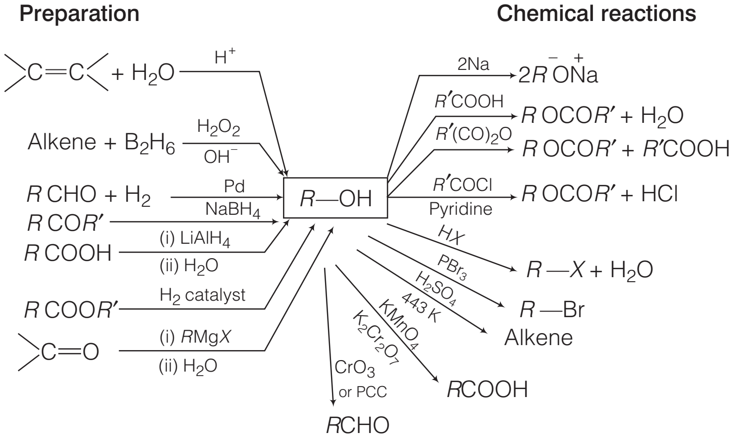
## CHAPTER

# 11

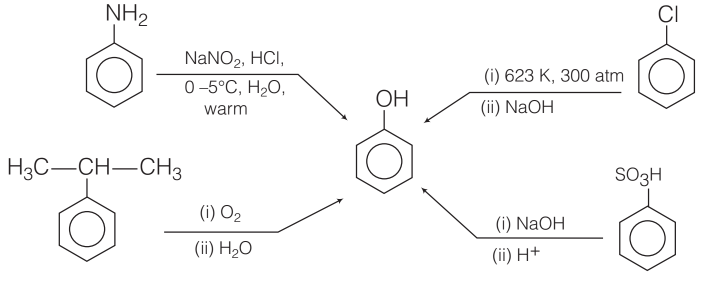
# Alcohols, Phenols and Ethers

## A Quick Recapitulation of the Chapter

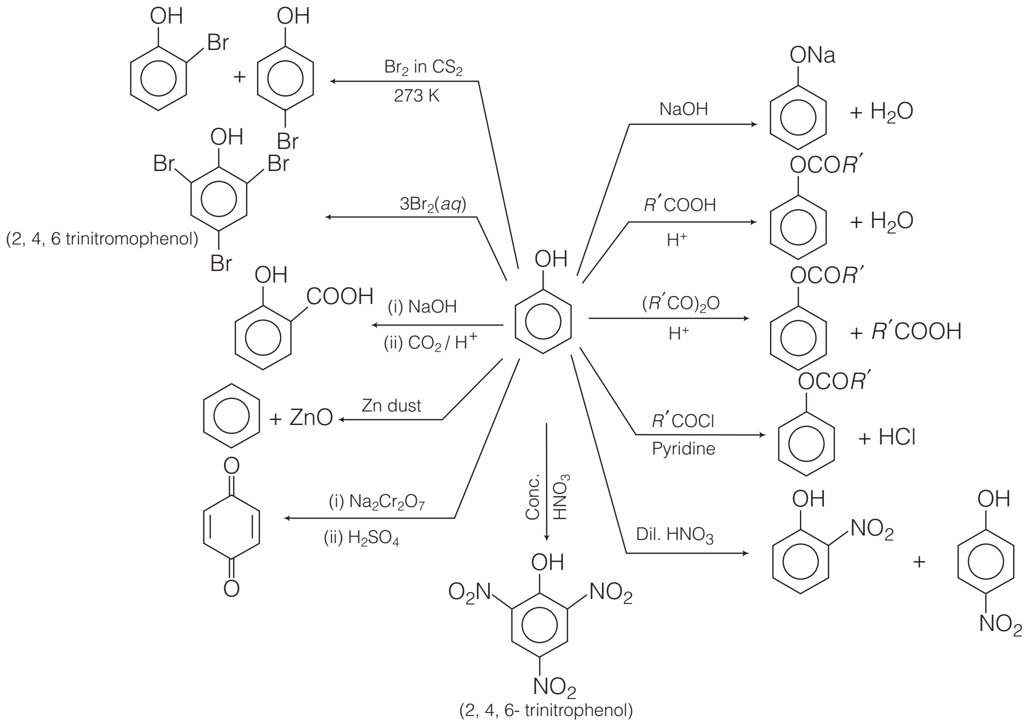
1. Alcohols are the hydroxy derivatives of alkanes with general formula $C_n H_{2n+1}OH$.
2. **Preparation and Chemical Reactions of Alcohols**



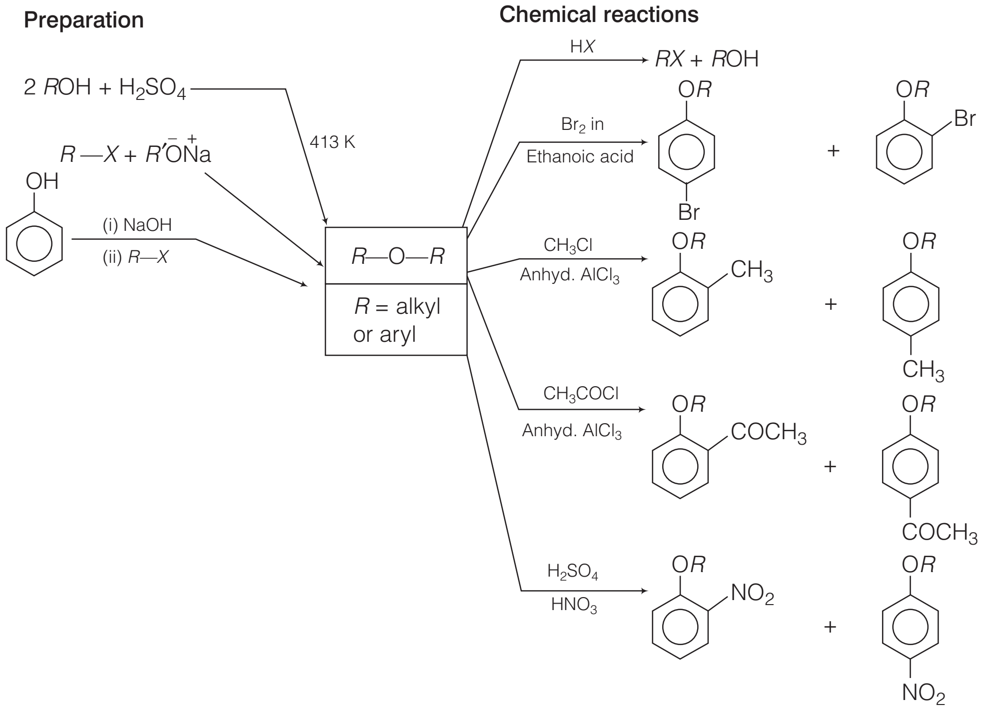
3. **Preparation of Phenol**



## 4. Chemical Reactions of Phenol



## 5. Preparation and Chemical Reactions of Ethers



# Objective Questions Based on NCERT Text

## Topic 1

## General Introduction

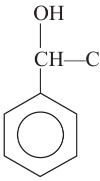
**1.** Which of the following compound containing hydroxyl group is used for polishing the wooden furniture?
(a) Anisole (b) Phenol
(c) Ethanol (d) All of these

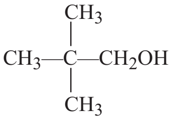
**2.** Which of the functional group is present in paper, cotton and sugar?
(a) $NH_2$ group (b) OH group
(c) COO$R$ group (d) $RX$ group

**3.** The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group yields another class of compounds known as
(a) alcohol (b) phenol (c) ethers (d) ester

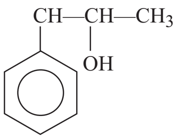
**4.** Which of the following alcohol contains $C_{sp^3}$ — OH bond?
(a) Allylic alcohol (b) Vinylic alcohol
(c) Phenols (d) None of these

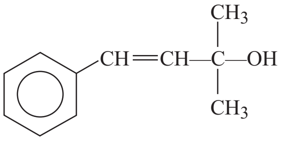
**5.** Identify the primary alcohol among the given options.

(a) 

(b) 

$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—CH_2OH$

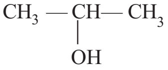
(c) 

(d) 

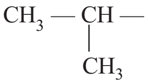
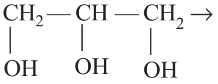
**6.** Which one of them is an incorrect match?
(a) Diethyl ether → simple ether
(b) $C_2H_5OC_6H_5 \rightarrow$ mixed ether
(c) $C_2H_5OCH_3 \rightarrow$ unsymmetrical ether
(d) $C_2H_5OC_2H_5 \rightarrow$ unsymmetrical ether

**7.** Select the incorrect statement from the following options.
(a) The common name of an alcohol is derived from the common name of the alkyl group by adding the word alcohol to it.
(b) The IUPAC name of an alcohol is derived from the name of the alkane from which the alcohol is derived by substituting 'e' of alkane with suffix 'ol'.
(c) The longest carbon chain is numbered starting at the end nearest to the hydroxyl group. The positions of the — OH group and other substituents are indicated by using the number of carbon atoms to which these are attached.
(d) In case of polyhydric alcohols the 'e' of alkane is not retained and ending di, tri 'ol' is added.

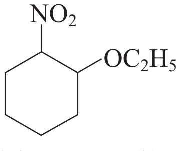
**8.** Observe the following table,

| **Compound** | **Common name** | **IUPAC name** |
|---|---|---|
| $CH_3$ — OH | Methyl alcohol | I |
| $CH_3CH_2CH_2OH$ | *n*-propyl alcohol | Propan-1-ol |
|  $CH_3—\underset{OH}{CH}—CH_3$ | II | Propan-2-ol |
| III | *n*-butyl alcohol | Butan-1-ol |

Identify I, II and III from the above table.
(a) I → methanol; II → *tert*-propyl alcohol;
II → $CH_3CH_2CH_2CH_2OH$
(b) I → methanol; II → propyl alcohol;
III → $CH_3CH_2CH_2OH$
(c) I → methanol; II → *iso*-propyl alcohol;
III → $CH_3CH_2CH_2CH_2OH$
(d) I → methanol; II → *tert*-propyl alcohol;
III → $CH_3CH_2CH_2OH$

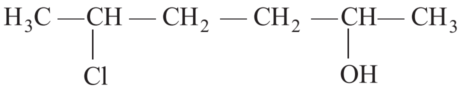
**9.** Select the incorrect match from the following options.
(a) Butan-2-ol → *sec*-butyl alcohol
(b)  $CH_3—\underset{CH_3}{CH}—CH_2OH \rightarrow$ *iso*-butyl alcohol
(c)  $\underset{OH}{CH_2}—\underset{OH}{CH}—\underset{OH}{CH_2} \rightarrow$ glycerol
(d) 1,1-dimethylethan–1– ol→ *iso* butyl alcohol

**10.** Which of the following statement(s) is/are true?
(a) If both the alkyl groups are the same in ethers, the prefix 'di' is added before the name of alkyl group
(b) Ethers are regarded as hydrocarbon derivatives, in which a hydrogen atom is replaced by an — O$R$ and OAr group. The larger $R$ group is chosen as the parent hydrocarbon
(c) Both (a) and (b)
(d) None of the above

**11.** IUPAC name of  is

(a) ethyl-2-nitrocyclohexane (b) 1-ethoxy-2-nitrocyclohexane
(c) 1-nitro-2-ethoxycyclohexane (d) 2-nitro-1-ethoxycyclohexane

**12.** Give IUPAC name of the compound given below



$H_3C-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_2-CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$

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

**13.** How many σ bonds are present in the $CH_3CH_2OH$?

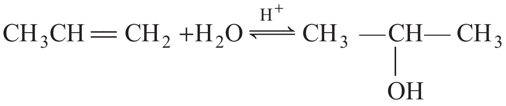
(a) 8
(b) 6
(c) 5
(d) 4

**14.** In ethers, the two bond pairs and two lone pairs of electrons on oxygen are arranged in a

(a) planar arrangement
(b) tetrahedral arrangement
(c) trigonal bipyramidal arrangement
(d) linear arrangement

## Topic 2
# Methods for Preparation of Alcohols and Phenols

**15.** Alkenes react with water in the presence of acid as catalyst to form alcohols.



$CH_3CH=CH_2+H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$

The reaction takes place in accordance with

(a) Hofmann elimination rule
(b) Saytzeff rule
(c) Markownikoff's rule
(d) Anti-Markownikoff's addition

**16.** Which of the following statement(s) is/are correct about hydroboration oxidation?

(a) Diborane reacts with alkenes to give trialkyl boranes as addition product which is oxidised to alcohol by $H_2O_2$ in the presence of aqueous NaOH
(b) The alcohol so formed can also be obtained by the addition of water to the alkene by Markownikoff's rule
(c) Alcohol is obtained in the poor yield
(d) All of the above

**17.** The reagent(s) used for the reduction of aldehydes and ketone into alcohols is/are

(a) finely divided metals such as Pt/Pd/Ni
(b) sodium borohydride
(c) lithium aluminium hydride
(d) All of the above

**18.** On reduction of aldehydes and ketones, the compounds formed are respectively.

(a) 1° alcohol; 2° alcohols
(b) 2° alcohols; 1° alcohol
(c) 1° alcohol; 3° alcohols
(d) 3° alcohols; 1° alcohol

**19.** The reaction of Grignard reagent with carbonyl compound is a nucleophilic addition reaction. This reaction on hydrolysis produces

(a) ester (b) alcohol
(c) carboxylic acid (d) ether

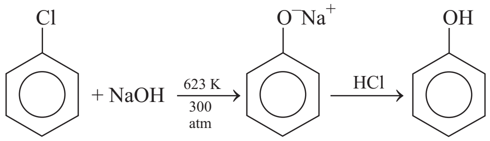
**20.** What is the another name for phenol?

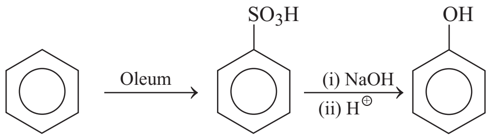
(a) Phenolic acid (b) Carbonic acid
(c) Both (a) and (b) (d) Carbolic acid

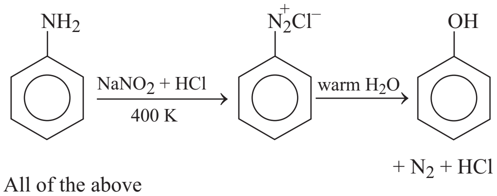
**21.** Which of the following hydrocarbon is used for the world wide production of phenol?

(a) *Iso*-butylbenzene (b) *Iso*-propylbenzene
(c) *Iso*-pentylbenzene (d) None of these

**22.** Identify which is/are the correct method(s) to synthesise the phenol?

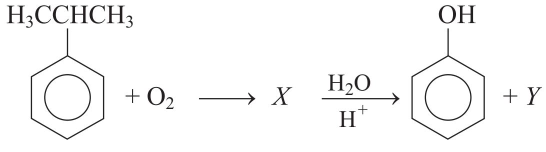
(a) 

(b) 

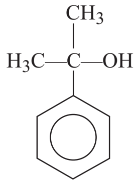
(c) 

(d) All of the above

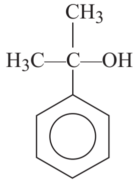
**23.** In the given reaction,



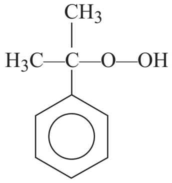
Choose '*X*' and '*Y*' for the reaction.

(a) 

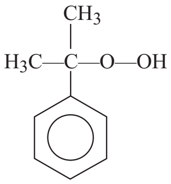
; $CH_3CH_2CH_3$

(b) 

; $CH_3COCH_3$

(c) 

; $CH_3CH_2CH_3$

(d) 

; $CH_3COCH_3$

## Topic 3

# Properties of Alcohols and Phenols

**24.** Select the incorrect option from the following regarding the physical properties of alcohol and phenol.

(a) The boiling point of alcohols and phenols are higher in comparison to hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses

(b) Ethanol and propane have comparable boiling points but differ only in the molecular masses

(c) The OH group in alcohols and phenols is involved in the intermolecular hydrogen bonding

(d) The trend of boiling point is ethanol > methoxymethane > propane

**25.** Alcohols and phenols react with active metals to yield

(a) alkoxides/phenoxides

(b) hydrogen

(c) nitrogen

(d) Both (a) and (b)

**26.** Which of the following reaction is correct?

(a) $\underset{\text{Acid}}{B} + \underset{\text{Base}}{H\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}R} \longrightarrow \underset{\text{Conjugate base}}{BH} + \underset{\text{Conjugate acid}}{\overset{-}{O}R}$

(b) $\underset{\text{Base}}{B} + \underset{\text{Acid}}{H\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}R} \longrightarrow \underset{\text{Conjugate acid}}{BH} + \underset{\text{Conjugate base}}{\overset{-}{O}R}$

(c) $\underset{\text{Acid}}{B} + \underset{\text{Base}}{H\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}R} \longrightarrow \underset{\text{Conjugate acid}}{BH} + \underset{\text{Conjugate base}}{\overset{-}{O}R}$

(d) $\underset{\text{Base}}{B} + \underset{\text{Acid}}{H\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}R} \longrightarrow \underset{\text{Conjugate base}}{BH} + \underset{\text{Conjugate acid}}{\overset{-}{O}R}$

**27.** Select the correct statement(s).

(a) Alcohols are weaker acids than water

(b) Water is a better proton donor than alcohol

(c) Sodium ethoxide is a stronger base than sodium hydroxide

(d) All of the above

**28.** Cresols are less acidic than phenols because

(a) electron releasing groups favour the formation of phenoxide ion resulting in the decrease in acidic strength

(b) electron withdrawing groups favour the formation of phenoxide ion resulting in the decrease in acidic strength

(c) electron releasing groups do not favour the formation of phenoxide ion resulting in the decrease in acidic strength

(d) electron withdrawing groups do not favour the formation of phenoxide ion resulting in the decrease in acidic strength

**29.** p$K_a$ values of some phenols and ethanol are given in table.

| Compound | Formula | p$K_a$ |
|---|---|---|
| *o*-nitrophenol | $o\text{-}O_2N-C_6H_4-OH$ | 7.2 |
| *p*-nitrophenol | $p\text{-}O_2N-C_6H_4-OH$ | 7.1 |
| phenol | $C_6H_5-OH$ | 10.0 |
| ethanol | $C_2H_5OH$ | 15.9 |

Select the incorrect statement(s) from the above table.

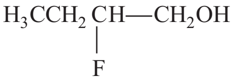
(a) The greater the p$K_a$ value, stronger is the acid
(b) Phenol is million times more acidic than ethanol
(c) Phenol is less acidic the *o*-nitrophenols
(d) *o*-and *p*-nitrophenol have nearly the equal acidic strength

**30.** Arrange the following compounds in the decreasing order of acidity.

(a) $H_2O > HC\equiv CH > ROH$
(b) $H_2O > ROH > HC\equiv CH$
(c) $HC\equiv CH > ROH > H_2O$
(d) $HC\equiv CH > H_2O > ROH$

**31.** Select the strongest acid among the following compounds.

(a) $FCH_2CH_2CH_2OH$

(b) 
$H_3CCH_2\underset{F}{CH}-CH_2OH$

(c) $CH_3CH_2CF_2CH_2OH$

(d) 
$CH_3\underset{F}{CH}CH_2CH_2OH$

**32.** Which of the following substrate reacts with alcohols and phenols to form esters?

(a) Carboxylic acids
(b) Acid chlorides
(c) Acid anhydrides
(d) All of the above

**33.** The reaction of alcohol/phenol with acid chloride is carried out in the presence of pyridine in order to

(a) neutralise HCl which is formed during the reaction
(b) shift the equilibrium to right hand side
(c) Both (a) and (b)
(d) None of the above

**34.** Phenols show the cleavage of C— O bond with

(a) Na
(b) K
(c) Zn
(d) Ca

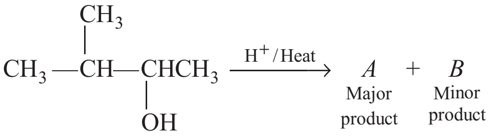
**35.** An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism? **(JEE Main 2013)**

(a) Secondary alcohol by $S_N1$
(b) Tertiary alcohol by $S_N2$
(c) Secondary alcohol by $S_N2$
(d) Tertiary alcohol by $S_N1$

**36.** Alcohols are converted to alkyl bromides by

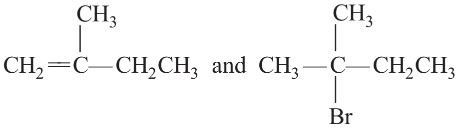
(a) $PBr_3$
(b) LAH
(c) $Br_2$
(d) None of these

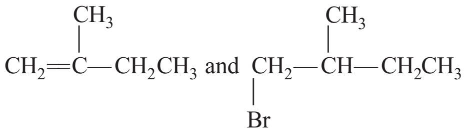
**37.** In the following reactions,

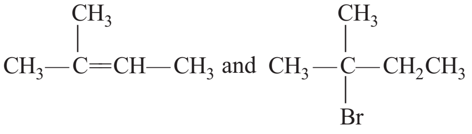
I. 
$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}CH_3 \xrightarrow{H^+/\text{Heat}} \underset{\substack{\text{Major}\\\text{product}}}{A} + \underset{\substack{\text{Minor}\\\text{product}}}{B}$

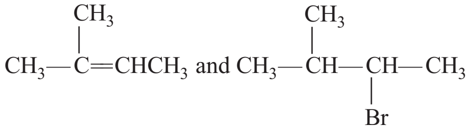
II. $A \xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}} \underset{\substack{\text{Major}\\\text{product}}}{C} + \underset{\substack{\text{Minor}\\\text{product}}}{D}$

The major products ($A$) and ($C$) are, respectively **(CBSE AIPMT 2011)**

(a) 
$CH_2=\overset{CH_3}{C}-CH_2CH_3$ and $CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2CH_3$

(b) 
$CH_2=\overset{CH_3}{C}-CH_2CH_3$ and $\underset{Br}{CH_2}-\overset{CH_3}{CH}-CH_2CH_3$

(c) 
$CH_3-\overset{CH_3}{C}=CH-CH_3$ and $CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2CH_3$

(d) 
$CH_3-\overset{CH_3}{C}=CHCH_3$ and $CH_3-\overset{CH_3}{CH}-\underset{Br}{CH}-CH_3$

**38.** Identify an appropriate reagent for the conversion of alcohol to carboxylic acid.

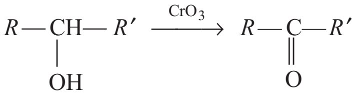
(a) PCC
(b) Anhydrous $CrO_3$
(c) Cu/573 K
(d) $KMnO_4/H^{\oplus}$

**39.** PCC is the

(a) complex of chromium trioxide with pyridine and HCl
(b) complex of chromium trioxide with ammonia and HCl
(c) complex of chromium dioxide with pyridine and HCl
(d) complex of chromium dioxide with ammonia and HCl

**40.** Which of the following option is/are true?

(a) $CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3CH_2CH_2CHO$

(b) 
$R-\underset{OH}{CH}-R' \xrightarrow{CrO_3} R-\underset{\|\atop O}{C}-R'$

(c) There is the cleavage of C— C bond in oxidation reaction by weak oxidising agents ($KMnO_4$) under weak reaction conditions

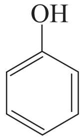
(d) All of the above

**41.** A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol. The enzyme responsible for the oxidation of aldehyde to acid is swamped allowing time for

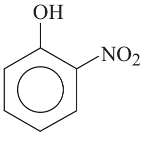
(a) liver to excrete methanol
(b) kidneys to excrete methanol
(c) liver to excrete methanal
(d) kidneys to excrete methanal

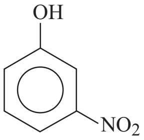
**42.** Electrophilic substitution reaction is given by the—OH group attached to the ring. It directs the incoming group at which position of the ring?

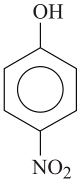
(a) *Ortho* and *meta*
(b) *Ortho* and *para*
(c) Only *ortho*
(d) Only *para*

**43.**  + dilute $HNO_3$ ⟶ ?

Select the product(s) formed in the given reaction.

(a) 

(b) 

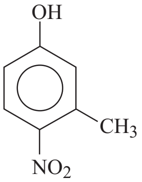
(c) 

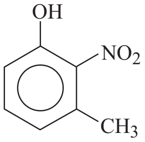
(d) Both (a) and (c)

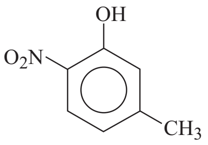
**44.** Which of the following statement(s) is/are true about picric acid?

(a) Picric acid is obtained in less quantity during the reaction of phenol with conc. $HNO_3$
(b) It is also prepared by treating phenol with conc. $H_2SO_4$ followed by conc. $HNO_3$
(c) Both (a) and (b)
(d) None of the above

**45.** What is the major product(s) formed by the mononitration of 3-methylphenol?

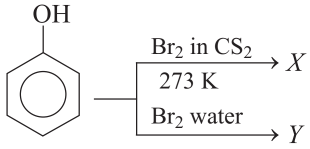
(a) 

(b) 

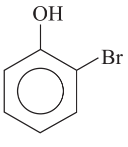
(c) 

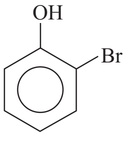
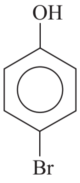
(d) Both (a) and (c)

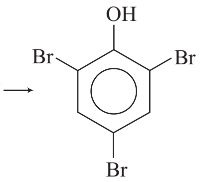
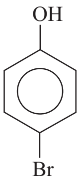
**46.** In the given reaction,

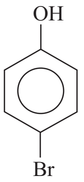
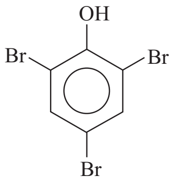


What is $X$ and $Y$ in the above reaction?

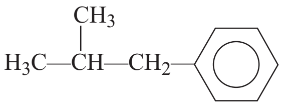
(a) $X$ ⟶  $Y$ ⟶ 

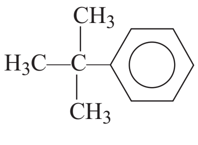
(b) $X$ ⟶  $Y$ ⟶ 

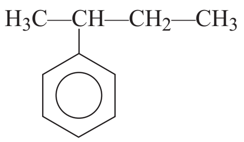
(c) $X$ ⟶  $Y$ ⟶ 

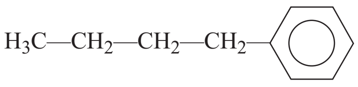
(d) $X$ ⟶  $Y$ ⟶ 

**47.** What is the major product formed during the reaction of benzene with *iso*propyl alcohol in the presence of conc. $H_2SO_4$?

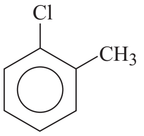
(a) 

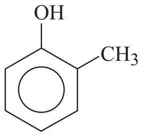
(b) 

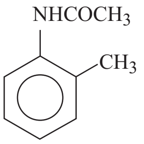
(c) 

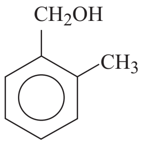
(d) 

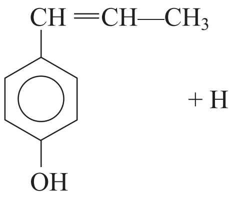
**48.** Electrophilic reagent reacts fastly with

(a) 

(b) 

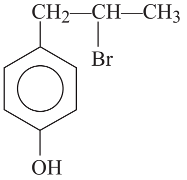
(c) 

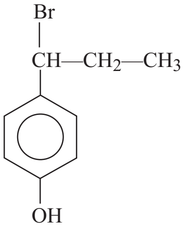
(d) 

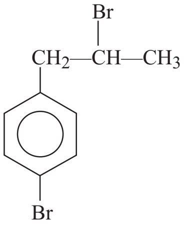
**49.** 

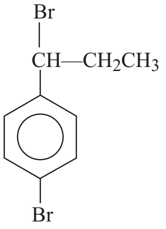
$+ HBr \longrightarrow ?$

What will be the product formed?

(a) 

(b) 

(c) 

(d) 

**50.** Select the incorrect statement about Kolbe's reaction.

(a) Phenoxide ion is less reactive than phenol towards electrophilic aromatic substitution

(b) A weak electrophile $CO_2$ is used in this reaction

(c) *Ortho*-hydroxybenzoic acid is formed as the main product

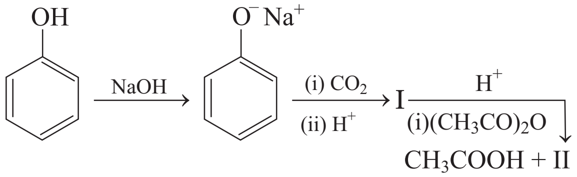
(d) Salicylic acid is formed as the main product

**51.** Salicylic acid and phenol can be distinguished by the use of

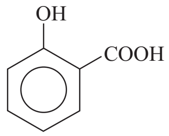
(a) bromine water (b) neutral $FeCl_3$

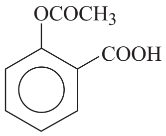
(c) 5% NaOH solution (d) $NaHCO_3$ solution

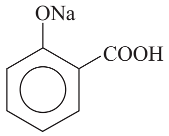
**52.** In the given reaction,

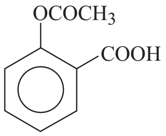


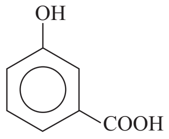
Identify I and II in the above reaction.

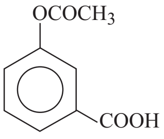
(a) (I) 

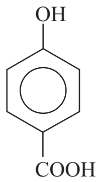
(II) 

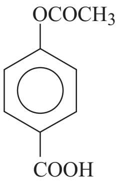
(b) (I) 

(II) 

(c) (I) 

(II) 

(d) (I) 

(II) 

**53.** The electrophile used in Reimer-Tiemann reaction is

(a) $CCl_3^{\oplus}$ (b) $:CCl_2$ (c) $Cl^{\oplus}$ (d) $H_2O$

**54.** $RCH_2CH_2OH \xrightarrow{?} RCH_2CH_2CH_2NH_2$

Identify the sequence of the reagents in order to carry out the above conversion.

(a) (i) $PBr_3$ (ii) KCN (iii) $LiAIH_4$

(b) (i) $PBr_3$ (ii) KCN (iii) $H_2$

(c) (i) HCN (ii) $PHr_3$ (iii) $LiAIH_4$

(d) (i) HCN (ii) $LiAIH_4$

## Topic 4

## Some Commercially Important Alcohols

**55.** Which of the following is also known as wood spirit?

(a) Ethanol (b) Propanol
(c) Methanol (d) Butanol

**56.** $X + H_2 \xrightarrow[\substack{200\text{-}300 \text{ atm} \\ 573-673\text{ K}}]{Y} CH_3OH$

What is $X$ and $Y$ in the given reaction?

| | $X$ | $Y$ |
|---|---|---|
| (a) | $CO_2$, | $ZnO - CrO_3$ |
| (b) | $CO$, | $ZnO - Cr_2O_3$ |
| (c) | $CO_2$, | $ZnO - Cr_2O_3$ |
| (d) | $CO$, | $ZnO - CrO_3$ |

**57.** Ethanol is commercially obtained by

(a) destructive distillation (b) fermentation
(c) vacuum distillation (d) All of these

**58.** $\underset{\text{(found in molasses)}}{\text{Sugar}} + H_2O \xrightarrow{X} \text{Glucose + fructose}$

$\underset{\text{(found in yeast)}}{\text{Glucose/fructose}} \xrightarrow{Y} \text{Ethanol} + CO_2$

Select the enzyme used in the above reactions.

(a) $X \rightarrow$ invertase, $Y \rightarrow$ zymase
(b) $X \rightarrow$ zymase, $Y \rightarrow$ invertase
(c) $X$ and $Y \rightarrow$ invertase
(d) $X$ and $Y \rightarrow$ zymase

**59.** The action of zymase is inhibited during fermentation if the percentage of alcohol formed exceeds

(a) 5% (b) 7%
(c) 10% (d) 14%

**60.** Denaturation of alcohol is the

(a) mixing of $CuSO_4$ (a foul smelling solid) and pyridine (to give the colour) to make the commercial alcohol unfit for drinking
(b) mixing of $CuSO_4$ (to give the colour) and pyridine (a foul smelling solid) to make the commercial alcohol unfit for drinking
(c) mixing of $Cu(OAc)_2$ and ammonia to make the commercial alcohol unfit for drinking
(d) mixing of $Cu(OAc)_2$ and pyridine to make the commercial alcohol unfit for drinking

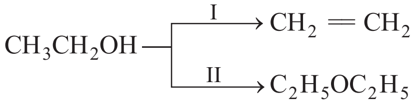
## Topic 5

## Preparation and Properties of Ethers

**61.** Which of the following method is used for the preparation of symmetrical and unsymmetrical ether?

(a) Williamson's synthesis (b) Riemer-Tiemann reaction
(c) Kolbe's reaction (d) None of these

**62.** Identify the reaction condition for the reaction to occur.



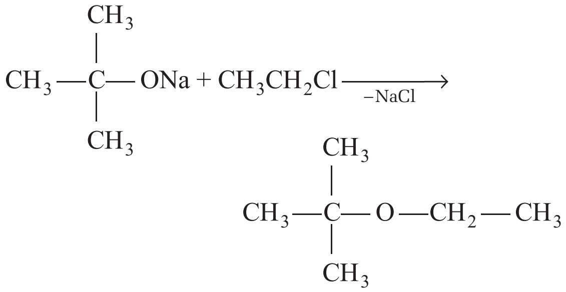
$$CH_3CH_2OH \begin{cases} \xrightarrow{\text{I}} CH_2 = CH_2 \\ \xrightarrow{\text{II}} C_2H_5OC_2H_5 \end{cases}$$

(a) I $\rightarrow H_2SO_4$, 443 K II $\rightarrow H_2SO_4$, 443 K
(b) I $\rightarrow H_2SO_4$, 413 K II $\rightarrow H_2SO_4$, 413 K
(c) I $\rightarrow H_2SO_4$, 443 K II $\rightarrow H_2SO_4$, 413 K
(d) I $\rightarrow H_2SO_4$, 413 K II $\rightarrow H_2SO_4$, 443 K

**63.** Williamson's synthesis involves which of the following type of mechanism when attack of an alkoxide ion on primary alkyl halide takes place?

(a) $S_N1$ (b) $S_N2$
(c) E1 (d) E2

**64.** The reaction,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa + CH_3CH_2Cl \xrightarrow[-NaCl]{} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2-CH_3$$

is called **(CBSE AIPMT 2015)**

(a) Williamson synthesis
(b) Williamson continuous etherification process
(c) Etard reaction
(d) Gattermann-Koch reaction

**65.** Among the following sets of reactants which one produces anisole? **(CBSE AIPMT 2014)**

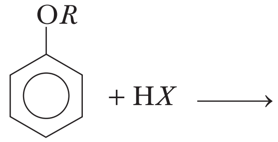
(a) $CH_3CHO$, $RMgX$
(b) $C_6H_5OH$, NaOH, $CH_3I$
(c) $C_6H_5OH$, neutral $FeCl_3$
(d) $C_6H_5-CH_3$, $CH_3COCl$, $AlCl_3$

**66.** Ethers have a net dipole moment because
(a) C—O bonds in ethers are non-polar
(b) C—O bonds in ethers are polar
(c) C—C bonds in ethers are polar
(d) C—C bonds in ethers are non-polar

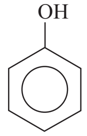
**67.** Select the correct increasing order of their boiling point.
(a) *n*-pentane, ethoxyethane, butan-1-ol
(b) ethoxyethane, *n*-pentane, butan-1-ol
(c) butan-1-ol, *n*-pentane, ethoxyethane
(d) ethoxyethane, butan-1-ol, *n*-pentane

**68.** The large difference in the boiling points of alcohols and ethers is due to the presence of
(a) van der Waals' forces in alcohols
(b) dipole-dipole interactions in alcohols
(c) hydrogen bonding in alcohols
(d) ion-ion interaction in alcohols

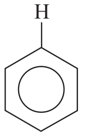
**69.** In the given reaction,



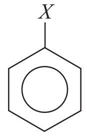
the product is/are

(a) 

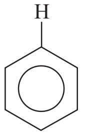
+ $RX$

(b) 

+ $RX$

(c) 

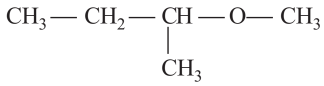
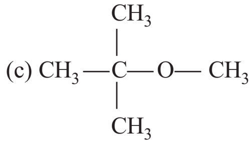
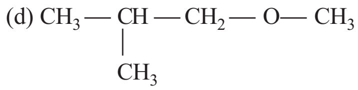
+ $ROH$

(d) 

+ $ROX$

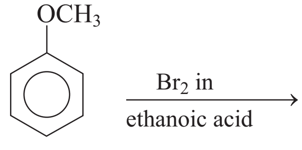
**70.** The order of reactivity of hydrogen halides with ether is as follows
(a) HBr > HI > HCl
(b) HCl > HBr > HI
(c) HI > HBr > HCl
(d) HCl > HI > HBr

**71.** The reaction of anisole with HI gives phenol rather than iodobenzene because
(a) the bond between O — $CH_3$ is weaker than O — $C_6H_5$
(b) the carbon of phenyl group is $sp^2$-hybridised and has a partial double bond character
(c) Both (a) and (b)
(d) None of the above

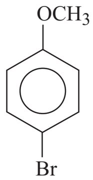
**72.** Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?
**(NEET 2013)**
(a) $CH_3-CH_2-CH_2-CH_2-O-CH_3$
(b) 
$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-O-CH_3$
(c) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-O-CH_3$
(d) 
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-O-CH_3$

**73.** Ethers are treated with an aqueous solution of I in order to remove peroxides from it. Identify the 'I' from the following options.
(a) KI (b) $Br_2$ (c) KCNS (d) $Na_2S_2O_3$

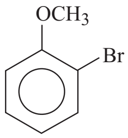
**74.** In the given reaction,



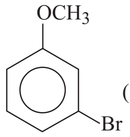
product formed is

(a) 

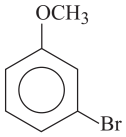
(90% yield)

(b) 

(90% yield)

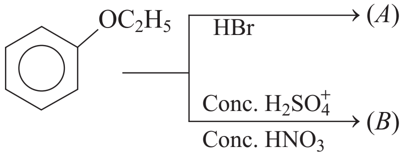
(c) 

(90% yield)

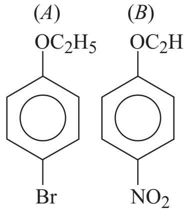
(d) 

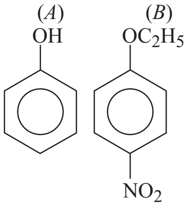
(10% yield)

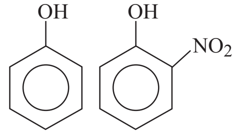
**75.** Predict the major product of the following reaction

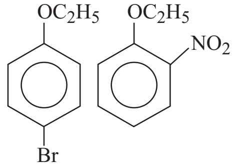


Choose the option with appropriate products from the codes given below.

(a) 

(b) 

(c) 

(d) 

# Special Format Questions

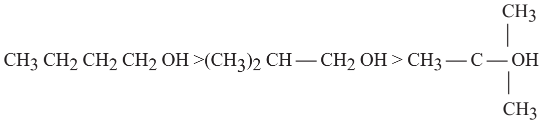
## I. More Than One Correct Option

**76.** Which of the following trends are correctly matched with properties mentioned?

(a) $CH_3CH_2OH > CH_3CH_2CH_2OH > CH_3CH_2CH_2CH_2OH$ (Solubility)

(b) $CH_3CH_2OH < CH_3CH_2CH_2OH < CH_3CH_2CH_2CH_2OH$ (Boiling point)

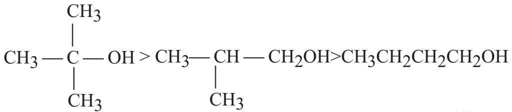
(c)



$$CH_3CH_2CH_2CH_2OH > (CH_3)_2CH—CH_2OH > CH_3—\underset{CH_3}{\overset{CH_3}{C}}—OH$$

(Boiling point)

(d)

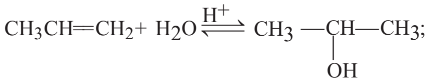


$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—OH > CH_3—\underset{CH_3}{CH}—CH_2OH > CH_3CH_2CH_2CH_2OH$$

(Boiling point)

**77.** Choose the correct pair of reactions and their name.

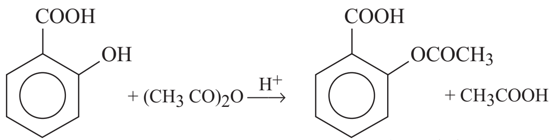
(a)



$$CH_3CH{=}CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3—\underset{OH}{CH}—CH_3$$

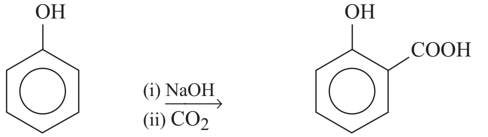
; Base catalysed hydration

(b)



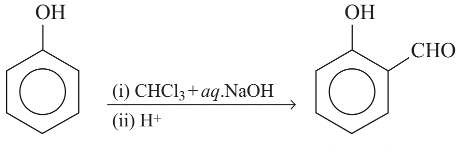
(Acetylation)

(c)



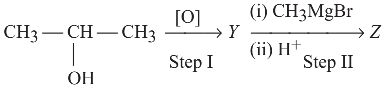
(Kolbe's reactions)

(d)



(Reimer–Tiemann reactions)

**78.** Regarding the given sequence of reactions



$$CH_3—\underset{OH}{CH}—CH_3 \xrightarrow[\text{Step I}]{[O]} Y \xrightarrow[\text{(ii) } H^+ \text{ Step II}]{\text{(i) } CH_3MgBr} Z$$

Choose the correct option from the following.

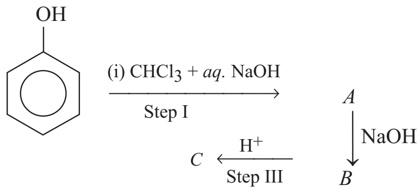
(a) Product $Z$ is 2-methylpropan – 2 –ol

(b) Product $Y$ is acetone

(c) Step II is nucleophilic addition followed by hydrolysis

(d) Step I is insertion of oxygen into C—C single bond.

**79.** Consider the following sequence of reactions



Choose the correct option.

(a) In step I, electrophile generated is carbene

(b) In — CHO group is introduced at *ortho*–position of benzene ring

(c) Product $C$ is salicylaldehyde

(d) Reaction is known as Friedel-Craft alkylation

## II. Statement Based Questions

**80.** Consider the following statements :

I. Solubility decreases with increase in size of alkyl/aryl groups.

II. Alcohols and phenols react with active in metals like Na, K etc., to produce corresponding alkoxides or phenoxides.

III. Alcohols act as Bronsted acid in the presence of strong acid.

IV. Alcohols react with both nucleophile and electrophiles.

Choose the correct option.

| | |
|---|---|
| (a) Only II | (b) II and III |
| (c) I, II and IV | (d) All of these |

**81.** Cosider the following compounds.

I. 3-chloromethyl-2-isopropylpentan-1-ol

II. 2,5-dimethylhexane-1,3-diol

III. 3-bromocyclohexanol

IV. Hex-1-en-3-ol

V. 2-bromo-3-methylpent-2-en-1-ol

Which of the following IUPAC names are considered as the isomeric alcohols of the molecular formula $C_6H_{12}OX$?

| | |
|---|---|
| (a) I, II and III | (b) II, III and IV |
| (c) I, IV and V | (d) III and V |

**82.** The acid catalysed hydration of alkene involves the following three steps.

I. Nucleophilic attack of water on carbocation.

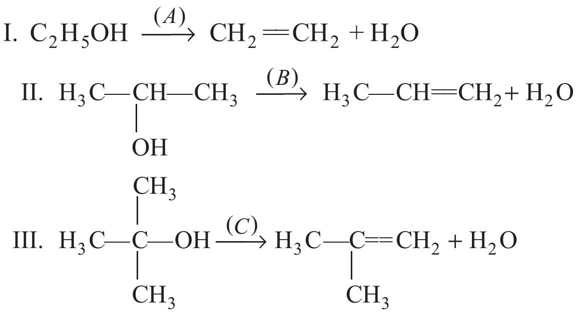
II. Protonation of alkene to form carbocation by the electrophilic attack of $H_3O^+$.

III. Deprotonation to form an alcohol.

Identify the sequence for the mechanism of reaction in the acid catalysed hydration of alkenes.

(a) I, II and III
(b) II, I and III
(c) III, I and II
(d) III, II and I

**83.** Consider the following reactions :



I. $C_2H_5OH \xrightarrow{(A)} CH_2{=}CH_2 + H_2O$

II. $H_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow{(B)} H_3C-CH{=}CH_2 + H_2O$

III. $H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH \xrightarrow{(C)} H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + H_2O$

Identify *A*, *B* and *C* in the given reaction.

| | *A* | *B* | *C* |
|---|---|---|---|
| (a) | 20% $H_3PO_4$, 358 K | 85% $H_3PO_4$, 440 K | $H_2SO_4$; 443 K |
| (b) | 85% $H_3PO_4$, 440 K | $H_2SO_4$; 443 K | 20% $H_3PO_4$, 358 K |
| (c) | $H_2SO_4$; 443 K | 85% $H_3PO_4$, 440 K | 20% $H_3PO_4$, 358 K |
| (d) | $H_2SO_4$; 443 K | 20% $H_2SO_4$; 358 K | 85% $H_3PO_4$, 440 K |

**84.** Consider the following steps :

**Step I** Formation of ethene by the elimination of a proton.

**Step II** Formation of protonated alcohol.

**Step III** Formation of carbocation.

Arrange the following steps in a sequence which are involved in the mechanism of dehydration of ethanol.

(a) I, II and III
(b) II, I and III
(c) II, III and I
(d) I, III and II

**85.** I. Methanol is a colourless liquid and highly poisonous in nature.

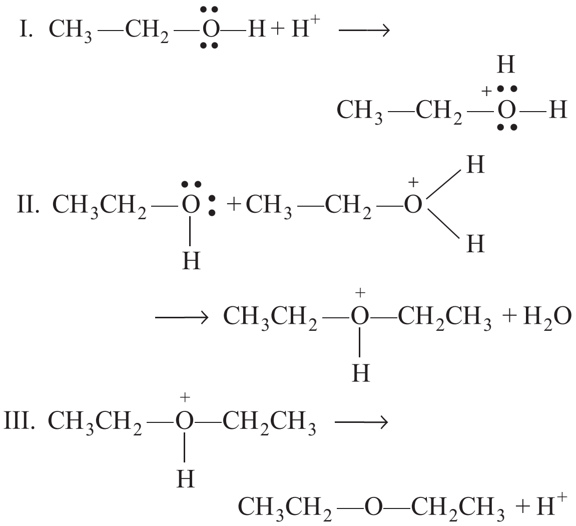
II. Ingestion of small quantities of methanol can cause blindness and its large quantities causes the death.

III. Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

Which of the following statement(s) is/are correct?

(a) Only I
(b) Only II
(c) Only III
(d) All of these

**86.** Consider the following mechanism and statements



I. $CH_3-CH_2-\underset{\cdot\cdot}{\ddot{O}}-H + H^+ \longrightarrow CH_3-CH_2-\underset{\cdot\cdot}{\overset{\displaystyle H}{\overset{+\cdot\cdot}{O}}}-H$

II. $CH_3CH_2-\underset{\displaystyle H}{\underset{|}{\ddot{O}}}\!: + CH_3-CH_2-\overset{+}{O}\begin{matrix}H\\H\end{matrix} \longrightarrow CH_3CH_2-\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}-CH_2CH_3 + H_2O$

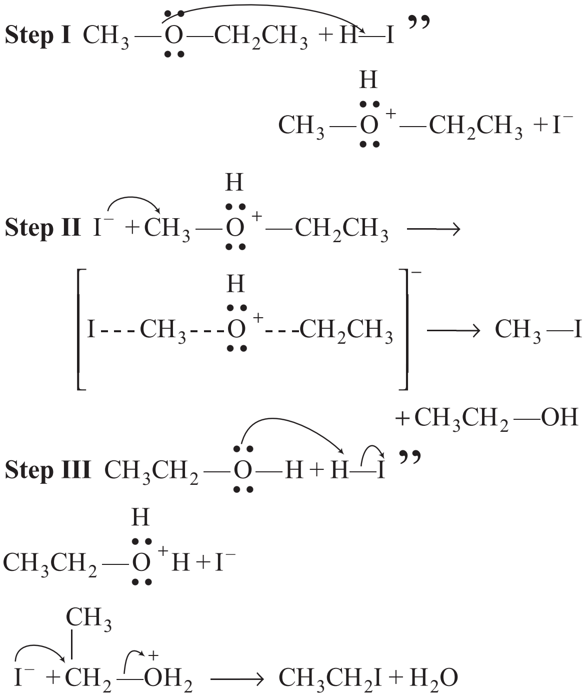
III. $CH_3CH_2-\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}-CH_2CH_3 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$

(i) It is a nucleophilic bimolecular reaction ($S_N2$)

(ii) The alkyl group should be unhindered and the temperature must be kept low in order to synthesise the ether.

(a) Only (i)
(b) Only (ii)
(c) Both (i) and (ii)
(d) Neither (i) in nor (ii)

**87.** The mechanism for the reaction of ether with the concentrated HI is as follows.



**Step I** $CH_3-\underset{\cdot\cdot}{\ddot{O}}-CH_2CH_3 + H-I$ ” $CH_3-\underset{\cdot\cdot}{\overset{\displaystyle H}{\ddot{O}}}{}^{+}-CH_2CH_3 + I^-$

**Step II** $I^- + CH_3-\underset{\cdot\cdot}{\overset{\displaystyle H}{\ddot{O}}}{}^{+}-CH_2CH_3 \longrightarrow \left[I\text{---}CH_3\text{---}\underset{\cdot\cdot}{\overset{\displaystyle H}{\ddot{O}}}{}^{+}\text{---}CH_2CH_3\right]^- \longrightarrow CH_3-I + CH_3CH_2-OH$

**Step III** $CH_3CH_2-\underset{\cdot\cdot}{\ddot{O}}-H + H-I$ ” $CH_3CH_2-\underset{\cdot\cdot}{\overset{\displaystyle H}{\ddot{O}}}{}^{+}H + I^-$

$I^- + \overset{\displaystyle CH_3}{\overset{|}{CH_2}}-\overset{+}{O}H_2 \longrightarrow CH_3CH_2I + H_2O$

Which of the following statement(s) is/are true about above mechanism?

I The reaction takes place with HBr or HI because these reagents are sufficiently acidic

II Iodide is a good nucleophile. It attacks the least substituted carbon of oxonium ion formed in step I and displaces an alcohol molecule by $S_N2$ mechanism

III When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide ($S_N2$ reaction)

Correct choice is

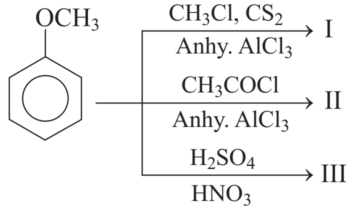
(a) I and II

(b) II and III

(c) I and III

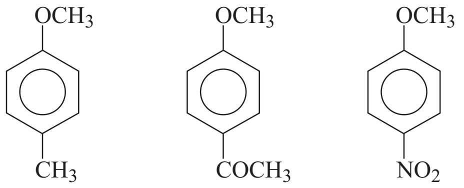
(d) I, II and III

**88.** Identify the minor product formed in the given reaction and choose the correct option from the codes given below.

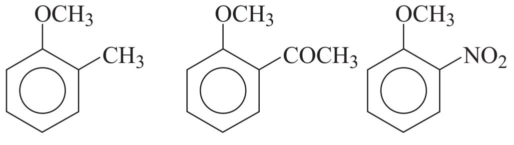


I II III

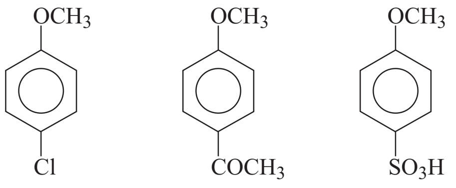
(a)



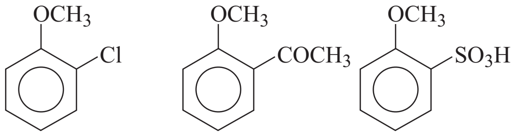
(b)



(c)

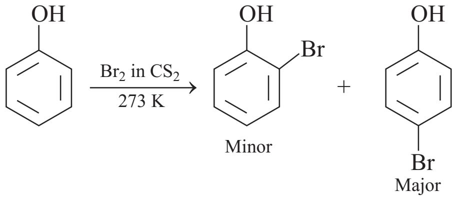


(d)

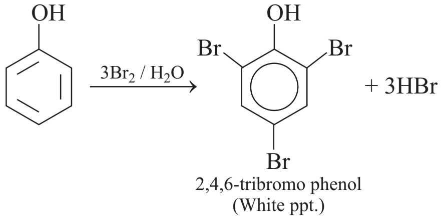


**89.** Which of the following reaction condition does not hold good with phenols?

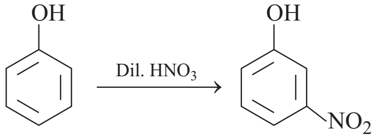
I.



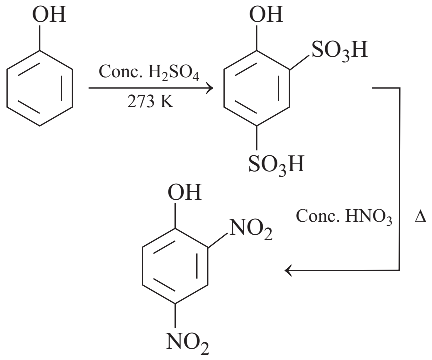
II.



III.



IV.



Choose the correct option.

(a) Only II

(b) Only III and IV

(c) I and II

(d) All of the above

**90.** Consider the following statements.

I. Alcohols undergo dehydration in the presence of protic acids such as $H_2SO_4, H_3PO_4$.

II. Dehydration of alcohols is the best method for the preparation of unsymmetrical ethers.

III. Phenols can be easily converted into ethers by Williamson's synthesis.

IV. Ethers are used as industrial solvents for oils, resins, guns etc.

Choose the correct option.

(a) Only I (b) III and IV

(c) I, III and IV (d) All of these

## III. Assertion-Reason Type Questions

■ **Directions** (Q. Nos. 91-115) *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) Both A and R are correct; R is the correct explanation of A.
(b) Both A and R are correct; R is not the correct explanation of A.
(c) A is correct; R is incorrect.
(d) R is correct; A is incorrect.

**91.** **Assertion** (A) The bond angle in alcohol is slightly more than the tetrahedral angle.

**Reason** (R) It is due to the repulsion between the unshared electron pair of oxygen.

**92.** **Assertion** (A) Carbon oxygen bond length of phenol is slightly less than that of methanol.

**Reason** (R) There exist a partial double bond character and $sp^2$-hybridisation of carbon to which oxygen is attached in phenol.

**93.** **Assertion** (A) The C— O bond length (141 pm) of ether is almost same as in alcohols.

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

**94.** **Assertion** (A) Commercially acids are reduced to alcohols by converting them to the esters followed by their reduction using catalylic hydrogenation.

**Reason** (R) $LiAlH_4$ can also reduce carboxylic acids to primary alcohols but $LiAlH_4$ is an expensive reagent and used for preparing special chemicals only.

**95.** **Assertion** (A) In alcohols, the boiling point decreases with decrease in the branching of the carbon chain.

**Reason** (R) There is the decrease in van der Waals' forces between the number of carbon atoms with decrease in the surface area.

**96.** **Assertion** (A) Alcohols and phenols are soluble in water.

**Reason** (R) There occurs a dipole-dipole interaction of OH group of alcohol and phenol with water molecules, which is responsible for their solubility in water.

**97.** **Assertion** (A) An alcohol is more volatile than an ether having the same molecular formula.

**Reason** (R) There is the intermolecular hydrogen bonding in alcohols.

**98.** **Assertion** (A) Dipole moment of phenol is smaller than that of methanol.

**Reason** (R) In phenol C— O bond is less polar whereas in methanol, C— O bond is more polar.

**99.** **Assertion** (A) Increasing order of acid strength of alcohol is

$$1° \text{ alcohol} > 2° \text{ alcohol} > 3° \text{ alcohol}$$

**Reason** (R) An electron releasing group increases the electron density on oxygen which tends to decrease the polarity of the O—H bond.

**100.** **Assertion** (A) Alcohols act as Bronsted bases.

**Reason** (R) It is due to the presence of shared electron pairs on oxygen which make them proton donors.

**101.** **Assertion** (A) Alcohols and water are weaker acids than phenols.

**Reason** (R) The delocalisation of negative charge makes the phenoxide ion more stable and favour the ionisation of phenol.

**102.** **Assertion** (A) Oxidation of alcohols is also known as dehydrohalogenation during oxidation.

**Reason** (R) There is the loss of dihydrogen from an alcohol molecule during oxidation.

**103.** **Assertion** (A) Methanol poisoned patients are prone to blindness and death.

**Reason** (R) In body, methanol is oxidised first to methanoic acid and then to methanal which may cause blindness and death.

**104.** **Assertion** (A) *o*-nitrophenol is less volatile than *p*-nitrophenol.

**Reason** (R) There is intramolecular hydrogen bonding in *o*-nitrophenol and intermolecular hydrogen bonding in *p*-nitrophenol.

**105.** **Assertion** (A) Picric acid is a strong acid.

**Reason** (R) Three electron withdrawing $NH_2$ groups are present in phenol to facilitate the release of hydrogen ion.

**106.** **Assertion** (A) Bromination of phenol takes place even in the absence of Lewis acid.

**Reason** (R) In phenol, OH group attached to benzene ring has highly deactivating effect.

**107.** **Assertion** (A) In the presence of air, phenol mixture becomes dark in colour.

**Reason** (R) Phenols are slowly oxidised to the dark coloured mixture containing quinones.

**108.** **Assertion** (A) Alcohols do not react with NaBr but when $H_2SO_4$ is added they form alkyl bromides.

**Reason** (R) Water is a good leaving group.

**109.** **Assertion** (A) Isopropyl alcohol is preferred over ethanol.

**Reason** (R) Isopropyl alcohol is used as an antiseptic for skin before giving injections.

**110.** **Assertion** (A) Ethers are not obtained during the dehydration of secondary and tertiary alcohols.

**Reason** (R) In the secondary and tertiary alcohols, elimination competes over substitution during dehydration.

**111.** **Assertion** (A) Diethyl ether has been replaced as an anaesthetic by other compounds.

**Reason** (R) Diethyl ether is highly expensive.

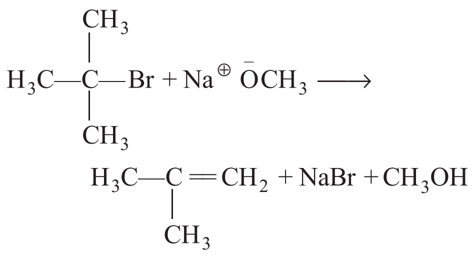
**112.** **Assertion** (A) 7.5 g of ethoxyethane and 9 g of butan-1-ol is miscible to almost same extent while pentane is essentially immiscible with water.

**Reason** (R) Alcohols and ethers can form hydrogen bonds with the water molecule.

**113.** **Assertion** (A) The cleavage of C—O bond in ethers takes place under drastic condition with excess of hydrogen halides.

**Reason** (R) Ethers are the most reactive among all the functional groups.

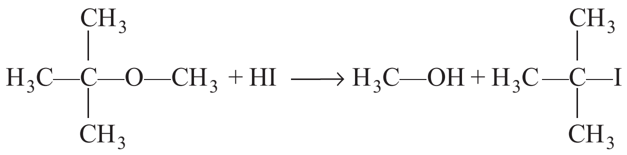
**114.** **Assertion** (A)



$$H_3C-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-Br + Na^{\oplus}\,\overset{-}{O}CH_3 \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{C}=CH_2 + NaBr + CH_3OH$$

**Reason** (R) Alkoxides are not only nucleophiles but also the strong base, so they can react with alkyl halide to form the eliminated product.

**115.** **Assertion** (A) Consider the reaction,



$$H_3C-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-O-CH_3 + HI \longrightarrow H_3C-OH + H_3C-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-I$$

**Reason** (R) The departure of leaving group creates a more stable carbocation and the reaction follows $S_N1$ mechanism.

## IV. Matching Type Questions

**116.** Match the following compounds given in Column I with their uses given in Column II and choose the correct option from the codes given below.

| **Column I**<br>(Compounds) | **Column II**<br>(Uses) |
|---|---|
| A. Alcohol | 1. Detergents |
| B. Phenol | 2. Antiseptics |
| C. Ether | 3. Fragrances |

**Codes**

| | A | B | C | | A | B | C |
|---|---|---|---|---|---|---|---|
| (a) | 2 | 1 | 3 | (b) | 3 | 1 | 2 |
| (c) | 1 | 2 | 3 | (d) | 2 | 3 | 1 |

**117.** Match the following structure given in Column I with their classification given in Column II and choose the correct option from the codes given below.

| **Column I**<br>(Alcohol) | **Column II**<br>(Classification) |
|---|---|
| A. $\geqslant C-OH$ | 1. Secondary alcohol |
| B. $>CH-OH$ | 2. Primary alcohol |
| C. $-CH_2OH$ | 3. Tertiary alcohol |

**Codes**

| | A | B | C | | A | B | C |
|---|---|---|---|---|---|---|---|
| (a) | 1 | 2 | 3 | (b) | 2 | 3 | 1 |
| (c) | 3 | 2 | 1 | (d) | 3 | 1 | 2 |

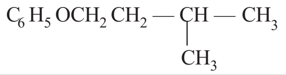
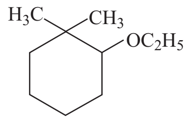
**118.** Match the following IUPAC names given in Column I with their common names given in Column II and choose the correct option from the codes given below.

| **Column I**<br>(IUPAC name) | **Column II**<br>(Common name) |
|---|---|
| A. 4-methyl phenol | 1. Resorcinol |
| B. Benzene-1,4-diol | 2. Catechol |
| C. Benzene-1,2-diol | 3. Quinol |
| D. 2-methyl phenol | 4. Phenol |
| | 5. *o*-cresol |
| | 6. *p*-cresol |

**Codes**

| | A | B | C | D |
|---|---|---|---|---|
| (a) | 6 | 3 | 2 | 5 |
| (b) | 3 | 6 | 5 | 2 |
| (c) | 1 | 2 | 5 | 6 |
| (d) | 6 | 5 | 2 | 1 |

**119.** Match the following compounds given in Column I with their names given in Column II and choose the correct option from the codes given below.

| **Column I**<br>(Compound) | **Column II**<br>(Name) |
|---|---|
| A. $C_6H_5OCH_3$ | 1. 2-ethoxy-1,1-dimethyl cyclohexane |
| B. $C_6H_5O(CH_2)_6CH_3$ | 2. Anisole |
| C.  $C_6H_5OCH_2CH_2-\underset{\underset{CH_3}{\mid}}{CH}-CH_3$ | 3. Phenyl isopentyl ether |
| D.  | 4. 1-phenoxyheptane |

**Codes**

| | A | B | C | D | | A | B | C | D |
|---|---|---|---|---|---|---|---|---|---|
| (a) | 1 | 2 | 3 | 4 | (b) | 4 | 3 | 2 | 1 |
| (c) | 2 | 3 | 4 | 1 | (d) | 2 | 4 | 3 | 1 |

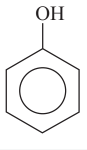
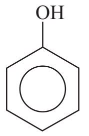
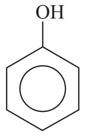
**120.** Match the following alcohols given in Column I with the product formed during their reaction with Cu/573 K in Column II and choose the correct option from the codes given below.

| **Column I**<br>(Alcohol) | **Column II**<br>(Product) |
|---|---|
| A. 1° alcohol | 1. Ketone |
| B. 2° alcohol | 2. Alkene |
| C. 3° alcohol | 3. Aldehyde |

**Codes**

| | A | B | C | | A | B | C |
|---|---|---|---|---|---|---|---|
| (a) | 3 | 1 | 2 | (b) | 2 | 1 | 3 |
| (c) | 2 | 3 | 1 | (d) | 3 | 2 | 1 |

**121.** Match the following reactants and reagents given in Column I with the products given in Column II and choose the correct option from the codes given below.

| | **Column I** | **Column II** |
|---|---|---|
| A. |  + Zn | 1. Benzene |
| B. |  $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$ | 2. Salicylaldehyde |
| C. |  $\xrightarrow[\text{(ii) NaOH}]{\text{(i) CHCl}_3 + \text{aq. NaOH}}$<br>(iii) $H^{\oplus}$ | 3. Benzoquinone |

**Codes**

| | A | B | C | | A | B | C |
|---|---|---|---|---|---|---|---|
| (a) | 3 | 1 | 2 | (b) | 1 | 3 | 2 |
| (c) | 1 | 2 | 3 | (d) | 3 | 2 | 1 |

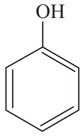
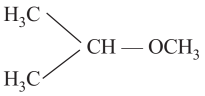
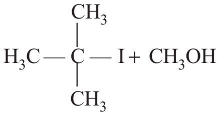
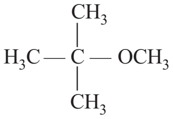
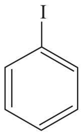
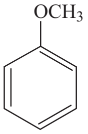
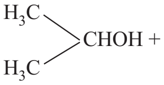
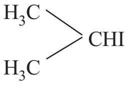
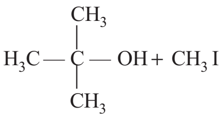
**122.** Match the Column I with Column II and choose the correct option from the codes given below.

| **Column I**<br>(Distinguish) | **Column II**<br>(By reagent) |
|---|---|
| A. Methanol and diethyl ether | 1. Lucas reagent |
| B. Methanol and ethanol | 2. Sodium metal |
| C. Phenol and cyclohexanol | 3. Iodoform test |
| D. *n*-propyl alcohol and *tert*-butyl alcohol | 4. Ferric chloride |

**Codes**

| | A | B | C | D |
|---|---|---|---|---|
| (a) | 2 | 4 | 3 | 1 |
| (b) | 2 | 3 | 4 | 1 |
| (c) | 2 | 3 | 1 | 4 |
| (d) | 3 | 2 | 1 | 4 |

**123.** Match the starting materials given in Column I with the products formed by these (given in Column II ) in the reaction with HI and choose the correct option from the codes given below.

| **Column I** | **Column II** |
|---|---|
| A. $CH_3-O-CH_3$ | 1.  + $CH_3I$ |
| B.  | 2.  $H_3C-C(CH_3)_2-I + CH_3OH$ |
| C.  $H_3C-C(CH_3)_2-OCH_3$ | 3.  + $CH_3OH$ |
| D.  | 4. $CH_3-OH + CH_3-I$ |
| | 5.  + $CH_3I$ |
| | 6.  + $CH_3OH$ |
| | 7.  $H_3C-C(CH_3)_2-OH + CH_3I$ |

**Codes**

| | A | B | C | D |
|---|---|---|---|---|
| (a) | 4 | 3 | 2 | 1 |
| (b) | 3 | 5 | 6 | 3 |
| (c) | 4 | 3 | 6 | 1 |
| (d) | 4 | 5 | 2 | 1 |

# NCERT & NCERT Exemplar Questions

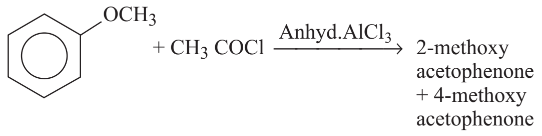
## NCERT

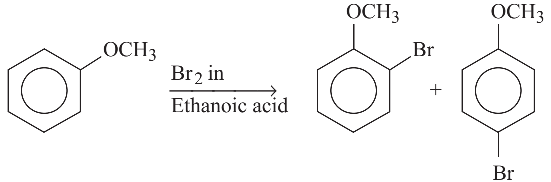
**124.** Explain why is *ortho*-nitrophenol more acidic than *ortho*-methoxyphenol?
(a) Due to H–bonding in *ortho*-nitrophenol
(b) Due to H–bonding in *ortho*-methoxyphenol
(c) Due to the presence of $-I$ group in *ortho*-nitrophenol
(d) Due to the presence of $+I$ group in *ortho*-methoxyphenol

**125.** Name the reagents used for butan-2-one to butan-2-ol conversion:
(a) $NaBH_4$
(b) $LiAlH_4$
(c) Raney nickel
(d) Both (a) and (b)

**126.** Preparation of ethers by acid dehydration of secondary or tertiary alcohol is not a suitable method. Give reason.
(a) Due to presence of more basic alcohols
(b) Due to steric hindrance
(c) Due to formation of more stable carbocation
(d) Due to formation of less stable carbocation

**127.** Which of the following equation is the correct representation of Friedel-Craft's acetylation of anisole?

(a)


(b)


(c) Both (a) and (b)

(d) None of the above

## NCERT Exemplar

**128.** 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

**129.** How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?
(a) 1 (b) 2
(c) 3 (d) 4

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

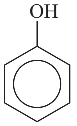
$$R\text{—OH} + HCl \xrightarrow{ZnCl_2} R\text{—Cl} + H_2O$$

(a) 1° > 2° > 3° (b) 1° < 2° > 3°
(c) 3° > 2° > 1° (d) 3° > 1° > 2°

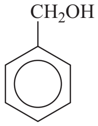
**131.** $CH_3CH_2OH$ can be converted into $CH_3CHO$ by
(a) catalytic hydrogenation
(b) treatment with $LiAlH_4$
(c) treatment with pyridinium chlorochromate
(d) treatment with $KMnO_4$

**132.** The process of converting alkyl halides into alcohols involves
(a) addition reaction
(b) substitution reaction
(c) dehydrohalogenation reaction
(d) rearrangement reaction

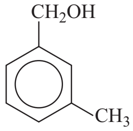
**133.** Which of the following compounds is aromatic alcohol?



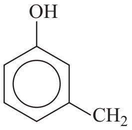
*A*



*B*



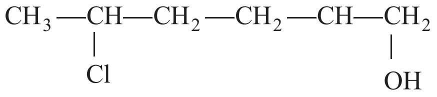
*C*



*D*

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

**134.** Give IUPAC name of the compound given below.

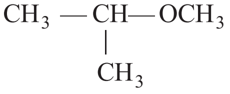


$$CH_3\text{—}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{—}CH_2\text{—}CH_2\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}CH_2$$

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

**135.** IUPAC name of *m*- cresol is.
(a) 3-methylphenol (b) 3-chlorophenol
(c) 3-methoxyphenol (d) benzene-1, 3-diol

**136.** IUPAC name of the compound



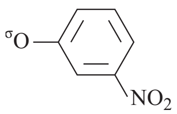
$$CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}OCH_3 \text{ is}$$

(a) 1-methoxy-1-methylethane
(b) 2-methoxy-2-methylethane
(c) 2-methoxypropane
(d) isopropylmethyl ether

**137.** Which of the following species can act as the strongest base?

(a) $^{s}$OH (b) $^{s}$O*R*

(c) $^{s}OC_6H_5$ (d)



**138.** 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) $C_2H_5OH$

**139.** Phenol is less acidic than

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

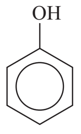
(c) *o*-methylphenol (d) *o*-methoxyphenol

**140.** Which of the following is most acidic?

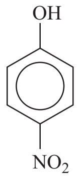
(a) Benzyl alcohol (b) Cyclohexanol

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

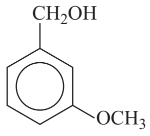
**141.** Mark the correct order of decreasing acid strength of the following compounds.



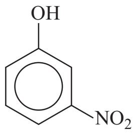
(I)



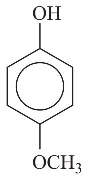
(II)



(III)



(IV)



(V)

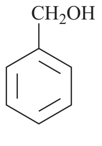
(a) V > IV > II > I > III

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

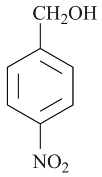
(c) IV > V > III > II > I

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

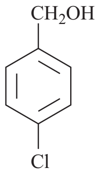
**142.** Mark the correct increasing order of reactivity of the following compounds with HBr / HCl.



(I)



(II)



(III)

(a) I < II < III

(b) II < I < III

(c) II < III < I

(d) III < II < I

**143.** 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, pentan-1-ol, butan-1-ol

(d) Propan-1-ol, butan-1-ol, pentan-1-ol, butan-2-ol

# Answers

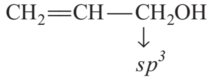
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1.** | (c) | **2.** | (b) | **3.** | (c) | **4.** | (a) | **5.** | (b) | **6.** | (d) | **7.** | (d) | **8.** | (c) | **9.** | (d) | **10.** | (c) | **11.** | (b) | **12.** | (a) | **13.** | (a) | **14.** | (b) | **15.** | (c) |
| **16.** | (a) | **17.** | (d) | **18.** | (a) | **19.** | (b) | **20.** | (d) | **21.** | (b) | **22.** | (d) | **23.** | (d) | **24.** | (b) | **25.** | (d) | **26.** | (b) | **27.** | (d) | **28.** | (c) | **29.** | (a) | **30.** | (b) |
| **31.** | (c) | **32.** | (d) | **33.** | (c) | **34.** | (c) | **35.** | (d) | **36.** | (a) | **37.** | (c) | **38.** | (d) | **39.** | (a) | **40.** | (b) | **41.** | (b) | **42.** | (b) | **43.** | (d) | **44.** | (c) | **45.** | (d) |
| **46.** | (b) | **47.** | (b) | **48.** | (b) | **49.** | (b) | **50.** | (a) | **51.** | (d) | **52.** | (a) | **53.** | (b) | **54.** | (a) | **55.** | (c) | **56.** | (b) | **57.** | (b) | **58.** | (a) | **59.** | (d) | **60.** | (b) |
| **61.** | (a) | **62.** | (c) | **63.** | (b) | **64.** | (a) | **65.** | (b) | **66.** | (b) | **67.** | (b) | **68.** | (c) | **69.** | (a) | **70.** | (c) | **71.** | (c) | **72.** | (c) | **73.** | (a) | **74.** | (a) | **75.** | (b) |
| **76.** | (abc) | **77.** | (bcd) | **78.** | (abc) | **79.** | (abc) | **80.** | (c) | **81.** | (d) | **82.** | (b) | **83.** | (c) | **84.** | (c) | **85.** | (d) | **86.** | (c) | **87.** | (d) | **88.** | (b) | **89.** | (c) | **90.** | (c) |
| **91.** | (d) | **92.** | (a) | **93.** | (b) | **94.** | (b) | **95.** | (d) | **96.** | (c) | **97.** | (d) | **98.** | (a) | **99.** | (a) | **100.** | (c) | **101.** | (a) | **102.** | (d) | **103.** | (c) | **104.** | (d) | **105.** | (c) |
| **106.** | (c) | **107.** | (a) | **108.** | (a) | **109.** | (b) | **110.** | (a) | **111.** | (c) | **112.** | (a) | **113.** | (c) | **114.** | (a) | **115.** | (a) | **116.** | (c) | **117.** | (d) | **118.** | (a) | **119.** | (d) | **120.** | (a) |
| **121.** | (b) | **122.** | (b) | **123.** | (d) | **124.** | (c) | **125.** | (d) | **126.** | (b) | **127.** | (a) | **128.** | (d) | **129.** | (a) | **130.** | (c) | **131.** | (c) | **132.** | (b) | **133.** | (c) | **134.** | (c) | **135.** | (a) |
| **136.** | (c) | **137.** | (b) | **138.** | (a) | **139.** | (b) | **140.** | (d) | **141.** | (b) | **142.** | (c) | **143.** | (a) | | | | | | | | | | | | | | |

# Hints & Explanations

**1.** (*c*) Ordinary spirit used for polishing wooden furniture is chiefly a compound containing hydroxyl group, i.e. ethanol.

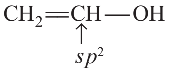
**2.** (*b*) The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds containing — OH groups.

**4.** (*a*) Allylic alcohol



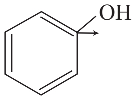
$CH_2{=}CH{-}\underset{\underset{sp^3}{\downarrow}}{CH_2}OH$

Vinyl alcohol

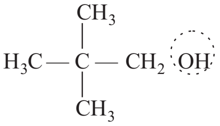


$CH_2{=}\underset{\underset{sp^2}{\uparrow}}{CH}{-}OH$

Phenol



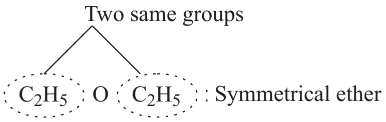
**5.** (*b*) Primary alcohols contain $-CH_2OH$ group. So



$H_3C{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2\,OH$

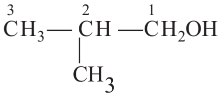
is a primary alcohol

**6.** (*d*)



**7.** (*d*) For naming polyhydric alcohols the word 'e' of an alkane is retained and the suffix 'ol' is added. The number of —OH groups is indicated by adding the multiplicative prefix, di, tri etc, before 'ol'.

**9.** (*d*) Structure of *iso*-butyl alcohol is



$\overset{3}{C}H_3{-}\underset{\underset{CH_3}{|}}{\overset{2}{C}H}{-}\overset{1}{C}H_2OH$

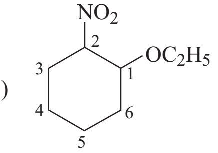
2-methyl propan-1-ol

**10.** (*c*) If both the alkyl groups are same in ethers, the prefix 'di' is added before the name of the alkyl group, e.g., $C_2H_5OC_2H_5$ is diethylether.

According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an —O*R* or —OAr group, where, *R* and Ar represents alkyl and aryl groups respectively.

The larger (*R*) group is chosen as the parent hydrocarbon.

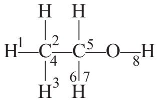
**11.** (*b*)



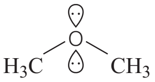
1-ethoxy-2-nitrocyclohexane

**12.** (*a*) 5-chlorohexan-2-ol is the IUPAC name of given compound.

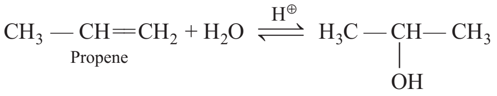
**13.** (*a*) Single bond contains only one σ bond so 8σ bonds are present in the ethanol.



**14.** (*b*) In ethers, the four electron pairs, i.e. the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement.
e.g .



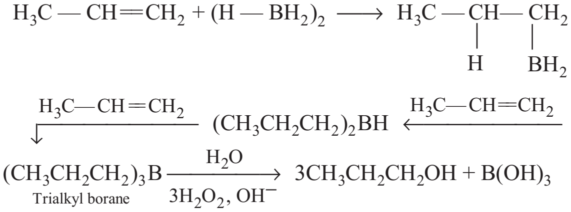
**15.** (*c*) Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markownikoff's rule.



$$\underset{\text{Propene}}{CH_3-CH{=}CH_2} + H_2O \overset{H^{\oplus}}{\rightleftharpoons} H_3C-\underset{\underset{OH}{|}}{CH}-CH_3$$

Propan–2–ol

**16.** (*a*) Diborane $(B_2H_6)$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



$$H_3C-CH{=}CH_2 + (H-BH_2)_2 \longrightarrow H_3C-\underset{\underset{H}{|}}{CH}-\underset{\underset{BH_2}{|}}{CH_2}$$

$$\xleftarrow{H_3C-CH=CH_2} (CH_3CH_2CH_2)_2BH \xleftarrow{H_3C-CH=CH_2}$$

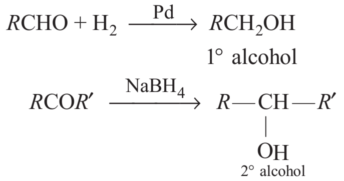
$$\underset{\text{Trialkyl borane}}{(CH_3CH_2CH_2)_3B} \xrightarrow[3H_2O_2,\ OH^-]{H_2O} 3CH_3CH_2CH_2OH + B(OH)_3$$

The alcohol is formed by the addition of water to the alkene in a way opposite to the Markownikoff's rule. In this reaction, alcohol is obtained in excellent yield.

**17.** (*d*) Aldehydes and ketones are reduced to the corresponding alcohols by the addition of hydrogen in the presence of catalysts (catalytic hydrogenation). The usual catalyst is finely divided metal such as platinum, palladium or nickel.

Alcohols are also prepared by treating aldehydes and ketones with sodium borohydride $(NaBH_4)$ or lithium aluminium hydride $(LiAlH_4)$.

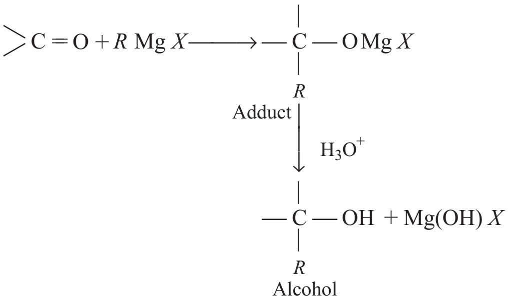
**18.** (*a*) Aldehydes yield primary alcohols whereas ketones give secondary alcohols on reduction.



$$RCHO + H_2 \xrightarrow{Pd} \underset{1^\circ \text{ alcohol}}{RCH_2OH}$$

$$RCOR' \xrightarrow{NaBH_4} \underset{2^\circ \text{ alcohol}}{R-\underset{\displaystyle OH}{\underset{|}{CH}}-R'}$$

**19.** (*b*) The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of this adduct yields an alcohol.



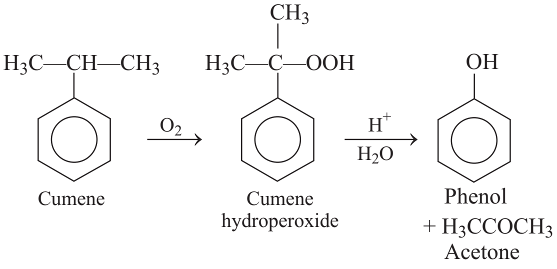
$$>C=O + R\,Mg\,X \longrightarrow \underset{\text{Adduct}}{-\underset{R}{\overset{|}{\underset{|}{C}}}-OMg\,X} \xrightarrow{H_3O^+} \underset{\text{Alcohol}}{-\underset{R}{\overset{|}{\underset{|}{C}}}-OH} + Mg(OH)\,X$$

**20.** (*d*) Phenol was also known as carbolic acid as it was first isolated in the early nineteenth century from coal tar.

**21.** (*b*) Phenol is manufactured from the hydrocarbon cumene. Cumene is also called *iso*-propylbenzene.

**22.** (*d*) Phenols are prepared from all the given reactions.

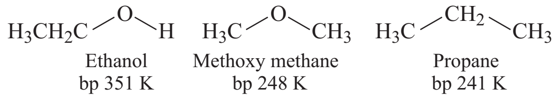
**23.** (*d*) Cumene is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone a by-product of this reaction, is also obtained in large quantities by this method.



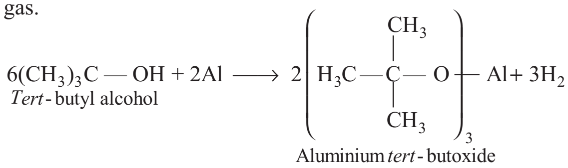
**24.** (*b*) The —OH group in alcohols and phenols is involved in the intermolecular hydrogen bonding which is responsible for high boiling point of alcohols and phenols.

Thus, the boiling points of alcohols and phenols are higher in comparison to other class of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses.

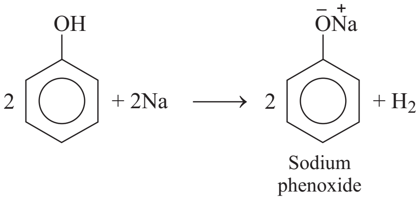
The boiling point varies as



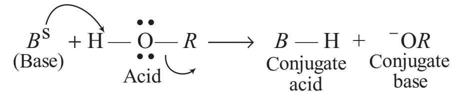
**25.** (*d*) Alcohols and phenols react with active metals such as Na, K, Al to yield corresponding alkoxides/phenoxide and hydrogen gas.



$$\underset{\textit{Tert}\text{-butyl alcohol}}{6(CH_3)_3C-OH} + 2Al \longrightarrow \underset{\text{Aluminium } \textit{tert}\text{-butoxide}}{2\left(H_3C-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O\right)_3 Al} + 3H_2$$



**26.** (*b*) Alcohols and phenols are Bronsted acids, i.e. they can donate a proton to a stronger base $(B\colon)$.



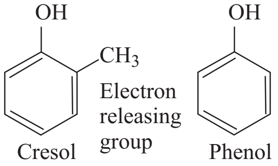
$$\underset{\text{(Base)}}{B^{S}} + \underset{\text{Acid}}{H-\ddot{\underset{\cdot\cdot}{O}}-R} \longrightarrow \underset{\substack{\text{Conjugate}\\ \text{acid}}}{B-H} + \underset{\substack{\text{Conjugate}\\ \text{base}}}{{}^-OR}$$

**27.** (*d*) Alcohols are weaker acids than water.

$$\underset{\text{Base}}{RO^{S}} + \underset{\text{Acid}}{H_2O} \longrightarrow \underset{\substack{\text{Conjugate}\\ \text{acid}}}{R-O-H} + \underset{\substack{\text{Conjugate}\\ \text{base}}}{{}^-OH}$$

This reaction shows that water is better proton donor (i.e. stronger acid) than alcohols. An alkoxide ion is a better proton acceptor than hydroxide ion which suggests that alkoxides are stronger bases. Sodium ethoxide is a stronger base than sodium hydroxide.

**28.** (*c*) Electron releasing groups, such as alkyl groups, do not favour the formation of phenoxide ion resulting in the decrease of acid strength that's why cresols are less acidic than phenol.



**29.** (*a*) Since, $pK_a = -\log K_a$ and $K_a$ is the measure of acidic strength. So, greater the $pK_a$ value, weaker is the acid.

**30.** (*b*) A stronger acid displaces a weaker acid from its salt. Since, $H_2O$ displaces $ROH$ from $RONa$ and both $H_2O$ and alcohol displace acetylene from sodium acetylide. Therefore, water is the strongest acid followed by alcohol while acetylene is the weakest acid. $H_2O > ROH > HC \equiv CH$.

**31.** (*c*) $CH_3CH_2CF_2CH_2OH$ is the strongest acid due to more *I*-effect of two fluorine atoms.

**32.** (*d*) Alcohols and phenols react with carboxylic acids and their derivations like acid chlorides and acid anhydrides to form esters.

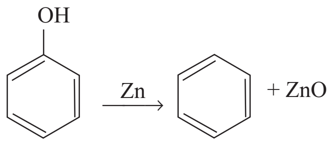
$$Ar/ROH + R'COOH \xrightarrow{H^+} Ar/ROCOR' + H_2O$$

$$Ar/ROH + (R'CO)_2O \xrightarrow{H^+} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{\text{Pyridine}} R/ArOCOR' + HCl$$

**33.** (*c*) The reaction of alcohol/Phenol with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side.

**34.** (*c*) The reactions involving cleavage of C—O bond take place only in alcohols. Phenols show this type of reaction only with zinc.



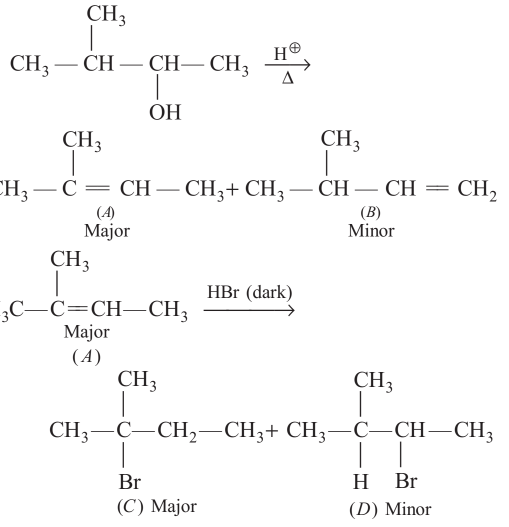
**35.** (*d*) The reaction of alcohol with Lucas reagent is mostly an $S_N1$ reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction.

Since 3° $R$—OH forms 3° carbocation (most stable), hence it will react fastest.

**36.** (*a*) Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide.

$$R-OH \xrightarrow{PBr_3} 3R-H_3PO_3$$

**37.** (*c*)



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{OH}{|}}{C}H-CH_3 \xrightarrow[\Delta]{H^{\oplus}}$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{\text{Major}}{(A)}}{C}}=CH-CH_3+CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{\text{Minor}}{(B)}}{C}H}-CH=CH_2$$

$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{(A)}{\text{Major}}}{C}}=CH-CH_3 \xrightarrow{\text{HBr (dark)}}$$

$$\underset{(C)\ \text{Major}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_2-CH_3}+\underset{(D)\ \text{Minor}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3}$$

**38.** (*d*) $RCH_2OH \xrightarrow[{[O]}]{\text{Oxidation}} \underset{\text{Aldehyde}}{RCHO} \longrightarrow \underset{\text{Carboxylic acid}}{RCOOH}$

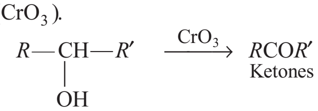
Strong oxidising agents such as acidified $KMnO_4$ are used for getting carboxylic acids from alcohols directly.

**39.** (*a*) PCC (pyridinium chlorochromate) is the complex of chromium trioxide with pyridine and HCl.

**40.** (*b*) A better reagent for the oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate. However it does not affect olefinic bond. So

$$H_3C \leftarrow CH{=}CH-CH_2OH \xrightarrow{PCC} CH_3-CH{=}CH-CHO$$

Secondary alcohols are oxidised to ketones by chromic anhydride ($CrO_3$).



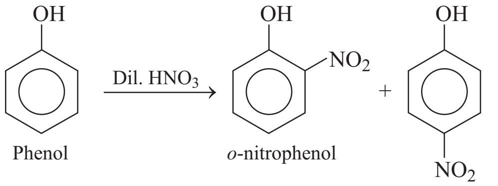
$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow{CrO_3} \underset{\text{Ketones}}{RCOR'}$$

Secondary alcohol

Under strong reaction conditions such as strong oxidising agents like $KMnO_4$ and elevated temperatures, cleavage of various C—C bonds in oxidation reaction takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

**42.** (*b*) The —OH group attached to the benzene ring activates it towards electrophilic substitution reaction. Also, it directs the incoming group to *ortho* and *para* positions of the ring as these positions become electron rich due to the resonance effect caused by the —OH group.

**43.** (*d*) Nitration of phenol with dilute nitric acid at low temperature (298 K), yield a mixture of *ortho* and *para* nitrophenols.

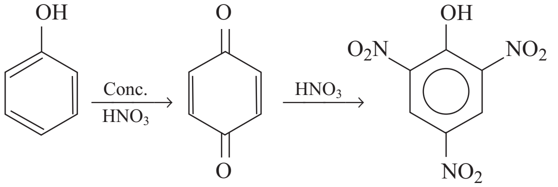


Phenol

*o*-nitrophenol

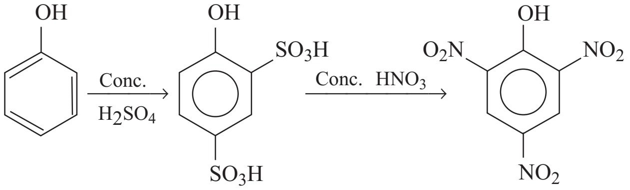
*p*-nitrophenol

**44.** (*c*) When phenol directly reacts with conc. $HNO_3$, it gets first converted into quinone because conc. $HNO_3$ oxidises phenol. Hence, picric acid obtained is low in yield.



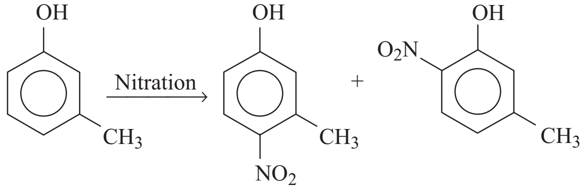
2, 4, 6- trinitrophenol
or picric acid

Picric acid can also be prepared by treating phenol with conc. $H_2SO_4$ (which converts it to phenol-2,4-disulphonic acid) and then with concentrated nitric acid.

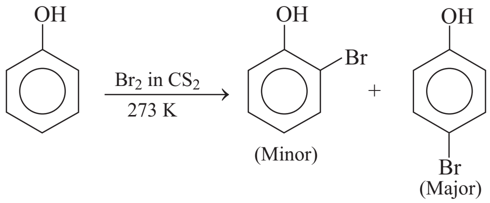


Picric acid

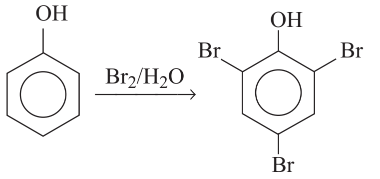
**45.** (*d*) Since, OH and $CH_3$ groups are *ortho* and *para*-directing.



**46.** (*b*) When the reaction of phenol is carried out in solvents of low polarity such as $CHCl_3$ or $CS_2$ and at low temperature, monobromophenols are formed.

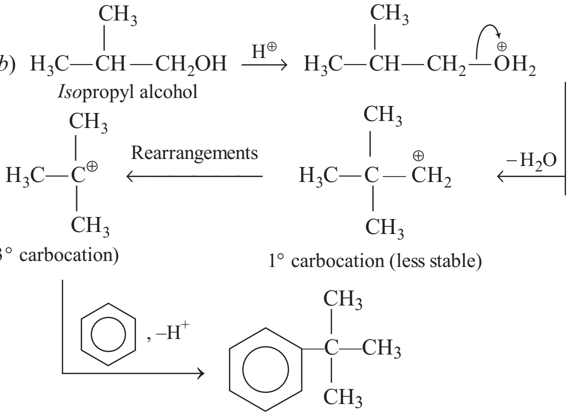


While phenol on reaction with $Br_2$ / $H_2O$ produces 2,4,6-tribromophenol.



2,4,6-tribromophenol

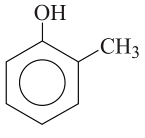
**47.** (*b*)



*tert*-butylbenzene

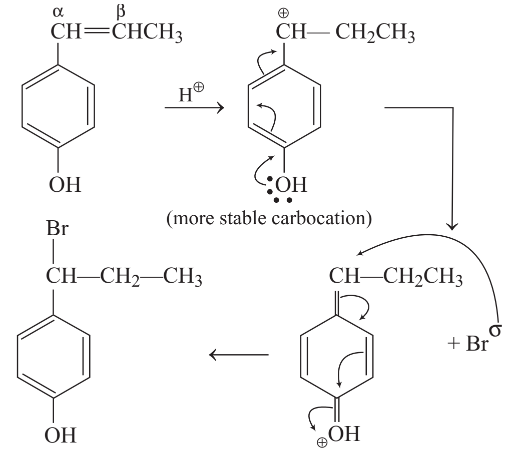
**48.** (*b*) Electron donating effect decreases in the order

$$OH > OCH_3 > NHCOCH_3 > CH_3 > CH_2OH$$

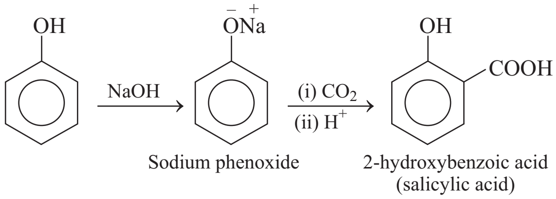


–OH is the strong electron donating group and hence *o*-cresol is most reactive towards electrophilic reagents.

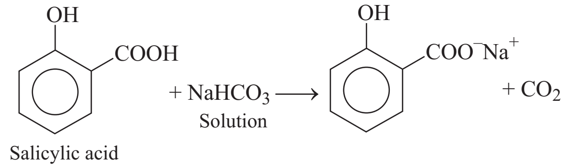
**49.** (*b*)

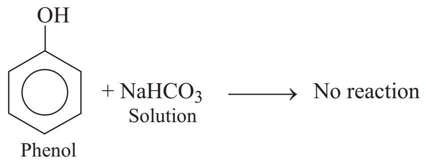


**50.** (*a*) Phenoxide ion generated by treating phenol with NaOH is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with $CO_2$, (a weak electrophile) and *ortho*-hydroxybenzoic acid is formed as the main product. **(Kolbe's reaction)**

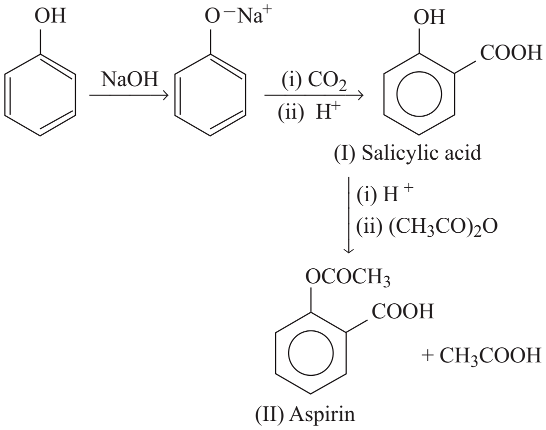


**51.** (*d*)





**52.** (*a*)



**53.** (*b*) Reimer-Tiemann reaction is an electrophilic substitution reaction. The electrophile generated here is $CCl_2$.

$$HO^- + CHCl_3 \;\text{’’}\; H_2O + CCl_3^- \longrightarrow \underset{\substack{\text{Dichlorocarbene}\\ \text{(electrophile)}}}{:CCl_2} + Cl^-$$

**54.** (*a*) $RCH_2CH_2OH + PBr_3 \longrightarrow RCH_2CH_2Br \xrightarrow{KCN}$

$$RCH_2CH_2CH_2NH_2 \xleftarrow{LiAlH_4} RCH_2CH_2CN$$

**55.** (*c*) Methanol, $CH_3OH$, is known as 'wood spirit' as it is produced by destructive distillation of wood.

**56.** (*b*) Most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature in the presence of $ZnO—Cr_2O_3$ catalyst.

$$\underset{\text{water gas}}{CO + 2H_2} \xrightarrow[\substack{200-300\text{ atm}\\ 573-673\text{ K}}]{ZnO—Cr_2O_3} CH_3OH$$

**58.** (*a*) The sugar in sugarcane is converted to glucose and fructose, in the presence of an enzyme, called invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase which is found in yeast.

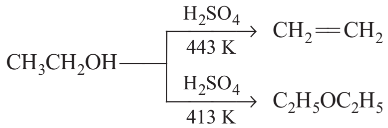
**59.** (*d*) The action of zymase is inhibited once the percentage of alcohol formed exceeds the 14 per cent.

**60.** (*b*) The commercial alcohol is made unfit for drinking by mixing some copper sulphate in it (to give it colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

**61.** (*a*) **Williamson's synthesis** is used for the preparation of symmetrical as well as unsymmetrical ethers.

$$RX + RO^{-}Na^{+} \longrightarrow ROR + NaX$$

**62.** (*c*) Ethanol is dehydrated to ethene in the presence of $H_2SO_4$ at 443 K. At 413 K, ethoxyethane is the main product.

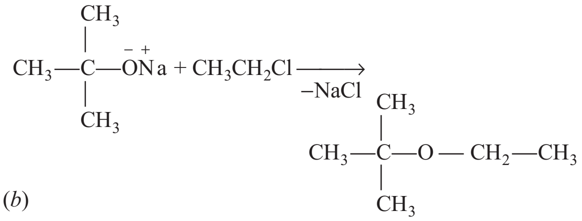


$$CH_3CH_2OH \begin{cases} \xrightarrow[443\ K]{H_2SO_4} CH_2{=}CH_2 \\ \xrightarrow[413\ K]{H_2SO_4} C_2H_5OC_2H_5 \end{cases}$$

**63.** (*b*) Williamson's synthesis involves the $S_N2$ mechanism when attack of an alkoxide ion on primary alkyl halide takes place.

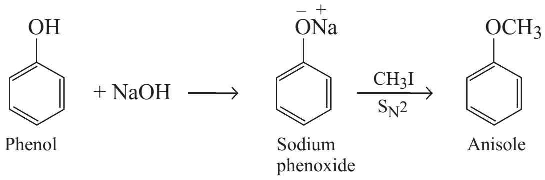
$$\overset{+}{R}-\overset{-}{X} + R\overset{-}{O}\overset{+}{Na} \xrightarrow{S_N2} ROR + NaX$$

**64.** (*a*) The reaction of alkyl halides with sodium alkoxide or sodium phenoxide to form ethers is called Williamson synthesis. Here, in this reaction alkyl halide should be primary and alkoxide, may be bulkier as shown below,



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{-}{O}\overset{+}{Na} + CH_3CH_2Cl \xrightarrow[-NaCl]{} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_2-CH_3$$

**65.** (*b*)



**66.** (*b*) The C—O bonds in ethers are polar and thus, ethers have a net dipole moment.

**67.** (*b*) The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular masses but are much lower than the boiling point of alcohols.

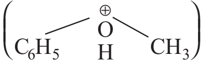
| | *n*-pentane | Ethoxyethane | Butan-1-ol |
|---|---|---|---|
| Boiling point | 309.1 | 307.6 | 390 |

**68.** (*c*) The large difference in the boiling points of alcohols and ethers is due to the presence of H-bonding interaction in alcohols.

**69.** (*a*) Alkyl aryl ethers are cleaved at the alkyl oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.

**70.** (*c*) The order of reactivity of hydrogen halides is as follows HI > HBr > HCl. The cleavage of ethers take place with concentrated HI or HBr at high temperature.

**71.** (*c*) In case of anisole, methylphenyloxonium ion



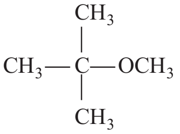
$$\left(C_6H_5-\underset{H}{\overset{\oplus}{O}}-CH_3\right)$$

is formed by the protonation of an ether.

The bond between O — $CH_3$ is weaker than the bond between O — $C_6H_5$ because the carbon of phenyl group is $sp^2$-hybridised and there is a partial double bond character. Therefore, the attack by $I^-$ ion breaks $OCH_3$ bond to form $CH_3I$. Phenols do not react further to give halides because the $sp^2$-hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

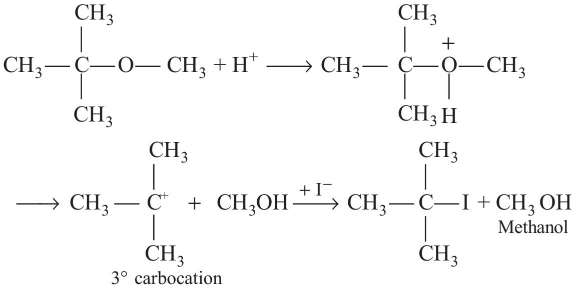
**72.** (*c*) The ether which gives more stable carbocation gives $CH_3OH$ as one of the product with hot concentrated HI.

The order of stability of carbocation is 3° > 2° > 1°.



Thus, $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OCH_3$ gives $CH_3OH$ as one of the product.

The reaction proceeds as



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 + H^+ \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_3$$

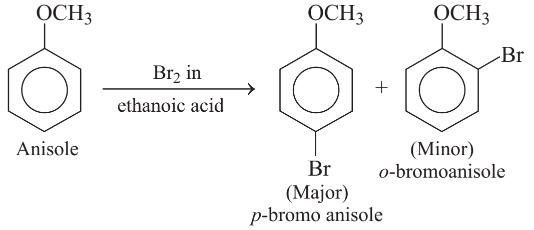
$$\longrightarrow \underset{3^\circ\ \text{carbocation}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}}} + CH_3OH \xrightarrow{+I^-} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-I + \underset{\text{Methanol}}{CH_3OH}$$

**73.** (*a*) KI is added to remove peroxides from Ethers. Ether peroxide oxidises KI into $I_2$ and itself gets reduced to ether.

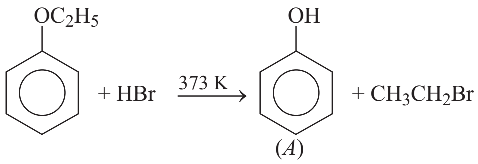
$$2I^- \longrightarrow I_2 + 2e^-$$

$$\text{Ether peroxide} + 2e^- \longrightarrow \text{Ether} + O_2$$

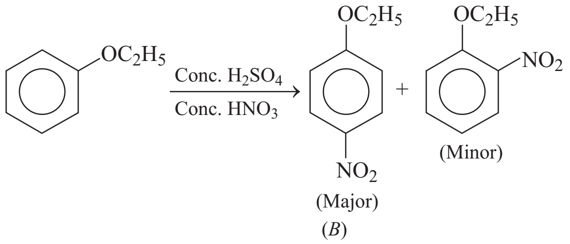
**74.** (*a*) Anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to activation of benzene ring by the methoxy group. *para* isomer is obtained in 90% yield.



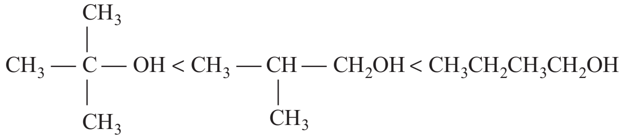
**75.** (*b*)



$C_6H_5$ — O bond has some double bond character with benzene ring due to resonance and hence, it is stronger than O — $C_2H_5$ bond. Cleavage of weaker O — $C_2H_5$ bond occurs to yield phenol and bromoethane.



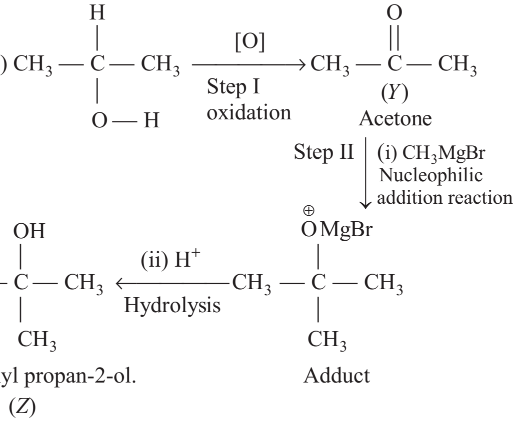
**76.** (*a*, *b*, *c*) Solubility of alcohols decreases with increase in size of alkyl group. Boiling points of alcohols increase with increase in the number of carbon atoms and decrease with increase of branching in carbon chain. The correct trends of boiling point is



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH < CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2OH < CH_3CH_2CH_3CH_2OH$$

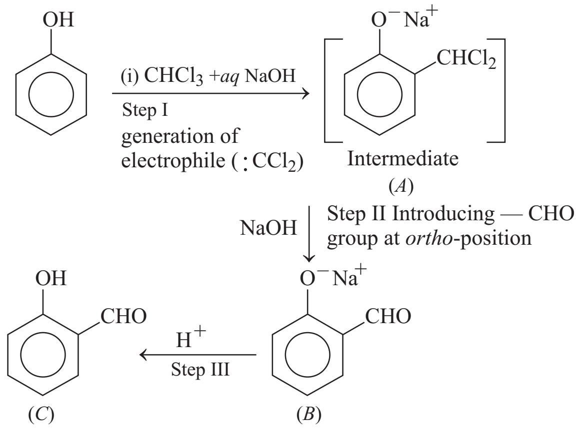
**77.** (*b*, *c*, *d*) is acid catalysed hydration where other reactions are correctly matched with their names.

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



2-methyl propan-2-ol.
(*Z*)

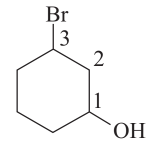
**79.** (*a*, *b*, *c*)



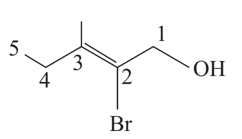
Salicylaldehyde
This reaction is known as Reimer–Tiemann reaction.

**80.** (*c*) In the presence of strong acids, alcohols act as Bronsted bases because they can accept a proton from strong acids to form protonated alcohols. Other given statements are true.

**81.** (*d*) Possible structural formula of $C_6\,H_{12}O\cdot X$ alongwith their correct IUPAC nomenclature among the given options are as follows



3-bromocyclohexanol



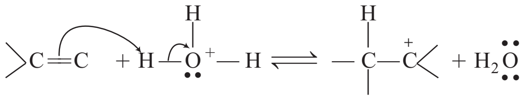
2-bromo 3-methylpent 2-en1-ol

When out of $X = Bre$ when the given options only these two are correct isomeric structures and nomenclature of organic compound.

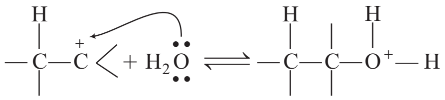
**82.** (*b*) The mechanism of the given reaction involves the following three steps.

**Step I** Protonation of alkene to form carbocation by electrophilic attack of $H_3O^+$.

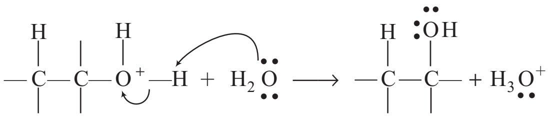
$$H_2O + H^+ \longrightarrow H_3O^+$$



**Step II** Nucleophilic attack of water on carbocation.



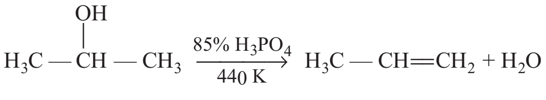
**Step III** Deprotonation to form an alcohol.



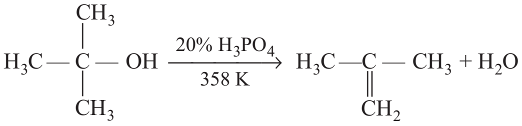
**83.** (*c*) Ethanol undergoes dehydration by heating it with concentrated $H_2SO_4$ at 443 K.

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} H_2C{=}CH_2 + H_2O$$

Secondary and tertiary alcohols are dehydrated under milder conditions.



$$H_3C-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} H_3C-CH{=}CH_2 + H_2O$$



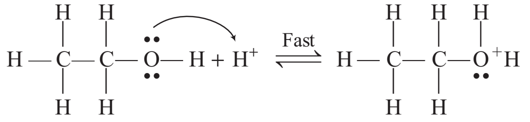
$$H_3C-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} H_3C-\underset{CH_2}{\underset{\|}{C}}-CH_3 + H_2O$$

The relative ease of dehydration of alcohols follows the order tertiary > secondary > primary.

**84.** (*c*) The mechanism of dehydration of ethanol involves the following steps :

**Mechanism**

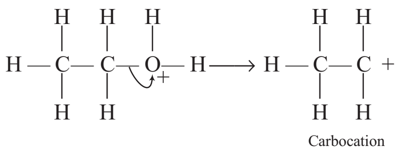
**Step I** Formation of protonated alcohol.



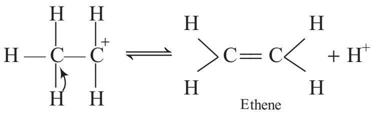
(Ethanol)

Protonated alcohol (Ethyl oxonium ion)

**Step II** Formation of carbocation : It is the slowest step and hence, the rate determining step of the reaction.



**Step III** Formation of ethene by elimination of a proton.



The acid used in step I is released in step III.

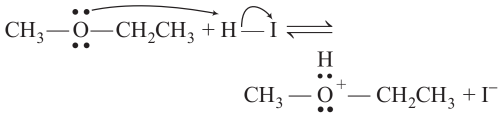
To drive the equilibrium to the right, ethene is removed as it is formed.

**85.** (*d*) Methanol is a colourless liquid and boils at 337 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and its large quantities causes even death. It is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

**86**. (*c*) The formation of an ether is a nucleophilic bimolecular reaction ($S_N2$) involving the attack of alcohol molecule on a protonated alcohol. The alkyl group in ether should be unhindered and the temperature should be low otherwise the reaction favours the formation of alkene.

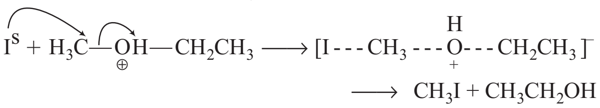
**87.** (*d*) The reaction of an ether with concentrated HI starts wtih protonation of ether molecule.

**Step I**



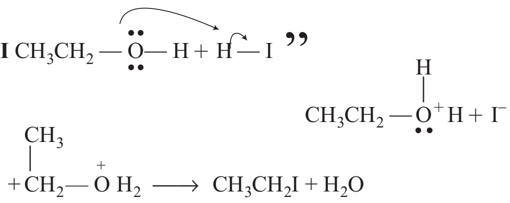
The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

**Step II** Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by $S_N2$ mechanism. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide ($S_N2$ reaction).

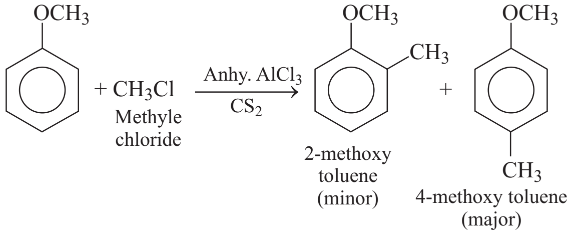


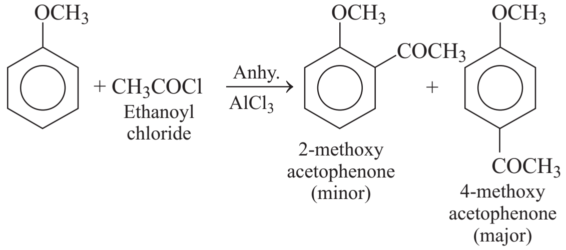
When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

**Step III**

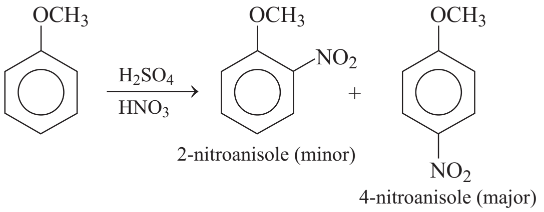


**88.** (*b*) Anisole undergoes Friedel-Crafts' reaction,

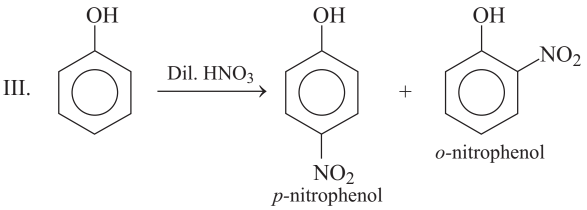


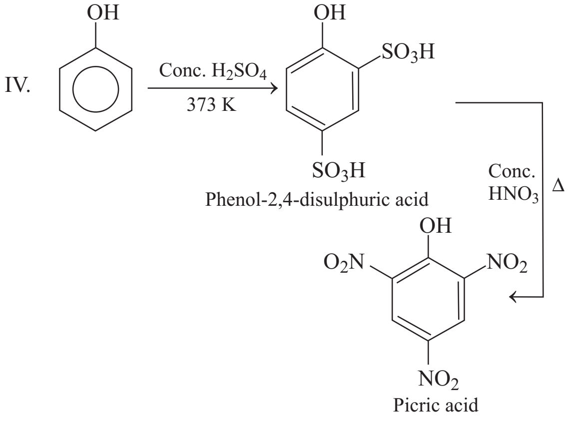


Anisole reacts with a mixture of concentrated sulphuric and nitric acid to yield a mixture of *ortho* and *para* nitroanisole.



**89.** (*c*) Reactions III and IV show the wrong products with phenols.





**90.** (*c*) Dehydration of alcohols is not the suitable method for the preparation of unsymmetrical ethers since complex mixture is obtained. This method is suitable for the preparation of ethers having primary alkyl groups only.

**91.** (*d*) The bond angle in alcohols is slightly less than the tetrahedral angle ($109°28'$). It is due to the repulsion between the unshared electron pairs of oxygen.

**92.** (*a*) In phenols, the —OH group is attached to $sp^2$-hybridised carbon atom of an aromatic ring. So, the carbon oxygen bond length (136 pm) in phenol is slightly less than that in methanol.

**93.** (*b*) The bond angle in ether is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (–*R*) groups. The C— O bond length (141 pm) is almost the same as in alcohols.

**94.** (*b*) Carboxylic acids are reduced to the primary alcohols in excellent yields by lithium aluminium hydride, a strong reducing agents.

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$$

$LiAlH_4$ is an expensive reagent and therefore, used for preparing special chemicals only.Commercially, acids are reduced to alcohols by converting them to esters followed by their reduction using hydrogen in the presence of catalyst.

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{catalyst}]{H_2} RCH_2OH + R'OH$$

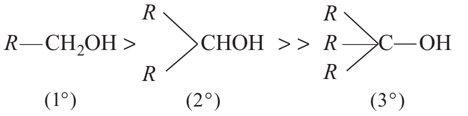
**95.** (*d*) The boiling point of alcohols and phenols increases with increase in the number of carbon atoms (increase in van der Waals' forces). In alcohols, the boiling point decreases with increase of branching in carbon chain (because of decrease in van der Waals' forces with decrease in surface area).

**96.** (*c*) Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules.
The solubility decreases with increase in size of the alkyl/aryl groups. Several lower molecular mass alcohols are miscible with water in all proportions.

**97.** (*d*) Ether is more volatile than an alcohol due to the intermolecular hydrogen bonding between the alcohol molecules.

**98.** (*a*) Dipole moment of phenol is smaller than that of methanol because in phenol, Ar group is – *I*-effect showing group while in methanol — $CH_3$ is + *I*-effect group, resulting the greater polarity and hence greater dipole moment of methanol.

**99.** (*a*) An electron releasing group ($CH_3$, $C_2H_5$) increases electron density on oxygen tending to decrease the polarity of OH bond. This decreases the acidic strength. For this reason, the acid strength of alcohols decreases in the following order.



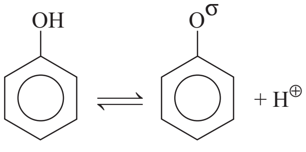
$$\underset{(1°)}{R-CH_2OH} > \underset{(2°)}{R_2CHOH} >> \underset{(3°)}{R_3C-OH}$$

**100.** (*c*) Alcohols act as Lewis base due to the presence of unshared electron pairs on oxygen which makes them proton acceptors and electron pair donors.

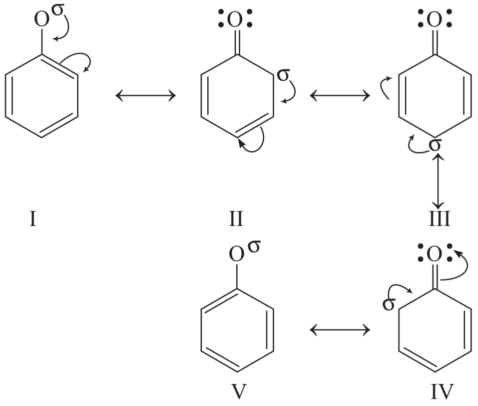
**101.** (*a*) The reaction of phenol with aqueous NaOH indicates that phenols are stronger acids than alcohols and water.

The ionisation of an alcohol and a phenol takes place as follows

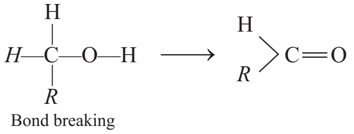
$$R-\ddot{O}H \;”\; RO^{s} + H^{\oplus}$$



In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structure I–V) makes phenoxide ion more stable and favours the ionisation of phenol.



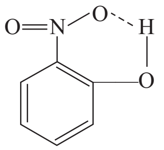
**102.** (*d*) Oxidation of alcohols involve the formation of a carbon oxygen double bond with cleavage of an O—H and C—H bonds.



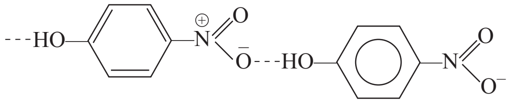
Such a cleavage and formation of bonds occur in the oxidation reactions. These are known as dehydrogenation reactions as these involve the loss of dihydrogen from an alcohol molecule.

**103.** (*c*) In the body, methanol is oxidised first to methanal and then to methanoic acid which may cause blindness and death.

**104.** (*d*) *o*-nitrophenol is more volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



*o*-nitrophenol (intramolecular H-bonding)



*p*-nitrophenol
(intermolecular H-bonding)

**105.** (*c*) 2,4,6-trinitrophenol (picric acid) is a strong acid due to the presence of three electron withdrawing $NO_2$ groups which facilitate the release of hydrogen ion.

**106.** (*c*) In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of OH group attached to the benzene ring.

**107.** (*a*) In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.

**108.** (*a*) $R-OH + NaBr \not\longrightarrow R-Br + \bar{O}H$ because $\bar{O}H$ is not a good leaving group. But when $H_2SO_4$ is added, water is released after reaction. As it is a neutral molecule, it also act as a good leaving group.

$$R-OH \xrightarrow{H_2SO_4} R-\overset{r}{O}H_2 \xrightarrow{NaBr} R-Br + H_2O$$

**109.** (*b*) Isopropyl alcohol is preferred over ethanol because it has less drying effect on the skin. It is used as cooling and soothing agent for bed ridden patients and athletes. It is also used as an antiseptic for skin before giving injections.

**110.** (*a*) The dehydration of secondary and tertiary alcohols takes place to give ethers is unsuccessful as elimination competes over substitution and as a consequence alkene are easily formed.

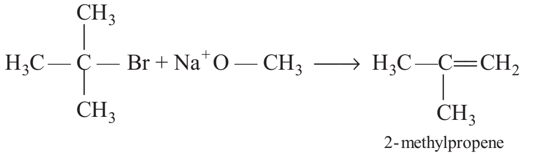
**111.** (*c*) Diethyl ether has been used widely as an inhalation anaesthetic but due to its slow effect and an unpleasant recovery period, it has been replaced by the other compounds.

**112.** (*a*) Ethoxyethane and butan-1-ol are miscible to almost the same extent, i.e. 7.5 and 9 g per 100 mL of water respectively while pentane is essentially immiscible with water. This is due to the fact that oxygen of either can form the hydrogen bond with the water molecule.

**113.** (*c*) Ethers are the least reactive among all the functional groups. That's why the cleavage of C—O bond in ethers takes place under drastic conditions with excess of hydrogen halides.

$$R-O-R + HX \longrightarrow RX + ROH$$
$$ROH + HX \longrightarrow RX + H_2O$$

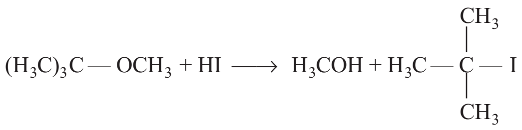
**114.** (*a*)



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Br + Na^+O-CH_3 \longrightarrow \underset{\text{2-methylpropene}}{H_3C-\underset{\displaystyle CH_3}{C}=CH_2} + NaBr + CH_3OH$$

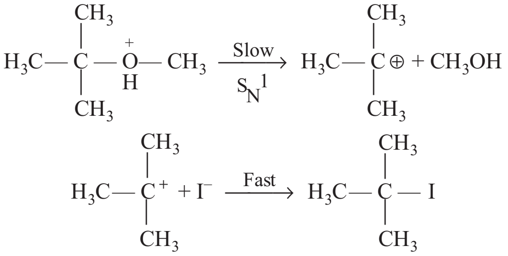
If tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. It is because alkoxides are not only nucleophiles but also the strong bases. They react with alkyl halides leading to elimination reactions.

**115.** (*a*)



$$(H_3C)_3C-OCH_3 + HI \longrightarrow H_3COH + H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-I$$

When one of the alkyl part of ether is a tertiary group, the halide formed is a tertiary halide.

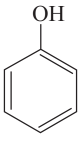


$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{+}{\underset{H}{O}}-CH_3 \xrightarrow[S_N1]{Slow} H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\oplus + CH_3OH$$

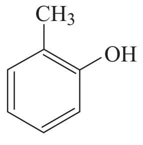
$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}} + I^- \xrightarrow{Fast} H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-I$$

**116.** (*c*) Alcohols, phenols and ethers are the basic compounds used for the formation of detergents, antiseptics and fragrances respectively.

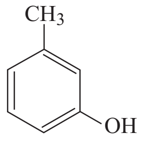
**118.** (*a*) A → 6; B → 3; C → 2; D → 5.



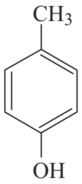
Phenol



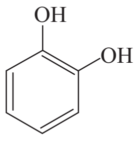
*o*-cresol
(2-methylphenol)



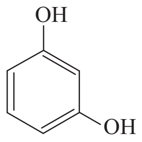
*m*-cresol
(3-methylphenol)



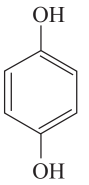
*p*-cresol
(4-methylphenol)



Catechol
(Benzene-1,2-diol)

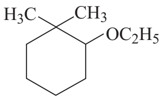


Resorcinol
(Benzene-1,3-diol)

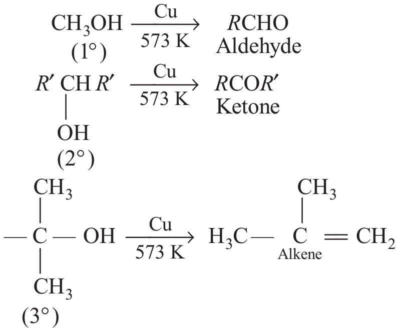


Hydroquinone or quinol
Benzene-1,4-diol

**119.** (*d*) A → 2; B → 4; C → 3; D → 1.

| Compound | Common name | IUPAC name |
|---|---|---|
| $C_6H_5OCH_3$ | Methyl phenyl ether (Anisole) | Methoxybenzene (Anisole) |
| $C_6H_5O(CH_2)_6-CH_3$ | Heptyl phenyl ether | 1-phenoxyheptane |
| $C_6H_5OCH_2CH_2-\underset{\displaystyle CH_3}{CH}-CH_3$ | Phenyl isopentyl ether | 3-methylbutoxy-benzene |
|  | – | 2-ethoxy-1, 1-dimethyl cyclohexane |

**120.** (*a*)

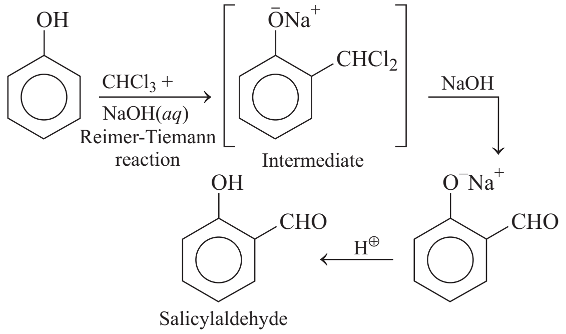


$$\underset{(1°)}{CH_3OH} \xrightarrow[573\ K]{Cu} \underset{\text{Aldehyde}}{RCHO}$$

$$\underset{(2°)}{R'\underset{\displaystyle OH}{CH}R'} \xrightarrow[573\ K]{Cu} \underset{\text{Ketone}}{RCOR'}$$

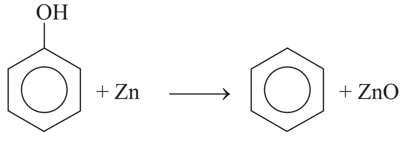
$$\underset{(3°)}{H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH} \xrightarrow[573\ K]{Cu} H_3C-\overset{\displaystyle CH_3}{\underset{\text{Alkene}}{C}}=CH_2$$

**121.** (*b*) A → 1, B → 3, C → 2

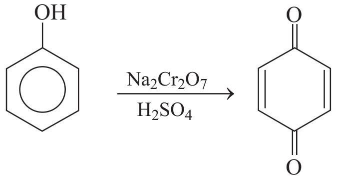


Salicylaldehyde

Phenol is converted to benzene on heating with Zn dust.



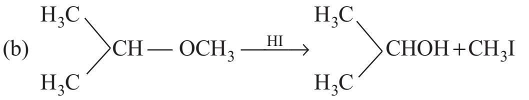
Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone.



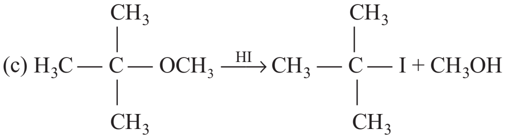
**122.** (*b*) A → 2; B → 3; C → 4; D → 1

**123.** (*d*) A → 4; B → 5; C → 2; D → 1

(a) $CH_3-O-CH_3 \xrightarrow{HI} CH_3OH + CH_3I$

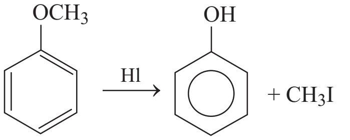


(b) $\underset{H_3C}{\overset{H_3C}{>}}CH-OCH_3 \xrightarrow{HI} \underset{H_3C}{\overset{H_3C}{>}}CHOH+CH_3I$

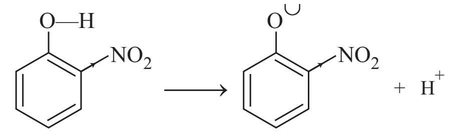


(c) $H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3 \xrightarrow{HI} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-I+CH_3OH$

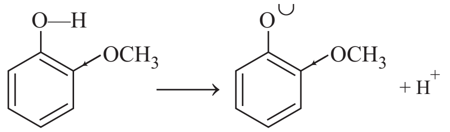
(d)

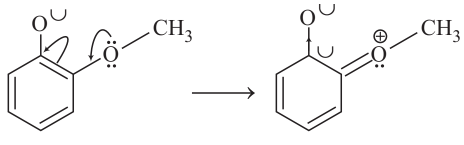


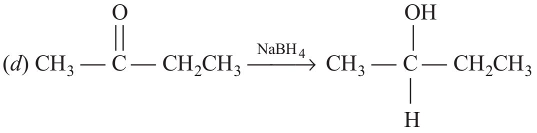
**124.** (*c*) Nitro ($NO_2$) group is electron withdrawing whereas methoxy ($OCH_3$) group is electron releasing in nature. *o*-nitrophenol produces $H^+$ ions easily but methoxyphenol does not. This is because *o*-nitrophenoxide ion is stabilised due to resonance. This is not true with *o*-methoxyphenoxide ion. The two negative charges repel each other thereby destabilising it.



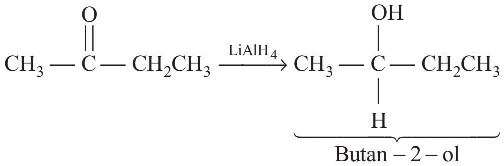
*o*-nitrophenol







**125.** (*d*) $CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_3 \xrightarrow{NaBH_4} CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2CH_3$

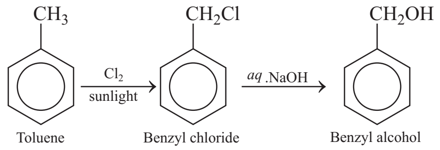


$CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_3 \xrightarrow{LiAlH_4} \underbrace{CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2CH_3}_{\text{Butan – 2 – ol}}$

**126.** (*b*) Ethers are formed as a result of acidic dehydration by $S_N2$ mechanism (from primary alcohols). If secondary or tertiary alcohols are used, due to steric hindrance, alkenes are formed and not ethers.

**127.** (*a*) Reaction first is acetylation while second (b) is bromination.

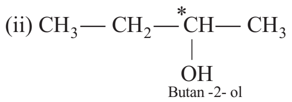
**128.** (*d*) Monochlorination of toluene in sunlight gives benzyl chloride. On hydrolysis with *aq*. NaOH, benzyl chloride shows nucleophilic substitution reaction to give benzyl alcohol.



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

(i) $\underset{\text{Butan – 1–ol}}{CH_3CH_2-CH_2-CH_2OH}$

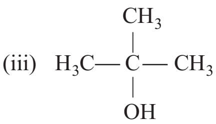
No carbon is chiral in this compound as none of the four carbon is bonded to four different substituents.



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

Butan -2- ol

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



(iii) $H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

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).

**130.** (*c*) The given reaction is nucleophilic substitution reaction in which —OH group is replaced by —Cl. Tertiary alcohols, when react with HCl in the 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°.

**131.** (*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.

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

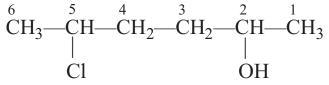
**132.** (*b*) An addition reaction is a reaction where two or more molecules combine to form a larger one. These reactions occur to change the unsaturated compound to saturated compound. In dehydrohalogenation reaction, alkyl halides give alkenes.

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.

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

**133.** (*c*) Phenol is also known as carbolic acid. It cannot be considered as an 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, in compounds (*B*) and (*C*), —OH group is bonded to $sp^3$-hybridised carbon which in turn is bonded to benzene ring. So these are aromatic alcohols.

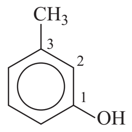
**134.** (*c*)



$$\overset{6}{C}H_3—\underset{Cl}{\overset{5}{C}H}—\overset{4}{C}H_2—\overset{3}{C}H_2—\underset{OH}{\overset{2}{C}H}—\overset{1}{C}H_3$$

The correct IUPAC name of the compound is 5-chlorohexan-2-ol.

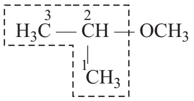
**135.** (*a*) The structure of *m*–cresol is



*m*-cresol

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

**136.** (*c*)

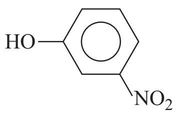


$$H_3\overset{3}{C}—\underset{\overset{|}{\overset{1}{C}H_3}}{\overset{2}{C}H}—OCH_3$$

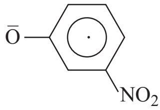
IUPAC name of the above compound is 2-methoxypropane.

**137.** (*b*) Weakest acid has the strongest conjugate base. *R*OH is the acid of $RO^-$ conjugate base, *R*OH is the acid of $^-OH$,

$C_6H_5OH$ is the acid of $C_6H_5O^-$ and



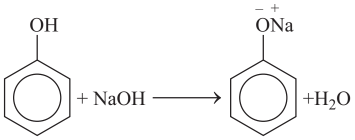
is the acid of



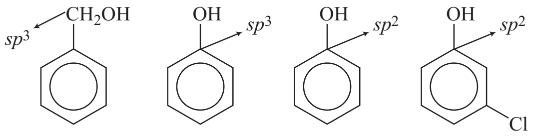
Among all these acids,

*R*OH is the weakest acid. Therefore, the strongest base is $RO^-$.

**138.** (*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.



**140.** (*d*) α 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.



Benzyl alcohol Cyclo hexanol Phenol *m*-chloro phenol

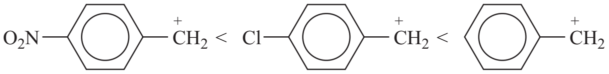
Presence of electron withdrawing group increases the acidic strength. So, *m*-chlorophenol is most acidic among all the given compounds.

**142.** (*c*) Reaction of the given compounds with HBr/HCl is a nucleophilic substitution reaction. It follows $S_N1$ mechanism.$S_N1$ 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.

**143.** (*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, the correct increasing order of boiling point is:

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