# Alcohols, Phenols and Ethers

### Fastrack Revision

▶ Alcohols and Phenols: Alcohols and phenols are formed when a hydrogen atom in hydrocarbon, aliphatic and aromatic respectively, is replaced by hydroxyl group.

#### Classification of Alcohols and Phenols

➤ In alcohols, the —OH group is attached to sp³ hybridised carbon.

➤ In phenols, the —OH group is attached to sp² hybridised carbon.

#### Preparation of Alcohols

#### ► From Alkenes

By acid catalysed hydration in accordance with Markownikov's rule:

$$CH_3$$
— $CH$ 
 $CH_2$ 
 $+H_2O$ 
 $\stackrel{H^+}{\longleftarrow}$ 
 $CH_3$ — $CH$ 
 $OH$ 

> By Hydroboration-Oxidation:

$$CH_{3} - CH_{2} - CH_{2} + (H_{2} - BH_{2})_{2} - CH_{3} - CH_{2} - CH_{2}$$

$$H BH_{2}$$

$$CH_{3} - CH_{2} - CH_{2})_{3}B \leftarrow CH_{3} - CH_{2} - CH_{2} - CH_{2} - CH_{2}$$

$$3H_{1}O_{2},OH_{1} + H_{1}O$$

$$3CH_{3}CH_{2}CH_{2}OH + B(OH)_{3}$$

#### ► From Carbonyl Compounds

> By reduction of aldehydes and ketones:

 Aldehydes yield primary alcohols whereas ketones give secondary alcohols, when subjected to reduction. > By reduction of carboxylic acids and ester:

RCOOH 
$$\xrightarrow{(i) \text{UAIH}_4} \text{RCH}_2\text{OH}$$
  
RCOOR'  $\xrightarrow{\text{H}_2} \text{RCH}_2\text{OH} + \text{R'OH}$ 

#### ► From Grignard's Reagent:

The reaction produces a primary alcohol with methanol, a secondary alcohol with aldehydes (except methanal) and tertiary alcohol with ketones.

$$\begin{array}{c} \text{HCHO} + \text{RMgX} \longrightarrow \text{RCH}_2\text{OMgX} \xrightarrow{H_2\text{O}} \text{RCH}_2\text{OH} + \text{Mg} < \bigvee_{\text{OH}} \\ \text{RCHO} + \text{R'MgX} \xrightarrow{H_2\text{O}} \text{R} \xrightarrow{\text{CH}} \text{OMgX} \xrightarrow{H_2\text{O}} \xrightarrow{\text{NIg(OH)X}} \\ \\ \text{R} \xrightarrow{\text{CH}} \text{OH} \\ \\ \text{RCOR} + \text{R'MgX} \longrightarrow \text{R} \xrightarrow{\text{C}} \text{OMgX} \xrightarrow{H_2\text{O}} \text{R} \xrightarrow{\text{R'}} \\ \\ \text{R} \xrightarrow{\text{C}} \text{CH} \longrightarrow \text{OH} \\ \\ \text{RCOR} \xrightarrow{\text{R'MgX}} \xrightarrow{\text{R}} \text{C} \xrightarrow{\text{C}} \text{OMgX} \xrightarrow{\text{Mg(OH)X}} \text{R} \xrightarrow{\text{C}} \text{C} \longrightarrow \text{OH} \\ \\ \text{RCOR} \xrightarrow{\text{R'MgX}} \xrightarrow{\text{R'MgX}} \text{R} \xrightarrow{\text{C}} \text{C} \longrightarrow \text{OH} \\ \\ \text{R'} \xrightarrow{\text{NIg(OH)X}} \text{R} \xrightarrow{\text{C}} \text{C} \longrightarrow \text{OH} \\ \\ \text{R'} \xrightarrow{\text{R'}} \xrightarrow{\text{R'}} \xrightarrow{\text{R'}} \text{R'} \xrightarrow{\text{R'}} \xrightarrow{\text{R'}} \text{R'} \xrightarrow{\text{R'}} \xrightarrow{\text$$

#### ► Hydrolysis of Alkyl Halldes:

- ightharpoonup R—X + KOH(aq) ightharpoonup ROH + KX
- ➤ Ease of hydrolysis of alkyl halides is R—I > R—Br > R—Cl and t > s > p alkyl halides.
- ► Hydrolysis of Ethers:

$$R - O - R + H_2O \xrightarrow{H_2SO_4} 2ROH$$

From Primary Amines: By treatment with nitrous acid.

$$RNH_2 + HONO \xrightarrow{(NaNO_2 + HCI)} ROH + N_2 + H_2O$$

➤ Methylamine does not give methyl alcohol when treated with HNO₂. It gives CH₃OCH₃ and CH₃ONO.

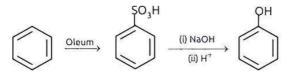
▶ By Alcoholic Fermentation:

$$\begin{array}{ccc} C_{12}H_{22}O_{11}+H_2O & \xrightarrow{Invertase} & C_6H_{12}O_6 + C_6H_{12}O_6 \\ Sucrose & Glucose & Fructose \\ \hline C_6H_{12}O_6 & \xrightarrow{Zymase} & 2C_2H_5OH + 2CO_2(g) \\ Glucose & and fructose & Elithyl alcohol \\ \end{array}$$

#### Preparation of Phenols

► From Haloaranos:

#### From Benzene Sulphonic Acid:



#### ► From Diazonium Salts:

#### ▶ From Cumene:

$$H_3C$$
 $CH$ 
 $CH_3$ 
 $H_3C$ 
 $CH$ 
 $O_2$ 
 $Cumene$ 
 $O_3$ 
 $Cumene$ 
 $O_3$ 
 $Cumene$ 
 $O_4$ 
 $O_4$ 
 $O_5$ 
 $O_5$ 
 $O_7$ 
 $O_8$ 
 $O_8$ 

#### **Physical Properties of Alcohols**

- ➤ Lower alcohols are colourless liquids, members from C<sub>5</sub> - C<sub>11</sub> are oily liquids and higher members are waxy solids.
- ➤ The hydroxyl groups in alcohols can form H-bonds with water, so alcohols are miscible with water. The solubility decreases with increase in molecular mass.
- ➤ Boiling points of alcohols are higher than expected because of the presence of intermolecular hydrogen bonding in the polar molecules.

[The boiling point decreases in the order  $1^{\circ} > 2^{\circ} > 3^{\circ}$  as the van der Waals' forces of attraction decreases.]

#### **Physical Properties of Phenols**

- ➤ These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.
- > Phenol is also called carbolic acid.
- Because of the presence of polar —OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.

#### Acidity of Alcohols and Phenols

- Alcohols are weaker acids than water due to + I group present in alcohols, which decreases the polarity of —OH bond.
- Acid strength of alcohols

$$R-CH_2OH > R > CH-OH >> R > C-OH$$
Primary Secondary

- ➤ Electron releasing group increases electron density on oxygen to decrease the polarity of —OH bond.
- Order of acidity is RCOOH > H<sub>2</sub>CO<sub>3</sub> > C<sub>6</sub>H<sub>5</sub>OH > H<sub>2</sub>O > R—OH.
- Phenol is more acidic than alcohols due to stabilisation of phenoxide ion through resonance.

#### Chemical Reactions of Alcohols and Phenols

► Reactions Involving Cleavage of O—H Bond:

(a) Reaction with Metal:

$$2R-O-H+2Na \longrightarrow 2R-O-Na+H_2$$

$$2 \longrightarrow + 2 \times 3 \longrightarrow 2 \longrightarrow + H_2$$
Sodium phenoxide

#### (b) Esterification:

$$Ar/R$$
— $O$ — $H$  +  $R'COOH$   $\stackrel{H^+}{\Longleftrightarrow}$   $Ar/R$ — $OCOR'$  +  $H_2O$ 

$$Ar/R$$
— $OH$  +  $(R'CO)_2O$   $\stackrel{H^+}{\Longleftrightarrow}$   $Ar/R$ — $OCOR'$  +  $R'COOH$ 
 $R/Ar$ — $OH$  +  $R'COCI$   $Pyridine$   $R/Ar$ — $OCOR'$  +  $HCI$ 

The reaction with R'COOH and  $(R'CO)_2O$  is reversible, so conc.  $H_2SO_4$  is used to remove water.

#### ▶ Reactions Involving Cleavage of C—O Bond in Alcohols:

➤ In these reactions, the reactivity order of different alcohols is:

Methyl alcohol Primary alcohol Secondary alcohol Tertiary alcohol

Alkyl group due to +I effect increases the electron density on the carbon and oxygen atom of C—OH bond. As a result, the bond cleavage becomes easy.

(a) Reaction with Halogen Acids: Alcohols can be converted into haloalkanes by the action of halogen acids.

$$R \longrightarrow OH + HX \longrightarrow R \longrightarrow X + H_2O$$
 (where X  $=$  Cl, Br, I)

> For a given alcohol, order of reactivity of HX is:

> For a given halogen acid, order of reactivity of alcohols ie:

#### Tertiary > Secondary > Primary Lucas Test

Primary alcohols		Secondary alcohols	Tertiary alcohols
RCH <sub>2</sub> OH	Anhy.ZnCl <sub>2</sub> No reaction	R <sub>2</sub> CH OH OUNCHEL ANNY DICE 2 RICHEL	R <sub>3</sub> C—OH  cont. HCl Anhy.2nCl <sub>2</sub> R <sub>3</sub> CCl
No reaction and hence, no white cloudiness or turbidity at room temperature.		White cloudiness or turbidity appears within about 5 minutes.	White cloudiness or turbidity appears immediately.

#### (b) Reaction with Phosphorus Halides:

ROH + PCl<sub>5</sub> 
$$\longrightarrow$$
 RCI + POCl<sub>3</sub> + HCI  
3ROH + PBr<sub>3</sub>  $\xrightarrow{P/Br_2}$   $\longrightarrow$  3RBr + H<sub>3</sub>PO<sub>3</sub>  
3ROH + PI<sub>4</sub>  $\xrightarrow{P/I_2}$   $\longrightarrow$  3RI + H<sub>3</sub>PO<sub>3</sub>

#### (c) Reaction with Thionyl Chloride:

$$ROH + SOCI_2 \longrightarrow RCI + SO_2 \uparrow + HCI \uparrow$$

#### ► Dehydration of Alcohols:

➤ The ease of dehydration is 3° > 2° > 1°.

$$C_2H_5OH \xrightarrow{H_2SO_4} CH_2 = CH_2 + H_2O$$

$$\begin{array}{c} \text{CH}_{3} \\ \mid \\ \text{CH}_{3} - \text{C} - \text{OH} & \xrightarrow{20\% \text{ H}_{2}\text{SO}_{4}} \rightarrow \text{CH}_{3} - \text{C} & \text{III} \text{CH}_{2} + \text{H}_{2}\text{C} \\ \mid \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \end{array}$$

➤ Oxidation Reactions: Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline KMnO<sub>4</sub> and acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. A common reagent that selectively oxidises a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate (PCC).

▶ Dehydrogenation:

#### Some Reactions of Phenols

▶ Electrophilic Substitution Reactions: The —OH group attached to the benzene ring activates it towards electrophilic substitution at *ortho* and *para* positions.

#### (a) Halogenation:

$$\begin{array}{cccc} & & & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$$

$$\begin{array}{c}
OH \\
& \xrightarrow{Br_1, 0^*C} \\
& \xrightarrow{CS_2}
\end{array}$$

$$\begin{array}{c}
OH \\
& \xrightarrow{Br_1, 0^*C}
\end{array}$$

$$\begin{array}{c}
OH \\
& \xrightarrow{Br_1, 0^*C}
\end{array}$$

$$\begin{array}{c}
OH \\
& \xrightarrow{Bromophenol}$$

$$\begin{array}{c}
PBromophenol
\end{array}$$

#### (b) Sulphonation:

#### (c) Nitration:

$$\xrightarrow{\text{conc. HNO}_{3}} \xrightarrow{\text{conc. HNO}_{3}} O_{2}N \xrightarrow{\text{NO}_{2}} NO_{2}$$

$$\downarrow NO_{2}$$

$$\downarrow NO_{2}$$

$$\downarrow NO_{2}$$

$$\downarrow A,6-Trinitrophenol (picric acid)$$

#### (d) Reimer-Tiemann Reaction:

#### ► Kolbe's Reaction:

#### ▶ Reaction with Zinc Dust:

#### ► Oxidation:

$$\begin{array}{c}
OH \\
& \longrightarrow \\$$

#### ► Fries Rearrangement:

#### Uses of Alcohols and Phenols

- ▶ 100% ethanol is absolute alcohol and 95% ethanol is rectified alcohol.
- ► A mixture of 20% ethanol and 80% gasoline is the power alcohol.
- ► Alcohols are used as solvents, antifreeze agent, in the preparation of medicines as preservatives, etc.
- Phenols are used to prepare bakelite, plastic for manufacturing of dyes and drugs in medicines in the preparation of phenolphthalein, etc.

#### Ethers

▶ Ethers are the organic compounds in which two alkyl or aryl groups are attached to a divalent oxygen, known as ethereal oxygen. These are represented by the general formula R—O—R" where R may be alkyl or aryl groups. e.g.,

$$\begin{array}{cccc} \text{CH}_3 & \text{--}\text{O} & \text{--}\text{CH}_3, & \text{C}_2\text{H}_5 & \text{--}\text{O} & \text{--}\text{C}_2\text{H}_5 \\ \text{Dimethyl ether} & \text{Diethyl ether} & \text{CH}_3 & \text{--}\text{O} & \text{--}\text{C}_3\text{H}_7 \\ \text{Ethyl methyl ether} & \text{Methyl $n$-propyl ether} \end{array}$$

#### Preparation of Ethers

#### ▶ By Dehydration of Alcohols:

Williamson's Synthesis: Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.

$$CH_{3}CH_{2}Br + CH_{3}CH_{2}ONa \longrightarrow CH_{3}CH_{2}OCH_{2}CH_{3} + NaBr$$

$$CH_{3}$$

$$CH_{3}Br + H_{3}C - C - ONa \longrightarrow CH_{3} - O - C - CH_{3} + NaBr$$

$$CH_{3}$$

$$CH_$$

#### Physical Properties of Ethers

- > Ethers are polar but insoluble in H<sub>2</sub>O.
- Ethers have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.

Alkoxy bonzono

#### **Chemical Reactions of Ethers**

#### ► Reaction with HX:

The order of reactivity of hydrogen halides is as follows:

#### ► Halogenation:

$$\begin{array}{ccc} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 & \xrightarrow{\text{Cl}_2} & \text{CH}_3\text{CHCIOCH}_2\text{CH}_3 \\ & (\alpha\text{-Monochloro diathyl ather}) \\ \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + 10\text{Cl}_2 & \xrightarrow{\text{(light)}} & \text{C}_2\text{Cl}_5\text{OC}_2\text{Cl}_5 & +10\text{HCl}_2\\ & (\text{excess}) & (\text{Perchlorodiethyl ether}) \\ \end{array}$$

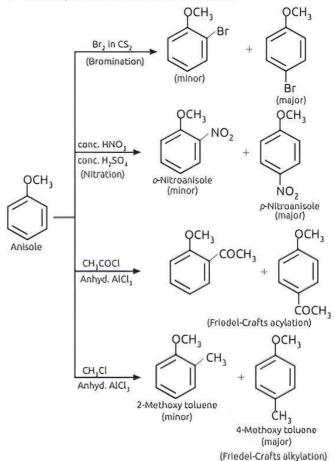
#### ► Reaction with PCI<sub>s</sub>:

$$\mathsf{R} {\longleftarrow} \mathsf{O} {\longleftarrow} \mathsf{R} + \mathsf{PCl}_{\mathsf{S}} \xrightarrow{\quad \Delta \quad} \mathsf{2RCl} + \mathsf{POCl}_{\mathsf{3}}$$

#### ▶ Reaction with CO:

$$ROR + CO \xrightarrow{BF_3/150^{\circ}C} RCOOR$$

#### ► Electrophilic Substitution Reactions:



Ethyl phenyl ester  $C_6H_4OC_2H_5$  is also known as phenetole.

#### Uses of Ethers

- Dimethyl ether is used as refrigerant and as a solvent at low temperature.
- Diethyl ether is used as an anaesthesia in surgery.

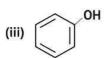


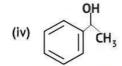
### **Practice** Exercise



### Multiple Choice Questions

- Q1. Identify the secondary alcohols from the following set:
  - (i) CH<sub>2</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>
- $(C_2H_5)_3COH$ (ii)





(CBSE SQP 2021 Term-1)

- a. (i) and (iv)
- b. (i) and (iii)
- c (i) and (ii)
- d. (i), (iii) and (iv)
- Q 2. The C O H bond angle in alcohol is:

(CBSE 2021 Term-1)

- a. slightly greater than 109°28'
- b. slightly less than 109°28'
- c. slightly greater than 120°
- d. slightly less than 120°
- Q 3. The catalyst used for the preparation of methyl alcohol from water gas is:
  - a. CuO + ZnO + NiO
- b.  $CuO + ZnO + Cr_2O_3$
- C Al, O,
- d.  $CuO + Fe_2O_3$
- Q 4. What is the product formed when butanol reacts with HCl and ZnCl,?
  - a. 1-chlorobutane
- b. 2-chlorobutane
- c. Butane
- d. Butene
- Q S. In the reaction R—OH + HCl  $\xrightarrow{ZnCl_1}$  RCl + H<sub>2</sub>O, what is the correct order of reactivity of alcohol?

(CBSE 2023)

- a.  $1^{\circ} < 2^{\circ} < 3^{\circ}$
- b.  $1^{\circ} > 3^{\circ} > 2^{\circ}$
- c.  $1^{\circ} > 2^{\circ} > 3^{\circ}$
- d.  $3^{\circ} > 1^{\circ} > 2^{\circ}$
- Q 6. Which of the following alkenes on acid catalysed hydration gives a tertiary alcohol? (CBSE 2023)
  - a. 2-butene
- b. 2-methylpropene
- c. Propene
- d. 1-butene
- Q7. Lucas reagent is:
  - a. conc. HCl + anhyd. ZnCl<sub>2</sub>
  - b. Pd + BaSO,
  - c. dil HCl + anhyd. ZnCl<sub>2</sub>
  - d. None of the above
- Q8. Lucas reagent is used to differentiate which monohydric alcohol?
  - a. Primary
- b. Secondary
- c. Tertlary
- d. All of these
- Q 9. The boiling points of alcohols are higher than those of hydrocarbons of comparable masses due (CBSE SQP 2021 Term-1)
  - a. hydrogen bonding
  - b. ion-dipole interaction
  - c dipole-dipole interaction
  - d. van der Waal's forces

Q 10. Which of the following is optically inactive?

(CBSE 2021 Term·1)

- a. (+)-Butan-2-ol
- b. (-)-Butan-2-ol
- c. (±)-Butan-2-ol
- d. (+)-2-Bromobutane
- Q 11. Lower molecular mass alcohols are:

(CBSE SQP 2021 Term-1)

- a. miscible in limited amount of water
- b. miscible in excess of water
- c. miscible in water in all proportions
- d. Immiscible in water
- Q 12. What would be the reactant and reagent used to obtain 2, 4-dimethyl pentan-3-ol?

(CBSE SQP 2021 Term·1)

- a. Propanal and propyl magnesium bromide
- b. 3-methylbutanal and 2-methyl magnesium bromide
- c. 2-dimethylpropanone and methyl magnesium
- d. 2-methylpropanal and isopropyl magnesium
- Q13. During dehydration of alcohols to alkenes by heating with concentrated  $H_2SO_4$ , the initiation step is: (CBSE SQP 2021 Term-1)
  - a. protonation of alcohol molecule
  - b. formation of carbocation
  - c. elimination of water
  - d. formation of an ester
- Q 14. In the following reaction,
  - CH<sub>3</sub>—CH = CH CH<sub>2</sub>OH The product formed is: (CBSE 2021 Term-1)
  - a. CH<sub>3</sub>—CHO and CH<sub>3</sub>CH<sub>2</sub>OH
  - b. CH<sub>3</sub>—CH ···· CH—COOH
  - c. CH<sub>3</sub>—CH ∞ CH—CHO
  - d. CH<sub>3</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CHO
- Q15. For the conversion of propene into 1-propanol, which of the following reagents and conditions should be used? (CBSE 2023)
  - a. Conc. H<sub>2</sub>SO<sub>4</sub>; H<sub>2</sub>O and heat
  - b. B<sub>2</sub>H<sub>A</sub>; H<sub>2</sub>O<sub>2</sub>/OH-
  - c. Dilute H2SO4
  - d. H20/H4
- Q 16. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields: (NCERT EXEMPLAR)
  - a. o-cresol
- b. m-cresol
- c. 2.4-dihydroxytoluene d. benzyl alcohol
- Q 17. Which of the following compounds will react with sodium hydroxide solution in water?

(NCERT EXEMPLAR)

- a. C<sub>6</sub>H<sub>0</sub>OH
- b. C<sub>6</sub>H<sub>6</sub>CH<sub>2</sub>OH

- c. (CH<sub>2</sub>)<sub>3</sub>C—OH
- d. C<sub>2</sub>H<sub>n</sub>OH

# Q 18. Anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst: (CBSE SQP 2023-24)

- a. due to the activation of benzene ring by the methoxy group
- b. due to the de-activation of benzene ring by the methoxy group
- c. due to the increase in electron density at *ortho* and *para* positions
- d. due to the formation of stable carbocation

## Q 19. Long time nitration of phenol with mixture of conc. HNO<sub>x</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> gives:

- a. o-nitrophenol
- b. p-nitrophenol
- c. picric acid
- d. nitrobenzene

## Q 20. o-hydroxy benzyl alcohol when reacted with PCl<sub>3</sub> gives the product as (IUPAC name):

(CBSE SQP 2021 Term-1)

- a. o-hydroxy-benzyl chloride
- b. 2-chloromethylphenol
- c. o-chloromethylchlorobenzene
- d. 4-hydroxymethylphenol

## Q 21. The major product of acid catalysed dehydration of 1-methylcyclohexanol is: (CBSE SQP 2022-23)

- a. 1-methylcyclohexane
- b. 1-methylcyclohexene
- c. 1-cyclohexylmethanol
- d. 1-methylenecyclohexane

## Q 22. What would be the major product of the following reaction?

$$C_6H_5$$
— $CH_2$ — $OC_6H_5 + HBr$ — $\rightarrow A + B$ 
(CBSE SQP 2022-23)

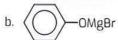
- a.  $A = C_6H_5CH_2OH$ ,  $B = C_6H_6$
- b.  $A = C_6 H_5 C H_2 O H$ ,  $B = C_6 H_5 B r$
- c.  $A = C_6H_5CH_3$ ,  $B = C_6H_5Br$
- d.  $A = C_6H_9CH_2Br$ ,  $B = C_6H_9OH$

## Q 23. In the reaction $\longrightarrow$ Br $\xrightarrow{\text{Mg}}$ 'Y' $\xrightarrow{\text{H}_2\text{O}}$ 'Y

#### Compound 'Y' is:

(CBSE 2021 Tarm-1)







## Q 24. Phenol does not undergo nucleophilic substitution reaction easily due to: (CBSE SQP 2021 Tarmi-1)

- a. acidic nature of phenol
- b. partial double bond character of C OH bond
- c. partial double bond character of C C bond
- d. Instability of phenoxide ion

## Q 25. Which of the following reactions is used to prepare salicylaldehyde? (CBSE SQP 2021 Tarm-1)

- a. Kolbe's reaction
- b. Etard reaction
- c. Reimer-Tiemann reaction
- d. Stephen's reduction

Q 26. Major product formed in the following reaction.

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$(CBSE 2021 Tarmi-1)$$

## Q 27. Which of the following observation is shown by 2-phenyl ethanol with Lucas reagent?

(CBSE SQP 2023-24)

- a. Turbidity will be observed within five minutes
- b. No turbidity will be observed
- c. Turbidity will be observed immediately
- d. Turbidity will be observed at room temperature but will disappear after five minutes
- Q 28. When diethyl ether is heated with excess of HI, it produces: (CBSE 2023)
  - a. ethanol b. iodoform
  - c. methyl lodide d. ethyl lodide

## Q 29. Williamson's synthesis of preparing dimethyl ether is an: (CBSE SQP 2021 Tarm-1)

- a. S,,1 reaction
- b. Elimination reaction
- c.  $S_N 2$  reaction
- d. Nucleophilic addition reaction

## Assertion & Reason Type Questions

**Directions (Q. Nos. 30-38):** Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:

- a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
- Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
- c. Assertion (A) is true but Reason (R) is false.
- d. Assertion (A) is false but Reason (R) is true.
- Q 30. Assertion (A): Addition reaction of water to but-1-ene in acidic medium yields butan-2-ol. Reason (R): Addition of water in acidic medium proceeds through the formation of primary carbocation.
- Q 31. Assertion (A): IUPAC name of the compound

is 2-Ethoxy-2-methylethane.

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

**Q 32.** Assertion (A): Alcohols react both as nucleophiles and electrophiles.

**Reason (R):** The bond between C—O is broken when alcohols react as nucleophiles.

(CBSE SQP 2023-24)

**Q 33.** Assertion (A): *p*-nitrophenol is more acidic than phenol.

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

**Q 34.** Assertion (A): Bond angle in ethers is slightly less than the tetrahedral angle.

**Reason (R):** There is a repulsion between the two bulky (—R) groups.

Q 35. Assertion (A): Boiling points of alcohols are higher in comparison to ethers of comparable molecular masses.
Reason (R): They can form intermolecular hydrogen

**Reason (R):** They can form intermolecular hydrogen bonding.

- **Q 36.** Assertion (A): Alcohols have higher boiling points than ethers of comparable molecular masses.
  - **Reason (R):** Alcohols and ethers are isomeric in nature.
- **Q 37.** Assertion (A): An ether is more volatile than an alcohol of comparable molecular mass.

Reason (R): Ethers are polar in nature.

(CBSE SQP 2022-23)

Q 38. Assertion (A): (CH<sub>3</sub>)<sub>3</sub>COH when heated with conc. H<sub>2</sub>SO<sub>4</sub> gives isobutylene as the main product and not di-tertiary butyl ether.

**Reason (R):** All alcohols readily dehydrates with conc. H<sub>2</sub>SO<sub>4</sub>.

### Answers

- L (a)(i) and (iv)
  - (I) CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH<sub>3</sub> (secondary)
  - (ii) (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>COH (tertiary)

- 2. (b) slightly less than 109°28'.
- 3. (b)  $CuO + ZnO + Cr_2O_3$
- 4. (b) 2-chlorobutane
- 5. (a) Lucas test is used to recognise whether the given alcohol is primary, secondary or tertiary in nature. In this reaction, the carbocation is formed as an intermediate and thus the stability and ease of carbocation formation determine the rate of the reaction as that's the slow step of the mechanism. Since, the stability of tertiary carbocation is the most due to hyperconjugation effect. Hence, the order of reactivity is 3° > 2° > 1° or 1° < 2° < 3°.</p>
- **6.** (b) On acid catalysed hydration. 2-methylpropene gives a tertiary alcohol.

$$\begin{array}{c} \mathsf{CH_3} \\ \mathsf{I} \\ \mathsf{CH_3-C} \\ \mathsf{unim} \\ \mathsf{CH_2} \\ & \mathsf{H} \\ \end{array} \xrightarrow{\mathsf{H}_2\mathsf{O}} \mathsf{CH_1-C} \\ \mathsf{CH_3-C} \\ \mathsf{CH_3-C}$$

r-butyl alcoho

- 7. (a) conc. HCl + anhyd. ZnCl<sub>2</sub>
- 8. (d) All of these
- (a) hydrogen bonding Alcohols form intermolecular hydrogen bonds while hydrocarbons do not.

- 10. (c) (±)-Butan-2-ol is optically inactive because it is both dextrorotatory and laevorotatory and hence forms a racemic mixture in which the net rotation of plane polarised light towards the right is cancelled by the left one, so it becomes optically inactive.
- (c) miscible in water in all proportions
   Lower molecular mass alcohols are able to form hydrogen bonds with water.
- 12. (d) 2-methylpropanal and isopropyl magnesium iodide

$$\begin{array}{c} H \\ \downarrow \\ CH_3 - CH - C = O + (CH_3)_2 CHMgl \longrightarrow \\ CH_3 \\ CH_3 \\ 2\text{-methylpropanal} \end{array}$$

$$(CH_3)_2CH$$
  $CH_3)_2CH$   $CH_3)_2CH$   $CH_3)_2CH$   $CH_3)_2CH$   $CH_3)_2$   $CH_3)_2CH$   $CH_3)_2$   $CH_3$ 

13. (a) protonation of alcohol molecule.

The various steps of the mechanism are given below:

Step 1: Formation of protonated alcohol

Protonated alcohol (ethyl oxonium ion)

**Step 2:** Formation of carbocation. It is the slowest step and hence the rate determining step of the reaction.

**Step 3**: Formation of ethene by elimination of a proton.

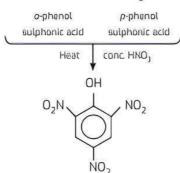
$$H \longrightarrow H$$
 $H \longrightarrow H$ 
Ethene

- **14**. (c) CH₃—CH∞CH—CHO
- 15. (b) B<sub>2</sub>H<sub>6</sub> along with hydrogen peroxide reacts with propene and convert it into 1-propanol. The reaction is known as a hydroboration reaction and it follows anti-Markovnikov's rule. Thus, alcohol group gets attached to the terminal carbon atom.
- 16. (d) benzyl alcohol

17. (a) C<sub>6</sub>H<sub>5</sub>OH

Phenols are more acidic than alcohols, thus they will react with sodium hydroxide solution in water.

- (a) Due to the activation of benzene ring by the methoxy group
- 19. (c) picric acid



Picric acid

20. (b) 2-chloromethylphenol

21. (b) 1-methylcyclohexene

According to Saytzeff rule, highly substituted alkene is the major product. Here, dehydration reaction takes place and alkene is formed due to the removal of a water molecule. So, 1-methylcyclohexene is the major product.

22. (d) 
$$A = C_6H_5CH_2Br$$
,  $B = C_6H_5OH$ 

$$C_6H_5CH_2OC_6H_9 + HBr \longrightarrow C_6H_5CH_2Br + C_6H_9OH$$

$$HgBr \qquad OH$$

- 24. (b) partial double bond character of C OH bond
- 25. (c) Reimer-Tiemann reaction.

  Kolbe's reaction is used to prepare salicylic acid.

  Etard reaction is used to prepare benzaldehyde.

  Reimer-Tiemann reaction is used to prepare salicylaldehyde.

  Stephen's reduction is used to prepare aldehyde.

26. (d) 
$$CH_3 - C - Br + NaOCH_3 \rightarrow$$

$$CH_3 - C = CH_2 + NaBr + CH_3OH$$

$$CH_3 - C = CH_2 + NaBr + CH_3OH$$

$$CH_3 - C = CH_2 + NaBr + CH_3OH$$

$$CH_3 - C = CH_2 + NaBr + CH_3OH$$

- **27.** (b) No turbidity will be observed, the given compound is a primary alcohol.
- **28.** (d) Diethyl ether on heating with HI gives ethyl lodide.  $CH_3CH_3CCH_3CH_3 + 2HI \longrightarrow 2CH_3CH_3I + H_3O$
- 29. (c) S<sub>N</sub>2 reaction
- **30.** (c) Assertion (A) is true but Reason (R) is false.

  Addition of water to but-1-ene in acidic medium yields butan-2-ol. Hence, the assertion is true but reason is false because the addition of water proceeds through formation of secondary carbocation.
- 31. (d) Assertion (A) is false but Reason (R) is true.
- **32.** (c) Alcohols react both as nucleophiles and electrophiles. When alcohols react as nucleophiles, the bond between O—H is broken. Hence, assertion is true but reason is false.
- **33.** (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
- 34. (d) Assertion (A) is false but Reason (R) is true.

  The bond angle in ethers is slightly greater than the tetrahedral angle. So, assertion is false but reason is true that is there is a repulsion between the two bulky (—R) groups.
- **35.** (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not a correct explanation of Assertion (A).
- **36.** (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not a correct explanation of Assertion (A).
- 37. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

  Assertion (A) and Reason (R) are two different

statements about ethers. The correct reason is that hydrogen bonding does not exist amongst ether molecules.

- **38.** (c) Reason is false because higher is the stability of carbocation, more easily it can be dehydrated. Thus, dehydration of alcohols follows the order:
  - 3° alcohol > 2° alcohol > 1° alcohol



#### Case Study Based Questions >

#### Case Study 1

A phenol contains—OH group(s) directly attached to carbon atom(s) of an aromatic system ( $C_6H_5OH$ ). In phenols, the -OH group is attached to  $sp^2$ -hybridised carbon of an aromatic ring. The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and (ii)  $sp^3$ -hybridised state of carbon to which oxygen is attached.

It can be prepared by various means or methods. Some important methods are alkali fusion of sulphonates, hydrolysis of diazonium salts, decarboxylation of salicyclic acid and from Grignard reagent. Commercially, it is prepared from Dow's process and from cumene. In Dow's process, phenol is obtained when chlorobenzene is heated with 6-8% NaOH at 623 K under 320 atm pressure. Aerial oxidation of cumene produces cumene hydroperoxide which upon subsequent hydrolysis with an aqueous acid gives phenol and propanone.

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of the sodium salt gives phenol.

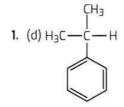
Diazonium salts are hydrolysed to phenols by warming with water by treating with dilute acids.

#### Read the given passage carefully and give the answer of the following questions:

#### Q1. The structural formula of cumene is:

- Q 2. 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 the above
- Q 3. The name of product which is obtained by the decarboxylation of sodium salt of salicylic acid with soda-lime is:
  - a. phenol
- b. toluene
- c. benzene
- d. benzoic acid
- Q 4. Which of the following reagents is used for the conversion of benzene sulphonic acid to phenol?
  - a. CaCO<sub>3</sub>
- b. NaOH, HCl
- c. Ca(OH)<sub>2</sub>
- d. None of these

#### Answers



- 2. (b) Iso-propylbenzene
- 3. (a) Phenol
- 4. (b) NaOH. HCl

#### Case Study 2

Alcohols and Phenols are acidic in nature. Electron withdrawing groups in phenol increase its acidic strength and electron donating groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to give alkyl halides. On oxidation primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. The presence of -OH groups in phenols activates the ring towards electrophilic substitution. Various important products are obtained from phenol like salicylaldehyde, salicylic acid, pierie acid etc.

#### Read the given passage carefully and give the answer of the following questions:

(CBSE 2021 Term-1)

Q 1. Which of the following alcohols is resistant to oxidation?

a. 
$$CH_{3}$$
— $CH_{3}$ — $CH$ — $CH$ — $CH$ — $CH$ — $CH$ 

c. CH<sub>3</sub>CH<sub>3</sub>OH

## Q 2. Which of the following group increases the acidic character of phenol?

a. CH<sub>3</sub>O

b. CH<sub>3</sub>

c. NO<sub>2</sub>

d. All of these

#### Q 3. Consider the following reaction:

$$X \leftarrow \underbrace{\text{(i) NaOH}_{1}, CO_{3}}_{\text{(ii) H}^{\circ}} \xrightarrow{\text{(ii) CHCL}_{3} \leftrightarrow \text{ad}_{2}NaOH} Y$$

#### The products X and Y are

a. 
$$\chi = \bigcirc$$
OH
COOH
$$X = \bigcirc$$
OH
OH
COOH
$$X = \bigcirc$$
OH
COOH
CHO
OH
CHO

#### 1. (a) Tertiary alcohols do not undergo oxidation.

**Answers** 

Thus, 
$$CH_3$$
— $C$ —OH being a tertiary alcohol is  $CH_3$ — $CH_3$ 

resistant to oxidation.

- **2.** (c) —NO<sub>2</sub>. —CN. —X (halogens). etc.. groups will increase the acidic character of phenol
- 3. (d) Kolbe's reaction:

#### Reimer-Tlemann Reaction:

#### Case Study 3

Alkene hydration is a catalytic process that involves the addition of water across the double bond of an alkene to produce an alcohol. This is most direct and atom-economical approach to the synthesis of alcohols. Acid-catalysed alkene hydration is the most well-known hydration process. This process is used industrially with several different acidic species as the catalyst, including zeolites, oxides, phosphoric acid and sulphuric acid. There are several major drawbacks with this catalytic process. The first drawback is the acidic environment which is very corrosive and can lead to degradation of reactors or the need to use specially engineered and expensive reactors to resist the acidic conditions. Another drawback is the acidic environment required for hydration which is not suitable for alkenes with acidsensitive functional groups. Thus, this process is typically only used with simple alkenes such as ethylene, propylene and butene. The final and biggest drawback is the selectivity of the reaction. Acid catalysed hydration follows Markovnikov's rule which states that the proton will add to the carbon with the most hydrogens attached to it. Therefore, starting with propylene, acid-catalysed hydration will always be selective for internal alcohols (secondary or tertiary). Except for ethanol, primary alcohol cannot be synthesized by acidcatalysed hydration. Generally, primary alcohols are the more valuable commodity industrially. Therefore, different synthetic strategies have to be

$$\mathsf{CH}_2 = \mathsf{CH}_2 + \mathsf{H}_2\mathsf{O} \xrightarrow{\mathsf{Cutalyst}} \mathsf{CH}_3\mathsf{CH}_2\mathsf{OH}$$

invented for the synthesis of primary alcohols.

Hydration of ethylene

## Read the given passage carefully and give the answer of the following questions:

- Q L When propene reacts with water under acidic condition, what is the product formed?
- Q 2. What is the product formed when propyne in the presence of HgSO<sub>4</sub> and sulphuric acid is hydrated?
- Q 3. Methylpropene when undergoes hydration in presence of acid catalyst, what is the product obtained? Also give its structure.

OR

But-1-ene (P) on acidic condition hydration will produce 'X' compound, which on dehydration produce 'Y', acidic condition hydration of 'Y' will produce 'Z'. What happens when X reacts with Na?

#### Answers

- 1. Propan-2-ol
- 2. Propanone
- 3. 2-methylpropan-2-ol is obtained and its structure is

X on reaction with Na. does not produce H<sub>2</sub> gas.

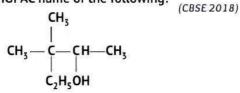


#### Very Short Answer Type Questions >

- Q1. Write the following compounds in increasing order of their acidic strength.
  - (i) Phenol
- (ii) o-cresol
- (iii) *m*-cresol
- (iv) p-cresol

**Ans.** p-cresol < m-cresol < o-cresol < phenol

Q 2. Write the IUPAC name of the following:



Ans. 3, 3-dimethylpentan-2-ol

Q 3. Write the IUPAC name of the following compound:

Ans. 2-bromo-3-methylbut-2-en-1-ol

Q 4. Give the IUPAC name of the compound:

Ans. 2-Bromo-3-methylbut-2-en-1-ol

Q 5. Write the IUPAC name of the compound.

Ans. 2-Methylhexan-1, 3, 5-triol.

Ans.

Q 6. Give the structures and IUPAC names of the phenols (NCERT EXERCISE)

of molecular formula C<sub>7</sub>H<sub>8</sub>O.

OH OH OH CH<sub>3</sub> 2-Methylphenol 3-Mothylphenol 4-IAuthylphenol

Q 7. Write the IUPAC name of the compound:

$$\begin{array}{c} \mathsf{CH_3} {\longleftarrow} \mathsf{O} {\longleftarrow} \mathsf{CH_2} {\longleftarrow} \mathsf{CH_2} {\longleftarrow} \mathsf{CH_3} \\ | \\ \mathsf{CH_3} \end{array}$$

Ans. 1-Methoxy-2-methylbutane.

Q 8. Complete the following chemical reaction:

$$\begin{array}{c|c} \text{CH}_{3} & \\ \downarrow & \\ \text{CH}_{3} & \text{C} & \text{OH} & \xrightarrow{\text{H}_{2}\text{SO}_{4}} ? & \xrightarrow{\text{O}_{2}} ? & \xrightarrow{\text{H}_{2}/\text{Ni}} ? \\ \downarrow & \\ \text{CH}_{3} & \\ \text{CH}_{3} & \\ \end{array} ?$$

Ans. 
$$CH_3$$
 $CH_3$ 
 $CH_3$ 

Q 9. Write the reaction of secondary alcohol when passed through copper at 573 K.

Q 10. How will you convert propanone to tertiary butyl alcohol?

Ans. 
$$CH_3$$
— $C$ — $CH_3$  +  $CH_3$ MgBr  $\longrightarrow$ 

$$\begin{bmatrix}
OMgBr\\I\\CH_3$$
— $C$ — $CH_3\end{bmatrix}$ 

$$\xrightarrow{H_2OM^*}$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

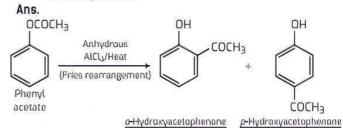
 $(CH_3)_3COH + Mg(OH)Br$ tert-butyl alcohol

Q 11. How will you convert ethanol to propanone?

Ans. 
$$CH_3CH_2OH \xrightarrow{KMnO_4/OH^-} CH_3COOH \xrightarrow{Ca(OH)_2} \xrightarrow{heat}$$

$$(CH_3COO)_2Ca \xrightarrow{D\otimes till} COCH_3 \xrightarrow{Propariono} CH_3COCH_3$$

Fries reaction to illustrate Q 12. Give chemical rearrangement.



Q 13. Butan-1-ol has higher boiling point than diethyl ether. Assign reason.

Ans. Both are functional isomers. However, intermolecular hydrogen bonding is present in butan-1-ol molecules while it is absent in the molecules of diethyl ether. Therefore, boiling point of alcohol (390 K) is higher as compared to that of ether (308 K).

## Q 14. Which compound is formed when a secondary alcohol is oxidised?

**Ans.** A <u>ketone is formed</u> as a result of oxidation. For example,

## Q 15. Write the chemical reactions of ethanol with PCl<sub>5</sub> and PCl<sub>7</sub> separately.

Ans. 
$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$
Ethanol  $Chloroethano$ 

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$
Ethanol  $Chloroethano$ 

#### Q 16. How will you prepare benzene from phenol?

Ans. Phenol upon reduction with zinc dust forms benzene.

## Q 17. Give the structures of A, B and C in the following reactions:

$$CH_3Br \xrightarrow{KCN} A \xrightarrow{LIAIH_4} B \xrightarrow{HNO_2} C$$

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{H\text{NO}_3} \text{CH}_3\text{CH}_2\text{OH} \\ \text{Ethyl anilne} \\ \text{(B)} \end{array}$$

## Q 18. Write any two differences between methyl alcohol and ethyl alcohol.

Ans. (i) Upon heating with  $I_2$  and  $Na_2CO_3$  solution. ethyl alcohol gives a yellow precipitate of iodoform but methyl alcohol does not.

(ii) Methyl alcohol is highly poisonous in nature but ethyl alcohol is not.

## Q 19. Arrange the following compounds in increasing order of their acidic strength:

4-Nitrophenol, Phenol, 2, 4, 6-trinitrophenol.

Ans. Phenol < 4-Nitrophenol < 2, 4, 6-trinitrophenol

## Q 20. How will you distinguish between benzyl alcohol and phenol?

Ans. Both can be distinguished as under:

- (i) Phenol turns <u>blue litmus red</u> but benzyl alcohol does not.
- (ii) Phenol gives a white precipitate with bromine water but benzyl alcohol does not.

#### Q 21. How will you convert propanone to propan-2-ol?

Ans. 
$$CH_3 - CH_3 + H_2 \xrightarrow{Pd} CH_3 - CH_3 - CH_3$$
Propanana

## Q 22. What happens when sodium salicylate is heated with sodalime?

Ans. Phenol is formed as the product and the reaction is known as decarboxylation reaction.

#### Q 23. How will you convert ethanol to propan-2-ol?

Ans. 
$$CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3 \xrightarrow{C} -H \xrightarrow{(OH_2MgBr)} CH_3$$

$$CH_3CH_2OH \xrightarrow{(Oxidation)} CH_3 \xrightarrow{(OH_2MgBr)} CH_3 \xrightarrow{($$

#### Q 24. How will you convert phenol to acetophenone?

#### Q 25. How will you convert propane to propan-1-ol?

Ans. 
$$CH_3$$
— $CH_2$   $CH_2$   $(R-O-O-R)$ 

$$CH_3$$
— $CH_2$ — $CH_2$ Br  $CH_3$ — $CH_3$ — $CH_2$ — $CH_2$ DH Propan-1-ol

#### Q 26. Complete the following:

$$C_2H_5OH \xrightarrow{Cu/573 K} X \xrightarrow{CH_3M_0Br} Y$$

Ans. 
$$C_2H_5OH \xrightarrow{Cu/573 \text{ K}} CH_3 \xrightarrow{C} H \xrightarrow{CH_3MgBr}$$

Ethanol (X)

$$CH_3 \xrightarrow{C} H_3OH \xrightarrow{CH_3MgBr} OH \xrightarrow{CH_3MgBr} OH \xrightarrow{CH_3} CH_3 \xrightarrow{C} CH_3 \xrightarrow{C} CH_3$$

#### Q 27. How will you convert propene to propan-2-ol?

Ans. 
$$CH_3$$
— $CH = CH_2 + H_2O$   $\xrightarrow{H^2}$   $CH_3$ — $CH$ — $CH_3$ 
 $OH$ 
Propuno 2: ol

#### Q 28. Unlike phenols, alcohols can be easily protonated. Explain.

Ans. In phenols, the <u>lone electron pairs</u> on the oxygen atom are involved in conjugation with the pi electrons

of the ring. Hence, these are delocalised and are not easily available for protonation. On the other hand, in alcohols the electron pairs on the oxygen atom are not involved in any conjugation. These are localised and are readily available for protonation.

## Q 29. How will you distinguish between methanol and ethanol by colour test?

**Ans.** Ethanol gives a <u>yellow precipitate of iodoform</u> on warming with iodine and sodium carbonate while methanol fails to react.

$$C_2H_9OH + 4I_2 + 3Na_2CO_3 \xrightarrow{Warm} CHI_3 + HCOONa + 5NaI + 2H_2O + 3CO_3$$

Q 30. What is function of anhydrous ZnCl<sub>2</sub> in the Lucas test of alcohols?

Ans. 
$$-C \longrightarrow OH + HCl(g) \xrightarrow{2nCl_2 (anhyd)} -C \longrightarrow Cl + H_2O$$
Allohol Allohol

Anhydrous  $ZnCl_2$  is a dehydrating agent and absorbs molecules of  $H_2O$  formed in the reaction. This enables the reaction to proceed in the forward direction.

## Q 31. Why is acid catalysed dehydration of tertiary butyl alcohol faster than that of *n*-butyl alcohol?

Ans. Acidic dehydration of alcohol involves the formation of carbocation which is more stable than the *n*-butyl carbocation formed in case of *n*-butyl alcohol therefore, tertiary butyl alcohol is more reactive than *n*-butyl alcohol.

## Q 32. Predict the product of the reaction between HBr and but-2-en-1-ol.

Ans. 
$$CH_3$$
— $CH$   $CH$   $CH_2$   $CH_2$   $CH_3$   $CH_3$   $CH_4$   $CH_4$   $CH_5$   $CH_5$   $CH_6$   $CH_6$   $CH_6$   $CH_7$   $CH_8$   $CH_8$ 

#### Q 33. Alcohols can act both as acids and base. Explain.

Ans. Alcohols can act as acids in strongly basic medium by releasing H\* ion. Similarly, they can act as Lewis bases in the acidic medium.

## Q 34. Sodium metal can not be used for drying alcohols. Assign reason.

Ans. Sodium metal reacts with alcohol to evolve hydrogen gas. Moreover, it also catches fire in air.

Therefore, it can not be used for drying alcohol.

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$$
  
Ethanol Sod ethoxide

# Q 35. Ethyl alcohol and dimethyl ether are isomeric but alcohol is a liquid at room temperature while ether is a gas. Explain.

Ans. Ethyl alcohol molecules are associated due to intermolecular hydrogen bonding but the same is not present in the molecules of dimethyl ether. As a result of association, ethyl alcohol is a liquid at room temperature while dimethyl ether is a gas.

#### Q 36. How do you account for the miscibility of ethoxyethane with water?

Ans. Ethoxyethane is miscible in water to small extent because of intermolecular hydrogen bonding in their molecules. Energy released during attraction accounts for the miscibility of ether in water.

## Short Answer Type-I Questions

## Q1. Boiling point of alcohols increases with increase in molecular weight. Explain.

Ans. With increase in molecular weight of alcohols, chain size *l.e.*, surface area increases. Due to which van der Waals' forces increases. Hence, a large amount of energy is required to break these forces. Thus, boiling points of alcohols increase with increase in molecular weight (or molar mass).

## Q 2. How will you prepare alcohol from alkyl halides and alkenes? Write chemical equations.

**Ans.** (I) Alkyl halldes react with aqueous KOH to form alcohols. For example.

(ii) Alkene upon acidic hydration form alcohols. For example.

#### Q 3. Note the structures of the products when butan-2ol reacts with the following:

(i) CrO<sub>3</sub>

(CBSE 2017)

- Q 4. Outline the synthesis of the following alcohols from the indicated starting material:
  - (i) Isopropyl alcohol from propane
  - (ii) n-Butyl alcohol from ethyne.

$$\begin{array}{c} \begin{array}{c} H_2 \\ \hline \text{Undlar's} \\ \text{Catalyst} \end{array} \rightarrow \begin{array}{c} H_2 C = \text{CHC}_2 H_5 \\ \hline \text{But-1-ene} \end{array} \rightarrow \begin{array}{c} B_2 H_5 \\ \hline H_3 O_2 / \text{OHT} \\ \hline \text{($n$-butyl alcahol)} \end{array}$$

## Q 5. How will you distinguish between allyl alcohol and n-propyl alcohol?

Ans. Allyl alcohol will give white turbidity with Lucas reagent immediately, but n-propyl alcohol does not react at room temperature. Actually in allyl alcohol, the allyl carbocation left after the release of OH ion is resonance stabilised which means that C—OH bond can be very easily cleaved by HCL But the C—OH bond cleavage is not so easy in n-propyl alcohol because n-propyl carbocation is not resonance stabilised.

$$\begin{array}{c} \text{CH}_2 & = \text{CH} - \text{CH}_2 - \text{OH} \xrightarrow{\text{H}^{\bullet} \text{(Acid)}} \text{CH}_2 & = \text{CH} \\ -\text{CH}_2 - \text{OH}_2 \xrightarrow{\text{H}_2\text{O}} \text{(CH}_2 = \text{CH} - \text{CH}_2 \leftrightarrow \text{CH}_2 = \text{CH}_2) \end{array}$$

Q 6. Give the product of reaction of ethyl alcohol with conc. H<sub>2</sub>SO<sub>4</sub> at (i) 0°C, (ii) room temperature (iii) 130°C, (iv) 180°C.

Ans. (i) 
$$C_2H_5 \overset{\bullet}{\circ} H + H_2SO_4 \xrightarrow{0.C} \begin{pmatrix} C_2H_5 \overset{\bullet}{\circ} H \\ H \end{pmatrix} HSO_4^-$$
Ethykronium hydrogensulphate

(ii) 
$$C_2H_9OH + H_2SO_4$$
 Remarkation  $C_2H_9HSO_4 + H_2O_4$  Ethythydrogunaulphate

(III) 
$$C_2H_6OH + HOC_2H_6 \xrightarrow{O+_2SO_4} C_2H_6 \xrightarrow{O} C_2H_8 + H_2O$$

# Q 7. The compound C<sub>4</sub>H<sub>10</sub>O is produced on reaction of an alkane with H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O which is not resolvable into optical isomers. Identify the compound.

Ans. The molecular formula of the compound and the reaction conditions suggest that the compound is an alcohol and not an ether. Since it is not resolvable, it is symmetrical and is tertiary butyl alcohol. The corresponding alkane is isobutane.

The alcohol has been formed as follows:

$$\begin{array}{c} \text{CH}_{3} & \text{CH}_{3} \\ | \\ \text{CH}_{3} & \text{C} \\ | \\ \text{CH}_{3} & \text{CH}_{3} \\ | \\ \text{Isobutane} \end{array} \rightarrow \begin{array}{c} \text{CH}_{3} \\ | \\ \text{CH}_{4} \\ | \\ \text{CH}_{5} \\ | \\ \text{$$

#### Q 8. At room temperature, tertiary alcohols form white turbidity very fast with Lucas reagent while primary alcohols do not. Give reason.

Ans. A carbocation intermediate is formed when HCl(g) reacts with an alcohol in the presence of anhydrous ZnCl<sub>2</sub> (dehydrating agent). Since tertiary carbocation is very stable while primary carbocation is rather unstable therefore, tertiary alcohols react very fast with Lucas reagent to form white turbidity immediately while the primary alcohols do not react at room temperature.

## Q 9. Explain why does propanol has higher boiling point than butane? (NCERT EXERCISE)

Ans. Propanol (Propan-1-ol) and butane are of comparable molecular masses 60u and 58u respectively but the boiling point of propanol is higher because of the presence of intermolecular hydrogen bonding in the molecules. However, it is not present in butane due to the absence of polar OH group. The only attractive forces are weak van der Waals' forces. Therefore, the boiling point of propanol (391 K) is more than that of butane (309 K).

## Q 10. Write the mechanism of hydration of ethene to yield ethanol. (NCERT EXERCISE)

Ans. Ethene does not react with water as such. Water being little polar, is not in a position to provide H\* ion for initial electrophilic attack on ethene. The reaction is carried in the presence of H<sub>2</sub>SO<sub>4</sub>. The acid provides proton (H\*) for the initial electrophilic attack.

$$H$$
— $OSO_3H$ + $CH_2$ — $CH_2$ — $CH_3$ — $CH_2$ + $OSO_3H$   
Ethyl carbocation

In the second, H<sub>2</sub>O attack the carbocation in preference to HSO, ion as a nucleophile.

$$H \longrightarrow O \longrightarrow H + CH_3 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow O \longrightarrow H$$

$$\longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow$$

Q1L 3, 3-Dimethyl butan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as the major product. Suggest a suitable mechanism.

Ans. The mechanism is as under:

3.3-Dimethylbutan-2-ol

$$\begin{array}{c} \text{CH}_3 \\ \text{Carbocation} \\ \text{CH}_3 \\ \text{CH}_4 \\ \text{CH}_4 \\ \text{CH}_5 \\ \text{$$

$$CH_3$$
 $-H^{\uparrow}$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

Q 12. What is the structure of the major product when-3-Ethylpent-2-ene is reacted with Hg(OAc)2/H2O; NaBH,?

Ans. The reaction is known as oxymercurationdemercuration and proceeds as follows:

$$C_{2}H_{5}$$

$$|$$

$$CH_{3}-CH_{2}-C \stackrel{\text{deg}(O \land c)_{2}/H_{2}O}{\longrightarrow}$$

$$3-60 \text{ Modernt-} 2-6 \text{ Note } 2$$

Q13. (i) Arrange the following compounds in the increasing order of their acid strength: p-cresol, p-nitrophenol, phenol

(ii) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_2 \stackrel{\text{\tiny MSO}^+}{-} CH_3 \stackrel{-}{-} CH_2^+ + H_2O$$

(CBSE 2017)

**Ans.** (i) p-cresol < p-nitrophenol

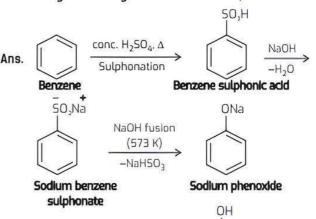
- Q 14. How will you convert ethyl amine to ethyl alcohol and vice-versa?
- Ans. Ethyl amine to ethyl alcohol

$$\begin{array}{c} C_2H_5NH_2 + HONO \xrightarrow{\text{(NoNO}_2/HCl)} & C_2H_5OH + H_2O + N_2 \\ \text{Ethyl amine} & \text{Ethyl alcohol} \end{array}$$

Ethyl alcohol to ethyl amine

$$\begin{array}{ccc} C_2H_5OH & \xrightarrow{PCl_B} & C_2H_5Cl & \xrightarrow{NH_2(alc.)} & C_2H_5NH_2 \\ \text{Ethyl alcohol} & & \text{Ethyl chlorido} & & \text{Ethyl amino} \end{array}$$

Q 15. You are given benzene, conc. H<sub>2</sub>SO<sub>4</sub> and NaOH. Write the equations for the preparation of phenol using these reagents. (NCERT EXERCISE)



dil HCl

Phenol

- Q 16. How the following will be obtained? (Write chemical equations only).
  - (i) Picric acid from phenol.
  - (ii) Benzoquinone from phenoL

OH Ans. furning HNOD ⊕ ∃H₂O conc HoSQL.A Phenol NO2 2. 4. 6-billitro phenol (plaric acid) OH Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Phenol Benzoquinone

- Q 17. Write the chemical equation involved in the following reactions:
  - (i) Reimer-Tiemann reaction
  - (ii) Acetylation of salicylic acid

(CBSE 2023)

Ans. (i) Reimer-Tiemann reaction

(ii) Acetylation of salicylic acid

$$\begin{array}{c|c}
 & O \\
 & C \\
\hline
 & OH \\
 & + (CH_3CO)_2O \\
 & OH \\
 & Acetic \\
 & anhydride
\end{array}$$

$$\begin{array}{c}
 & O \\
 & C \\
\hline
 & OH \\
 & C \\
\hline
 & OH \\
 & OH \\
 & Aspirin \\
 & OH \\
 & C \\
 & OH \\$$

- Q 18. Write the chemical equation involved in the following:
  - (i) Kolbe's reaction
  - (ii) Williamson synthesis

(CBSE 2023)

Ans. (i) Kolbe's reaction

Alkyl

Ether

(ii) Williamson synthesis

 $R \longrightarrow X + RONa \longrightarrow R -$ 

Sodlum

$$\begin{array}{c} \text{holide} & \text{olkoxide} \\ \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 - \text{C} - \text{ONa} + \text{CH}_3 \text{Br} - \rightarrow \text{CH}_3 - \text{O} - \text{C} - \text{CH}_3 + \text{NaB} \\ \text{CH}_3 & \text{CH}_3 \\ \end{array}$$

r-butyl methyl ether

-0 - R + NaX

- Q 19. (i) Write the mechanism of the following reaction:  $CH_3CH_2OH \xrightarrow[-443\ K]{H^+} CH_2 == CH_2 + H_2O$ 
  - (ii) Write the equation involved in Reimer-Tlemann reaction. (CBSE 2023)
- Ans. (i) The mechanism involved is as under:

  Step I: Formation of protonated alcohol

CH<sub>3</sub>CH<sub>2</sub>— 
$$\stackrel{\longleftarrow}{O}$$
H + H  $\stackrel{\vdash}{\leftarrow}$   $\stackrel{\vdash}{\leftarrow}$  CH<sub>3</sub> — CH<sub>2</sub> —  $\stackrel{\longrightarrow}{O}$  — H

Step II: Formation of carbocation

$$CH_3CH_2 \stackrel{H}{\longleftarrow} O^* - H^{SLOW} CH_3 - CH_2 + H_2O$$

Step III: Formation of ethene by elimination of a

$$\begin{array}{c|c} \hline \\ \hline \\ H \\ \hline \\ H \\ \hline \\ H \\ \hline \\ H \\ \end{array} \begin{array}{c} H \\ \hline \\ H \\ \hline \\ H \\ \end{array} \begin{array}{c} H \\ \hline \\ H \\ \hline \\ H \\ \end{array} \begin{array}{c} H \\ \hline \\ H \\ \hline \\ Ethene \\ \end{array} \begin{array}{c} H \\ \hline \\ H \\ \end{array} \begin{array}{c} H \\ \hline \end{array} \begin{array}{c} H \\ \hline \\ \end{array} \begin{array}{c} H \\ \hline \end{array} \begin{array}{c} H \\ \end{array} \begin{array}{c} H \\ \hline \end{array} \begin{array}{c} H \\ \end{array} \begin{array}{$$

(ii) Reimer-Tlemann reaction:

- Q 20. Write the names of the reagents and equations for the preparation of the following ethers by Williamson's synthesis:
  - (i) 1-Propoxypropane
  - (ii) 2-Methoxy-2-methylpropane
  - (iii) Ethoxybenzene
  - (iv) Methoxyethane.

(NCERT EXERCISE)

Ans. (i) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br + CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>ONa ---->
1-Branopropano Sod propoxido

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> + NaBr 1-Propoxypropane

$$\begin{array}{c} \mathsf{CH_3} & \mathsf{CH_3} \\ \mathsf{I} & \mathsf{I} \\ \mathsf{II} & \mathsf{CH_3} & \mathsf{CH_3} \\ \mathsf{Bromomethane} & \mathsf{CH_3} & \mathsf{CH_3} \\ \mathsf{CH_3} & \mathsf{CH_3} \\ \mathsf{Sod-2-methyl-} & \mathsf{2-Mathoxy-2-methyl-2-propoxide} \\ \end{array}$$

(iii) Sod. ethoxide 
$$C_2H_5Br \longrightarrow C_2H_5$$
 + NaBr

- (iv)  $C_2H_6ONa + CH_3Br \longrightarrow C_2H_6 \longrightarrow CH_3 + NaBr$ Sod ethawide Bromomethane Methawyethane
- Q 21. Account for the following:
  - (i) Phenol is a stronger acid than an alcohol.
  - (ii) The boiling point of alcohols decreases with increases in branching of alkyl chain. (CBSE 2023)
- Ans. (i) This is due to stabilisation of phenoxide ion through resonance. Presence of electron withdrawing group increases the acidity of phenol by stabilising phenoxide ion while presence of electron releasing group decreases the acidity of phenol by destabilising phenoxide ion.

- (ii) This is because attraction decreases with decrease in surface area, hence boiling point decreases. In other words, on increasing the molecules, the van der Waals' force decreases that is less boiling point is required to separate molecules to each other.
- Q 22. Write the mechanism of acid dehydration of ethanol to yield ethene. (CBSE 2023)
- Ans. Acid dehydration of ethanol to yield ethene

The mechanism involves the following steps:

Step I: Formation of protonated alcohol

$$CH_3 - CH_2 - Q - H + H^{\circ} \xrightarrow{Fast} H$$
 $H_3C - CH_2 - Q^{\circ} - H$ 

Step II: Formation of carbocation

$$H_3C - CH_2 \xrightarrow{C} 0^+ - H \xrightarrow{Slow} H_3 - C - CH_2 + H_2O$$

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

$$H - CH_2 \longrightarrow H C = C < H + H^2$$

- Q 23. Predict the products of the following reactions: (CBSE 2023)
  - (i)  $CH_3CH_2OH \xrightarrow{Cu/573K}$
  - (ii)  $C_6H_5OH \xrightarrow{Br_1(aq.)}$

Ans. (I)  $CH_3CH_2OH \xrightarrow{Cu/573K} CH_2CH_2 + H_2$ Ethene

(ii) 
$$C_6H_6OH \xrightarrow{Br_2(aq_i)} Br$$
Phenol

2.4.6-tribromophenol

- Q 24. Write equations for the following chemical reactions:
  - (i) Phenol reacts with Br<sub>2</sub> in the presence of CS<sub>2</sub>
  - (ii) Ethanol is heated at 573 K in the presence of Cu.

(II) 
$$CH_3$$
— $CH_2$ — $OH$ — $CU$ 
 $573K$   $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_2$ 

Q 25. Complete the following:

(i) 
$$+ CH_3Cl \xrightarrow{Anhyd.} AlCl_3$$

OH

 $+ H_2SO_4 \xrightarrow{373 \text{ K}}$ 

Ans. OH OH OH CH3
Phenol + CH3Br AlCl3
O-cresol CH3
P-cresol

Q 26. Write the mechanism of the following reaction:

$$CH_2 = CH_2 + H_2O \xrightarrow{H'} CH_3CH_2OH$$
 (CBSE 2023)

Ans. The mechanism of the reaction is as follows:

**Step I:** Protonation of alkene to form carbocation by electrophilic attack of H<sub>3</sub>O<sup>\*</sup>:

$$CH_2 = CH_2 + H + O + H + C + H_2 O + H + C + H_2 O + H + C + H_3 O + H + C + H_3 O + H + H_3 O + H_3 O + H + H_3 O + H_3 O$$

Step II: Nucleophilic attack of water on carbocation:

$$H - C - C + H + H_2 = H - C - C - D^* - H$$

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

$$H - C - C - C - H + H_2 = H - C - C - H + H_2 = H + H_$$

Q 27. Give chemical test to distinguish between:

(I) OH OH 
$$CH_2OH$$

(II)  $H_3C-CH-CH_3$  and  $OH$ 

Ans. (I) Add a few drops of blue litmus separately to the solutions of both the compounds taken in two test tubes. The solution which changes the colour of blue litmus to red is that of phenol The

- solution which does not bring about any colour changes is that of cyclohexanol.
- (ii) Treat both the solutions separately with Lucas reagent which is a mixture of HCl(g) and anhydrous ZnCl<sub>2</sub>. The compound that gives white fumes after sometimes is propan-2-ol while the other is benzyl alcohol.

#### Q 28. Give reasons for the following:

- (i) p-nitrophenol is more acidic than p-methylphenol.
- (ii) (CH<sub>3</sub>)<sub>3</sub>C Br on reaction with NaOCH<sub>3</sub> gives alkene as the main product and not an ether.

  (CBSE 2023)
- Ans. (I) —NO<sub>2</sub> group is an electron withdrawing group while the methyl group (—CH<sub>3</sub>) is an electron donating group. The presence of nitro group decreases the electron density in the —OH bond. As a result, it is easier to lose a proton and hence para-nitrophenol is more acidic than para-methylphenol.
  - (ii) This is because <u>alkoxide</u> is not only a nucleophile <u>but also a strong base</u>. It gives elimination product when the alkyl halide is tertiary.

#### Q 29. How will you convert:

Benzyl chloride

- (i) ethyl magnesium chloride to propan-1-ol?
- (ii) benzyl chloride to benzyl alcohol?

Ans. (I) 
$$C_2H_5MgCI + HC = 0 \longrightarrow HC = 0$$

## Q 30. Phenol is acidic while cyclohexanol is natural. Justify.

Benzyl alcohol

Ans. In phenol, the oxygen atom of  $O \longrightarrow H$  group becomes electron deficient due to the conjugation of electron pairs on it with the  $\pi$  electron pairs of ring. Therefore,  $H^{\circ}$  can be released. However, in cyclohexanol, the electron pairs on the oxygen atom are not involved in any conjugation with the ring since it has no  $\pi$  electron pairs.

Therefore, the release of H° ion is quite difficult. This is the reason why phenol is acidic while cyclohexanol is acidic.

# Q 31. Explain how does —OH group attached to a carbon atom of benzene ring activates it towards electrophilic substitution? (NCERT EXERCISE)

Ans. The OH group exerts + M (or + R) effect on the ring under the influence of attacking electrophile.

As a result, there is an increase in the electron density in the ring particularly at the ortho and poro positions. The electrophilic substitution readily takes place at these positions when electrophile attacks.

## Short Answer Type-II Questions

Q 1. Write only chemical equations of the following: The dehydration reactions of primary, secondary and tertiary alcohols.

Ans. (i) Dehydration of primary alcohol:

(II) Dehydration of secondary alcohol:

OH
$$CH_{3} \longrightarrow CH \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH \longrightarrow CH_{2} + H_{2}O$$
Propan-2-ol
$$Propan-2-ol$$

(iii) Dehydration of tertiary alcohol:

$$\begin{array}{c} \text{CH}_{3} & \text{CH}_{3} \\ \mid & \mid \\ \text{CH}_{3} - \text{CH}_{3} - \text{CH} & \xrightarrow{20\% \text{H}_{3} \text{PQ}_{1}} \text{CH}_{3} - \text{CH} = \text{CH}_{2} + \text{H}_{2}\text{O} \\ \text{CH}_{3} & \xrightarrow{2\text{-mathyl propon-2-ol}} \end{array}$$

#### Q 2. Explain the reason for the following:

- (i) Aqueous solution of alcohols is non-conductor of electricity.
- (ii) Phenol is more acidic in comparison to cyclohexanol.
- Ans. (I) Alcohols are covalent molecules, so their aqueous solution or molten state contains no ions. Because of the absence of free ions, their aqueous solution is non-conductor of electricity.
  - (II) The phenoxide ion formed after the removal of a proton from phenol is stabilised by resonance whereas in case of cyclohexanol resonance is not possible. So, the formed alkoxide ion does not stabilise. Hence, its tendency to lose a proton is less as compared to phenol. So, it is less acidic as compared to phenol

Q 3. When 3-methyl butan-2-ol is treated with HBr, the following reaction takes place.

$$\begin{array}{c} \operatorname{Br} \\ | \\ \operatorname{CH}_3 \longrightarrow \operatorname{CH} \longrightarrow \operatorname{CH} \longrightarrow \operatorname{CH}_3 \longrightarrow \operatorname{CH}_3 \longrightarrow \operatorname{CH}_2 \longrightarrow \operatorname{CH}_2 \longrightarrow \operatorname{CH}_3 \\ | \\ \operatorname{CH}_3 \longrightarrow \operatorname{CH}_3 \longrightarrow \operatorname{CH}_3 \longrightarrow \operatorname{CH}_3 \\ \end{array}$$

Give a mechanism for this reaction. (NCERT EXERCISE)

Ans. The given alcohol is <u>protonated</u> in the first step and the protonated alcohol <u>lose</u> a water molecule to give a 2° carbocation (I) in second step. The secondary (2°) carbocation formed in step II <u>rearranges</u> to a more stable tertiary carbocation (II) by a hydride ion shift from third carbon atom. The more stable carbocation (II) is then attacked by the nucleophile (Br¯) to give the product.

Q 4. What is Lucas reagent ? How is it used to test primary, secondary and tertiary alcohols ?

(product)

Ans. A mixture of anhydrous and concentrated HCl is called Lucas reagent. It is used to distinguish between primary, secondary and tertiary alcohols.

- In this test, take 3-4 mL alcohol and add 2-3 mL Lucas reagent to it.
- (i) If there appears immediate turbidity in cold. the alcohol is a tertiary (3°) alcohol.
- (ii) If the turbidity appears after 5-10 minutes, the alcohol is a secondary (2°) alcohol
- (iii) If no turbidity appears in cold, the alcohol is a primary (1°) alcohol.
- Q 5. Name the reagents used in the following reactions.
  (NCERT EXERCISE)
  - (i) Oxidation of a primary alcohol to carboxylic acld.
  - (ii) Oxidation of a primary alcohol to aldehyde.
  - (iii) Bromination of phenol to 2,4,6-tribromophenol.
  - (iv) Benzyl alcohol to benzoic acid.
  - (v) Dehydration of propan-2-ol to propene.
  - (vi) Butan-2-one to butan-2-ol.

Ans. (i) Acidified potassium dichromate or neutral, acidic or alkaline potassium permanganate.

(ii) Pyridinium chlorochromate (PCC).  $C_6H_6\stackrel{\leftarrow}{N}NHCl\ CrO_3^-$  (in  $CH_2Cl_2$ ) or pyridinium dichromate (PDC)  $(C_6H_5\stackrel{\leftarrow}{N}H)_2\ CrO_7^{2-}$ 

- (iii) Bromine water I.e., Br<sub>2</sub>/H<sub>2</sub>O.
- (iv) Acidified or alkaline potassium permanganate.
- (v) Conc. H<sub>2</sub>50<sub>a</sub> at 433-443 K and <u>85% phosphoric</u> acid at 443 K.
- (vi) NI/H2 or NaBH4 or LIALH4.
- Q 6. What happens when (write only chemical equations)
  - (i) Methyl alcohol reacts with acetyl chloride?
  - (ii) Ethyl alcohol reacts with Red P and bromine?
  - (iii) Ethyl alcohol reacts with acetic anhydride.

(ii) This reaction takes place in the following manner:

Step I: 
$$P_4 + 6Br_2 \longrightarrow 4PBr_3$$

or  $P_4 + 10Br_2 \longrightarrow 4PBr_4$ 

Step II:  $C_2H_5OH + PBr_5 \longrightarrow C_2H_5Br + POBr_3 + HCl$ 

or  $3C_2H_0OH + PBr_3 \longrightarrow 3C_2H_0Br + H_0PO_3$ 

(III)  $C_2H_5OH + (CH_3CO)_2O \longrightarrow CH_3COOC_2H_5 + CH_3COOH_3COOC_3H_3 + CH_3COOC_3H_3COOC_3H_3 + CH_3COOC_3H_3COO$ 

Q 7. Phenol and ethanol both contain —OH group. Explain phenol is acidic while ethanol is neutral.

Ans. Acidity means tendency to give a proton. Phenol and ethanol (alcohol) both have a proton for donation. In phenol, —OH group is attached to the benzene nucleus, so the phenoxide ion formed after losing a proton, gets stabilised by resonance. Thus, acidic nature of phenol is due to resonance

stabilisation of phenoxide ion. The resonating structures of phenoxide ion is obtained by the delocalisation of electrons that do not carry any positive charge at oxygen atom. Thus, phenoxide ion becomes more stable as compared to non-lonised phenol. That's why phenol readily gives a proton to form more stable phenoxide ion and thus, shows acidity.

Resonating structures of phenoxide ion

In case of ethanol ( $C_2H_5OH$ ), ethoxide ion ( $C_2H_5O^-$ ) does not exhibit resonance, so it is less stable. Thus, ethanol can not give a proton by the following reaction:

(Not possible)

That's why ethyl alcohol is neutral

- Q 8. Write the equations for the following reaction:
  - Salicylic acid is treated with acetic anhydride in the presence of conc. H<sub>2</sub>SO<sub>4</sub>.
  - (ii) Tert butyl chloride is treated with sodium ethoxide.
  - (iii) Phenol is treated with chloroform in the presence of NaOH. (CBSE SQP 2022-23)
- **Ans.** (i) When salicylic acid is treated with acetic anhydride in the presence of conc.  $H_2SO_4$ , aspirin is formed.

(ii) When tert. Butyl chloride is treated with sodium ethoxide. 2-methylpropene is formed.

$$(CH_3)_3CCI \xrightarrow{\text{Softum}} (CH_3)_2C \xrightarrow{\text{caso}} CH_2$$
2-methylpropene

(iii) When phenol is treated with chloroform in the presence of NaOH, o-hydroxybenzaldehyde will be formed.

$$\begin{array}{c}
\text{OH} \\
\text{ONa} \\
\text{ONa} \\
\text{CHCl}_{2}
\end{array}$$

$$\begin{array}{c}
\text{NaOH} \\
\text{Intermediate}
\end{array}$$

$$\begin{array}{c}
\text{NaOH} \\
\text{ONa}
\end{array}$$

- Q 9. Write the name of the reaction, structure and IUPAC name of the product formed when:
  - (i) phenol reacts with CHCl<sub>3</sub> in the presence of NaOH followed by hydrolysis.
  - (ii) CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH(CH<sub>3</sub>)ONa reacts with C<sub>2</sub>H<sub>5</sub>Br. (CBSE SQP 2023-24)
- **Ans.** (i) The given reaction is Reimer-Tlemann reaction. The

2-hydroxy benzaldehyde.

(ii) The given reaction is <u>Williamson synthesis</u>. The product formed is  $CH_3CH_2CH_4$  CH $_3CH_4$  with  $CH_3$  CH $_3$ 

IUPAC name 2-ethoxy-2-methylpentane.

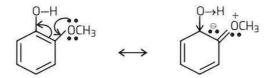
- Q 10. Explain why is *ortho*-nitrophenol more acidic than *ortho*-methoxyphenol? (NCERT EXERCISE)
- **Ans.** Due to strong —R and —I effects of NO<sub>2</sub> group, in O—H bond electron density decreases, making the removal of a proton easy.

$$O \rightarrow H$$
 $O \rightarrow H$ 
 $O \rightarrow H$ 
 $O \rightarrow H$ 
 $O \rightarrow H$ 
 $O \rightarrow G$ 
 $O \rightarrow$ 

After losing a proton. ortho-nitrophenoxide lon becomes stabilised by resonance.

Ortho-nitrophenoxide ion being stabilised by resonance, makes the *ortho*-nitrophenol a strong acid.

Contrary to this. —OCH<sub>3</sub> group shows +R effect and hence, raise the electron density in O—H bond. making the removal of a proton difficult.



Thus, after the loss of a proton, *ortho*methoxyphenoxide ion is formed, which is destabilised by resonance.

Here both the negative charges repel each other, hence the o-methoxyphenoxide ion becomes unstable.

Thus, ortho-nitrophenol is more acidic as compared to ortho-methoxyphenol

#### Q 11. Give IUPAC name of the following ethers:

- (ii) CH,OCH,CH,Cl
- (iii)  $O_2N-C_6H_4-OCH_5(p)$
- (iv) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>
  H<sub>3</sub>C CH<sub>3</sub>

(vi) OC<sub>2</sub>H<sub>5</sub>

(NCERT EXERCISE)

- Ans. (i) 1-ethoxy-2-methyl propane
  - (ii) 2-chloro-1-methoxyethane
  - (iii) 4-nitroanisole
  - (iv) 1-methoxypropane
  - (v) 1-ethoxy-4, 4-dimethylcyclohexane
  - (vi) ethoxybenzene.

#### Q 12. How do you convert the following: (Any three)

- (i) Phenol to 2-hydroxybenzaldehyde
- (ii) Anisole to 2-methoxyacetophenone
- (iii) Propene to propan-2-ol
- (iv) Ethanol to ethanal

(CBSE 2023)

Ans. (i) Treatment of phenol with chloroform in presence of aqueous NaOH or KOH at 70°C followed by hydrolysis gives 2-hydroxybenzaldehyde as the major product.

This reaction is called Reimer-Tiemann reaction.

2-hydroxy benzaldehyde

(ii) Anisole undergoes <u>Friedel-Crafts reaction</u> *i.e.*, acyl group is introduced at *ortho* and paro positions by <u>reaction</u> with acyl halide in the presence of anhyd. AlCl<sub>3</sub>(a lewis acid) as catalysts.

(iii) The conversion of propene to propan-2-ol undergoes Markovnikov's rule. Propene in the presence of acid and water produces propan-2-ol

acetophenone (Major)

$$CH_3$$
 —  $CH = CH_2 + H_2 SO_4 \xrightarrow{H_2 O} Boil$ 
 $H_3C \longrightarrow CH_2 \longrightarrow CH_3$ 
 $OH$ 

Propen-2-ol

(iv) Ethanol can be oxidised to ethanal by using the reagent, PCC or Pyridinium chlorochromate.

- Q 13. (i) Write hydroboration-oxidation reaction with an example.
  - (ii) Write the products of the following reaction:

- (iii) Why is p-nitrophenol more acidic than phenol?
- Ans. (i) Hydroboration-oxidation reaction: Diborane (BH<sub>3</sub>)<sub>2</sub> reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by

hydrogen peroxide in the presence of aqueous sodium hydroxides.

$$\begin{array}{c} \text{CH}_{3} - \text{CH} & \text{SMM} & \text{CH}_{2} + (\text{H} - \text{BH}_{2})_{2} - \rightarrow \\ & \text{CH}_{3} - \text{CH}_{2} - \text{CH}_{2} - \text{BH}_{2} \\ & \downarrow \text{CH}_{3} - \text{CH} & \text{CM}_{2} + (\text{CH}_{2} - \text{CH}_{2})_{3} \text{BH} \\ & \leftarrow \begin{array}{c} \text{CH}_{1} - \text{CH} = \text{CH}_{2} \\ & \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} \\ & \text{CH}_{3} - \text{CH}_{2} - \text{CH}_{2} \\ & \text{Propan-Hol} \end{array}$$

(iii) The polarity of O—H bond decreases due to decrease in electron density of the O—H bond of p-nitrophenol. The electron withdrawing group (—NO) withdraws electrons and disperses the negative charge. Hence, NO group stabilises the phenoxide ion making p-nitrophenol more acidic than phenol.

#### Q 14. (i) What happens when phenol reacts with:

- (a) conc. HNO,
- (b) CHCl<sub>3</sub> in presence of aqueous NaOH followed by acidification?
- (ii) Why does the reaction of CH, ONa with

(CH<sub>3</sub>)<sub>3</sub>C—Br give 2-methylpropene and not

$$(CH_3)_3C - OCH_3?$$
 (CBSE 2023)  
OH OH NO<sub>2</sub>
Ans. (I) (a)  $CONC + HNO_3$ 

I NO<sub>2</sub> 2. 4. 6-trìnltrophenol (Picric acid)

(b) CHCl<sub>3</sub> + CHCl<sub>2</sub> | Intermediate

(II) This is because  $CH_3ONa$  is not only a nucleophile but it is also a strong base. When it reacts with  $(CH_3)_3C$  — Br, it gives elimination product yielding 2-methyl propene and not an ether  $(CH_3)_3C$  —  $OCH_3$ .

Q 15. (i) Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow{H'} CH_3 - CH_2 - O - CH_2 - CH_3 + H_2O$$

(ii) Why *ortho*-nitrophenol is steam volatile while *para*-nitrophenol is not? (CBSE 2023)

Ans. (i) The mechanism of the given reaction involves the following steps:

Step I: 
$$CH_3 - CH_2 - OH + H \longrightarrow CH_3CH_2 - O - H$$

Step II: 
$$CH_3 - CH_2 - \ddot{O} + CH_3 - CH_2 - \ddot{O} + CH_3 - CH_2 - CH_3 + H_2O$$

Step III: 
$$CH_3CH_2 \longrightarrow O^* + CH_3 \longrightarrow CH_3 \longrightarrow CH_3CH_2 \longrightarrow CH_3CH_2 \longrightarrow CH_2CH_3 + H^*$$

(ii) Ortho-nitrophenol is steam volatile due to intermolecular hydrogen bonding while paranitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules. Intramolecular hydrogen bonding takes place in *ortho*-nitrophenol because of NO<sub>2</sub> and OH molecules in close proximity to each other.

#### Q 16. What happens when:

- (i) anisole is treated with CH3Cl/anhydrous AlCl3?
- (ii) phenol is oxidised with Na2Cr2O7/H+?
- (iii) (CH<sub>3</sub>)<sub>3</sub>C OH is heated with Cu/573 K?
  Write chemical equation in support of your answer. (CBSE 2023)

Ans. (i) The products formed are 2-methoxy toluene (minor) and 4-methoxy toluene (major).

 The product formed <u>is benzoquinone</u>, a conjugated diketone.

(iii) The product formed is isobutylene.

#### Q 17. Explain the following:

- Ethers are kept in coloured bottles filled upto brim.
- (ii) C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>OCH<sub>3</sub> both have same molar mass but C<sub>2</sub>H<sub>5</sub>OH is liquid at room temperature and CH<sub>3</sub>OCH<sub>3</sub> is gas.
- (iii) What is power alcohol? What is its use?
- Ans. (i) Ether, mainly diethyl ether is highly volatile. It slowly reacts with atmospheric oxygen to form peroxides in the presence of sunlight.

$$\begin{array}{c}
C_2H_5 \\
C_2H_5
\end{array}$$

$$\begin{array}{c}
0 + \frac{1}{2}O_2 \xrightarrow{\text{air. light}} & C_2H_5 \\
C_2H_5 & O \longrightarrow O
\end{array}$$

These peroxides are <u>highly explosive even in low</u> concentrations.

In order to stop this reaction, ethers are kept in coloured bottles filled upto brim, because coloured bottles stop the light and completely filled bottle does not have air.

(ii) C<sub>2</sub>H<sub>9</sub>OH forms giant molecule by the aggregation through intermolecular H-bonding. Due to its high molar mass, it exists in liquid form.

whereas intermolecular H-bonds are not formed among  $CH_{\frac{1}{2}}$ —O— $CH_{\frac{1}{2}}$  molecules. That's why it exists in gaseous state.

- (iii) Power alcohol: A mixture of rectified spirit with petrol or gasoline is used as a fuel in the motor. Here alcohol is used to generate power, so it is called power alcohol in general, power alcohol is a mixture of 80% rectified spirit and 20% gasoline or petrol.
- Q 18. Write the mechanism of the reaction of HI with methoxymethane. (NCERT EXERCISE)
- **Ans.** Equimolar amounts of methoxymethane and HI form a mixture of methyl alcohol and methyl iodide. The mechanism of the reaction is as follows:

If HI is in excess, then the methanol formed in step II gets converted into methyl lodide by following mechanism.

#### Step III:

Step IV: 
$$\begin{array}{c} H \\ -+ \\ CH_3 \\ \hline \\ Methoxymethane \\ \end{array}$$
  $\begin{array}{c} H \\ S_{W}^2 \\ Slow \\ Methyl \\ Iodide \\ \end{array}$ 

- Q 19. How will you obtain the following ? (Give only chemical equations).
  - (i) Ethyl alcohol from diethyl ether.
    - (ii) Diethyl ether from ethyl iodide.
    - (iii) Ethyl acetate from diethyl ether.

Ans. (i) 
$$C_2H_5O-C_2H_5 \xrightarrow{H_2O} 2C_2H_5OH$$

Distinct other

(ii) 
$$C_2H_5I$$
  $\xrightarrow{C_2H_5ON_0}$   $C_2H_5O$   $C_2H_5$  + NaI Single local decrease  $\Delta$  Diethyl other

(III) 
$$(C_2H_5)_2O \xrightarrow{\text{CLCOCH}_3} CH_3 \xrightarrow{\text{CH}_3} CH_3 - C \xrightarrow{\text{C}} O \xrightarrow{\text{C}_2H_5} + C_2H_5C$$

O

Ethyl acetate

- Q 20. Give one chemical test to distinguish between the following:
  - (i) Phenol and 1-propanol
  - (ii) Ethanol and dimethyl ether
  - (iii) 1-propanol and 2-methyl-2-propanol.

(CBSE 2019)

- Ans. (i) On adding neutral FeCl<sub>3</sub> to the both compounds, phenol gives violet colouration while, 1-propanol does not
  - (ii) On adding I<sub>2</sub>/NaOH(aq) to both the compounds. ethanol gives yellow precipitate while ether does
  - (III) On adding HCl and ZnCl, to both the compounds. 2-methyl-2-propanol gives turbidity immediately while 1-propanol does not.
- Q 21. Write the products of the following reactions:

(ii) 
$$CH_3 - CH_2 - O - CH_3 + HI - \rightarrow$$

OH

(iii)  $+ Br_2 \xrightarrow{CS_2}$ 

OCH<sub>3</sub>

(iii)  $+ CH_3COCl \xrightarrow{anhyd.AlCl_3}$  (CBSE 2019)

Q 22. Write the structure of the main product in the following reactions: (CBSE 2018)

(ii) 
$$CH_{2}$$
— $C$ — $OCH_{3}$   $NaBH_{4}$   $O$ 
 $CH$ = $CH_{2}$   $H_{2}O$   $H'$ 
 $CH$ = $CH_{2}$   $H_{2}O$   $H'$ 

Ans. (i)  $CH$ = $CH_{2}$   $CH$ = $CH_{3}$   $CH$ = $CH_{4}O$   $CH$ = $CH_{5}O$   $CH$ 

- Q 23. Write the equation for the reaction of HI with:
  - (i) 1-Propoxypropane
- (ii) Methoxybenzene
- (iii) Benzyl ethyl ether.

Benzyl ethyl

ether

(NCERT EXERCISE)

Ethanol

Benzyl

lodide

Q 24. Write the reactions of Williamson's synthesis of 2-ethoxy-3-methoxypentane starting from ethanol and 3-methylpentan-2-ol. (NCERT INTEXT)

Ans. In the Williamson's synthesis, the reactants are alkyl halide and sodium salt of an alcohol. In order to avoid the formation of alkene during the reaction, the alkyl halide should be primary while sodium salt must be of branched chain alcohol. In the present case, alkyl halide must be derived from ethanol upon heating with halogen acid (e.g., HBr).

Similarly, the branched chain alcohol must react with sodium metal to form the corresponding sodium salt.

The product of Williamson's synthesis is formed as a result of the following reaction:

Q 25. Predict the products of the following reactions:

(i) 
$$CH_3$$
— $CH$ = $CH_2$ - $\frac{(i)D_2H_6}{(ii)3H_2O_2/OH^-}$ 

(ii) 
$$C_6H_5$$
—OH —  $Br_2$  (aq.)

(iii) 
$$CH_3$$
— $CH_2$ — $OH$ — $\xrightarrow{573 \text{ K}}$ 

Ans. (i) 
$$CH_3 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow O10 \longrightarrow H_3 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow CH_2 OH_3 \longrightarrow CH_3 \longrightarrow CH$$

(II) 
$$C_6H_5$$
—OH— $\frac{Br_2(pq)}{Phenol}$   $C_6H_2(Br_3)OH$ 

(III) 
$$CH_3$$
— $CH_2$ — $OH$ — $CW/673K$   $\rightarrow CH_2$ = $CH_2+H_2O$ 
Ethanol

- Q 26. Given chemical tests to distinguish between:
  - (i) Isopropyl alcohol and n-propyl alcohol
  - (ii) Phenol and alcohol
  - (iii) Methyl ethanoate and ethyl ethanoate.
- Ans. (I) Isopropyl alcohol gives yellow precipitate of iodoform on heating with I<sub>2</sub> and NaOH solution while n-propyl does not.
  - (II) Phenol gives a characteristic violet/red colouration with neutral FeCl<sub>q</sub> while alcohol (e.g., ethyl alcohol) does not respond to this test.

(iii) Both are esters and upon hydrolysis in the acidic medium, they form methanol and ethanol respectively.

$$CH_3COOCH_3 + H_2O \xrightarrow{H^T} CH_3COOH + CH_3OH$$
Methyl ethanoate Methanol

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^4} CH_3COOH + CH_3OH$$
Methyl ethanoate Ethanol

Ethanol and methanol can be further distinguished by <u>iodoform</u> test (given by ethanol and not by methanol).

- Q 27. Dehydration of alcohol to form an alkene is always carried out with concentrated H<sub>2</sub>SO<sub>4</sub> and not with concentrated HCl or HNO<sub>3</sub>. Explain.
- Ans. Under the acidic conditions, alcohol is <u>initially</u> protonated and then loses H<sub>2</sub>O to form a carbocation. If HCl is used. Cl<sup>-</sup> ion being a strong nucleophile substitutes to form alkyl chloride. However, HSO<sub>4</sub> ion released by H<sub>2</sub>SO<sub>4</sub> is a very weak nucleophile and cannot participate in the nucleophilic substitution. It will rather act as a base and eliminate a proton to form alkene as the product as follows:

$$R - CH_{2} - CH_{2} - CI$$

$$R - CH_{2} - CH_{2} - CI$$

$$Albyl chlorida$$

$$Carbocation$$

$$R - CH_{2} - CH_{2} - CI$$

$$Carbocation$$

$$R - CH_{2} - CH_{2} - CI$$

$$Albyl chlorida$$

$$R - CH_{2} - CH_{2} - CI$$

$$Albyl chlorida$$

$$R - CH_{2} - CH_{2} - CI$$

$$Albyl chlorida$$

$$R - CH_{2} - CH_{2} - CI$$

$$Albyl chlorida$$

Concentrated HNO $_3$  is a powerful oxidising agent. It will cause oxidation of alcohol to aldehyde and then to acid. Thus, out of the mineral acids listed, dehydration is carried by concentrated  $H_2SO_2$ . Even phosphoric acid can be used.

- Q 28. Show how will you synthesise:
  - (i) 1-phenylethanol from a suitable alkene
  - (ii) Cyclohexylmethanol using an alkyl halide by  $S_N^2$  reaction
  - (iii) Pentan-1-ol using a suitable alkyl halide.

Ans. (i) 
$$C_6H_6$$
— $CH$ = $CH_2$  +  $H_2O$   $\xrightarrow{(H^3)}$   $C_6H_6$ — $CH$ — $CH_3$   $OH$ 

Helphonyllathanol

Q 29. (i) Draw the structural formulas and write IUPAC names of all the isomeric alcohols with the molecular formula,  $C_5H_{12}O$ .

- (ii) Classify the isomers of alcohols given in part(i) as primary, secondary and tertiary alcohols.
- **Ans.** (i) The molecular formula  $C_5H_{12}O$  represents eight isomeric alcohols. These are:

(a) 
$$CH_3$$
  $CH_2$   $CH_2$ 

(e) 
$$\overset{\text{S}}{\text{CH}_3}$$
— $\overset{\text{A}}{\text{CH}_2}$ — $\overset{\text{3}}{\text{CHO}}$ — $\overset{\text{2}}{\text{CH}}$ — $\overset{\text{1}}{\text{CH}_3}$ 
OH

$$\begin{array}{c|c} & CH_{3} \\ CH_{3} & CH_{2} & CH_{2} \\ CH_{3} & CH_{2} \\ CH_{3} & CH_{3} \\ CH_{4} & CH_{3} \\ CH_{4} & CH_{4} \\ CH_{5} & CH_{5} \\$$

2-Methylbutan-2-ol

(h) 
$$\overset{\S}{C}H_3$$
— $\overset{4}{C}H_2$ — $\overset{3}{C}H$ — $\overset{2}{C}H_2$ — $\overset{1}{C}H_3$ 
OH
Pontion-3-ol

- (ii) Primary: (a), (b), (c), (d); Secondary: (e), (f), (h); Tertlary: (g)
- Q 30. Write the structures of the products of the following reactions:

(iii) 
$$CH_3$$
— $CH_2$ — $CH$ — $CHO$ — $\stackrel{N\alpha BH_4}{\longrightarrow}$   $CH_3$ 

**Ans.** (i) The acidic hydration of propene gives <u>propan-2-ol</u> (isopropyl alcohol).

(ii) NaBH<sub>4</sub> is a weak reducing agent. It brings about reduction of the ketonic group to secondary alcoholic group. However, it does not affect ester group.

(iii) NaBH<sub>4</sub> reduce aldehydic group to a <u>primary</u> alcoholic group.

Q 31. An organic compound A with the molecular formula (+)  $C_4H_9Br$  undergoes hydrolysis to form (±)  $C_4H_9OH$ . Give the structure of A and write the mechanism of the reaction. (CBSE SQP 2023-24)

Ans. Structure of A is: 
$$C_2H_5$$
 —  $CH$  —  $CH_3$  I Br

Mechanism of the reaction:

Step II: 
$$H_3C - C_2H_5 \xrightarrow{\text{Slow}} H_3C - C_2H_5 \xrightarrow{\text{Slow}} H_3C - C_2H_5$$

Step II:  $H_3C - C_2H_5 \xrightarrow{\text{Slow}} H_3C - C_2H_5$ 



#### Long Answer Type Questions

- Q1. (i) Out of t-butyl alcohol and n-butanol, which one will undergo acid catalysed dehydration faster and why?
  - (ii) Carry out the following conversions:
    - (a) Phenol to salicylaldehyde
    - (b) t-butylchloride to t-butyl ethyl ether
    - (c) Propene to Propanol

(CBSE 2020)

Ans. (I) <u>t-butyl alcohol:</u> because it <u>forms more stable 3°</u> carbocation than 1°carbocation.

(ii) (a) Phenol to salicylaldehyde

(b) t-butyl chloride to t-butyl ethyl ether

$$(CH_3)_3C.Cl + NaOH(aq) \longrightarrow (CH_3)_3COH$$
 $\stackrel{c-butyl}{chloridg} \longrightarrow (CH_3)_3CONa$ 
 $\downarrow C_2H_6Cl$ 
 $(CH_3)_3COC_2H_6$ 
 $\downarrow C_2H_6Cl$ 

(c) Propene to Propanol

$$\mathsf{CH_3CH} = \mathsf{CH_2} \xrightarrow{\quad (0) \, \mathsf{B_2H_6} \quad} \mathsf{CH_3CH_2CH_2OH}$$

$$\mathsf{Propens}$$

$$\mathsf{Propens}$$

- Q 2. (i) Give the mechanism for the formation of ethanol from ethene.
  - (ii) Predict the reagent for carrying out the following conversions:
    - (a) Phenol to benzoquinone
    - (b) Anisole to p-bromoanisole
    - (c) Phenol to 2, 4, 6-tribromophenol.

(CBSE 2020)

Ans. (I) Mechanism for the formation of Ethanol from Ethene:

**Step 1:** Protonation of alkene to form carbocation by electrophilic attack of  $H_3O^*$ 

Step 2: Nucleophilic attack of water on carbocation.

$$-\frac{H}{C} + H_{2}O \longrightarrow -\frac{H}{C} - C - C - O - H$$

Step 3: Deprotonation to form an alcohol.

- (ii) (a)  $K_2Cr_2O_7 + H_2SO_4/Na_2Cr_2O_7 + H_2SO_4$ 
  - (b) Br<sub>2</sub> in CH<sub>3</sub>COOH
  - (c) Bromine water (aq. Br<sub>2</sub>).
- Q 3. (i) Give IUPAC name of CH<sub>x</sub>—CH—CH—CHO.
  - (ii) How can you distinguish between ethanol and ethanal?
  - (iii) How will you convert the following:
    - (a) Toluene to benzoic acid
    - (b) Ethanol to propan-2-ol
    - (c) Propanol to 2-hydroxypropanoic acid

(CBSE 2019)

Ans. (I) IUPAC name: But-2-enal

- (ii) On adding Tollen's reagent to both the compounds, ethanol gives silver mirror while ethanol does not.
- (iii) (a) Toluene to benzoic acid

(b) Ethanol to propan-2-ol

$$\begin{array}{c} \mathsf{CH_3CH_2OH} \xrightarrow{\mathsf{PCC.A}} \mathsf{CH_3CHO} \\ \xrightarrow{(\mathfrak{l}) \; \mathsf{CH_3} M \mathfrak{g} \mathfrak{G} r} & \mathsf{CH_3CH(OH)} \; \mathsf{CH_3} \\ \xrightarrow{(\mathfrak{l}) \; \mathsf{H_3O}^*} & \mathsf{CH_3CH(OH)} \; \mathsf{CH_3} \end{array}$$

(c) Propanol to 2-hydroxypropanoic acid

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHO} & \xrightarrow{\text{HANO}_4} & \text{CH}_3\text{CH}_2\text{COOH} \\ \text{Propanol} & \xrightarrow{\text{(ii) NaOH(aq)}} & \text{CH}_3\text{CH(OH) COOH} \\ & \xrightarrow{\text{3-hydras/propanols add}} \end{array}$$

- Q 4. (i) Give IUPAC name of salicylic acid.
  - (ii) Chloroacetic acid is more acidic than acetic acid. Why?
  - (iii) Write the products formed when (CH<sub>3</sub>)<sub>3</sub>C—CHO reacts with the following:
    - (a) zinc amalgam with dilute hydrochloric acid
    - (b) concentrated sodium hydroxide solution
    - (c) semicarbazide and a weak acid. (CBSE 2019)

Ans. (i) 2-hydroxybenzolc acid.

(ii) Chlorine being a strong electron withdrawing group uses inductive effect to pull the negative charge towards itself, resulting in reduced negative charge density on the oxygen atom. hence stabilising the conjugate base of

<u>chloroacetic acid</u> which in turn make it a stronger acid than acetic acid as the ease of releasing the hydrogen to the base is increased.

- (III) (a)  $(CH_3)_3C$ — $CH_3$ 
  - (b)  $(CH_3)_3C$ — $CH_2OH$  and  $(CH_3)_3C$ —COONa
  - (c)  $(CH_3)_3C$ —CH= $NNHCONH_2$

Q 5. (i) Write the product(s) in the following reactions:

- (ii) Give simple chemical tests to distinguish between the following pairs of compounds:
  - (a) Ethanol and Phenol
  - (b) Propanol and 2-methylpropan-2-ol

(CBSE 2017)

$$\begin{array}{c|c} \mathsf{CH_3} & \mathsf{CH_3} \\ | & | \\ \mathsf{(b)} \, \mathsf{CH_3} & \mathsf{CH} \, \mathsf{--O-CH_2} \, \mathsf{--CH_3} & \mathsf{--H} \\ \mathsf{2-othoxy propand} & | & \mathsf{--C-H_3} \\ \mathsf{H} \\ \mathsf{2-todapropand} \\ \end{array}$$

+ CH<sub>3</sub>CH<sub>2</sub>OH

(c) 
$$CH_{1}$$
— $CH$ — $CH$ — $CH_{2}$ — $OH$ 

But 2-207-bol

 $CH_{3}$ — $CH$ — $CH$ — $CHO$ 

(II) (a) Ethanol and Phenol: Iodoform test is used to distinguish ethanol. Ethanol reacts with NaOH solution containing Iodine. On heating, it gives a yellow precipitate of Iodoform while phenol does not react.

$$\text{CH}_3\text{CH}_2\text{OH} + 6\text{NaOH} * 3\text{I}_2 \xrightarrow{\text{lodoform}} \downarrow + \text{HCOONa}$$

$$\text{GUNANOI} \qquad \qquad + 5\text{NaI} + 5\text{HO}_2$$

$$\bigcirc$$
 OH + NaOH + I<sub>2</sub>  $\longrightarrow$  No reaction.

(b) Propanol and 2-methylpropan-2-ol

Propanol is 1° alcohol while 2-methylpropan-2-ol is 2° alcohol. Victor-Meyer's test is used to distinguish both of them. In this test, first the given alcohol is treated with  $P/I_2$  and

then with AgNO<sub>2</sub> and HNO<sub>2</sub>. The final product obtained gives different colour with NaOH. By identifying the colour produced, the alcohols are identified.

$$\begin{array}{c} \text{RCH}_2\text{OH} \xrightarrow{P/l_2} \text{RCH}_2\text{I} \xrightarrow{AgNO_2} \text{R}_2\text{CHNO}_2 \\ \text{1' alcohol} \\ \xrightarrow{O=N-OH} \text{R} \xrightarrow{C} \text{C} \xrightarrow{NO_2} \xrightarrow{NaOH} \text{Blood red} \\ \text{Colour} \\ \text{N} \xrightarrow{OH} \\ \text{Blood red colour} \\ \text{R} \xrightarrow{CHOH} \xrightarrow{P/l_2} \xrightarrow{R} \text{CH} \xrightarrow{I} \xrightarrow{AgNO_2} \text{R}_2\text{CHNO}_2 \\ \text{R} \xrightarrow{O=N-OH} \text{R} \xrightarrow{C} \text{C} \xrightarrow{No_2} \xrightarrow{NaOH} \text{Blood red colour} \\ \text{N} \xrightarrow{O} \end{array}$$

- Q 6. (i) Write the formula of reagents used in the following reactions:
  - (a) Bromination of phenol to 2, 4, 6-tribromophenol.
  - (b) Hydroboration of propene and then oxidation to propanol.
  - (ii) Arrange the following compound groups in the increasing order of their property indicated:
    - (a) p-nitrophenol, ethanol, phenol (acidic character)
    - (b) propanol, propane, propanal (boiling point)
    - (c) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_3$$
  $CH_2$   $OH_2$   $CH_3CH_2OH$   $CH_3CH_2OH$ 

(CBSE 2017

Ans. (I) (a) Bromine in presence of water can carry out bromination of phenol to give 2, 4, 6-tribromophenol.

(b) Diborane (BH<sub>2</sub>)<sub>2</sub> reacts with propene to give tripropylborane as addition product which on oxidation with alkaline H<sub>2</sub>O<sub>2</sub> give alcohols.

$$\begin{array}{c} \mathsf{3CH_3} \mathbf{\longleftarrow} \mathsf{CH} \mathbf{\longleftarrow} \mathsf{CH_2} \xrightarrow{\quad \mathsf{B_2H_6} \quad} (\mathsf{CH_3} \mathbf{\longleftarrow} \mathsf{CH_2} \mathbf{\longleftarrow} \mathsf{CH_2})_{\mathsf{3}} \\ \mathbf{Propene} \end{array}$$

$$-8$$
  $\xrightarrow{H_2O_2/OH^-}$  B(OH)<sub>3</sub> + 3CH<sub>3</sub>  $-CH_2$   $-CH_2$   $-OH$ 

(II) (a) Electron withdrawing groups such as —NO<sub>2</sub>. increases the acidic character while electron releasing group such as —CH<sub>2</sub>. decreases the acidic character. Moreover, the phenoxide ion, produced by the loss of a proton by phenol is stabilised by resonance due to delocalisation of the negative charge on the benzene ring. Therefore, the increasing order of acidic character is:

(b) Alcohols (CH<sub>3</sub>CH<sub>2</sub>OH) undergoes strong hydrogen bonding while hydrocarbon such as propane does not exhibit hydrogen bonding. Aldehydes show hydrogen bonding but not stronger than alcohols.

(increasing order of boiling point)

(c) In given reaction, alcohol acts as nucleophile and attacks on carbocation (CH<sub>2</sub> — CH<sub>2</sub> — 0 H<sub>2</sub>) to form the compound:

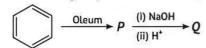
It is the intermediate step, involved in the preparation of ethers.



### **Chapter** Test

#### **Multiple Choice Questions**

QL In the following sequence of reaction,



#### The compound Q formed will be:

- a. aniline
- b. phenol
- c. benzaldehyde
- d. benzene sulphonic acid
- Q 2. Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)	Catechol	(i)	ОН
(B)	Resorcinol	(ii)	ОН
(C)	p-cresol	(iii)	ОН
(D)	Quinol	(iv)	OH CH <sub>3</sub>

- a. (A)  $\rightarrow$  (II), (B)  $\rightarrow$  (III), (C)  $\rightarrow$  (iv), (D)  $\rightarrow$  (I)
- b. (A)  $\rightarrow$  (I). (B)  $\rightarrow$  (II). (C)  $\rightarrow$  (III). (D)  $\rightarrow$  (IV)
- c. (A)  $\rightarrow$  (iv), (B)  $\rightarrow$  (iii), (C)  $\rightarrow$  (ii), (D)  $\rightarrow$  (i)
- d. (A)  $\rightarrow$  (ii), (B)  $\rightarrow$  (iv), (C)  $\rightarrow$  (i), (D)  $\rightarrow$  (iii)
- Q 3. The correct order of strength of acidity of the following compounds is:

- a. (ii) > (i) > (iii) > (iv)
- b. (i) > (ii) > (iii) > (iv)
- c. (iv) > (iii) > (ii) > (i)
- d. (iv) > (iii) > (i) > (ii)

Q 4. Give IUPAC name of the compound given below:

- a. 2-Chloro-5-hydroxyhexane
- b. 2-Hydroxy-5-chlorohexane
- c. 5-Chlorohexan-2-ol
- d. 2-Chlorohexan-5-ol

#### **Assertion and Reason Type Questions**

**Directions (Q. Nos. 5-6):** Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:

- a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
- b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
- c. Assertion (A) is true but Reason (R) is false.
- d. Assertion (A) is false but Reason (R) is true.
- Q 5. Assertion (A): C<sub>2</sub>H<sub>5</sub>OH is a weaker base than phenol but is a stronger nucleophile than phenol. Reason (R): In phenol, the lone pair of electrons on oxygen is withdrawn towards the ring due to resonance.
- **Q 6.** Assertion (A):  $CH_3OCH_3$  and  $C_2H_5OH$  has comparable molecular weight but boiling point of  $C_2H_5OH$  is more than dimethyl ether.

Reason (R): C<sub>2</sub>H<sub>5</sub>OH forms intermolecular H-bonding while CH<sub>3</sub>OCH<sub>3</sub> forms intramolecular H-bonding.

#### **Case Study Based Question**

Q7. Ethers are compounds with general formula  $C_nH_{2n+2}O$ . Ethers may be prepared by dehydration of alcohols and Williamson synthesis. Ethers are colourless, pleasant smelling and volatile liquids with lower boiling points than alcohols. The alkoxy group (—OR) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution. The C—O bond in ethers can be cleaved by hydrogen halides.

Read the given passage carefully and give the answer of the following questions:

- (i) Give the chemical equation for preparation of ether by Williamson synthesis.
- (ii) Diethyl ether does not react with sodium. Explain.

(iii) Write structures of the products of the following reaction:

Predict the products of the following reaction:

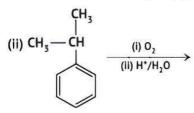
#### **Very Short Answer Type Questions**

- Q 8. What happens when phenol is heated with zinc dust?
- Q 9. How would you obtain ethane-1, 2-diol from ethanol?

#### **Short Answer Type-I Questions**

Q 10. Write the main product(s) in each of the following reaction:

(i) 
$$CH_3 - CH = CH_2 \xrightarrow{\text{(i) } B_2H_6}$$



- Q 11. Draw the structures of any two isomeric alcohols (other than  $1^{\circ}$  alcohols) having molecular formula of  $C_5H_{12}O$  and give their IUPAC names.
- Q 12. Write the mechanism of following reaction:

$$2CH_3CH_2OH \xrightarrow{conc. H_2SO_4} CH_3CH_2 \longrightarrow O \longrightarrow CH_2CH_3$$

#### **Short Answer Type-II Questions**

Q 13. (i) How will you synthesise the following alcohol from appropriate alkene?

(ii) Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow{H^\circ} 443K \rightarrow CH_2 \text{ mass } CH_2 + H_2O$$

- Q 14. How are the following conversions carried out?
  - (i) Benzyl chloride to Benzyl alcohol
  - (ii) Ethyl magnesium chloride to Propan-1-ol
  - (iii) Propene to Propan-2-ol.
- Q 15. Give reasons for the following:
  - (i) Protonation of phenol is difficult whereas ethanol easily undergoes protonation.
  - (ii) Boiling point of ethanol is higher than that of dimethyl ether.
  - (iii) Anisole on reaction with HI gives phenol and CH<sub>3</sub>—I as main products and not iodobenzene and CH<sub>2</sub>OH.

#### **Long Answer Type Questions**

- Q 16. (i) Account for the following:
  - (a) o-nitrophenol is more steam volatile than p-nitrophenol.
  - (b) t-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of t-butylmethylether.
  - (ii) Write the reaction involved in the following:
    - (a) Reimer-Tiemann reaction
    - (b) Friedel-Crafts alkylation of phenol
  - (iii) Give simple chemical test to distinguish between ethanol and phenol.
- Q 17. (i) (a) Write the products in the following reactions:

(b) 
$$CH_3$$
— $CH$ = $CH$ — $CH_2$ — $OH$   $\xrightarrow{PCC}$  ?

- (ii) Arrange the following compounds in the increasing order of the property indicated:
  - (a) p-nitrophenol, ethanol, phenol (acidic character).
  - (b) Propanol, propane, propanal (boiling point).
  - (c) Give simple chemical tests to distinguish between Propanol and 2-methylpropan-2-ol.