11

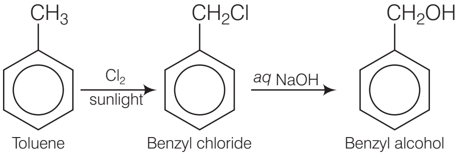
Alcohols, Phenols and Ethers

Multiple Choice Questions (MCQs)

Q. 1 Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields

(a) *o*-cresol
(b) *m*-cresol
(c) 2, 4- dihydroxytoluene
(d) benzyl alcohol

Ans. *(d)* Monochlorination of toluene in sunlight gives benzyl chloride. On hydrolysis with *aq*. NaOH, benzyl chloride shows nucleophilic substitution reaction to give benzyl alcohol.



So, the correct option is (d).

Q. 2 How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?

(a) 1
(b) 2
(c) 3
(d) 4

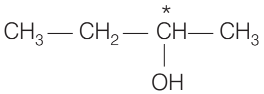
Thinking Process

To solve this question, it should keep in mind that, if all four groups or atoms attached to the carbon atom are different, such a carbon is called asymmetric carbon or chiral carbon or stereocentre.

Ans. *(a)* The three isomers of butanol are possible. Structural formula of these isomers are given below

(i) $\underbrace{CH_3CH_2 - CH_2 - CH_2OH}_{\text{Butan-1-ol}}$

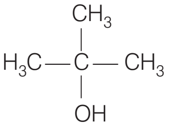
No carbon is chiral in this compound as none of the four carbon is bonded to four different substituents.

(ii) 

$$CH_3-CH_2-\overset{*}{C}H(OH)-CH_3$$

Butan-2-ol

In this compound, asterisk marked carbon is chiral carbon as all four substituents, attached to it are different.

(iii) 

$$H_3C-C(CH_3)(OH)-CH_3$$

2-methylpropan-2-ol

Here, again carbon is not chiral in nature.

So, only one alcohol is chiral in nature and the correct option is (a).

Q. 3 **What is the correct order of reactivity of alcohols in the following reaction?**

$$R—OH + HCl \xrightarrow{ZnCl_2} R—Cl + H_2O$$

(a) 1° > 2° > 3°

(b) 1° < 2° > 3°

(c) 3° > 2° > 1°

(d) 3° > 1° > 2°

Ans. ***(c)*** The given reaction is nucleophilic substitution reaction in which — OH group is replaced by — Cl. Tertiary alcohols, when react with HCl in presence of $ZnCl_2$, form tertiary carbocation.

This intermediate 3° carbocation is more stable than 2° carbocation as well as 1° carbocation. Higher the stability of intermediate, higher will be the reactivity of reactant molecule.

So, the order of reactivity of alcohols in the given reaction is 3° >2° >1° and correct option is (c).

Q. 4 **CH_3CH_2OH can be converted into CH_3CHO by ....**

(a) catalytic hydrogenation

(b) treatment with $LiAlH_4$

(c) treatment with pyridinium chlorochromate

(d) treatment with $KMnO_4$

Ans. ***(c)*** Ethanal (CH_3CHO) is an oxidised product of ethanol. Pyridinium chlorochromate ($C_5H_5\overset{+}{N}HCl\overset{-}{Cr}O_3$) oxidises primary alcohols to aldehydes. Strong oxidising agents such as $KMnO_4$ are used for getting carboxylic acid from alcohols.

The oxidation process can be stopped at the aldehyde stage if Cr(VI) reagents such as Collin's reagent ($CrO_3 \cdot 2C_5H_5N$), Corey's reagent or pyridinium chlorochromate and pyridinium dichromate [$(C_5H_5NH_2)^{2+}Cr_2O_7^{2-}$] in anhydrous medium are used as the oxidising agent. So, the correct option is (c).

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PCC} \underset{\text{Ethanal}}{CH_3CHO}$$

Q. 5 The process of converting alkyl halides into alcohols involves ....

(a) addition reaction
(b) substitution reaction
(c) dehydrohalogenation reaction
(d) rearrangement reaction

Ans. ***(b)*** An addition reaction is a reaction where two or more molecules combine to form a larger one. These reactions occur to change the unsaturated compound to saturated compound. In dehydrohalogenation reaction, alkyl halides give alkenes.

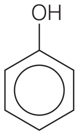
Rearrangement gives the structural isomers of the reactant while in substitution reaction one of the group or an atom is replaced by other group. Therefore, the process of converting alkyl halides into alcohols involves substitution reaction.

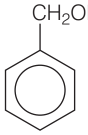
$$\underset{\text{Alkyl halide}}{R-X} \xrightarrow{OH^-} \underset{\text{Alcohol}}{R-OH}$$

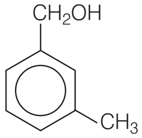
Reaction of alkyl halides

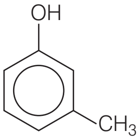
Primary alkyl halides – S_N^2
Secondary alkyl halides– S_N^1
Tertiary alkyl halides – S_N^1

Q. 6 Which of the following compounds is aromatic alcohol?


(*A*)


(*B*)


(*C*)

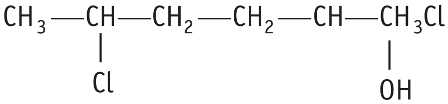

(*D*)

(a) *A*, *B*, *C*, *D*
(b) *A*, *D*
(c) *B*, *C*
(d) *A*

Ans. ***(c)*** Phenol is also known as, carbolic acid' cannot be considered as aromatic alcohol. It is quite separate branch of compound called phenols. So, compound (*A*) *i.e.,* phenol and compound (*D*) *i.e.,* a derivative of phenol cannot be considered as aromatic alcohol.

On the other hand, compound (*B*) and (*C*), — OH group is bonded to sp^3 hybridised carbon which inturn is bonded to benzene ring. Hence, the correct option is (c).

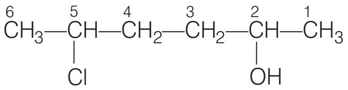
Q. 7 Give IUPAC name of the compound given below.



$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3Cl$$

(a) 2-chloro-5-hydroxyhexane
(b) 2-hydroxy-5-chlorohexane
(c) 5-chlorohexan-2-ol
(d) 2-chlorohexan-5-ol

Ans. ***(c)***



$$\overset{6}{CH_3}-\underset{\underset{Cl}{|}}{\overset{5}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\underset{\underset{OH}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

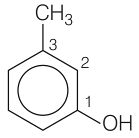
The correct IUPAC name of the compound is 5-chlorohexan-2-ol.
Hence, option (c) is the correct answer.

Q. 8 IUPAC name of m- cresol is ....

(a) 3-methylphenol (b) 3-chlorophenol

(c) 3-methoxyphenol (d) benzene-1, 3-diol

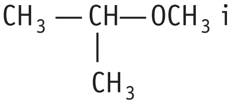
Ans. ***(a)*** The structure of *m*–cresol is



m-cresol

IUPAC name is 3-methylphenol because —OH is the functional group and the methyl is substituent.

Q. 9 IUPAC name of the compound is ....

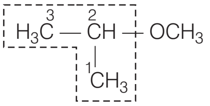


$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{CH}-OCH_3}$$

(a) 1-methoxy-1-methylethane (b) 2-methoxy-2-methylethane

(c) 2-methoxypropane (d) isopropylmethyl ether

Ans. ***(c)***

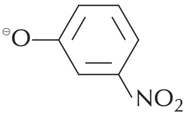


IUPAC name of the above compound is 2-methoxypropane and correct option is (c).

Q. 10 Which of the following species can act as the strongest base?

(a) $^{\ominus}OH$ (b) $^{\ominus}OR$

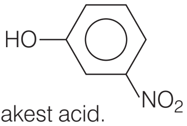
(c) $^{\ominus}OC_6H_5$ (d)



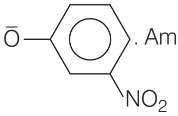
Thinking Process

To compare the species, the point to be noted that weak acid has strong conjugate base and vice-versa. Write the corresponding acid of the given base and choose the weakest acid among these.

Ans. ***(b)*** Weakest acid has the strongest conjugate base. ROH is the acid of RO^- conjugate base, HOH is the acid of ^-OH, C_6H_5OH is the acid of $C_6H_5O^-$ and



is the acid of



. Among all these acids, ROH is the weakest acid.

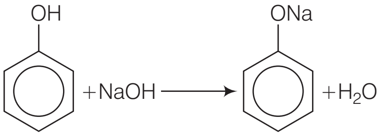
Therefore, the strongest base is RO^- and the correct option is (b).

Q. 11 Which of the following compounds will react with sodium hydroxide solution in water?

(a) C_6H_5OH (b) $C_6H_5CH_2OH$

(c) $(CH_3)_3COH$ (d) C_2H_5OH

Ans. *(a)* Phenol is more acidic in nature because by the loss of one proton, it gives phenoxide ion. This phenoxide ion is resonance stabilised. As phenoxide ion is a stable intermediate so, the tendency to give proton is more in phenol than the others. Phenols being more acidic than alcohols, dissolves in NaOH.



Therefore, option (a) is the correct.

Q. 12 Phenol is less acidic than ....

(a) ethanol (b) *o* - nitrophenol

(c) *o* - methylphenol (d) *o* - methoxyphenol

Thinking Process

This question is based on the acidic character of phenol. Electron withdrawing group at o - and p-position w.r.t. — OH group of phenol, increases the acidic strength.

Ans. *(b)* In *o*-nitrophenol, nitro group is present at *ortho* position. Presence of electron withdrawing group at *ortho* position increases the acidic strength. On the other hand, in *o*-methylphenol and in *o*-methoxyphenol, electron releasing group (— CH_3, — OCH_3) are present.

Presence of these groups at *ortho* or *para* positions of phenol decreases the acidic strength of phenols. So, phenol is less acidic than *o* - nitrophenol.

Q. 13 Which of the following is most acidic?

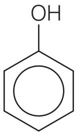
(a) Benzyl alcohol (b) Cyclohexanol

(c) Phenol (d) *m* - chlorophenol

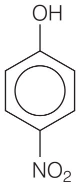
Ans. *(d)* Alpha carbon of benzyl alcohol and cyclohexanol is sp^3 hybridised while in phenol and *m*-chlorophenol, it is sp^2 hybridised. In *m*-chlorophenol electron withdrawing group (— Cl) is present at *meta* position.

Presence of electron withdrawing group increases the acidic strength. So, *m*-chlorophenol is most acidic among all the given compounds. The correct option is (d).

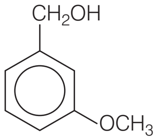
Q. 14 Mark the correct order of decreasing acid strength of the following compounds.



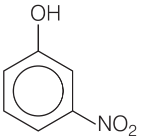
(I)



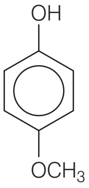
(II)



(III)



(IV)



(V)

(a) V > IV > II > I > III (b) II > IV > I > III > V

(c) IV > V > III > II > I (d) V > IV > III > II > I

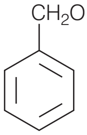
Ans. *(b)* Presence of electron withdrawing group on phenols, increases its acidic strength. So, both compounds *i.e., p*-nitrophenol (II) and *m*-nitrophenol (IV) are stronger acid than (I). If this — NO_2 group is present at *p*-position, then it exerts both $-I$ and — R effect but if it is present at *meta* position, then it exerts only $-I$ effect. Therefore, *p*-nitrophenol is much stronger acid then *m*-nitrophenol.

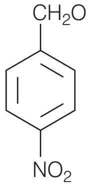
On the other hand, presence of electron releasing group on phenol, decreases its acidic strength. If — OCH_3 group is present at *meta* position, it will not exert $+R$ effect but exert $-I$ effect.

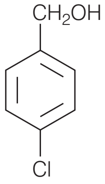
But, if it is present at *para* position, then it will exert $+R$ effect. Therefore, *m*-methoxy phenol is more acidic than *p*-methoxy phenol.

Hence, the correct option is (b).

Q. 15 Mark the correct increasing order of reactivity of the following compounds with HBr / HCl.


(I)


(II)


(III)

(a) I < II < III (b) II < I < III (c) II < III < I (d) III < II < I

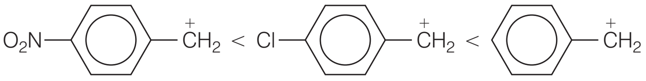
Thinking Process

This question is based on conceptual mixing of substitution reaction carbocation and reactivity. Nucleophilic substitution reactions depend upon the stability of carbocation. Higher the stability of carbocation (intermediate), higher will be the reactivity of reactant molecule.

Ans. *(c)* Reaction of the given compounds with HBr/HCl is a nucleophilic substitution reaction. It follows $S_N{}^1$ mechanism. $S_N{}^1$ mechanism depends upon the stability of carbocation. Presence of electron withdrawing group decreases the stability of carbocation. In compound (II) and (III) EWG is present at *para* position.

Since, — NO_2 group is a stronger EWG than — Cl. So, $NO_2—C_6H_5—\overset{+}{C}H_2$ carbocation will be less stable than $Cl—C_6H_5—\overset{+}{C}H_2$ carbocation.

Thus, the order of stability of carbocation is



Therefore, compound (II) is least reactive and correct option is(III).

Q. 16 Arrange the following compounds in increasing order of boiling point. Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(c) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(d) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

Thinking Process

This question is based on the boiling point of the compound. Boiling point increases with increase in the number of carbon atoms and decreases with increase of branching in carbon chain.

Ans. ***(a)*** Boiling point increases with increase in the number of carbon atoms because of increase in molecular mass. So, the boiling point of pentan-1-ol is more than that of all other given compounds. Further, among isomeric alcohols, 1° alcohols have higher boiling points than 2° alcohols because of higher surface area in 1° alcohols. Therefore, boiling point increase in the order

Propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol.

Here, the correct option is (a).

Multiple Choice Questions (More Than One Options)

Q. 17 Which of the following are used to convert RCHO into RCH_2OH?

(a) H_2/Pd

(b) $LiAlH_4$

(c) $NaBH_4$

(d) Reaction with RMgX followed by hydrolysis

Ans. ***(a, b, c)***

Conversion of aldehyde into alcohol is a reduction reaction. This reduction can be carried out by adding hydrogen in presence of finely divided metal catalyst such as platinum, palladium or nickel.

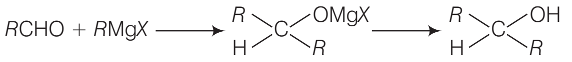
$$RCHO + \xrightarrow{H_2/Pd} RCH_2OH$$

It can also be prepared by using $NaBH_4$ and $LiAlH_4$ as a reducing agent.

$$RCHO \xrightarrow{NaBH_4} RCH_2OH$$

$$RCHO \xrightarrow{LiAlH_4} RCH_2OH$$

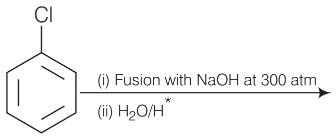
Reaction of RMgX with any aldehyde other than methanal gives secondary alcohols not the primary alcohols.



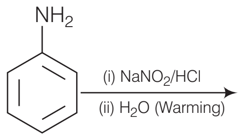
(Where, $R = — C_2H_5, C_3H_7$ etc.)

Q. 18 Which of the following reactions will yield phenol?

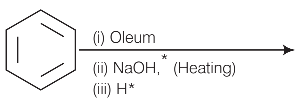
(a)



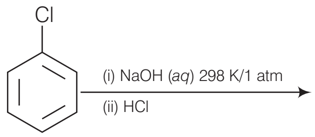
(b)



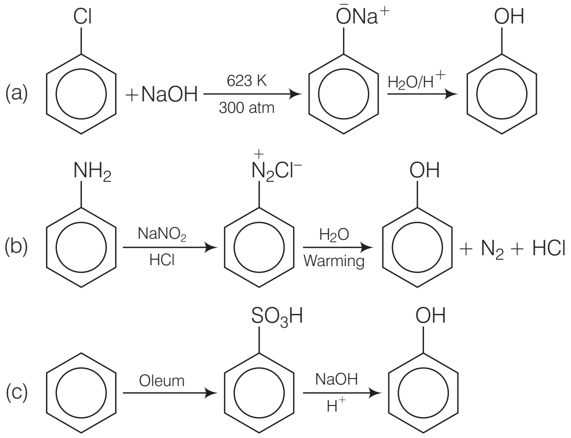
(c)



(d)



Ans. ***(a, b, c)***



Haloarenes are less reactive towards nucleophilic substitution reaction. Therefore, it requires very high temperature and pressure. Chlorobenzene does not undergo hydrolysis on treatment with *aq.* NaOH at 298 K and 1 atm.

Therefore, correct options are (a), (b) and (c).

Q. 19 **Which of the following reagents can be used to oxidise primary alcohols to aldehydes?**

(a) CrO_3 in anhydrous medium (b) $KMnO_4$ in acidic medium

(c) Pyridinium chlorochromate (d) Heat in the presence of Cu at 573K

Ans. ***(a, c, d)***

CrO_3 in anhydrous medium is used to oxidise primary alcohols to aldehydes.

$$RCH_2OH \xrightarrow{CrO_3\text{ (anhydrous)}} RCHO$$

Acidic $KMnO_4$ is a very strong oxidising agent. It oxidises primary alcohols into carboxylic acid.

$$RCH_2OH \xrightarrow{KMnO_4} RCOOH$$

Pyridinium chlorochromate $(C_6H_5\overset{+}{N}HClCrO_3^-)$ is a very good reagent for the oxidation of primary alcohols to aldehydes.

$$RCH_2OH \xrightarrow{PCC} RCHO$$

When the vapours of primary alcohols are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde is formed.

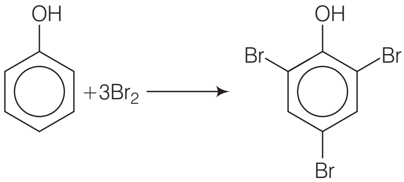
$$RCH_2OH \xrightarrow[573\text{ K}]{Cu} RCHO$$

Q. 20 **Phenol can be distinguished from ethanol by the reactions with ....**

(a) Br_2/water (b) Na (c) neutral $FeCl_3$ (d) All of these

Ans. ***(a, c)***

Ethanol does not react with Br_2/water while phenol gives 2, 4, 6-tribromophenol as white precipitate.



2, 4, 6-tribromophenol

Ethanol and phenol both react with sodium, so phenol cannot be distinguished from ethanol by the reaction with sodium.

Ethanol does not give any reaction with neutral $FeCl_3$ solution while phenol gives purple, blue or red colour when treated with neutral $FeCl_3$.

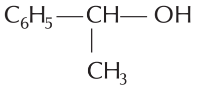
Therefore, correct options are (a) and (c).

Q. 21 Which of the following are benzylic alcohols?

(a) $C_6H_5—CH_2—CH_2OH$

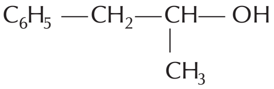
(b) $C_6H_5—CH_2OH$

(c)



$C_6H_5—\underset{\displaystyle CH_3}{\underset{|}{CH}}—OH$

(d)



$C_6H_5—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—OH$

Ans. ***(b, c)***

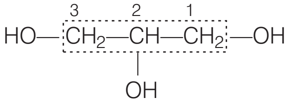
In benzylic alcohols, the — OH group is attached to a sp^3hybridised carbon atom next to an aromatic ring. In compound (a) and (d), the — OH group is attached to a sp^3 hybridised carbon atom but this carbon is not attached to the benzene ring.

On the other hand, in compound (a) and (c), the — OH group is attached to a sp^3 hybridised carbon atom next to an aromatic ring.

Short Answer Type Questions

Q. 22 What is the structure and IUPAC name of glycerol?

Ans. Glycerol is the trihydric alcohol. Structure of glycerol is

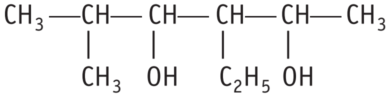


$$HO—\boxed{\overset{3}{C}H_2—\underset{\displaystyle OH}{\underset{|}{\overset{2}{C}H}}—\overset{1}{C}H_2}—OH$$

So, IUPAC name is — propan- 1, 2, 3-triol.

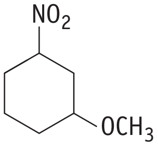
Q. 23 Write the IUPAC name of the following compounds.

(a)



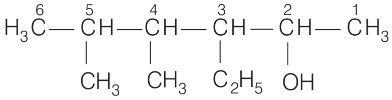
$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—\underset{\displaystyle OH}{\underset{|}{CH}}—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

(b)



Ans. The correct IUPAC name of the following compounds are given below

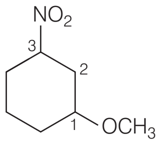
(a)



$$H_3\overset{6}{C}—\underset{\displaystyle CH_3}{\underset{|}{\overset{5}{C}H}}—\underset{\displaystyle CH_3}{\underset{|}{\overset{4}{C}H}}—\underset{\displaystyle C_2H_5}{\underset{|}{\overset{3}{C}H}}—\underset{\displaystyle OH}{\underset{|}{\overset{2}{C}H}}—\overset{1}{C}H_3$$

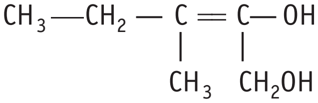
IUPAC name → 3-ethyl-5-methylhexan-2, 4-diol.

(b)



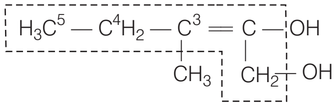
IUPAC name → 1-methoxy-3-nitrocyclohexane.

Q. 24 **Write the IUPAC name of the compound given below.**



$$CH_3—CH_2—\underset{CH_3}{\underset{|}{C}}=\underset{CH_2OH}{\underset{|}{C}}—OH$$

Ans. The IUPAC name of the compound given below is



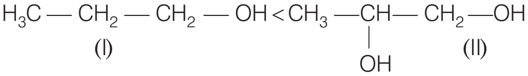
$$H_3C^5—C^4H_2—\underset{CH_3}{\underset{|}{C^3}}=\underset{CH_2—OH}{\underset{|}{C}}—OH$$

3-methylpent-2-ene-1, 2-diol.

Q. 25 **Name the factors responsible for the solubility of alcohols in water.**

Ans. *Solubility of alcohols in water depends upon the two factors.*

(i) **Hydrogen bonding** Higher the extent of hydrogen bonding, higher is the solubility. The hydrogen group of alcohol form hydrogen bonding. Solubility increases with increase in the number of — OH groups in alcohols of comparable molecular masses.



$$\underset{(I)}{H_3C—CH_2—CH_2—OH} < \underset{(II)}{CH_3—\underset{OH}{\underset{|}{CH}}—CH_2—OH}$$

(I) Compound (II) will form stronger H-bond due to two — OH group and hence has higher boiling point.

(ii) **Size of alkyl/aryl group** Higher the size of alkyl/aryl group (hydrocarbon part), lower is the extent of hydrogen bonding and lower is the solubility. Hence,

$$H_3C—CH_2—OH > CH_3CH_2—CH_2OH > CH_3CH_2CH_2—CH_2OH$$

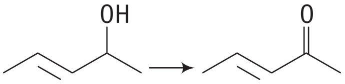
Q. 26 **What is denatured alcohol?**

Ans. Alcohol is used in large quantities in the manufacture of alcoholic liquors. Its continuous use damages the various vital organs. Therefore, to refrain the people from drinking alcohol, heavy excise duty is levied on the sale of alcoholic beverages. But, it is used in various industries as it is a very good solvent.

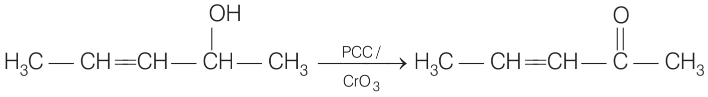
Therefore, industrial alcohol must be cheap. Thus, to provide cheaper alcohol to industries and to refrain people from drinking alcohol, it is mixed with some copper sulphate, pyridine, methyl alcohol or acetone.

Alcohol is made unfit for drinking by mixing some quantity of any of these substances in it. This is called denatured alcohol.

Q. 27 Suggest a reagent for the following conversion.



Ans. The given reactant is $H_3C—CH = CH—\overset{OH}{\overset{|}{C}}H—CH_3$. It is a secondary alcohol. Secondary alcohol (>CHOH) gives ketone when oxidises by CrO_3 or pyridinium chlorochromate without carrying out oxidation at the double bond.



$$H_3C — CH{=}CH— \overset{OH}{\overset{|}{C}}H— CH_3 \xrightarrow[CrO_3]{PCC/} H_3C — CH{=}CH— \overset{O}{\overset{||}{C}} — CH_3$$

Q. 28 Out of 2-chloroethanol and ethanol which is more acidic and why?

Ans. 2-chloroethanol is more acidic than ethanol. Due to – I effect (electron withdrawing group) of the Cl-atom electron density in O — H bond decreases. So, O — H bond of 2-chloroethanol becomes weaker than O — H bond of ethanol. Thus, 2-chloroethanol is more acidic than ethanol.

$$Cl \leftarrow CH_2 \leftarrow CH_2 \leftarrow O \leftarrow H > CH_3 \rightarrow CH_2 \rightarrow O \rightarrow H$$

Stronger acid due to – I effect of Cl.

Q. 29 Suggest a reagent for conversion of ethanol to ethanal.

Ans. Ethanol can be oxidises into ethanal by using pyridinium chlorochromate.

$(C_6H_5\overset{+}{N}HCl\overset{-}{C}rCrO_3)$ in CH_2Cl_2.

$$\underset{\text{Ethanol}}{H_3C— CH_2 —OH} \xrightarrow{PCC/CH_2Cl_2} \underset{\text{Ethanal}}{CH_3 — CHO}.$$

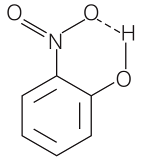
Q. 30 Suggest a reagent for conversion of ethanol to ethanoic acid.

Ans. Ethanol can be converted into ethanoic acid by using acidified $KMnO_4$ or $K_2Cr_2O_7$. Both $KMnO_4$ and $K_2Cr_2O_7$ are strong oxidising agents.

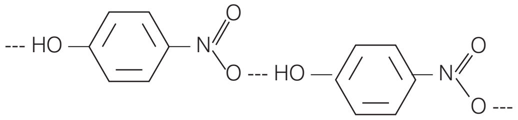
$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\substack{\text{Acidified}\\ KMnO_4}} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

Q. 31 Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain.

Ans. *o*-nitrophenol is more volatile than *p*-nitrophenol due to presence of intramolecular hydrogen bonding. In *para* nitrophenol intermolecular hydrogen bonding is present. This intermolecular hydrogen bonding causes the association of molecules.



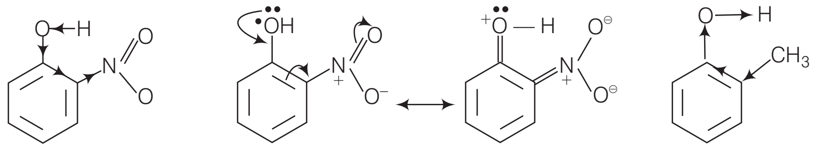
o-nitrophenol
(Intramolecular H-bonding)



p-nitrophenol
(Intermolecular H-bonding)

Q. 32 Out of o-nitrophenol and o-cresol which is more acidic?

Ans. The acidic character of alcohols is due to the polar nature of O — H bond. Higher the polarity of O — H bond, more will be the acidic strength. Due to – *I* and – *R* effect of nitro group, electron density decreases in the O — H bond of *o*-nitrophenol and thus polarity increases.

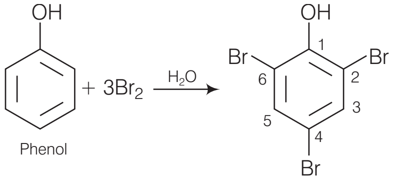


(– *I* effect) (– *R* effect) (+ *I* – effect)

Whereas due to + *I* effect of — CH_3 group, electron density increases in the O — H bond of *o*-cresol. Thus, O — H bond of *o*-nitrophenol is weaker than O — H bond of *o*-cresol and *o*-nitrophenol is more acidic than *o*-cresol.

Q. 33 When phenol is treated with bromine water, white precipitate is obtained. Give the structure and the name of the compound formed.

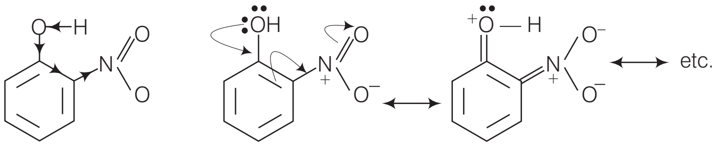
Ans. When phenol is treated with bromine water, white ppt. of 2, 4, 6 – tribromophenol is obtained.



2,4,6 – tribromophenol

Q. 34 Arrange the following compounds in increasing order of acidity and give a suitable explanation.
Phenol, o-nitrophenol, o-cresol

Ans. Nitro group shows – *I* and – *R* effect as follows



(– *I* effect) (– *R* effect)

Due to this – *I* and – *R* effect of *o*-nitrophenol, it is a stronger acid than phenol. On the other hand, —CH_3 group produces + *I* effect – *I* and – *R* effect increases the acidic strength by increasing the polarity of — OH bond while + *I* effect decreases the polarity due to increase in electron density on —OH bond. So, *o*-cresol is a weaker acid than phenol. Thus, the correct order is *o*-cresol < phenol < *o*-nitrophenol.

Q. 35 **Alcohols react with active metals e.g., Na, K etc., to give corresponding alkoxides. Write down the decreasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols.**

Thinking Process

This question is based on the concept of the acidity and reactivity. The acidic character of alcohols is due to the polar nature of the O — H *bond.*

Ans. An electron releasing group produces $+I$ effect so it increases the electron density on oxygen and decreases the polarity of O — H bond. As the number of alkyl group increases from 1° to 3° alcohols, the electron density on the O — H bond increases.

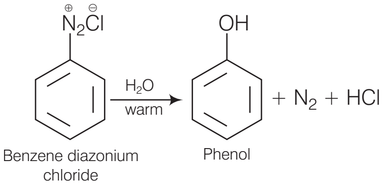
It will finally decrease the polarity and increase the strength of O — H bond in going from 1° to 3° alcohols. Thus, acidic strength decreases in the following order

$$\underset{1^\circ\text{ alcohol}}{RCH_2OH} > \underset{2^\circ\text{ alcohol}}{R_2CHOH} > \underset{3^\circ\text{ alcohol}}{R_3C{-}OH}$$

As we know that, sodium metal is basic in nature and alcohols are acidic in nature. Thus, reactivity of alcohol with sodium metal decreases with decrease in acidic strength. Therefore, the correct order is $1^\circ > 2^\circ > 3^\circ$.

Q. 36 **What happens when benzene diazonium chloride is heated with water?**

Ans. When benzene diazonium chloride is heated with water then phenol is formed.



Q. 37 **Arrange the following compounds in decreasing order of acidity.**

$$H_2O, ROH, HC\equiv CH$$

Ans. A stronger acid displaces a weaker acid from its salt. When $RONa$ is treated with H_2O, it forms ROH. So, water is a stronger acid than ROH.

$$\underset{\text{Stronger acid}}{HOH} + RONa \longrightarrow NaOH + \underset{\text{Weaker acid}}{ROH}$$

Similarly, when sodium ethynide is treated with water and alcohol, then acetylene is obtained.

$$\underset{\text{Stronger acid}}{HOH} + CH \equiv CNa \longrightarrow \underset{\text{Weak acid}}{HC \equiv CH} + NaOH$$

$$\underset{\text{Stronger acid}}{ROH} + HC \equiv CNa \longrightarrow \underset{\text{Weak acid}}{HC \equiv CH} + RONa$$

Thus, water and alcohol are stronger acid than ethyne and the decreasing order of acidity of given compounds are

$$HOH > ROH > HC \equiv CH$$

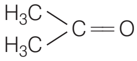
Q. 38 Name the enzymes and write the reactions involved in the preparation of ethanol from sucrose by fermentation.

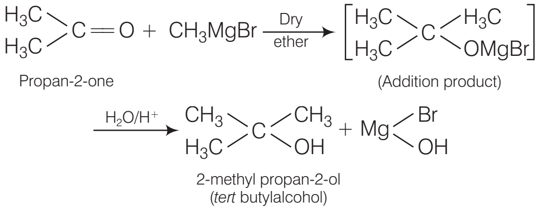
Ans. Sucrose is converted to glucose and fructose in the presence of an enzyme, invertase or sucrase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase. Both these enzymes are present in yeast.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase/sucrose}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose / Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2CH_3CH_2OH} + 2CO_2$$

Q. 39 How can propan-2-one be converted into tert-butyl alcohol?

Ans. Propan-2-one is a ketone. Its structural formula is  $(H_3C)_2C{=}O$ ketones when treated with Grignard reagent give tertiary alcohols.



Propan-2-one

(Addition product)

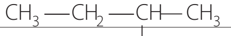
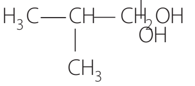
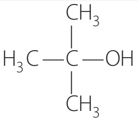
2-methyl propan-2-ol

(*tert* butylalcohol)

$$(H_3C)_2C{=}O + CH_3MgBr \xrightarrow[\text{ether}]{\text{Dry}} \left[(H_3C)_2C(H_3C)(OMgBr)\right] \xrightarrow{H_2O/H^+} (CH_3)(H_3C)C(CH_3)(OH) + Mg(Br)(OH)$$

Q. 40 Write the structures of the isomers of alcohols with molecular formula $C_4H_{10}O$. Which of these exhibits optical activity?

Ans. Some compounds can rotate the plane polarised light, when it is passed through their solution. Such compounds are called optically active compounds. The structures of the isomers of alcohols with molecular formula $C_4H_{10}O$ are as follows

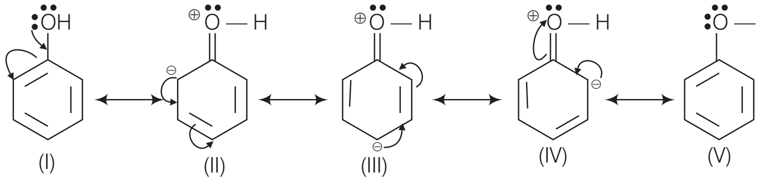
(i)	$CH_3 - CH_2 - CH_2 - CH_2 - OH$	Butan-1-ol
(ii)	 $CH_3-CH_2-\underset{OH}{CH}-CH_3$	Butan-2-ol
(iii)	 $H_3C-\underset{CH_3}{CH}-CH_2OH$	2-methylpropan-1-ol
(iv)	 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$	2-methylpropan-2-ol

The asymmetry of the molecule is responsible for the optical activity in a molecule. If all the four substituents attached to the carbon are different then the carbon is called asymmetric or chiral carbon and such a molecule is called asymmetric molecule.

In the above explained structure, it is only butan-2-ol which contains a chiral carbon and hence it is optically active.

Q. 41 Explain why is OH group in phenols more strongly held as compared to OH group in alcohols?

Ans. In phenols, the electron pairs on oxygen atom of — OH group are in conjugation (or resonance) with π electrons of the ring and the following resonating structures are possible



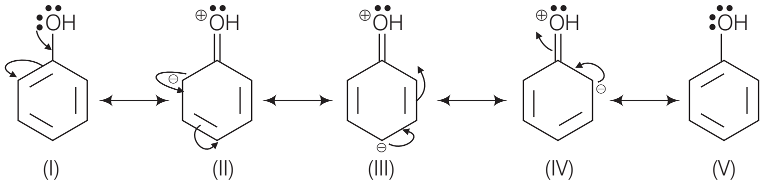
Out of these five resonating structures, II, III and IV structures contain a carbon-oxygen double bond character. In other words, carbon-oxygen bond in phenol acquires a partial double bond character due to resonance.

But in alcohols carbon-oxygen bond in alcohols is purely single bond. Therefore, — OH group in phenols is more strongly held as compared to — OH group in alcohols.

Q. 42 Explain why nucleophilic substitution reactions are not very common in phenols?

Ans. Resonance is an important factor in phenols. During resonance — OH group in phenol gives its electrons to the benzene ring. As a result of this, the electron density on benzene ring is very high. This increased electron density repels nucleophiles.

Therefore, nucleophiles cannot attack the benzene ring and phenols usually do not give nucleophilic substitution reaction.



Resonance in phenols

Q. 43 Preparation of alcohols from alkenes involves the electrophilic attack on alkene carbon atom. Explain its mechanism.

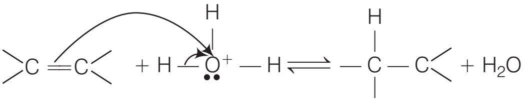
Ans. Preparation of alcohols from alkene by the hydration of alkenes in presence of sulphuric acid.

$$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$$

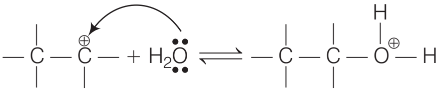
This addition reaction takes place in accordance with Markownikoff's rule.

Mechanism The mechanism of the reaction involves the following three steps

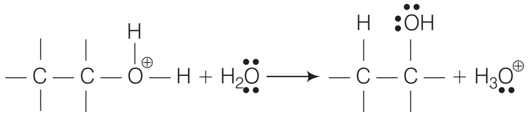
Step 1 Protonation of alkene to form carbocation by electrophilic attack of $H_3\overset{+}{O}$.



Step 2 Attack of water molecule to the secondary carbocation.



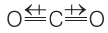
Step 3 Loss of the hydrogen from the protonated alcohol.



$$-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}{}^{\oplus}-\mathrm{H}+\mathrm{H_2\ddot{O}}\longrightarrow-\overset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\overset{\mathrm{\ddot{O}H}}{\overset{|}{\underset{|}{\mathrm{C}}}}-+\mathrm{H_3\ddot{O}}^{\oplus}$$

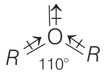
Q. 44 Explain why is O ═ C ═ O non-polar while R—O—R is polar?

Ans. CO_2 is a linear molecule. The dipole moment of two C ═ O bonds are equal and opposite and they cancel each other and hence the dipole moment of CO_2 is zero and it is a non-polar molecule.



$\mu = 0$

While for ethers, two dipoles are pointing in the same direction. These two dipoles do not cancel the effect of each other. Therefore, there is a finite resultant dipoles and hence *R*—O—*R* is a polar molecule.



$\mu \neq 0$

Q. 45 Why is the reactivity of all the three classes of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) different?

Ans. The reaction of alcohols with Lucas reagent (conc. HCl and $ZnCl_2$) follow S_N^1 mechanism. S_N^1 mechanism depends upon the stability of carbocations (intermediate). More stable the intermediate carbocation, more reactive is the alcohol.

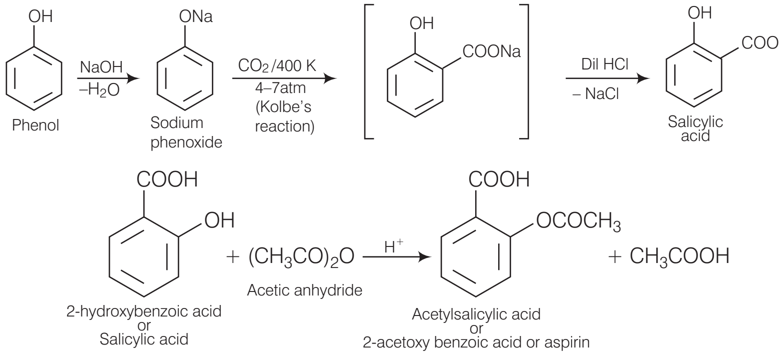
Tertiary carbocations are most stable among the three classes of carbocations and the order of the stability of carbocation is 3° > 2° > 1°. This order, inturn, reflects the order of reactivity of three classes of alcohols *i.e.,* 3° > 2° > 1°.

Thus, as the stability of carbocations are different so the reactivity of all the three classes of alcohols with Lucas reagent is different.

Q. 46 Write steps to carry out the conversion of phenol to aspirin.

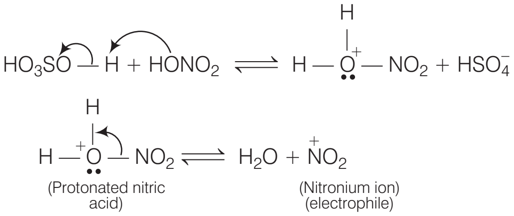
Ans. Aspirin can be prepared by the reaction of salicylic acid with acetic anhydride. Salicylic acid is prepared by the reaction of phenol with CO_2 and NaOH.

This process is known as Kolbe's reaction. The product salicylic acid is used in the preparation of aspirin. After wards, when salicylic acid is treated with acetic anhydride then acetyl group replaces the hydrogen of — OH group *i.e.,* acetylation occurs at — OH group of salicylic acid. *Reaction is as follows*



Q. 47 Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?

Ans. Nitration of benzene and phenol is an electrophilic substitution reaction. During nitration $\overset{+}{N}O_2$ (nitronium ion) is produced as an intermediate as follows



$$HO_3SO-H + HONO_2 \rightleftharpoons H-\overset{\overset{\displaystyle H}{|}}{\underset{\cdot\cdot}{\overset{+}{O}}}-NO_2 + HSO_4^-$$

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\cdot\cdot}{\overset{+}{O}}}-NO_2 \rightleftharpoons H_2O + \overset{+}{N}O_2$$

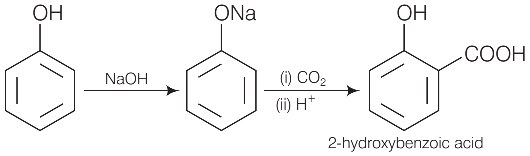
This nitronium ion (electrophile) attacks on benzene or on phenol. Phenol is more easily nitrated than benzene as the presence of — OH group in phenol increases the electron density at *ortho* and *para* positions in benzene ring by + *R* effect.

Since, the electron density is more in phenol than in benzene, therefore, phenol is more easily nitrated than benzene.

Q. 48 In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

Ans. In phenoxide ion, the ability to give lone pair of electrons to the benzene ring is more in comparison to phenols. Therefore, the reactivity of phenoxide ion towards electrophilic substitution reaction is more in comparison to phenols.

Thus, phenoxide ion being a stronger nucleophile reacts easily with CO_2 (weak electrophile) than phenols in Kolbe's reaction.



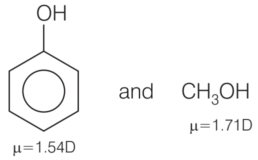
(Kolbe's reaciton)

Note *Kolbe's process is also known as Kolbe - Schmitt reaction. This reaction is precursor to aspirin.*

Q. 49 Dipole moment of phenol is smaller than that of methanol. Why?

Ans. Dipole moment depends upon the polarity of bonds. Higher the polarity of bonds in molecule, higher will be its dipole moment. In phenol carbon is sp^2 hybridised and due to this reason benzene ring is producing electron withdrawing effect.

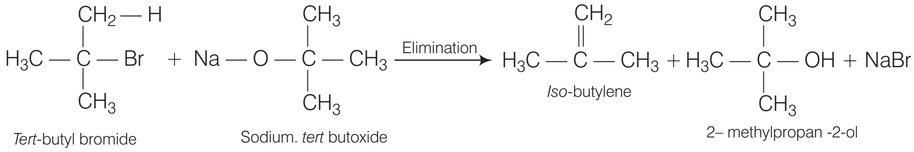
On the other hand, carbon of methanol is sp^3 hybridised and produces electron releasing effect (+ I effect). Thus, C — O bond in phenol is less polar than C — O bond in methanol and therefore, the dipole moment of phenol is smaller than that of methanol.



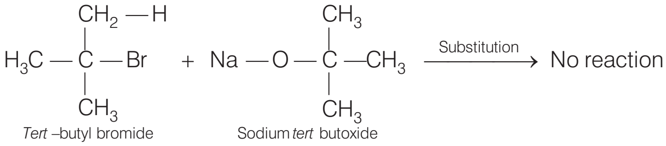
Q. 50 **Ethers can be prepared by Williamson synthesis in which an alkyl halide is reacted with sodium alkoxide. Di-tert -butyl ether can't be prepared by this method. Explain.**

Ans. In order to prepare di-*tert*-butyl ether, sodium *tert*-butoxide must be reacted with *tert*-butyl bromide. Alkoxides are not only nucleophiles but they are strong base as well. They react with 3° alkyl halides leading to the elimination reaction.

When *tert*-butyl-bromide reacts with sodium *tert*-butoxide instead of substitution, elimination takes place. As a result of this elimination reaction, *Iso* butylene is formed instead of di-*tert* butyl ether.



$$H_3C-\overset{CH_2-H}{\underset{CH_3}{C}}-Br + Na-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{\text{Elimination}} H_3C-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH + NaBr$$



$$H_3C-\overset{CH_2-H}{\underset{CH_3}{C}}-Br + Na-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{\text{Substitution}} \text{No reaction}$$

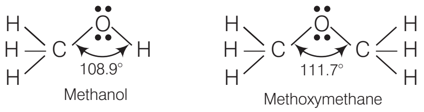
Q. 51 **Why is the C—O—H bond angle in alcohols slightly less than the tetrahedral angle whereas the C—O—C bond angle in ether is slightly greater?**

Thinking Process

To solve this question, it should keep in mind that the order of repulsion between electron pairs is → $lp-lp > lp-bp > bp-bp$.

Ans. The bond angle in $\mathrm{C}-\overset{\bullet\bullet}{\underset{\bullet\bullet}{\mathrm{O}}}-\mathrm{H}$ in alcohols is slightly less than tetrahedral angle (109° 28'). It is due to the repulsion between the unshared electron pairs of oxygen. In alcohols, two lone pair of electrons are present. Therefore, there is comparatively more repulsion and less bond angle.

The C—O—C bond angle in ether is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (– *R*) groups.



Q. 52 **Explain why low molecular mass alcohols are soluble in water?**

Ans. Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecule. The hydrocarbon part methoxy methane (*i.e.*, *R* group) tends to prevent the formation of hydrogen bonds.

Alcohols with lower molar mass will have smaller hydrocarbon part and therefore tendency to form hydrogen bonding is more and they are more soluble in water.

$$\underset{\text{(More soluble)}}{CH_3CH_2OH} > \underset{\text{(Less soluble)}}{CH_3CH_2CH_2OH}$$

Q. 53 Explain why p-nitrophenol is more acidic than phenol?

Ans. Nitro group of phenol produces $-I$ and $-R$ effect. Because of these two effects —NO_2 group is electron withdrawing in nature. So, the electron density in the O — H bond of *p*-nitrophenol decreases relative to the O — H bond of phenol.

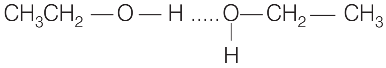
The decrease in electron density of the O — H bond of *p*-nitrophenol, the polarity of O — H bond is decrease and in turn make it more acidic than phenol.

Q. 54 Explain why alcohols and ethers of comparable molecular mass have different boiling points?

Ans. Boiling point depends upon the strength of intermolecular forces of attraction. Higher these forces of attraction, more will be the boiling point. Alcohols undergo intermolecular hydrogen bonding. So, the molecules of alcohols are held together by strong intermolecular forces of attraction.

But in ethers no hydrogen atom is bonded to oxygen. Therefore, ethers are held together by weak dipole-dipole forces, not by strong hydrogen bond.

Since, lesser amount of energy is required than to break weak dipole-dipole forces in ethers than to break strong hydrogen bonds in alcohol.

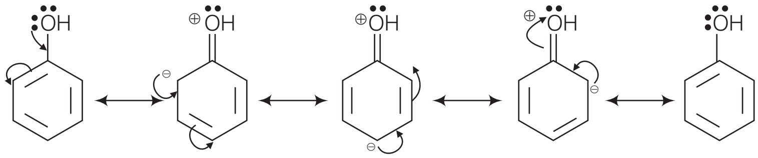


$$CH_3CH_2-O-H\ .....\underset{\substack{|\\ H}}{O}-CH_2-CH_3$$

Hydrogen bond in alcohols

Q. 55 The carbon-oxygen bond in phenol is slightly stronger than that in methanol. Why ?

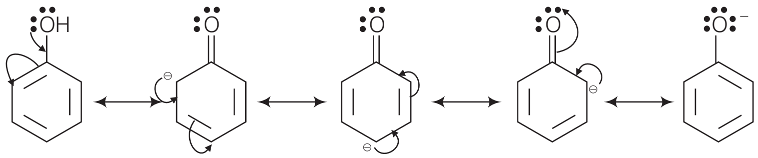
Ans. Positive resonance effect is observed in phenols. Due to this $+R$ effect, lone pair of electrons of —OH group are in conjugation with π electrons of the ring and the following resonance hybrid are obtained.



From the above resonating structure, it is very clear that C — O bond of phenol acquires some partial double bond character while the C — O bond of methanol is purely single bond. Therefore, the carbon-oxygen bond in phenol is slightly stronger than that in methanol.

Q. 56 Arrange water, ethanol and phenol in increasing order of acidity and give reason for your answer.

Ans. *The phenoxide ion obtained after the removal of a proton is resonance stabilised as follows*

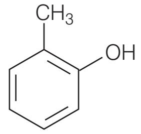
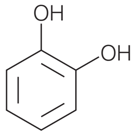
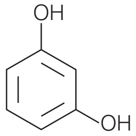
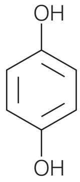
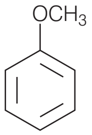
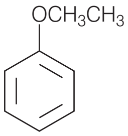


Whereas, the ethoxide ion obtained after the removal of a proton is not stabilised but destabilised due to $+I$ effect of $—C_2H_5$ group. Therefore, phenol is a stronger acid than ethanol. $+I$ effect of $CH_3 — CH_2$ group increase the electron density on $O — H$ bond in ethanol. As the electron density on the $O — H$ bond of ethanol is more than that of water. So, ethanol is a weaker acid than water. Thus, the increasing order of acidity is

$$\text{ethanol} < \text{water} < \text{phenol}$$

Matching The Columns

Q. 57 Match the structures of the compounds given in Column I with the name of the compounds given in Column II.

Column I	Column II
A. 	1. Hydroquinone
B. 	2. Phenetole
C. 	3. Catechol
D. 	4. *o*-cresol
E. 	5. Quinone
F. 	6. Resorcinol
	7. Anisole

Ans. **A.** → (4) **B.** → (3) **C.** → (6) **D.** → (1) **E.** → (7) **F.** → (2)

A. Cresols are organic compounds which are methyl phenols. There are three forms of cresol-*o*-cresol, *p* – cresol and *m* – cresol.

B. Catechol is also known as pyrocatechol. Its IUPAC name is 1, 2- dihydrobenzene. It is used in the production of pesticides, perfumes and pharmaceuticals.

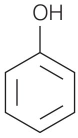
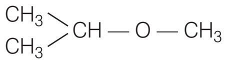
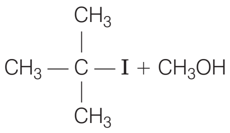
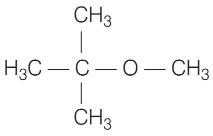
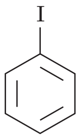
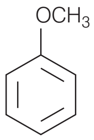
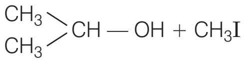
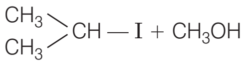
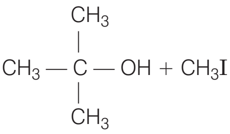
C. Its IUPAC name is 1, 3- dihydroxybenzene. Resorcinol is used to treat acne, seborrheic dermatitis and other skin disorder.

D. Hydroquinone is also known as quinol. Its IUPAC name is 1, 4- dihydroxybenzene. It is a white granular solid. It is a good reducing agent.

E. Anisole or methoxy benzene, is a colourless liquid with a smell reminiscent of anise seed.

F. Phenetole is an organic compound. It is also known as ethylphenyl ether. It is volatile in nature and its vapours are explosive in nature.

Q. 58 Match the starting material given in Column I with the products formed by these (Column II) in the reaction with HI.

Column I	**Column II**
A. CH_3-O-CH_3	1.  + CH_3I
B.  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH-O-CH_3$	2.  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I+CH_3OH$
C.  $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3$	3.  + CH_3OH
D. 	4. $CH_3-OH+CH_3I$
	5.  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH-OH+CH_3I$
	6.  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH-I+CH_3OH$
	7.  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH+CH_3I$

Ans. **A.** → (4) **B.** → (5) **C.** → (2) **D.** → (1)

A. $CH_3 — O — CH_3$ is a symmetrical ether so the products are CH_3I and CH_3OH.

B. In $(CH_3)_2CH — O — CH_3$ unsymmetrical ether, one alkyl group is primary while another is secondary. So, it follows $S_N{}^2$ mechanism. Thus, the halide ion attacks the smaller alkyl group and the products are

$$\begin{matrix} H_3C \\ H_3C \end{matrix} \!\!> CHOH + CH_3I$$

C. In this case, one of the alkyl group is tertiary and the other is primary. It follows $S_N{}^1$ mechanism and halide ion attacks the tertiary alkyl group and the products are $(CH_3)_3\ C — I$ and CH_3OH.

D. Here, the unsymmetrical ether is alkyl aryl ether. In this ether $O — CH_3$ bond is weaker than $O — C_6H_5$ bond which has partial double bond character due to resonance. So, the halide ion attacks on alkyl group and the products are $C_6H_5 — OH$ and CH_3I.

Q. 59 Match the items of Column I with items of Column II.

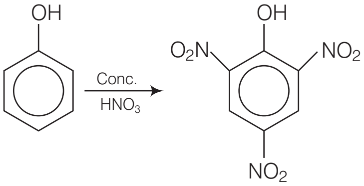
	Column I		Column II
A.	Antifreeze used in car engine	1.	Neutral ferric chloride
B.	Solvent used in perfumes	2.	Glycerol
C.	Starting material for picric acid	3.	Methanol
D.	Wood spirit	4.	Phenol
E.	Reagent used for detection of phenolic group	5.	Ethylene glycol
F.	By product of soap industry used in cosmetics	6.	Ethanol

Ans. **A.** → (5) **B.** → (6) **C.** → (4) **D.** → (3) **E.** → (1) **F.** → (2)

A. IUPAC name of ethylene glycol is ethane –1, 2 - diol. It is primarily used as raw material in the manufacturing of polyester fibers and fabric industry. A small percentage of it is used in antifreeze formulations.

B. Ethanol is a good solvent for fatty and waxy substances. Fats and waxes provide odour to the perfumes. Apart from being a good solvent, it is less irritating to the skin. So, it is used in perfumes.

C. Phenol is converted into picric acid (2, 4, 6-trinitro-phenol) by the reaction of phenol with conc. HNO_3.

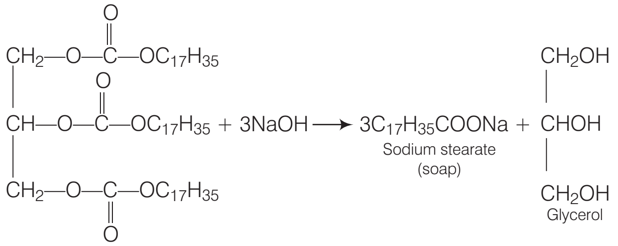


(Picric acid)

D. Methanol, CH_3OH is also known as 'wood spirit' as it was produced by the destructive distillation of wood.

E. Neutral ferric chloride give purple/red colour when treated with phenols. It is the reagent used for detection of phenolic group.

F. Soaps are prepared by the reactions of fatty acid with NaOH.



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-OC_{17}H_{35} \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-OC_{17}H_{35} \\ | \\ CH_2-O-\underset{\underset{O}{\|}}{C}-OC_{17}H_{35} \end{array} + 3NaOH \longrightarrow \underset{\text{Sodium stearate (soap)}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerol}}{\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}}$$

This glycerol (propan -1, 2, 3 - triol) is the by product of soap industry and used in cosmetics.

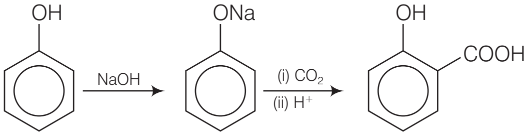
Q. 60 Match the items of Column I with items of Column II.

	Column I		Column II
A.	Methanol	1.	Conversion of phenol to *o* – hydroxysalicylic acid
B.	Kolbe's reaction	2.	Ethyl alcohol
C.	Williamson's synthesis	3.	Conversion of phenol to salicylaldehyde
D.	Conversion of 2° alcohol to ketone	4.	Wood spirit
E.	Reimer-Tiemann reaction	5.	Heated copper at 573K
F.	Fermentation	6.	Reaction of alkyl halide with sodium alkoxide

Ans. **A.** → (4) **B.** → (1) **C.** → (6) **D.** → (5) **E.** → (3) **F.** → (2)

A. Methanol is also known as 'wood spirit' as it was produced by the destructive distillation of wood.

B. In Kolbe's reaction, 2 – hydroxy benzoic acid (salicylic acid) is prepared by the reaction of phenol with CO_2 gas.

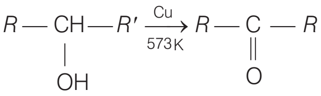


2-hydroxybenzoic acid
(salicylic acid)

C. Williamson synthesis is an important method for the preparation of ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.

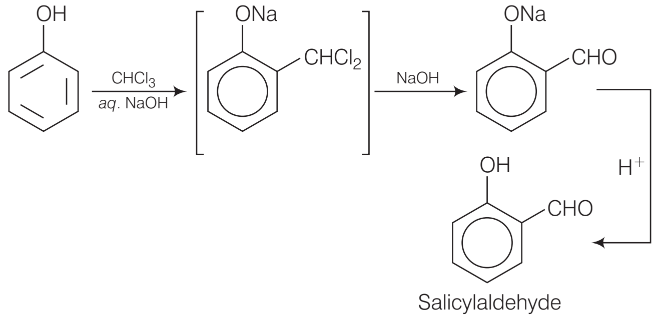
$$R-X + R-ONa \longrightarrow ROR + NaX$$

D. When a 2° alcohol is allowed to pass over heated copper at 573 K, dehydrogenation takes place and an ketone is formed.



$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow[573K]{Cu} R-\underset{\underset{O}{\|}}{C}-R$$

E. On treating phenol with chloroform in the presence of NaOH, an aldehydic group is introduced at *ortho* position of benzene ring



Salicylaldehyde

F. Ethanol is prepared by the fermentation of sugars.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Assertion and Reason

In the following questions a statement of Assertion (A) *followed by a statement of Reason* (R) *is given. Choose the correct answer out of the following choices.*

(a) Assertion and reason both are correct and reason is correct explanation of assertion.

(b) Assertion and reason both are wrong statements.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(e) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

Q. 61 Assertion (A) Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol.

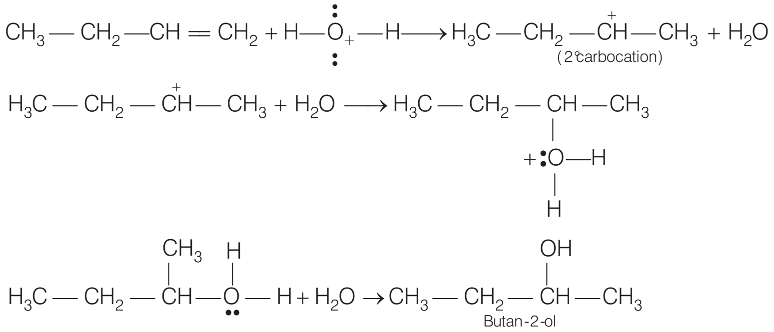
Reason (R) Addition of water in acidic medium proceeds through the formation of primary carbocation.

Ans. ***(b)*** Assertion and reason both are wrong statements.

Correct Assertion Addition reaction of water to but-1-ene in acidic medium yields butan-2-ol.

Correct Reason Addition of water in acidic medium proceeds through the formation of secondary carbocation.

Mechanism $H_2O + H^+ \longrightarrow H_3O^+$



$$CH_3-CH_2-CH=CH_2 + H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{}_{+}-H \longrightarrow H_3C-CH_2-\underset{(2^\circ\text{carbocation})}{\overset{+}{C}H}-CH_3 + H_2O$$

$$H_3C-CH_2-\overset{+}{C}H-CH_3 + H_2O \longrightarrow H_3C-CH_2-\underset{\substack{|\\ +\,:O-H\\ |\\ H}}{CH}-CH_3$$

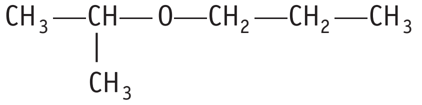
$$H_3C-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{H}{|}}{\underset{\cdot\cdot}{O}}-H + H_2O \rightarrow CH_3-\underset{\text{Butan-2-ol}}{CH_2-\overset{\overset{OH}{|}}{CH}}-CH_3$$

Q. 62 Assertion (A) p-nitrophenol is more acidic than phenol.

Reason (R) Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

Ans. *(a)* Assertion and reason both are correct and reason is correct explanation of assertion. *p*-nitrophenol is more acidic than phenol because nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

Q. 63 Assertion (A) IUPAC name of the compund



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_2-CH_2-CH_3$$ is 2-ethoxy-2-methylethane

Reason (R) In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by $-OR$ or $-OAr$ group [where, R = alkyl group and Ar = aryl group].

Ans. *(d)* Assertion is wrong statement but reason is correct statement.

Correct Assertion The IUPAC name of the given compound is 1-(2-propoxy) propane.

Q. 64 Assertion (A) Bond angle in ethers is slightly less than the tetrahedral angle.

Reason (R) There is a repulsion between the two bulky (– R) groups.

Ans. *(d)* Assertion is wrong statement but reason is correct statement.

Correct Assertion Bond angle in ether is slightly more than the tetrahedral angle.

Q. 65 Assertion (A) Boiling points of alcohols and ethers are high.

Reason (R) They can form intermolecular hydrogen-bonding.

Ans. *(b)* Assertion and reason both are wrong statements.

Correct Assertion Boiling points of alcohols are higher than that of ethers of comparable molecular mass.

Correct Reason Alcohols can form intermolecular hydrogen bonding while ethers cannot.

Q. 66 Assertion (A) Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

Reason (R) Lewis acid polarises the bromine molecule.

Ans. *(d)* Assertion is wrong statement but reason is correct statement.

Correct Assertion Bromination of benzene but not of phenol is carried out in presence of a Lewis acid.

Q. 67 Assertion (A) o-nitrophenol is less soluble in water than the m and p-isomers.

Reason (R) m and p-nitrophenols exist as associated molecules.

Ans. *(d)* Both assertion and reason are correct statements but reason is not correct explanation of assertion.

Correct Explanation Due to the presence of intramolecular hydrogen bonding, *o*-nitrophenol does not form hydrogen bonds with H_2O but *m* and *p*-nitrophenol form hydrogen bonds with water.

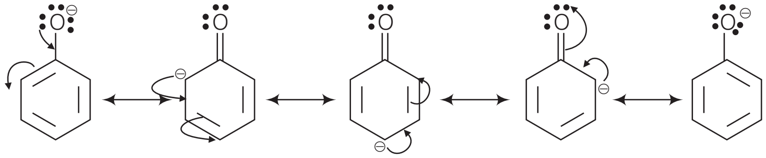
Q. 68 Assertion (A) Ethanol is a weaker acid than phenol.

Reason (R) Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

Ans. *(c)* Assertion is correct statement but reason is wrong statement.

Correct Reason Phenoxide ion is stabilised by resonance but ethoxide ion is not stabilised by resonance.

Resonance in phenoxide ion

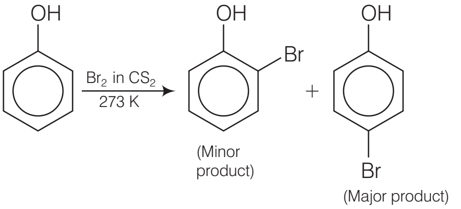


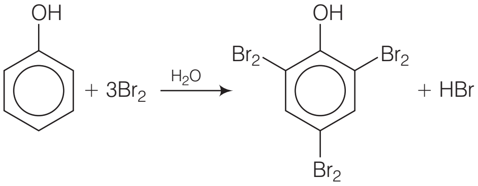
Q. 69 Assertion (A) Phenol forms 2, 4, 6-tribromophenol on treatment with Br_2 in carbon disulphide at 273K.

Reason (R) Bromine polarises in carbon disulphide.

Ans. *(b)* Assertion and reason both are wrong statements.

Correct Assertion Phenol form 2, 4, 6-tribromophenol on treatment with bromine in water.





2,4,6-tribromophenol

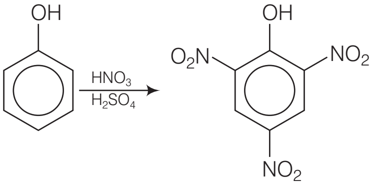
Correct Reason In water, phenol gives phenoxide ion. This phenoxide ion activates the ring towards electrophilic substitution reaction.

Q. 70 Assertion (A) Phenols give o-and p-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.

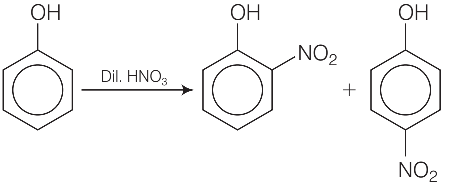
Reason (R) —OH group in phenol is o-,p-directing.

Ans. *(d)* Assertion is wrong statement but reason is correct statement.

Correct Assertion Phenols give *o* and *p*-nitrophenol on nitration with dil. HNO_3 at 298 K.



2, 4, 6-trinitrophenol



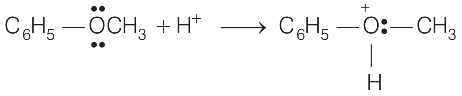
o-nitrophenol *p*-nitrophenol

Long Answer Type Questions

Q. 71 Write the mechanism of the reaction of HI with methoxybenzene.

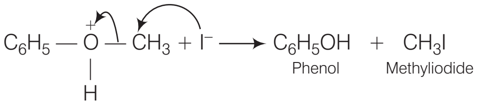
Ans. In case of alkyl aryl ethers, the products are always phenol and an alkyl halide because due to resonance C_6H_5 — O bond has partial double bond character. The mechanism is given below

Mechanism Protonation of anisole gives methylphenyl oxonium ion.



$$C_6H_5-\ddot{\underset{\cdot\cdot}{O}}CH_3 + H^+ \longrightarrow C_6H_5-\underset{\displaystyle H}{\overset{+}{O}}\!:\!-CH_3$$

In this ion, the bond between O — CH_3 is weaker than the bond between O — C_6H_5 which has partial double bond character. This partial double bond character is due to the resonance between the lone pair of electrons on the O - atom and the sp^2 hybridised carbon atom of the phenyl group. Therefore, attack by I^- ion exclusively breaks the weaker O — CH_3 bond forming methyl iodide and phenol.



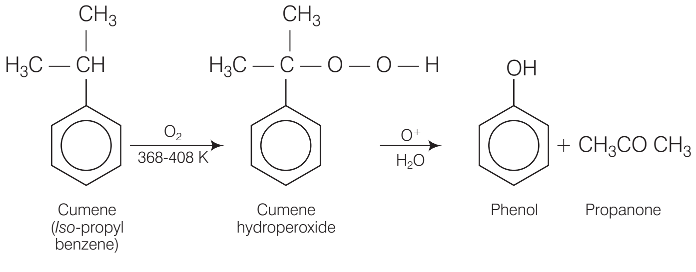
$$C_6H_5-\underset{\displaystyle H}{\overset{+}{O}}-CH_3 + I^- \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Methyliodide}}{CH_3I}$$

Q. 72 (a) Name the starting material used in the industrial preparation of phenol.

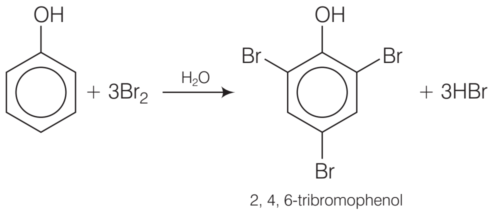
(b) Write complete reaction for the bromination of phenol in aqueous and non-aqueous medium.

(c) Explain why Lewis acid is not required in bromination of phenol?

Ans. **(a)** The starting material used in the industrial preparation of phenol is cumene.

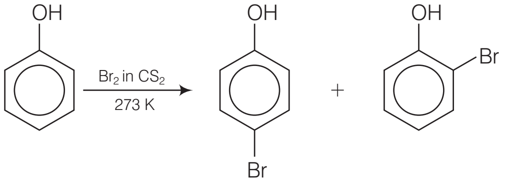


(b) Phenols when treated with bromine water gives polyhalogen derivatives in which all the hydrogen atoms present at *ortho* and *para* positions with respect to — OH group are replaced by bromine atoms.



2, 4, 6-tribromophenol
(white ppt.)

However, in non-aqueous medium such as CS_2, CCl_4, $CHCl_3$, monobromophenols are obtained.



Phenol 4-bromophenol 2-bromophenol

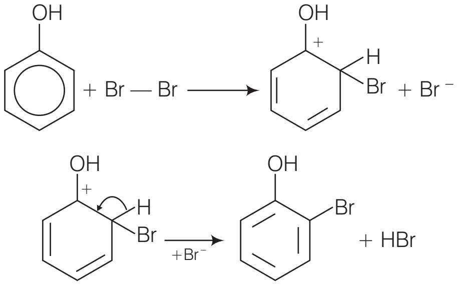
In aqueous solution, phenol ionises to form phenoxide ion. This ion activates the benzene ring to a very large extent and hence the substitution of halogen takes place at all three positions.

On the other hand, in non-aqueous solution ionisation of phenol is greatly suppressed. Therefore, ring is activated slightly and hence monosubstitution occur.

(c) Lewis acid is an electron deficient molecule. In bromination of benzene, Lewis acid is used to polarise Br_2 to form Br^+ electrophile.

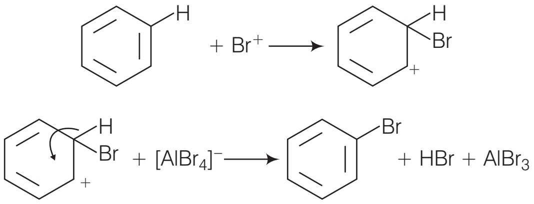
In case of phenol, oxygen atom of phenol itself polarises the bromine molecule to form Br^+ ion (electrophile). So, Lewis acid is not required in the bromination of phenol.

Mechanism of bromination of phenol



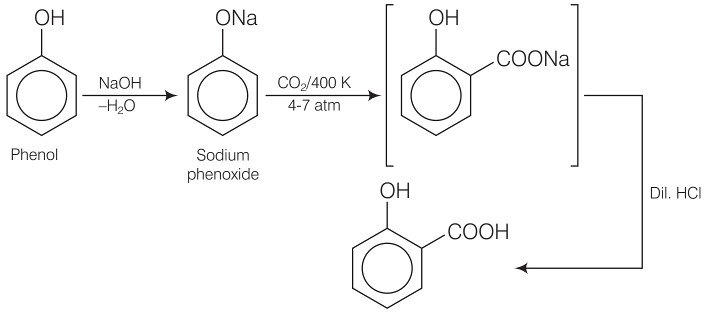
Mechanism of bromination of benzene

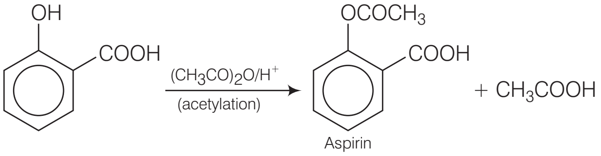
$$AlBr_3 + Br — Br \longrightarrow [AlBr_4]^- + Br^+$$



Q. 73 How can phenol be converted to aspirin?

Ans. Phenol is converted into salicylic acid. This salicylic acid is treated with acetic anhydride. On acetylation of salicylic acid, aspirin (acetyl salicylic acid) is formed.





Q. 74 Explain a process in which a biocatalyst is used in industrial preparation of a compound known to you.

Ans. Enzymes are biocatalyst. These biocatalysts (enzymes) are used in the industrial preparation of ethanol. Ethanol is prepared by the fermentation of molasses - a dark brown coloured syrup left after crystallisation of sugar which still contains about 40% of sugar.

The process of fermentation actually involves breaking down of large molecules into simple ones in the presence of enzymes. The source of these enzymes is yeast. The various reactions taking place during fermentation of carbohydrates are

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions *i.e.,* in absence of air. CO_2 gas is released during fermentation.

The action of zymase is inhibited once the percentage of alcohol formed exceeds 14 per cent. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.