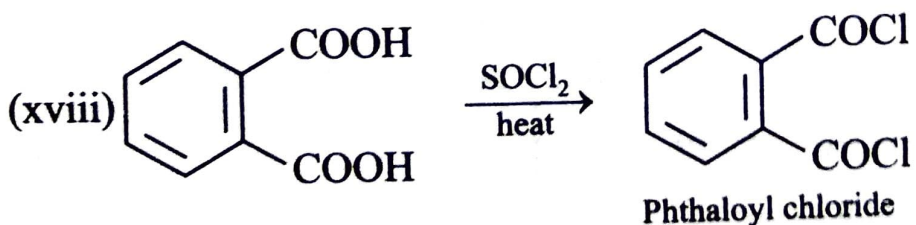
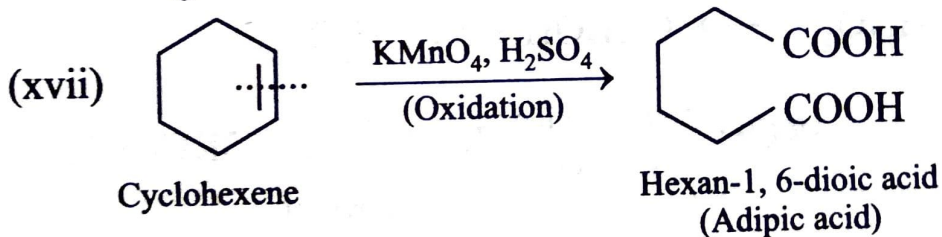
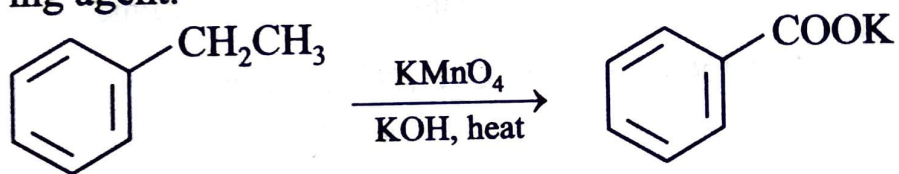


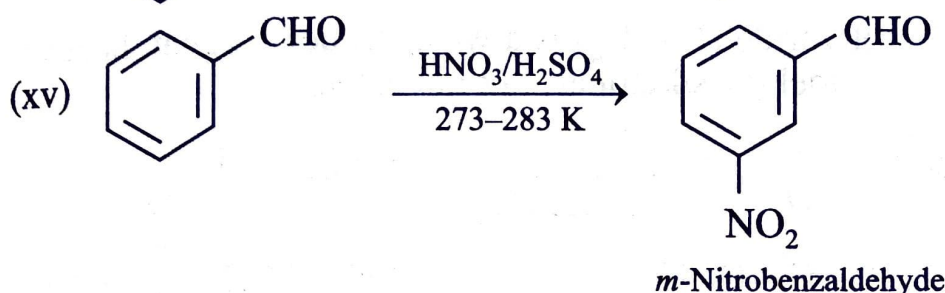
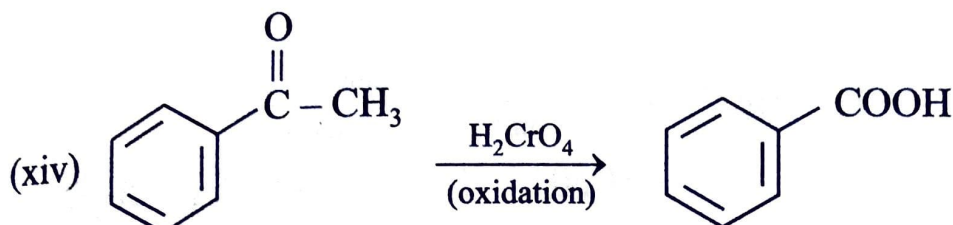
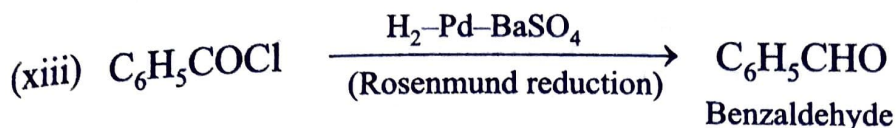
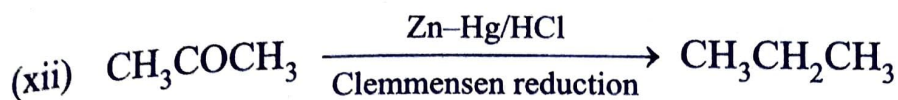
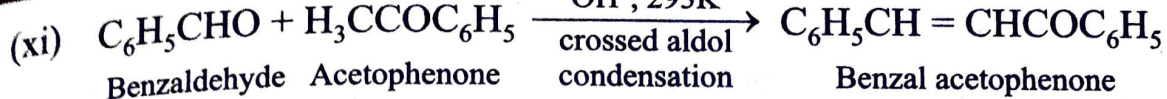
nucleophilic character is decreased due to resonance.



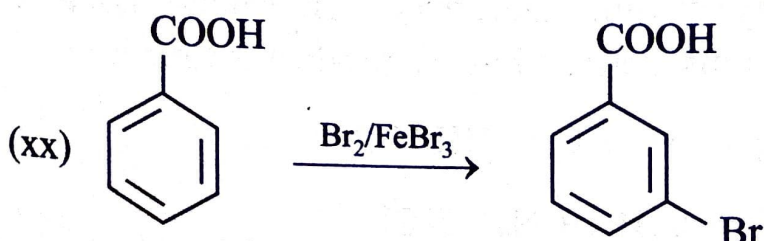
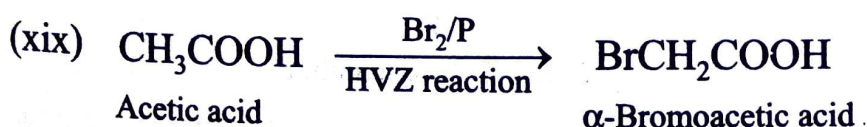
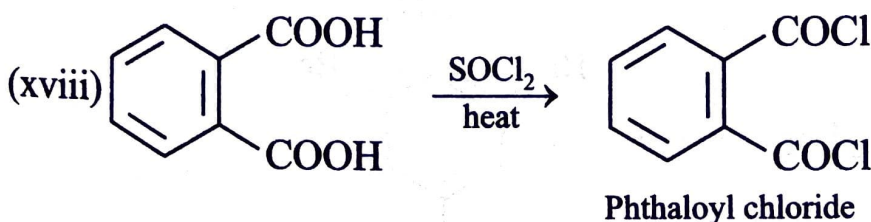
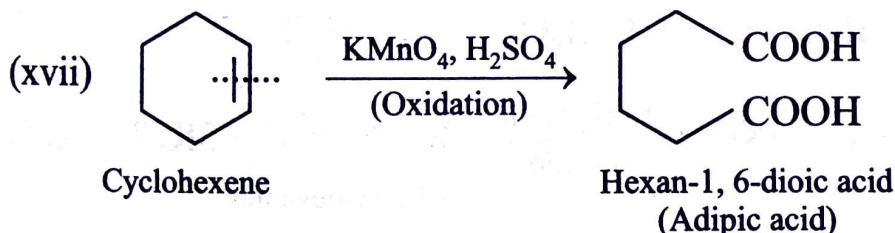
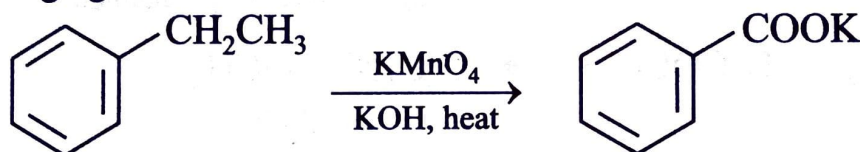


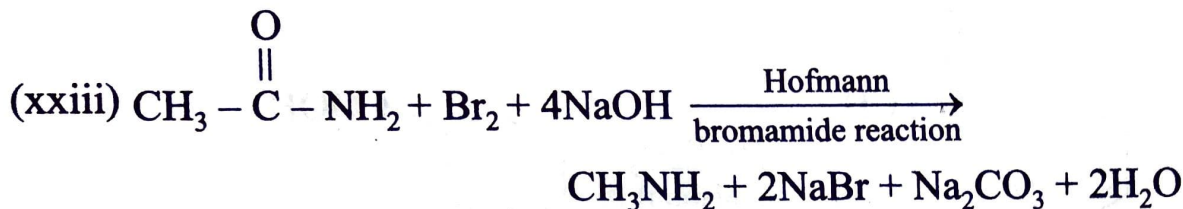
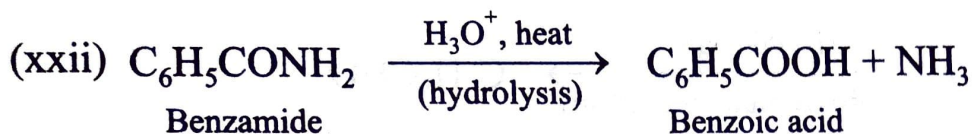
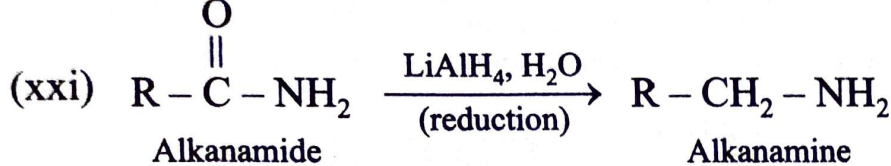
(xvi) Alkyl group present on benzene ring is always oxidised to $-\text{COOH}$ group, irrespective to its length, when oxidised by a strong oxidising agent.



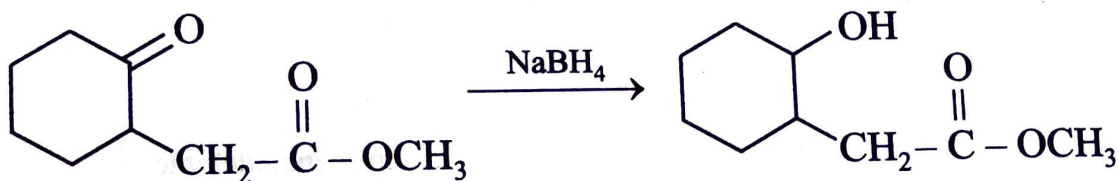


(xvi) Alkyl group present on benzene ring is always oxidised to $-COOH$ group, irrespective of its length, when oxidised by a strong oxidising agent.

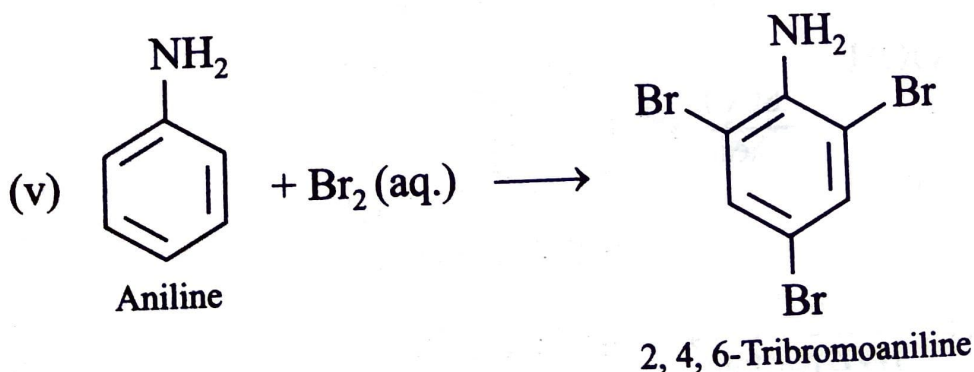
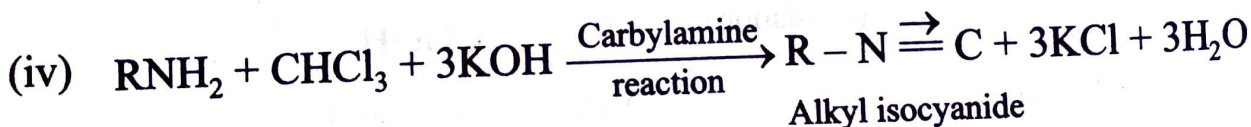
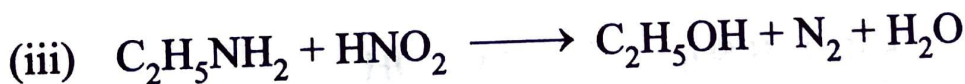
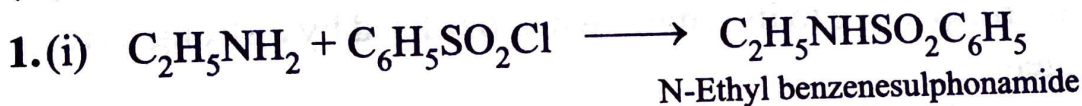




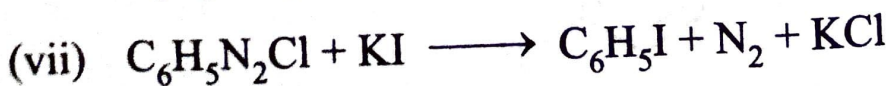
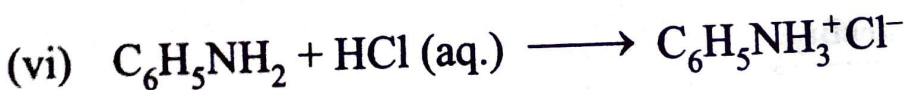
(xxiv) Sodium borohydride (NaBH_4) is a weak reducing agent, hence it reduces only aldehydes/ketones, but not esters.

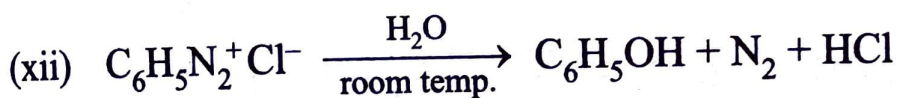
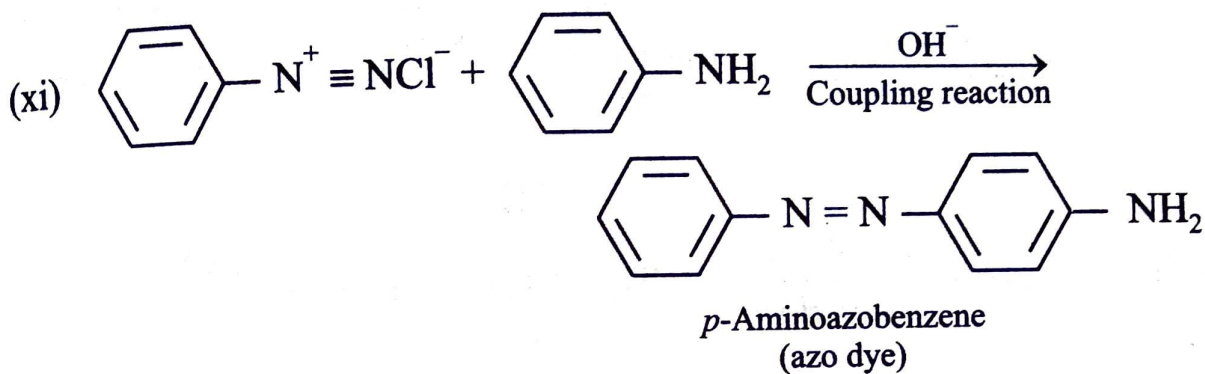
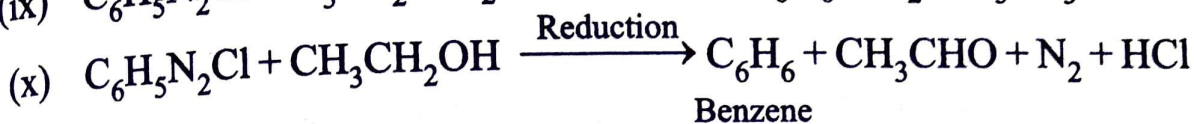
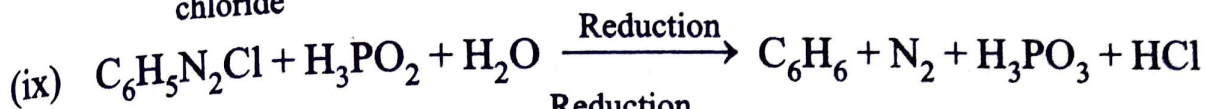
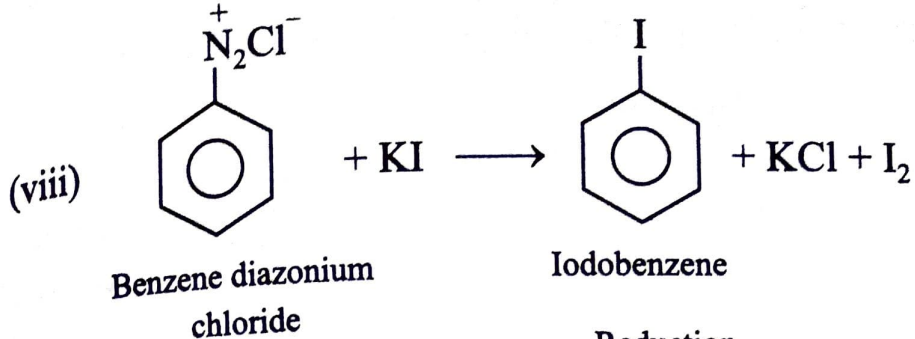


(D) Amines.

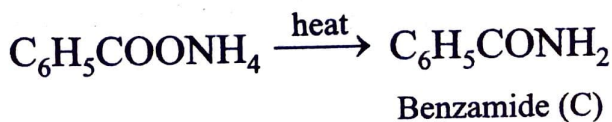
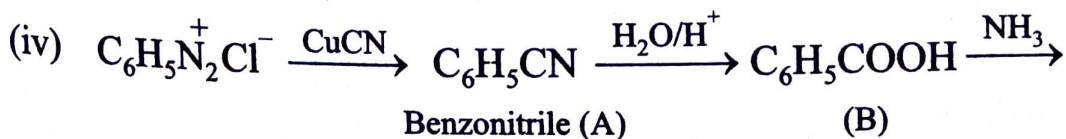
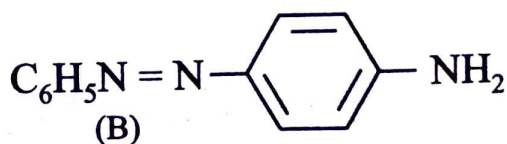
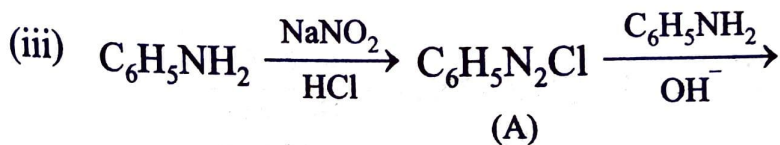
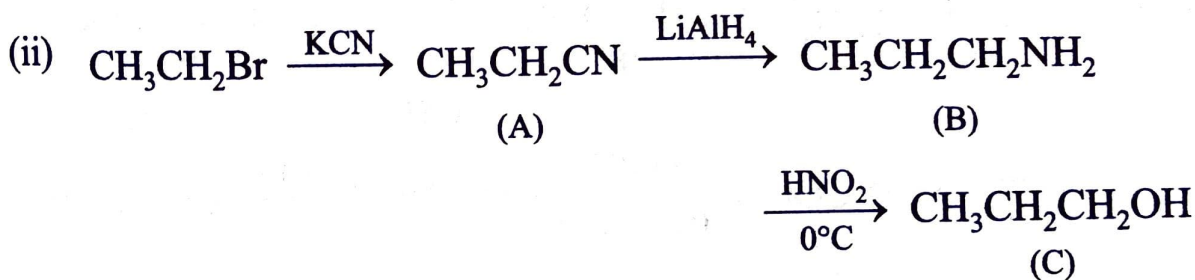
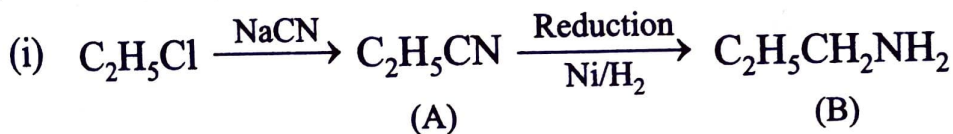


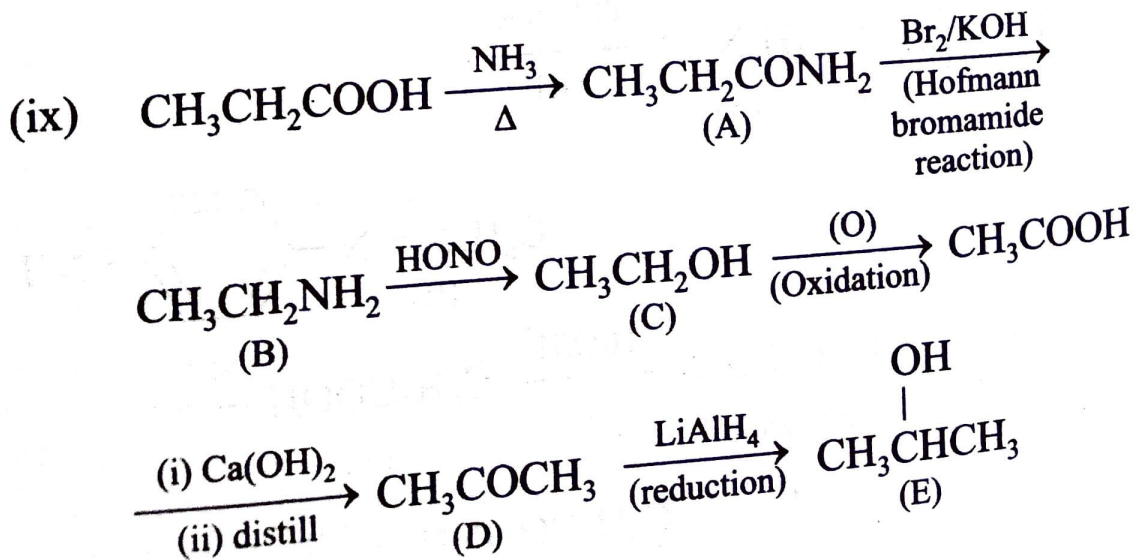
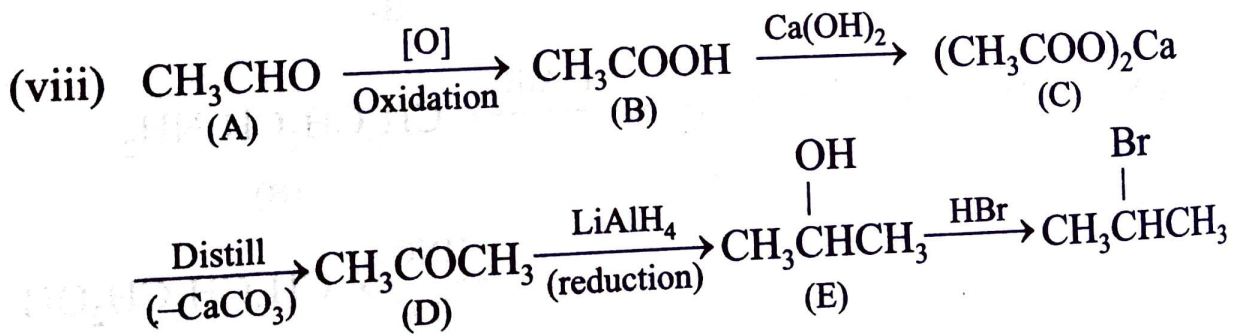
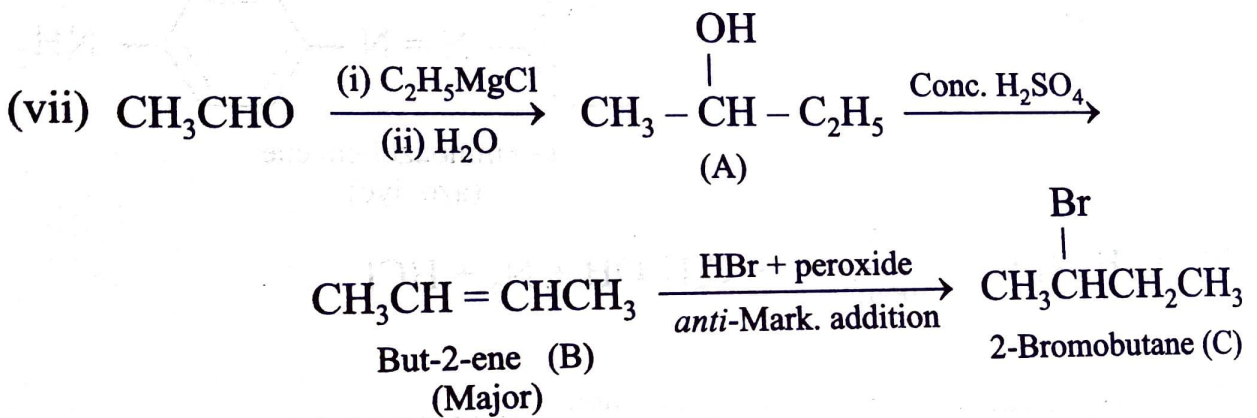
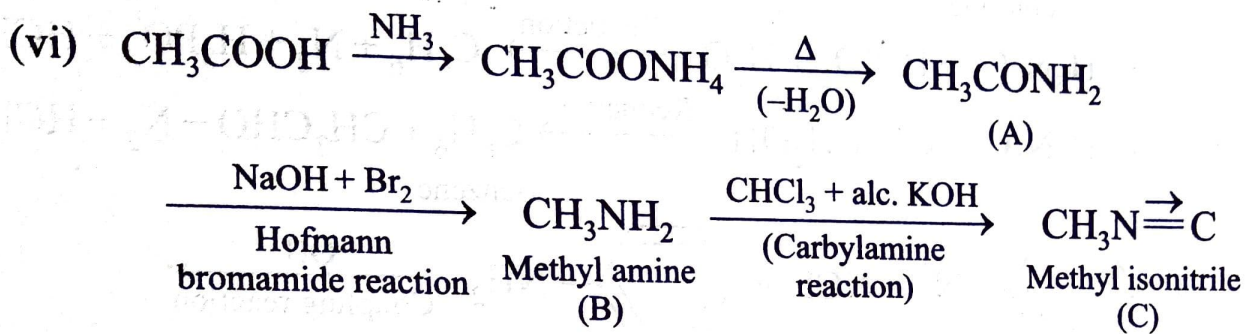
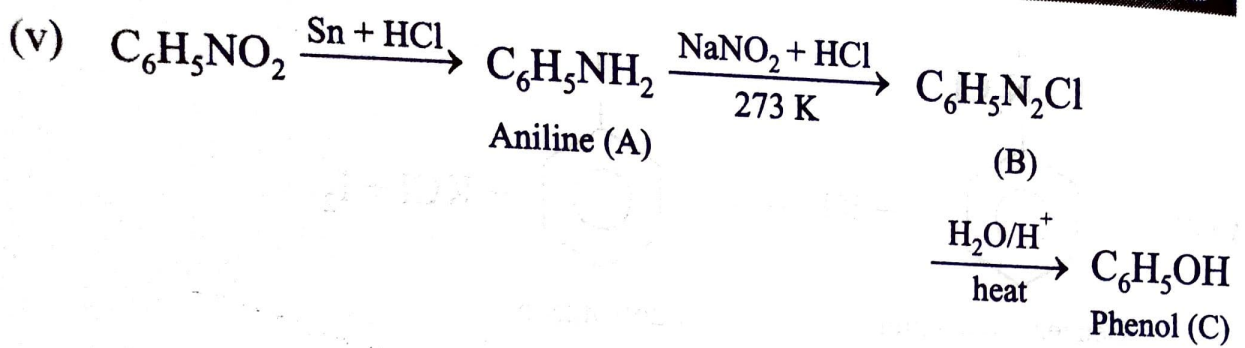
($-\text{NH}_2$ group is highly activating and aqueous Br_2 solution is highly ionising to give Br^+ ions, hence tribromo product is formed)

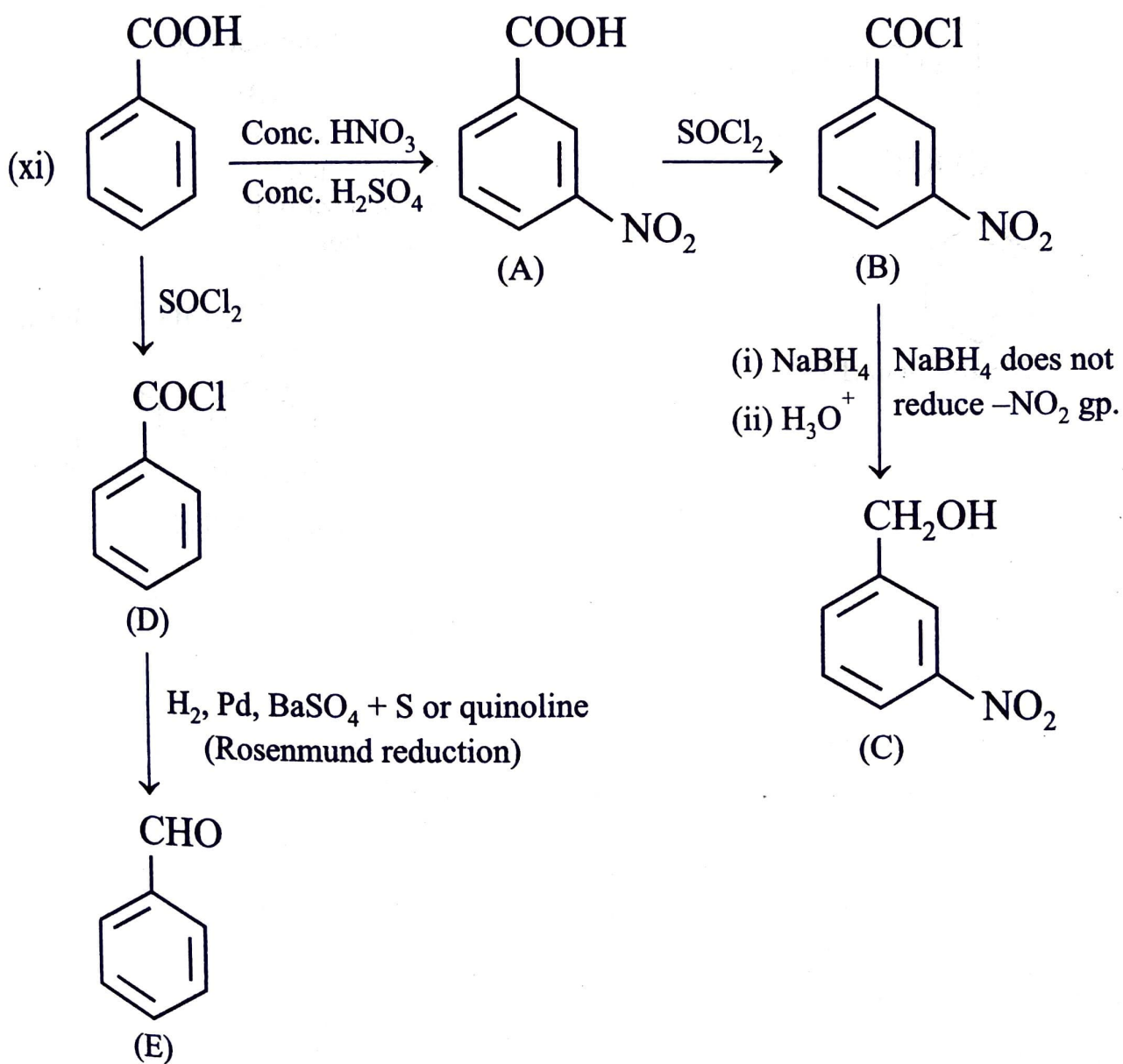
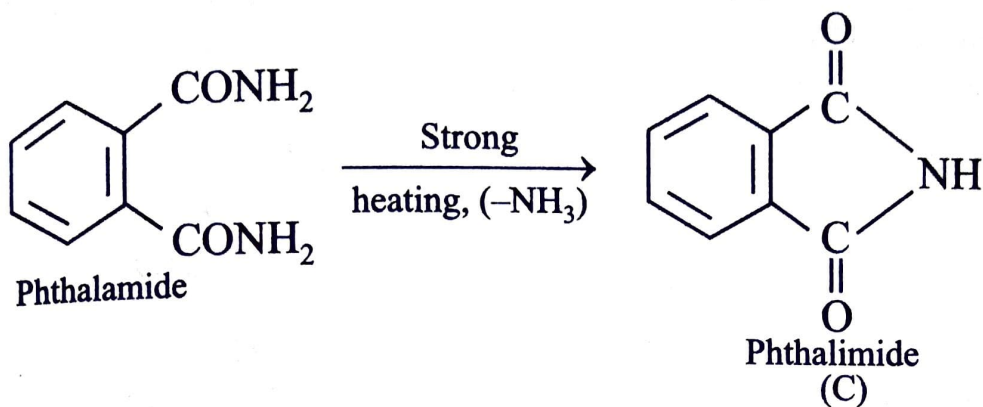
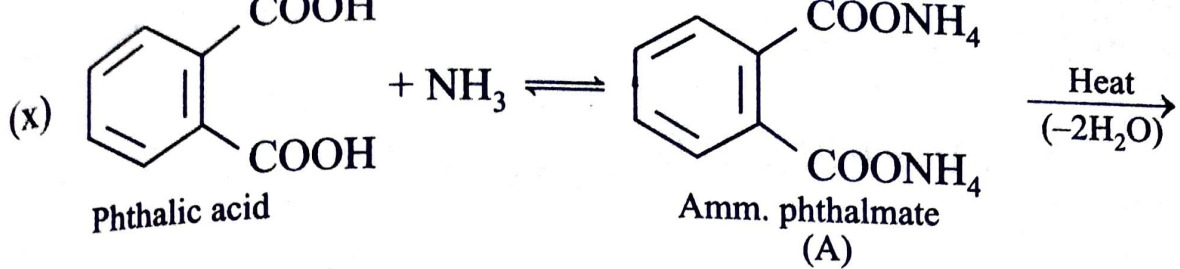


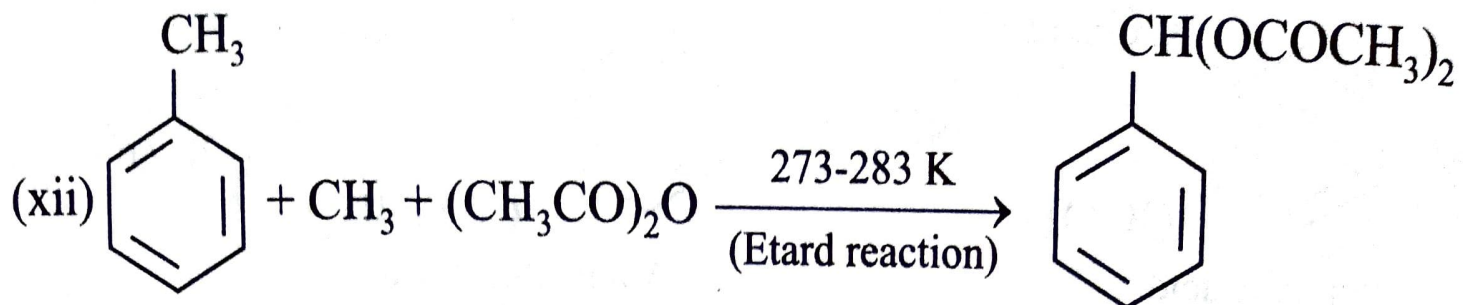


2.



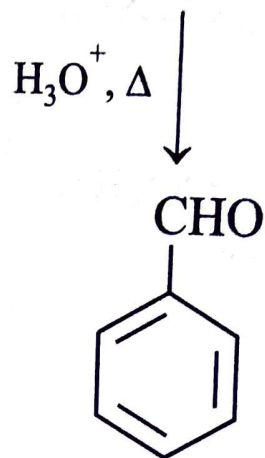






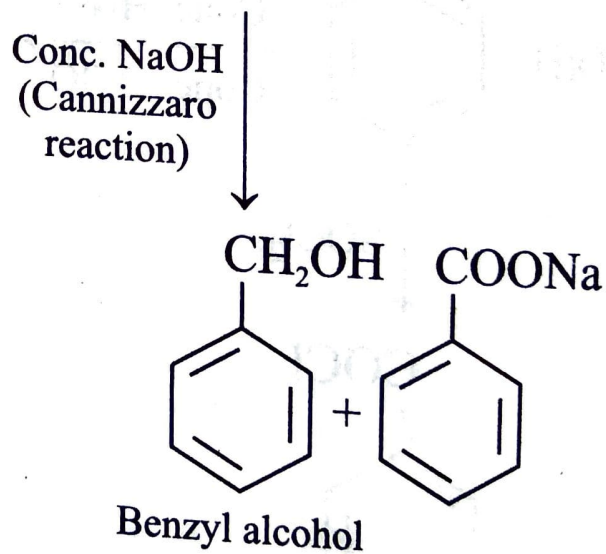
Benzylidene diacetate

(A)

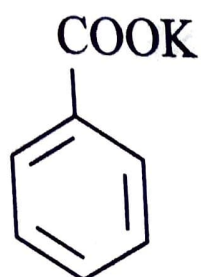
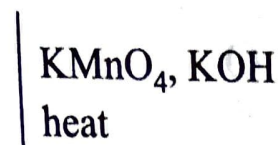


Benzaldehyde

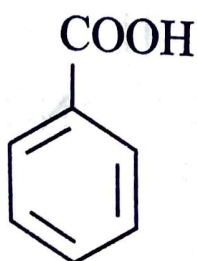
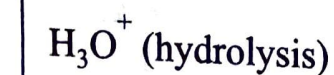
(B)



Benzyl alcohol



Pot benzoate (D)



Benzoic acid (E)

