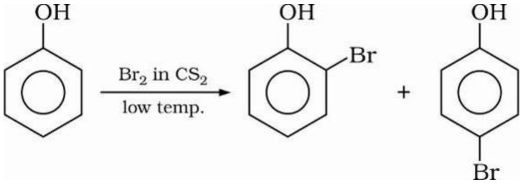
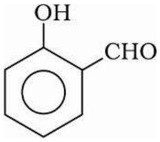
26.(B)



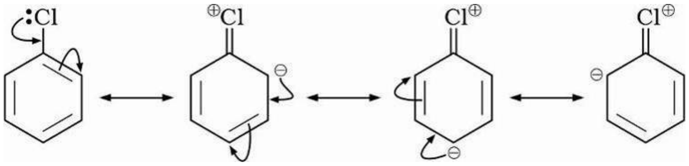
27.(C) The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised $-OH$ groups present both in alcohol and water. However, in higher alcohols the hydrocarbon part (alkyl chain) character increases and thus solubility in water decreases. When the ratio of C to OH is more than 4, alcohol have little solubility in water. So Statement I is correct but Statement II is not.

28. Fuse benzene sulphonic acid with NaOH then visualise Riemer-Tiemann reaction.



29. Nucleophilic

30.(BD)



Aryl halides are resonance stabilised and thus stable. The $C-X$ bond in aryl halide has a partial double bond character also due to resonance. Also, sp² hybridsed C is more electronegative which makes the $C-Cl$ bond shorter and stronger.

31.(CD) $C_2H_5Br + AgNO_2 \xrightarrow{OH^-} \underset{\substack{\text{Nitroethane}\\(\text{Major})}}{CH_3CH_2NO_2} + \underset{\substack{\text{Ethylnitrite}\\(\text{Minor})}}{CH_3CH_2ONO}$

32. % of $C = \frac{12}{44} \times \frac{0.308}{0.108} \times 100 = 77.77$;   % of $H = \frac{2}{18} \times \frac{0.072}{0.108} \times 100 = 7.40$;

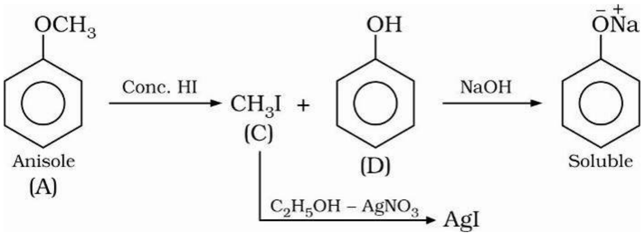
% of $O = 100 - (77.77 + 7.40) = 14.83$

Empirical formula of A and B

Element	% age	Relative number of atoms	Simplest ratio
C	77.77	77.77/12 = 6.48	6.48/0.92 = 7
H	7.40	7.40/1 = 7.40	7.40/0.92 = 8
O	14.43	14.83/16 = 0.92	0.92/0.92 = 1

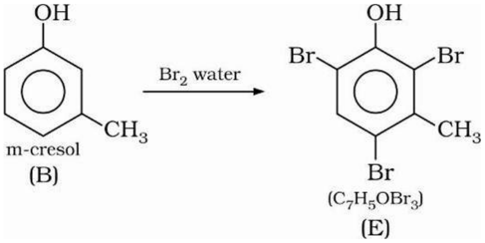
Empirical formula $= C_7H_8O$

➢ Since A is insoluble in NaOH and $NaHCO_3$ so it does not contain $-OH$ and $-COOH$ group. So it contains ether group. Also A on reaction with concentration HI forms compounds C and D which can be separated by means of ammoniacal $AgNO_3$ and out of C and D, D is soluble in NaOH so C and D are alkyl halides and phenol respectively. So A is anisole.



- $B(C_7H_8O)$ is soluble in NaOH so it is a phenol. Following reactions of B also confirm it to be a phenol.

  B when reacted with bromine water give the compound $E(C_7H_5OBr_3)$. On further bromination B yields tribromo product which indicates that B is m-cresol.



33.(B) $RSH + O_2 \xrightarrow{\Delta} CO_2(g) + H_2O(\ell) + SO_2(g)$

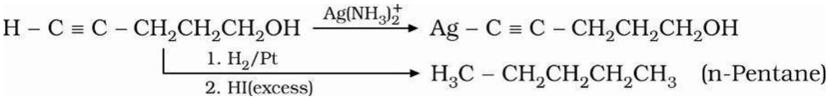
34. On standing in contact with air, ethers are converted into unstable peroxides which are highly explosive even in low concentration. Hence ethers are always purified before distillation which can be done by washing with a solution of ferrous salt or by distillation with conc. H_2SO_4.

35. Compound 'X' $\xrightarrow{\text{Lucas reaget}}$ No reaction at room temperature (1° alcohol)

$C_5H_8O \xrightarrow[\text{AgNO}_3]{\text{Ammoniacal}}$ ppt, X $\xrightarrow[\text{CH}_3\text{ MgBr}]{\text{Excess of}} CH_4$; X $\xrightarrow[\text{HI excess}]{H_2/Pt}$ n - pentane

Above information suggest that X has a terminal triple bond and it contain primary $-OH$ group.

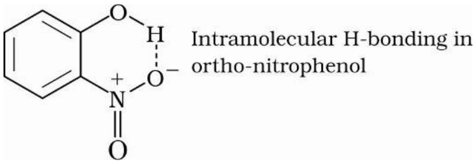
⇒



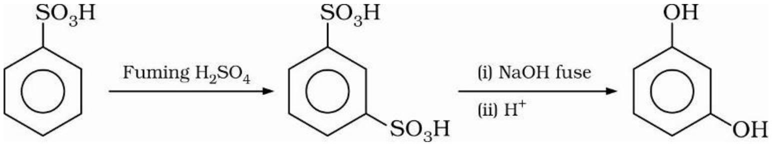
$$H-C\equiv C-CH_2CH_2CH_2OH \xrightarrow{Ag(NH_3)_2^+} Ag-C\equiv C-CH_2CH_2CH_2OH$$

$$H-C\equiv C-CH_2CH_2CH_2OH \xrightarrow[\text{2. HI(excess)}]{\text{1. }H_2/Pt} H_3C-CH_2CH_2CH_2CH_3 \quad \text{(n-Pentane)}$$

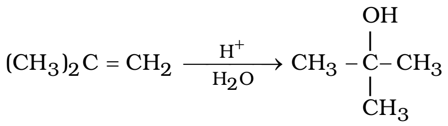
36. Ortho-nitrophenol : Due to intramolecular H-bonding.



37.



38. C must be isobutene.



$$(CH_3)_2C = CH_2 \xrightarrow[H_2O]{H^+} CH_3-\overset{\overset{\large OH}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3$$

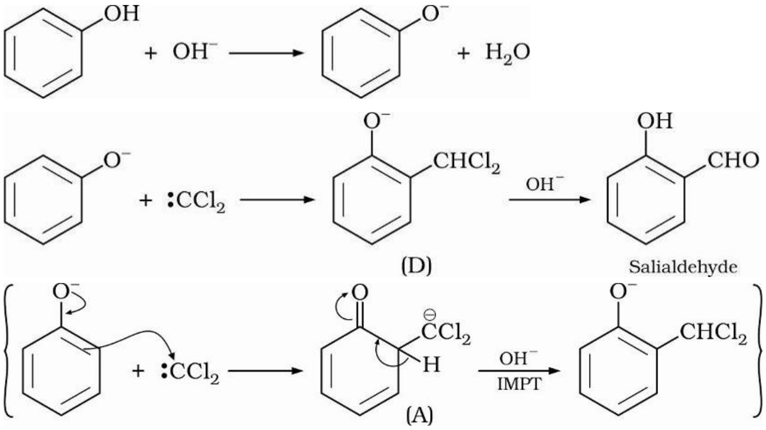
Tert-butyl alcohol has no chiral centre so no chance of resolution.

39. *n*-Butanol gives the following reaction in which the colour of $KMnO_4$ changes to brown. The brown colour is due to MnO_2.

$$\underset{n\text{-Butanol}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{(Purple)}}{KMnO_4} \longrightarrow \underset{\text{(Soluble in water}}{CH_3CH_2CH_2COOK} + \underset{\text{(brown)}}{MnO_2 \downarrow} + KOH$$

Tert-alcohols are not oxidised easily as they do not have α-H and so there is no change in purple colour of $KMnO_4$

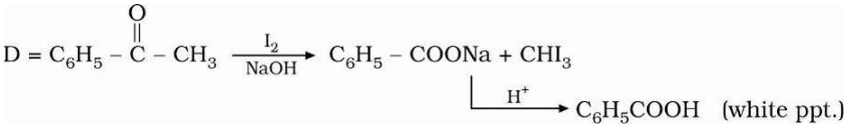
40.(AD) $CHCl_3 + OH^- \rightleftharpoons {}^-CCl_3 \longrightarrow Cl^- + :CCl_2$



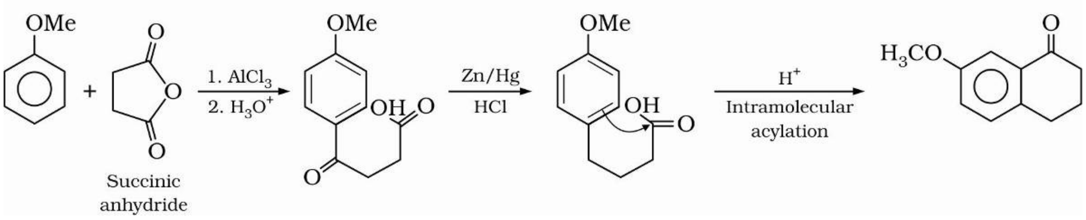
➢ Visualise mechanism of Riemer-Tiemann reaction.

41. E = C_6H_5COOH (benzoic acid)

⇒



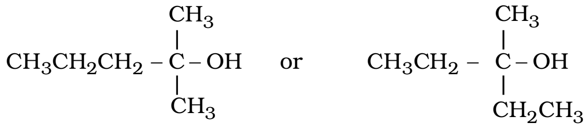
42.



43. $\underset{A}{C_6H_{10}O} \xrightarrow{2H_2} \underset{B}{C_6H_{14}O}$

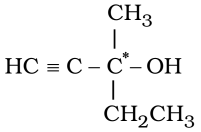
(i) Since B is resistant to oxidation, it must be tert, alcohol.

(ii) Since B is optically inactive, it must have at least two similar alkyl groups. The possible structure of alcohol *B* is either



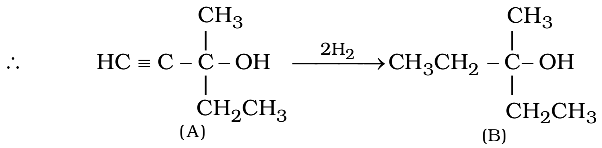
$$CH_3CH_2CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \quad \text{or} \quad CH_3CH_2-\underset{CH_2CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

Since (A) is an optically active, hence A should be :



$$HC\equiv C-\underset{CH_2CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C^*}}}}-OH$$

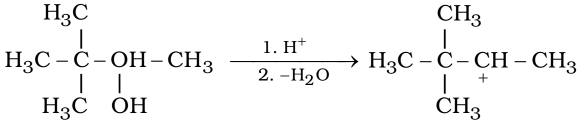
which contains a chiral C-atom.



$$\therefore \quad \underset{(A)}{HC\equiv C-\underset{CH_2CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH} \xrightarrow{2H_2} \underset{(B)}{CH_3CH_2-\underset{CH_2CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH}$$

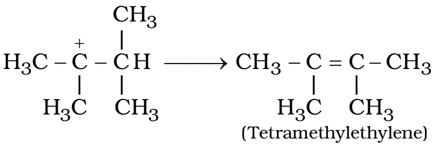
44. Various steps involved in the suggested mechanism are:

- Protonation of hydroxyl group followed by removal of H_2O to form a secondary (2°) carbocation.



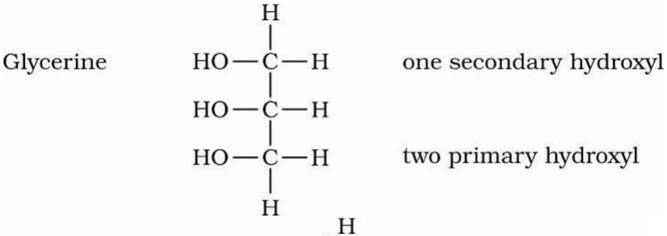
$$H_3C-\underset{H_3C}{\overset{H_3C}{\underset{|}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{OH}}-CH_3 \xrightarrow[2.\ -H_2O]{1.\ H^+} H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\overset{+}{C}H-CH_3$$

- Methide shift (CH_3^-) to get more stable carbocation followed by lose of proton to give an alkene.



$$H_3C-\underset{H_3C}{\underset{|}{\overset{+}{C}}}-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}H \longrightarrow \underset{(Tetramethylethylene)}{CH_3-\underset{H_3C}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3}$$

45.



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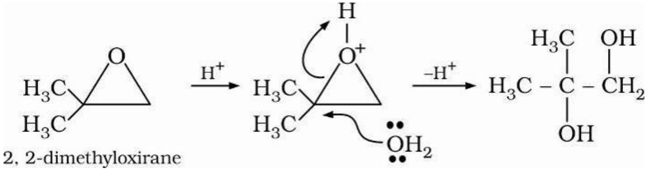


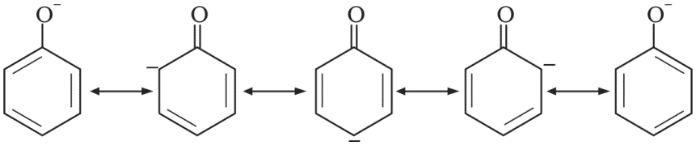
2, 2-dimethyloxirane

47.(C) The order of reactivity depends upon the stability of carbocation formed i.e. stability of carbocations.

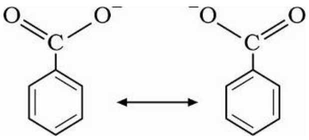
$$\underset{I}{FCH_2\overset{+}{C}HCH_3} < \underset{II}{FCH_2CH_2\overset{+}{C}HCH_3} < \underset{III}{CH_3\overset{+}{C}HCH_3} < \underset{IV}{Ph\overset{+}{C}H_2}$$

Thus, the order of reactivity of alcohols will be IV > III > II > I.

48. The resonating structures of phenoxide ion are:

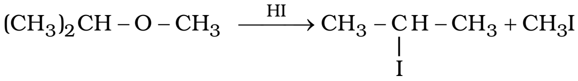


The resonating structures of benzoate ion are:



The benzoate ion is more stabilized because in it the negative charge is delocalised on more electronegative oxygen atom. In phenoxide ion the negative charge is on less electronegative carbon atom. Because of this benzoic acid is a stronger acid than phenol.

49.



$$(CH_3)_2CH-O-CH_3 \xrightarrow{HI} CH_3-\underset{\displaystyle I}{\underset{|}{C}}H-CH_3+CH_3I$$

50.(AD)