HINTS & SOLUTIONS

Oxygen Containing Organic Compounds-I

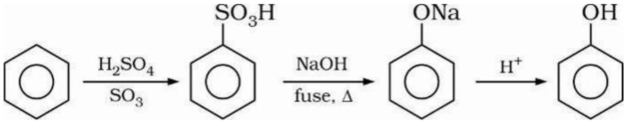
Daily Tutorial Sheet	**Level-0**

VERY SHORT ANSWER TYPE (1 MARK)

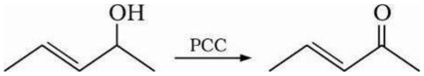
1. $C_6H_5-O-CH_2-CH_2-CH(CH_3)_2$

2. Phenol and Benzyl iodide.

3.



4.



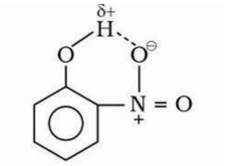
PCC : Pyridinium chlorochromate $(CrO_3/py/HCl)$ does not oxidise $>C=C<$ but oxidises 1° and 2° alcoholic group to aldehydes and ketones respectively.

5. Diethyl ether does not react with sodium because diethyl ether does not contain an active H-attached to oxygen like alcohols and phenols.

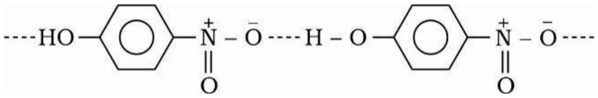
SHORT ANSWER TYPE-I (2 MARKS)

6. Hydrocarbon part is usually hydrophobic and does not allow H-bonding formation. So higher alcohols are not able to form effective H-bond in water as compared to lower ones, hence they are less soluble.

7. In o-nitrophenol, there exists 'intramolecular Hydrogen bonding' (chelation), which results in weak intermolecular forces. As a result, it is steam volatile.


intramolecular H-bonding

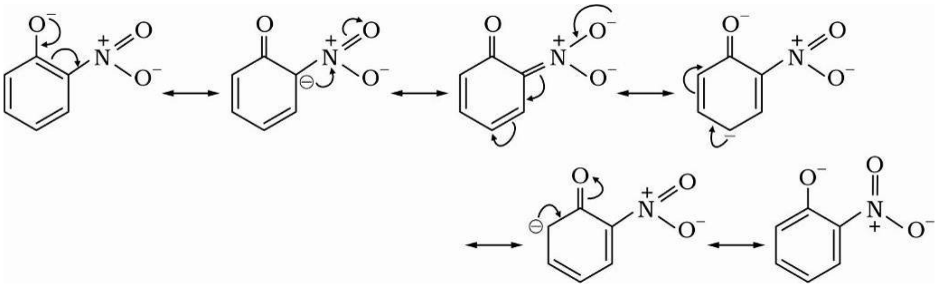
In p-nitrophenol, there exists intermolecular H-bonding with neighbouring molecules resulting in strong intermolecular forces. Hence it is not steam volatile.



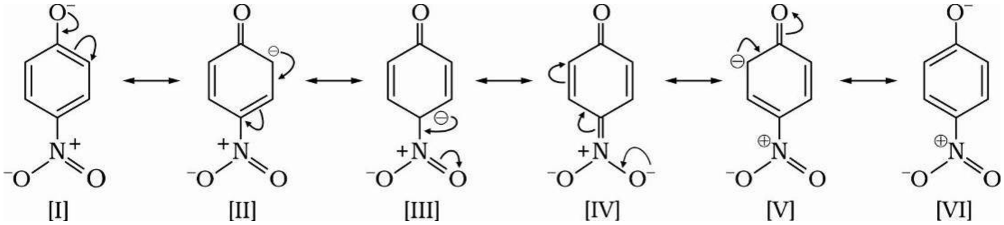
8. Phenol is acidic but weaker acid than H_2CO_3 (carbonic acid). Hence it cannot liberate CO_2 from $NaHCO_3$ solution.

SHORT ANSWER TYPE-II (3 MARKS)

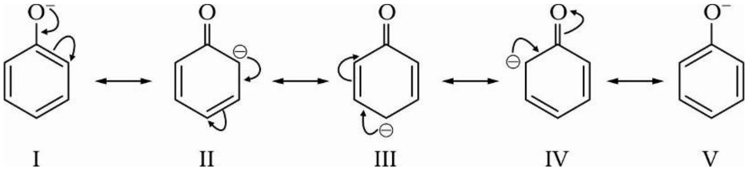
9. Resonating structures of o-nitrophenoxide ion



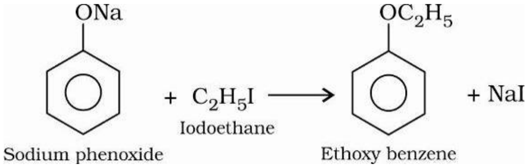
Resonating structures of p-nitrophenoxide ion



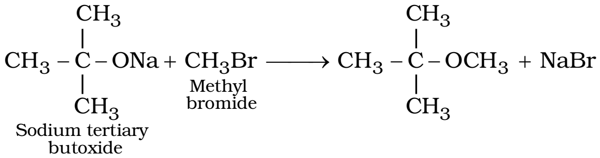
Resonating structure of phenoxide ion



10. **(a)** **(i)**



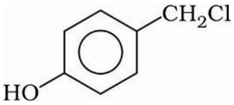
(ii)



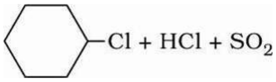
$$CH_3-\underset{\underset{\text{Sodium tertiary butoxide}}{CH_3}}{\overset{CH_3}{C}}-ONa + \underset{\text{Methyl bromide}}{CH_3Br} \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3 + NaBr$$

(b) In phenols, there is +ve charge on oxygen in three out of five resonating structures, therefore, it does not protonate easily. So lone pair is involved in resonance, and is not available for protonation.

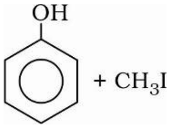
11. **(a)**



(b)



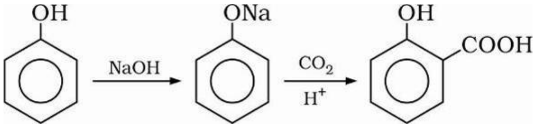
(c)



12. **(i)** $C_2H_5ONa + CH_3I \longrightarrow C_2H_5OCH_3 + NaI$

(ii) $CH_3COOH + CH_3CH_2OH \overset{H^+}{\rightleftharpoons} CH_3COOCH_2CH_3 + H_2O$

(iii)



13. **(i)** PCC **(ii)** $LiAlH_4$ **(iii)** Br_2/H_2O

14. **(i)** Because stability of carbocation is : 3° > 2° > 1°.

(ii) Grignard reagent reacts with water to form alkane $RMgX + HOH \longrightarrow RH + Mg(OH)X$

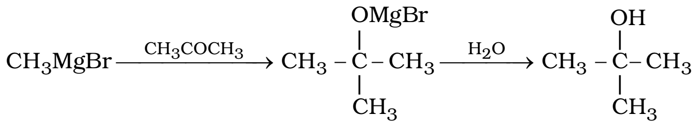
(iii) Phenoxide ion is less stable than acetate ion, as in acetate ion, −ve charge is delocalised over two oxygen atoms and gives equivalent resonating structures which contribute to greater stability.

(iv) It is due to positive charge on oxygen in three out of five resonating structure of phenol, alcohols are more Bronsted basic.

(v) It is because 1° alcohols are more acidic due to stability of RO^- whereas 3° alcohols are least acidic due to least stability of R_3CO^-.

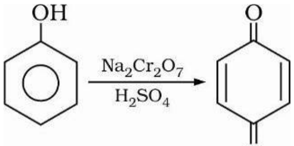
(vi) o-nitrophenol possess intramolecular H-bonding while p-nitrophenol possess intermolecular H-bonding.

15. **(a)**



$$CH_3MgBr \xrightarrow{CH_3COCH_3} CH_3-\overset{OMgBr}{\underset{CH_3}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3$$

(b)



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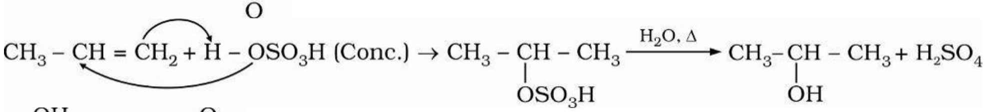
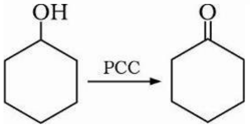
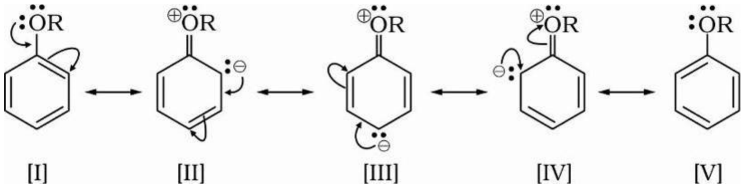


$$CH_3-CH=CH_2+H-OSO_3H\ (Conc.) \rightarrow CH_3-\underset{OSO_3H}{CH}-CH_3 \xrightarrow{H_2O,\ \Delta} CH_3-\underset{OH}{CH}-CH_3+H_2SO_4$$

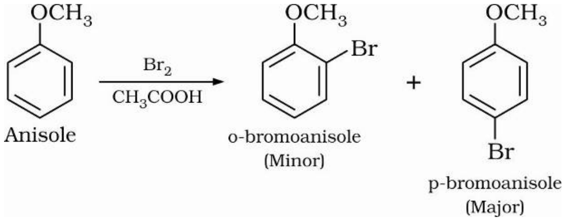
(d)



16. In aryl ether, $+R$ effect of the alkoxy group $(-OR)$ increases the electron density in the benzene ring thereby activating the benzene ring towards electrophilic substitution reactions.

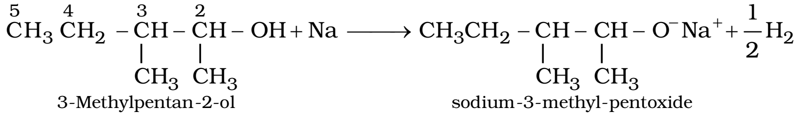


Electron density is more at o-and p-positions so o-and p-products are mainly formed during electrophilic substitution reactions.



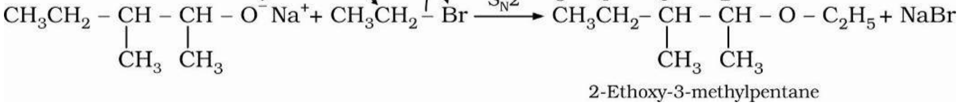
17. Alkyl halide should be primary for Williamson's synthesis. Hence, alkyl halide is derived from ethanol and the alkoxide ion form 3-Methylpentan-2-ol.

$$\underset{\text{Ethanol}}{CH_3CH_2OH}+HBr \xrightarrow{\Delta} \underset{\text{Ethyl bromide}}{CH_3CH_2Br}+H_2O$$



$$\overset{5}{CH_3}\,\overset{4}{CH_2}-\underset{CH_3}{\overset{3}{CH}}-\underset{CH_3}{\overset{2}{CH}}-OH+Na \longrightarrow CH_3CH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-O^-Na^+ +\frac{1}{2}H_2$$

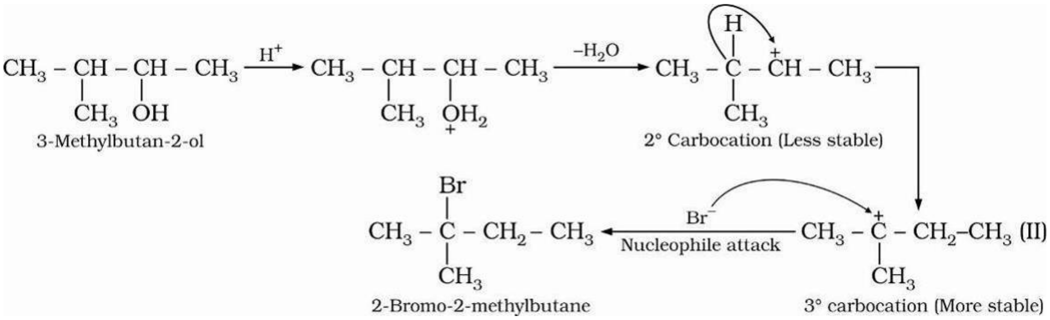
3-Methylpentan-2-ol sodium-3-methyl-pentoxide



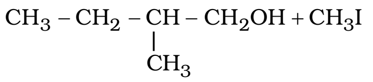
$$CH_3CH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-O^-Na^+ + CH_3CH_2-Br \xrightarrow{S_N2} \overset{5}{CH_3}\overset{4}{CH_2}-\underset{CH_3}{\overset{3}{CH}}-\underset{CH_3}{\overset{2}{CH}}-O-C_2H_5+NaBr$$

2-Ethoxy-3-methylpentane

18. We get a 2° carbocation by the protonation of 3-Methylbutan-2-ol followed by loss of H_2O. It is rearranged by 1, 2-hydride shift to form the more stable 3° carbocation (II). Nucleophilic attack by ion on this carbocation (II) gives the final product.

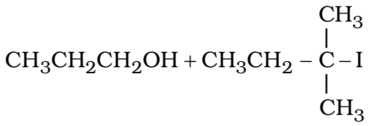


19. **(i)**



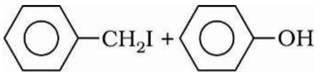
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH+CH_3I$ (S_N2)

(ii)



$CH_3CH_2CH_2OH+CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-I$ (S_N1)

(iii)



(S_N1)

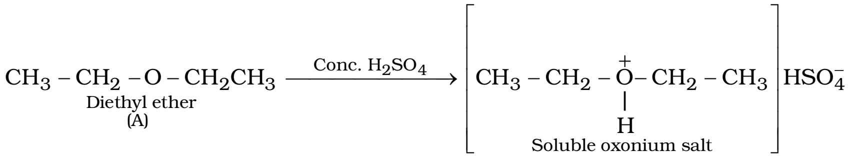
LONG ANSWER TYPE (5 MARKS)

20. **(i)** As compound A does not react with sodium metal or potassium permanganate, it cannot be alcohol.

(ii) As it dissolves in conc. H_2SO_4, it may be an ether.

(iii) As on heating with excess of HI, 'A' gives a single alkyl halide, therefore compound A must be symmetrical ether.

(iv) The only symmetrical ether having molecular formula $C_4H_{10}O$ is diethyl ether. Therefore, compound 'A' is diethyl ether $CH_3-CH_2-O-CH_2CH_3$.

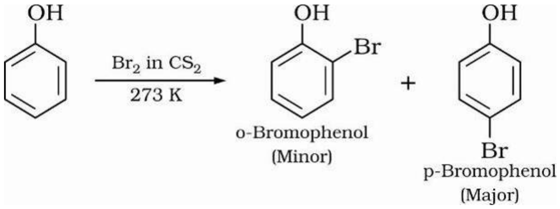


$$\underset{\substack{\text{Diethyl ether}\\ \text{(A)}}}{CH_3-CH_2-O-CH_2CH_3} \xrightarrow{\text{Conc. } H_2SO_4} \left[\underset{\text{Soluble oxonium salt}}{CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2-CH_3}\right]HSO_4^-$$

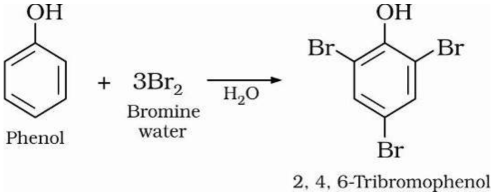
$$\underset{\substack{\text{Diethyl ether}\\ \text{(A)}}}{CH_3CH_2OCH_2CH_3}\xrightarrow[\Delta]{2\,HI}\underset{\text{Ethyl iodide}}{2CH_3CH_2-I}$$

21. **(a)** Cumene (Isopropyl benzene)

(b) Bromination of phenol in non-aqueous medium.

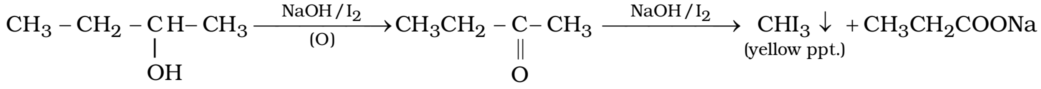


Bromination of phenol in aqueous medium



22. (A) (i) Iodoform Test :

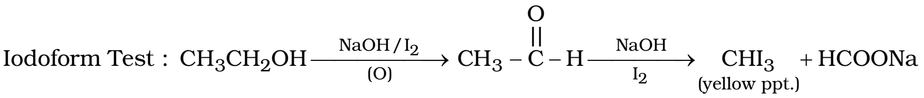
$$CH_3CH_2CH_2CH_2OH \xrightarrow[I_2]{NaOH} \text{No response to iodoform test}$$



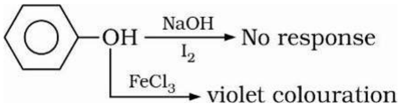
$$CH_3-CH_2-\underset{|}{\underset{OH}{C}}H-CH_3 \xrightarrow[(O)]{NaOH/I_2} CH_3CH_2-\overset{}{\underset{\underset{O}{||}}{C}}-CH_3 \xrightarrow{NaOH/I_2} \underset{\text{(yellow ppt.)}}{CHI_3\downarrow} + CH_3CH_2COONa$$

(ii) $\text{No colouration} \xleftarrow{\text{Methanol}} FeCl_3 \xrightarrow{\text{Phenol}} \text{violet colour}$

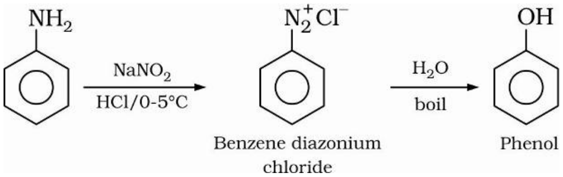
(iii)



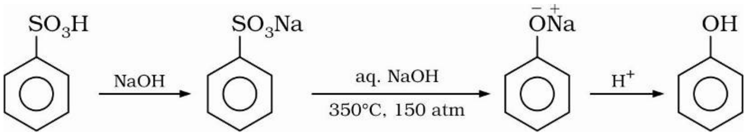
$$\text{Iodoform Test : } CH_3CH_2OH \xrightarrow[(O)]{NaOH/I_2} CH_3-\overset{\overset{O}{||}}{C}-H \xrightarrow[I_2]{NaOH} \underset{\text{(yellow ppt.)}}{CHI_3} + HCOONa$$



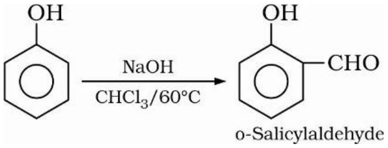
(B) (i)



(ii)



(C) (i)



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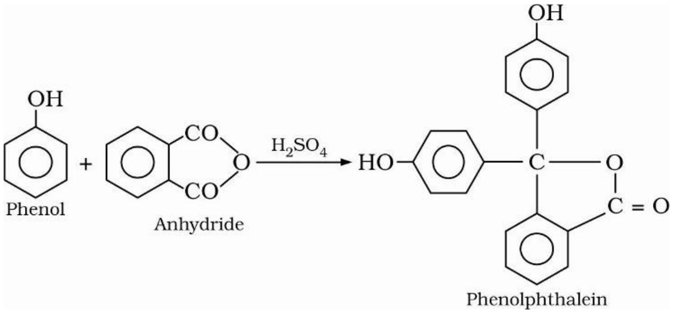

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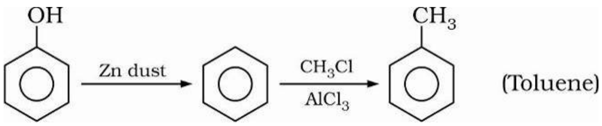
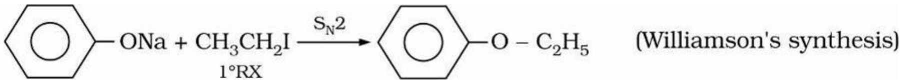


23. **(A)** **(i)** $CH_3CH_2CH_2Br + CH_3CH_2CH_2ONa \xrightarrow{S_N2} CH_3CH_2CH_2-O-CH_2CH_2CH_3$

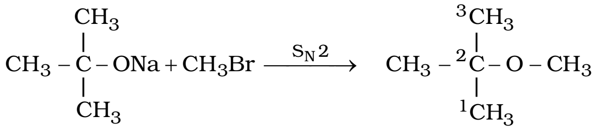
(Williamson's synthesis)

(ii)



(Williamson's synthesis)

(iii)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa + CH_3Br \xrightarrow{S_N2} CH_3-{}^2\underset{{}^1CH_3}{\overset{{}^3CH_3}{C}}-O-CH_3$$

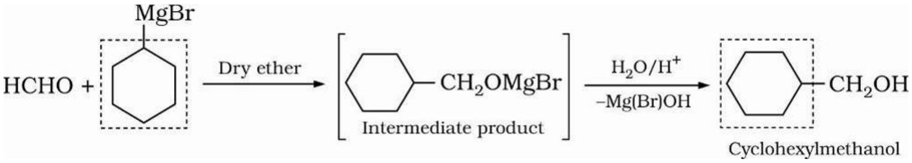
(Williamson's synthesis)

2-Methoxy-2-Methyl propane

(iv) $CH_3CH_2ONa + CH_3I \xrightarrow{S_N2} CH_3CH_2-O-CH_3$ (Williamson's Synthesis)

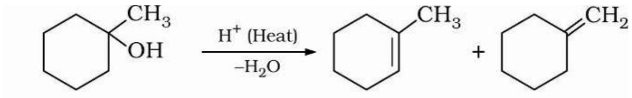
(B) **(i)** $$\underset{\text{Methanal}}{HCHO} + \underset{\text{Isopropyl magnesium bromide}}{\boxed{(CH_3)_2CH\ MgBr}} \xrightarrow{\text{Dry ether}} \underset{\text{Addition compound}}{[(CH_3)_2\ CH-CH_2OMgBr]} \xrightarrow[-Mg(Br)OH]{H_2O/H^+} \underset{\text{Isobutyl alcohol or 2-Methylpropan-1-ol}}{(CH_3)_2CH-CH_2OH}$$

(ii)



Cyclohexylmethanol

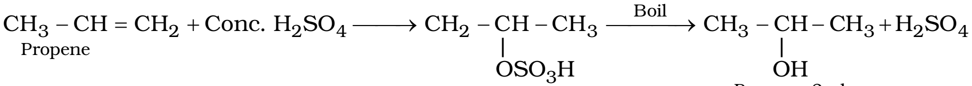
(C) **(i)**



1-Methylcyclohexanol (Major) (Minor)

(ii) $$\underset{\text{Butan-1-ol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow[-H_2O]{H^+,\ heat} \underset{\text{But-2-ene (Major)}}{CH_3-CH=CH-CH_3}$$

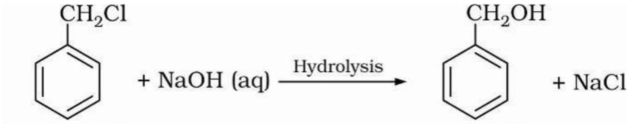
24. **(i)** Propene $\longrightarrow$ Propan-2-ol



$$\underset{\text{Propene}}{CH_3-CH=CH_2} + \text{Conc. } H_2SO_4 \longrightarrow CH_2-\underset{OSO_3H}{CH}-CH_3 \xrightarrow{\text{Boil}} CH_3-\underset{OH}{CH}-CH_3 + H_2SO_4$$

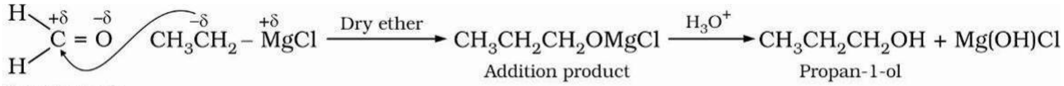
Isopropyl hydrogen sulphate Propane-2-ol

(ii) Benzyl chloride to Benzyl alcohol



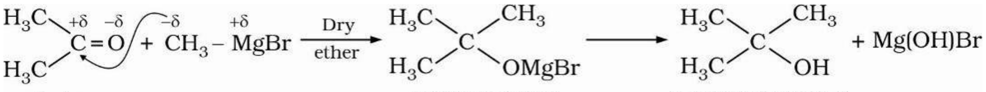
Benzyl chloride Benzyl alcohol

(iii) Ethyl magnesium chloride to Propan-1-ol



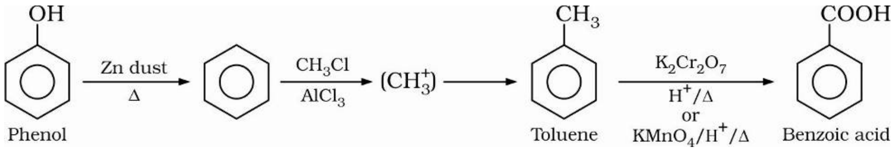
Formaldehyde

(iv) Methyl magnesium bromide 2-Methylpropan-2-ol

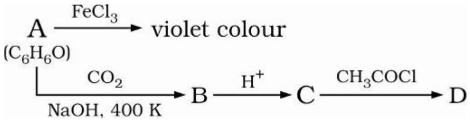


Acetone 2-Methylpropan-2-ol

25. **(i)**



(ii)



A is clearly phenol and under going Kolbe's reaction.