CHAPTER / 15

Alcohols

Topics Covered

- Classification of Alcohols
- Monohydric Alcohols
- Nomenclature of Monohydric Alcohol
- Isomerism in Alcohols
- General Methods of Preparation
- Phsycial Properties
- Chemical Properties
- Tests for Alcoholic —OH Group
- Manufacture of Red Methyl Alcohol from Destructive Distillation of Wood
- Manufacture of Ethyl Alcohol from Starchy Materials

An alcohol contains one or more hydroxyl group(s) (—OH), directly attached to carbon atom(s) of an aliphatic system having general formula, $C_nH_{2n+1}OH$.

Classification of Alcohols

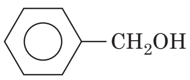
All alcohols, can be divided into two broad categories, i.e.

(i) **Aliphatic alcohols** A compound containing one or more hydroxyl group(s) (—OH group) directly attached to carbon atom(s) of an aliphatic system is known as aliphatic alcohol.

e.g. $\underset{\text{Methanol}}{CH_3OH}$, $\underset{\text{Ethanol}}{CH_3CH_2OH}$

(ii) **Aromatic alcohols** A compound containing hydroxyl group directly attached to side chain of an aromatic hydrocarbon is known as aromatic alcohol.

e.g.



Phenyl methanol

Alcohols can be further classified on the basis of number of —OH groups present in the molecule.

(i) **Monohydric** Alcohols having one hydroxyl group (—OH) attached to the carbon atom of a compound are monohydric alcohols.

e.g. $\underset{\text{Methanol}}{CH_3OH}$, $\underset{\text{Ethanol}}{CH_3CH_2OH}$

(ii) **Dihydric** Alcohols having two hydroxyl groups (—OH) attached to the two carbon atoms of a compound are dihydric alcohols. They are called as diols.

e.g.
$$\begin{array}{l} CH_2-OH \\ | \\ CH_2 \\ | \\ CH_2-OH \end{array}$$
Propan-1,3-diol

(iii) **Trihydric** Alcohols having three hydroxyl groups (—OH) attached to the three carbon atoms of a compound, are trihydric alcohols. They are called **triols**.

e.g.
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$
Gylycerol

(iv) **Polyhydric** Alcohols that have more than three —OH groups are said to be polyhydric alcohols.
$$\begin{array}{l} CH_2-OH \\ | \\ (CH-OH)_4 \\ | \\ CH_2OH \end{array}$$
Sorbitol

Monohydric Alcohols

The general formula of monohydric alcohols is $C_nH_{2n+1}OH$. On the basis of position of —OH group in the carbon chain, monohydric alcohols can be classified as:

(i) **Primary alcohols** In primary (1°) alcohols, the carbon which carries the —OH group, is attached with only one alkyl group, i.e. they contain $-CH_2OH$ group. e.g.

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH}, \quad \underset{\text{2 - methylpropan - 1- ol}}{\begin{array}{l} CH_3-CH-CH_2-OH \\ \quad\quad\;\; | \\ \quad\quad\; CH_3 \end{array}}$$

(ii) **Secondary alcohols** In secondary (2°) alcohols, the carbon carrying —OH group is joined directly to two alkyl groups, which may or may not be same. In other words, they have $>$CHOH group. e.g.

$$\underset{\text{Propan-2-ol}}{\begin{array}{c} \quad OH \\ \quad | \\ CH_3-CH-CH_3 \end{array}}, \quad \underset{\text{Butan-2-ol}}{\begin{array}{c} OH \quad\quad\quad\quad \\ | \quad\quad\quad\quad \\ CH_3-CH-CH_2-CH_3 \end{array}}$$

(iii) **Tertiary alcohols** In tertiary (3°) alcohols, the carbon atom carrying the —OH group is attached directly to three alkyl groups, which may or may not be same. In other words, they have $>$C—OH group.

$$\underset{\text{2-methylpropan-2-ol}}{\begin{array}{c} OH \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}}, \quad \underset{\text{2-methylbutan-2-ol}}{\begin{array}{c} \quad\quad\quad\quad OH \\ \quad\quad\quad\quad | \\ CH_3-CH_2-C-CH_3 \\ \quad\quad\quad\quad | \\ \quad\quad\quad\quad CH_3 \end{array}}$$

Nomenclature of Monohydric Alcohol

The common name of an alcohol is derived from common name of alkyl group and adding the word alcohol to it.

e.g. $CH_3OH \rightarrow \underbrace{CH_3 \text{ (methyl group) + alcohol}}_{\downarrow}$

Methyl alcohol

In **IUPAC system,** the name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by replacing 'e' of alkane with the suffix 'ol'.

The position of substituents are indicated by numerals. Steps for writing the IUPAC name of the alcohols are as follows:

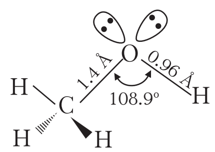
(i) Select the longest carbon chain (parent chain) containing —OH group.
(ii) The selected longest chain is numbered from the end nearest to the hydroxyl group.
(iii) Replace the 'e' of alkane by adding suffix 'ol'.
(iv) The positions of the —OH group and other substituents are indicated by using the numbers of carbon atoms to which these are attached.
(v) For naming polyhydric alcohols, the 'e' of alkane is retained and the ending or suffix 'ol' is added.
(vi) Indicate the number of —OH groups by adding prefix like di, tri, etc. before 'ol'.

Common and IUPAC Name of Some Alcohols

Compound	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-propyl alcohol	Propan-1-ol
$\begin{array}{c} OH \\ \vert \\ CH_3-CH-CH_3 \end{array}$	*iso*-propyl alcohol	Propan-2-ol
$CH_3CH_2CH_2CH_2-OH$	*n*-butyl alcohol	Butan-1-ol

Structure

In alcohols, the oxygen atom of —OH group is attached to sp^3-hybridised carbon atom, where C—O—H bond angle is 108°9' due to repulsion between the two lone pairs of oxygen.



Structure of Methyl Alcohol

Isomerism in Alcohols

Alcohols show four types of isomerism. These are as follows:

(i) **Chain isomerism** The isomers differ in the chain of carbon atoms attached to the hydroxyl group,

e.g. $C_4H_{10}O$ $\quad \underset{\text{Butan-1-ol}}{CH_3—CH_2—CH_2—CH_2—OH}$;

$$\underset{\text{2-methylpropan-1-ol}}{CH_3—\underset{\displaystyle CH_3}{\overset{|}{CH}}—CH_2OH}$$

(ii) **Position isomerism** The isomers differ in the position of hydroxyl group in the same carbon chain.

e.g. C_3H_8O $\quad \underset{\text{Propan-1-ol}}{CH_3—CH_2—CH_2—OH}$;

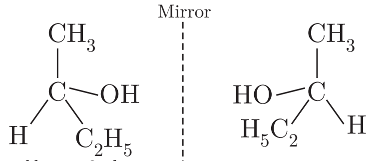
$$\underset{\text{Propan-2-ol}}{CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3}$$

(iii) **Functional isomerism** The isomers differ in the functional group, e.g.

C_2H_6O $\quad \underset{\text{Ethanol (Alcohol)}}{CH_3—CH_2—OH}$; $\quad \underset{\text{Methoxy methane (Ether)}}{CH_3—O—CH_3}$

(iv) **Stereo isomerism** Alcohols containing chiral carbon atom show optical isomerism. These optical isomers can rotate the plane polarised light in different directions. e.g. $C_4H_{10}O$

Mirror



d-butan-2-ol $\quad$ *l*-butan-2-ol

General Methods of Preparation

Monohydric alcohols can be prepared by the following ways :

1. Hydrolysis of Alkyl Halide

Haloalkanes when treated with aqueous solution of an alkali (NaOH/KOH) give corresponding alcohols.

$$\underset{\text{Haloalkane}}{R—X} + KOH(aq) \longrightarrow \underset{\text{Alcohol}}{R—OH} + KX$$

Sometime small amount of ether is also formed, so obtain good yield of alcohol is treat with moist Ag_2O (AgOH).

$$R—X + AgOH \xrightarrow{\Delta} R—OH + AgX$$

2. By Hydrolysis of Ester

On boiling esters with aqueous solution of sodium or potassium hydroxide, salt of carboxylic acid and alcohol are obtained.

$$R—\overset{\displaystyle O}{\overset{||}{C}}—O—R' + NaOH(aq) \xrightarrow{\text{Heat}} R—C—ONa + \underset{\text{Alcohol}}{R'—OH}$$

$$CH_3COOC_2H_5 + NaOH(aq) \xrightarrow{\text{Heat}} CH_3COONa + C_2H_5OH$$

This process is known as **saponification**.

3. By the Reduction of Aldehydes and Ketones

Aldehydes and ketones are reduced to the corresponding alcohols by:

(i) Addition of H_2 in the presence of a finely divided catalyst like Pt, Pd, Ni or Ru metals (catalytic hydrogenation).

$$R—CHO + H_2 \xrightarrow{\text{Ni/Pd}} R—CH_2OH$$

(ii) In presence of complex metal hydrides such as $LiAlH_4$, $NaBH_4$, etc. aldehydes yield primary alcohols, whereas ketones give secondary alcohols.

$$\underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!\!>C=O} \xrightarrow{NaBH_4} \underset{\text{2°-alcohol}}{\begin{matrix}R\\R'\end{matrix}\!\!>CH—OH}$$

$$\underset{\text{Aldehyde}}{R—CHO} \xrightarrow{LiAlH_4} \underset{\text{1° alcohol}}{R—CH_2OH}$$

(iii) Aldehydes and ketones can also be reduced to alcohols using sodium in ethanol.

$$R—\underset{\displaystyle O}{\underset{||}{C}}—H + 2H \xrightarrow{Na/C_2H_5OH} \underset{\text{(1° alcohol)}}{R—CH_2—OH}$$

$$\underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!\!>C=O} + 2H \xrightarrow{Na/C_2H_5OH} \underset{\text{2°-alcohol}}{\begin{matrix}R\\R'\end{matrix}\!\!>CH—OH}$$

This reaction is known as **Bouveault-Blanc reduction**.

4. By the Action of Grignard Reagents on Aldehydes and Ketones

The reactions using different aldehydes and ketones are as follows:

$$\underset{\text{Formaldehyde}}{HCHO} + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O/H^+} \underset{\text{1° alcohol}}{R\;CH_2OH} + Mg(OH)X$$

$$\underset{\text{Aldehyde}}{RCHO} + R'MgX \longrightarrow R—\overset{\displaystyle R'}{\overset{|}{C}}H—\overset{-}{O}\overset{+}{M}gX$$

$$\xrightarrow{H_2O/H^+} \underset{\text{2° alcohol}}{R—\overset{\displaystyle R'}{\overset{|}{C}}H—OH} + Mg(OH)X$$

$$\underset{\text{Ketone}}{RCOR'} + R''MgX \longrightarrow R—\underset{\displaystyle R''}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C}}}}—\overset{-}{O}\overset{+}{M}gX$$

$$\xrightarrow{H_2O/H^+} \underset{\text{3° alcohol}}{R—\underset{\displaystyle R''}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C}}}}—OH} + Mg(OH)X$$

Only formaldehyde yields primary alcohol on reaction with Grignard reagents, whereas all other aldehydes and ketones give secondary and tertiary alcohols, respectively.

5. From Aliphatic Primary Amines

Aliphatic primary amines react with nitrous acid to give primary alcohol.

$$NaNO_2 + HCl \xrightarrow{0\text{-}3°C} \underset{\text{Nitrous acid}}{HNO_2} + NaCl$$

$$R\text{—}NH_2 + HNO_2 \xrightarrow{0\text{-}3°C} R\text{—}OH + N_2\uparrow + H_2O$$

But this is not a good method for the preparation of 1° alcohols because a mixture of alkenes, alkyl halides, aldehydes are also produced along with alcohols.

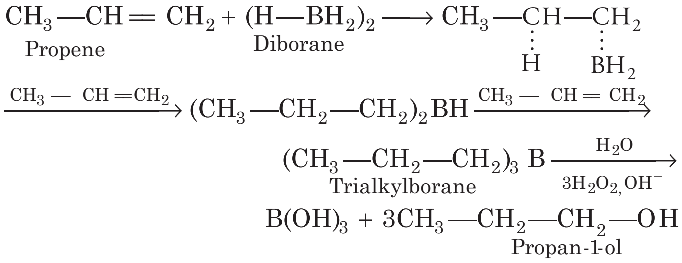
6. By Addition of Water (Hydration)

The term hydration refers to the addition of a molecule of water. Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition of water takes place in accordance with Markovnikov's rule. This rule states that negative part of the water molecule, i.e. OH^- part gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

$$\underset{\text{Propene}}{H_3C\text{—}CH{=}CH_2} + H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{Propan-2-ol}}{H_3C\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}CH_3}$$

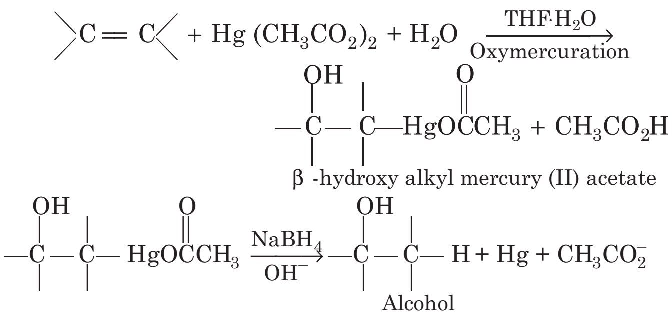
7. By Hydroboration-Oxidation

Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product which upon subsequent oxidation by H_2O_2 in the presence of aqueous sodium hydroxide give alcohols.



8. Oxymercuration-Demercuration Reaction

Mercury (II) acetate reacts with alkene in presence of water to give β-hydroxy alkyl mercury (II) acetate (this step is called oxymercuration and is carried out in a mixture of H_2O and THF as solvent) which is treated directly with $NaBH_4$ to form alcohol (this step is called demercuration).



The complete reaction is called oxymercuration-demercuration. It gives product in accordance with Markovnikov's rule without any rearrangement (without formation of carbocation).

Physical Properties

Some important physical properties are as follows :

1. Physical State

At room temperature, lower alcohols are colourless liquids with distinct smell and burning taste. The higher members are colourless, odourless waxy solids.

2. Boiling Points

The boiling points of alcohols increase with increase in number of C-atoms (due to increase in van der Waal's forces). In alcohols, the boiling point decreases with increase in branching in carbon chain because of decrease in van der Waal's forces with decrease in surface area.

3. Solubility

The solubility of alcohols in water is due to their ability to form H-bonds with water molecules. Solubility decreases with increase in size of alkyl/aryl (i.e. hydrophobic) groups.

4. Physiological Effects

Amongst all alcohols ethyl alcohol is least toxic. Drinking methyl alcohol can cause death or blindness.

Chemical Properties

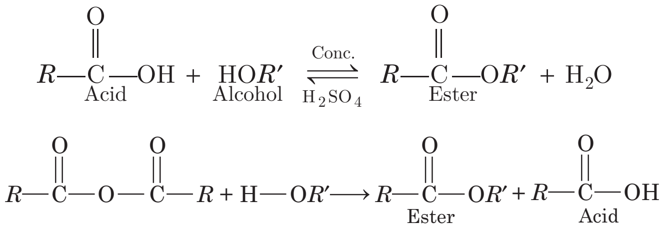
1. Reactions Involving Cleavage of O—H Bond

Some typical reactions of alcohols involving the cleavage of $O—H$ bond are as follows:

(i) **Reaction with alkali metals** Alcohols react with active metals like Na, K, Al to produce corresponding alkoxides with the evolution of hydrogen gas.

$$2R\text{—}O\text{—}H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R\text{—}\overset{-}{O}\overset{+}{Na}} + H_2\uparrow$$

(ii) **Reaction with carboxylic acid** (Esterification) Alcohols react with carboxylic acid, acid anhydride and acid chloride in the presence of concentrated sulphuric acid to form esters. This reaction is called **esterification**.



(iii) **Reaction with inorganic acids** Inorganic acids such as H_2SO_4, HCl, etc. react with alcohols form corresponding alkyl hydrogen sulphate, alkyl halide respectively

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

$$\underset{\substack{\text{Ethyl}\\\text{alcohol}}}{C_2H_5OH} + HCl \xrightarrow{\text{Anhyd. }ZnCl_2} \underset{\substack{\text{Ethyl}\\\text{chloride}}}{C_2H_5Cl} + H_2O$$

When ethyl alcohol is treated with equimolar amount of conc. H_2SO_4 at 100°C an inorganic ester is formed.

$$C_2H_5\text{—}OH + H_2SO_4 \longrightarrow C_2H_5\text{—}HSO_4 + H_2O$$

But in excess of H_2SO_4 at 140°C, diethyl ether is formed

$$C_2H_5\text{—}HSO_4 + HOC_2H_5 \longrightarrow C_2H_5OC_2H_5 + H_2SO_4$$

And at 160°C with excess of conc. H_2SO_4, ethylene is formed

$$C_2H_5\text{—}HSO_4 \xrightarrow[160^\circ C]{\Delta} \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

The order of reactivity of alcohols is 3° > 2° > 1°.

2. Reactions Involving Cleavage of C—OH Bond

The reactions involving cleavage of C—OH bond taking place in alcohols are as follows:

(i) **Reaction with phosphorus halides** Alcohols react with phosphorus halides, PCl_3, PCl_5, etc. to form corresponding haloalkanes.

$$CH_3CH_2OH + PCl_5 \longrightarrow \underset{\text{Chloroethane}}{CH_3CH_2Cl} + \underset{\substack{\text{Phosphorus}\\\text{oxychloride}}}{POCl_3} + HCl\uparrow$$

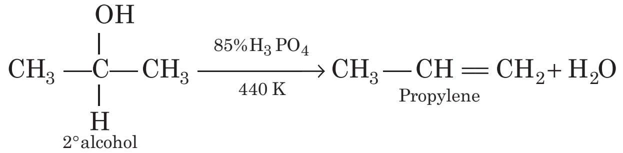
$$3CH_3CH_2OH + PCl_3 \longrightarrow \underset{\text{Chloroethane}}{3CH_3CH_2Cl} + \underset{\substack{\text{Phosphorus}\\\text{acid}}}{H_3PO_3}$$

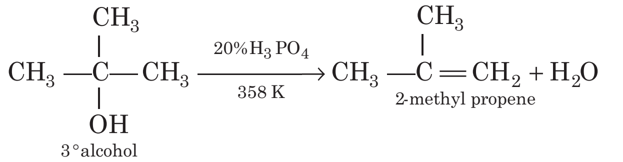
(ii) **Reaction with thionyl chloride** Alcohols react with thionyl chloride in the presence of pyridine to form chloroalkanes.

$$R\text{—}OH + \underset{\substack{\text{Thionyl}\\\text{chloride}}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Chloroalkane}}{R\text{—}Cl} + SO_2\uparrow + HCl\uparrow$$

(iii) **Dehydration** Alcohols undergo dehydration to form alkenes on treatment with a protic acid such as H_2SO_4 or H_3PO_4.

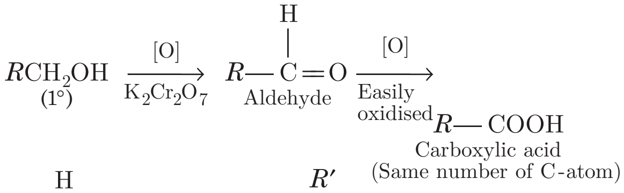
e.g. $$\underset{1^\circ\text{ alcohol}}{CH_3CH_2OH} \xrightarrow[443\text{ K}]{H_2SO_4} \underset{\text{Ethylene}}{CH_2 = CH_2} + H_2O$$

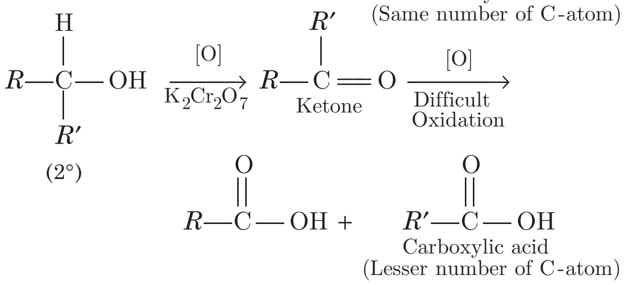




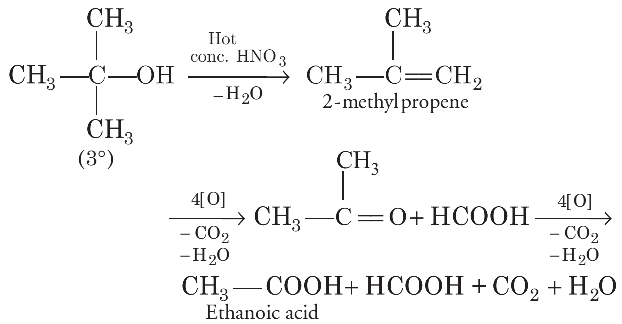
3. Reactions Involving both Alkyl and Hydroxyl Group

(i) **Oxidation** Primary and secondary alcohols are easily oxidised by $Na_2Cr_2O_7$ / $K_2Cr_2O_7$ /acidified $KMnO_4$ to form aldehydes and ketones containing same number of carbon atoms respectively. This process involves the formation of carbon-oxygen double bond with cleavage of O—H and C—H bonds.





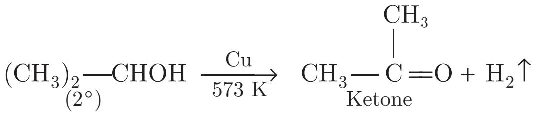
Tertiary alcohols are resistant to oxidation in alkaline solution. However, when subjected to vigorous oxidation with nitric acid give ketone containing lesser number of carbon atoms.

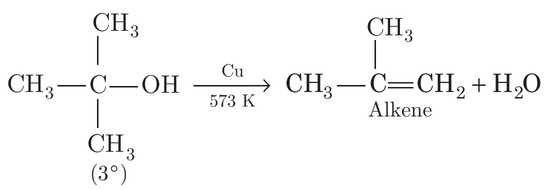


(ii) **Catalytic Dehydrogenation**

When vapours of alcohols are passed over heated copper at 573 K, primary and secondary alcohols undergo dehydrogenation to give aldehydes and ketones respectively, while tertiary alcohols undergo dehydration to give alkenes.

$$\underset{(1^\circ)}{CH_3\text{—}CH_2OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Aldehyde}}{CH_3\text{—}CHO} + H_2\uparrow$$



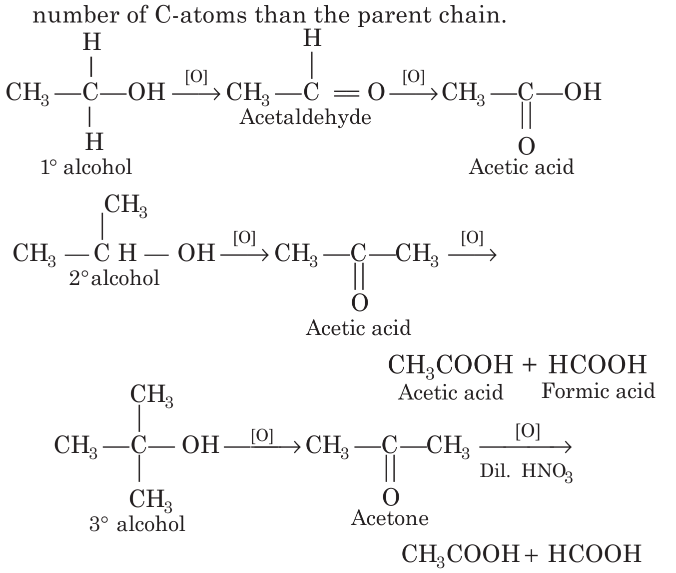


Distinction between 1°, 2° and 3° Alcohols

Distinction among 1°, 2° and 3° alcohols can be made by following methods:

1. Oxidation Method

- Oxidation reaction is used to distinguish between 1°, 2° and 3° alcohols.
- Primary alcohols are oxidised to aldehydes and then to acids.
- Secondary alcohols are oxidised to ketones and then to acids containing lesser number of carbon atoms than the parent alcohol under vigrous conditions.
- Tertiary alcohols can only be oxidised in acidic medium to give mixture of ketone and acid containing lesser number of C-atoms than the parent chain.



2. Catalytic Dehydrogenation

1° and 2° alcohol on treating with Cu or Ag, undergo dehydrogenation to give aldehydes and ketones respectively, while tertiary alcohols undergo dehydration to give alkenes.

$$1^\circ \text{ alcohol} \xrightarrow[300^\circ C]{Cu} \text{Aldehyde} + H_2\uparrow$$

$$2^\circ \text{ alcohol} \xrightarrow[300^\circ C]{Cu} \text{Ketone} + H_2\uparrow$$

$$1^\circ \text{ alcohol} \xrightarrow[300^\circ C]{Cu} \text{Alkene} + H_2\uparrow$$

3. Victor-Meyer's Test

In this test, the given alcohol is treated with red phosphorus and iodine to convert, it into the corresponding alkyl iodide which is then further treated with $AgNO_2$ to form nitroalkane, which is finally treated with nitrous acid and the resulting solution is made alkaline with *aq.*NaOH or KOH. Primary alcohols give blood red colour, secondary alcohols give blue colour and in case of tertiary alcohols, solution remains colourless.

Primary (1°) alcohol	Secondary (2°) alcohol	Tertiary (3°) alcohol
CH_3CH_2OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$
$\downarrow P/I_2$	$\downarrow P/I_2$	$\downarrow P/I_2$
CH_3CH_2I	$(CH_3)_2CH-I$	$(CH_3)_3C-I$
$\downarrow AgNO_2$	$\downarrow AgNO_2$	$\downarrow AgNO_2$
$CH_3CH_2NO_2$	$(CH_3)_2CHNO_2$	$(CH_3)_3C-NO_2$
$\downarrow HNO_2$	$\downarrow HNO_2$	$\downarrow HNO_2$
$R-C(=N-OH)-NO_2$ (Nitrolic acid)	$(CH_3)_2C(N{=}O)-NO_2$	(No reaction)
$\downarrow NaOH$	$\downarrow NaOH$	$\downarrow NaOH$
Blood red colouration	Blue colouration	No colour

4. Lucas Test

A small quantity of unknown alcohol is added to Lucas reagent (anhyd. $ZnCl_2$ + conc. HCl) at room temperature and the mixture is shaken turbidity appears due to the formation of insoluble alkyl chloride.

A tertiary alcohol forms turbidity immediately, secondary alcohol forms turbidity within five minutes and primary alcohol shows no turbidity at room temperature.

$$R_3COH \xrightarrow[\text{anhyd . } ZnCl_2]{\text{Conc.HCl} +} \underset{\text{Turbidity appears immediately}}{R_3CCl} + H_2O$$

$$R_2CHOH \xrightarrow[\text{anhyd . } ZnCl_2]{\text{Conc.HCl} +} \underset{\text{Turbidity appears in 5 min}}{R_2CHCl}$$

$$RCH_2OH \xrightarrow[\text{anhyd . } ZnCl_2]{\text{Conc.HCl} +} \text{No reaction}$$

Tests for Alcoholic –OH Group

The following tests can be performed in order to detect the presence of alcoholic group in an unknown organic compound.

(i) When a piece of sodium metal is added to an anhydrous compound, bubbles of hydrogen (H_2) gas are evolved

$$2ROH + 2Na \longrightarrow 2RONa + H_2\uparrow$$

(ii) When PCl_5 is added to the compund, it becomes warm due to evolution of HCl gas.

$$ROH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl\uparrow + \text{Heat}$$

(iii) Acetyl chloride (CH_3COCl) reacts with the compound containing hydroxyl group with evolution of HCl gas and formation of oily layer of ester.

$$CH_3OH + ClOCCH_3 \longrightarrow CH_3COOCH_3 + HCl\uparrow$$

(iv) The colour of orange cerric ammonium nitrate solution changes to a deep red colour when added to organic compound containing — OH group.

$$\underset{\text{Orange}}{(NH_4)_2Ce(NO_3)_6} + 2ROH \longrightarrow \underset{\text{Red}}{Ce(NO_3)_4(ROH)_2} + 2NH_4NO_3$$

Manufacture of Red Methyl Alcohol from Destructive Distillation of Wood

Commercially, methyl alcohol is manufactured by destructive distillation of wood. It involves decomposition of wood by heating to temperature of 450-500°C in absence of air. The products, obtained are **wood gas** consisting of CH_4, C_2H_6, CO, CO_2 and N_2, **pyroligneous acid** that contains H_2O, CH_3OH, CH_3COCH_3, CH_3COOH, **wood tar** and **wood charcoal**.

Recovery of Methyl Alcohol from Pyroligneous Acid

Methyl alcohol can be recovered form pyroligneous acid by removing acetone and acetic acid.

Following steps are involved in this process:

(i) **Removal of acetic acid** For removing acetic acid, pyroligneous acid is treated with lime milk that produces calcium salt of acetic acid. The resulting solution is then distilled that leaves calcium acetate as residue. It is further treated with conc. H_2SO_4 that gives acetic acid.

$$2CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + H_2O$$

$$(CH_3COO)_2Ca + H_2SO_4 \longrightarrow 2CH_3COOH + CaSO_4$$

(ii) **Removal of acetone** The distillates methyl alcohol and acetone obtained are subjected to fractional distillation. At 329 K acetone is collected and at 338 K methyl alcohol is collected.

(iii) **Purification of methyl alcohol** Methyl alcohol collected, contains small amount of acetone and water so, it is further treated with anhy. $CaCl_2$ and CH_3OH forming a crystalline compound. It is then decomposed by boiling in water to give free alcohol which is dried over quick lime and redistilled to obtain pure methyl alcohol.

Manufacture of Ethyl Alcohol from Starchy Materials

Ethyl alcohol can be commercially prepared by the fermentation process using starchy grains such as potatoes, barley, rice, wheat, etc. The different steps involved in this process are as follows:

(i) Saccharification

It is the process of conversion of starch into maltose, which on fermentation gives alcohol. The process of saccharification involves three steps.

(a) **Preparation of Malt Extract** Moist barley seeds are allowed to germinate in dark at the 15°C and then, temperature is raised to 60°C to check the growth. After that seeds are crushed and extracted with water. This is called malt extract, which contain the enzyme, diastase.

(b) **Mashing** Substances containing starch like potato, rice are heated in steam under high pressure to give a paste known as **mash**.

(c) **Hydrolysis** When mash and malt are added together and heated at 50°C in presence of water, hydrolysis takes and maltose is obtained.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

(ii) Alcoholic Fermentation

Solution of maltose is cooled to 30°C and then yeast is added containing **maltase** and **zymase.** Maltase converts maltose into glucose and zymase convert glucose into ethyl alcohol.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + H_2O \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2\uparrow$$

(iii) Distillation

The fermented ethyl alcohol contains water and impurities. So, pure ethanol can be obtained by fractional distillation.

Distinction of Ethanol from Methanol

(i) Ethanol can be distinguished from methanol as follows:

Iodoform Test When ethyl alcohol or any alcohol containing the group $CH_3—\overset{\overset{\large OH}{|}}{CH}—$ is heated with iodine and *aq*. NaOH or Na_2CO_3 solution at 333 K to 343 K, a yellow precipitate of iodoform is formed.

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3}\downarrow + HCOONa + 5NaI + 5H_2O$$

$$CH_3OH + I_2 + NaOH \xrightarrow{\Delta} \text{No reaction}$$

(ii) On oxidation, ethanol gives acetic acid but methanol gives formic acid.

PRACTICE QUESTIONS

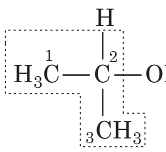
Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 What is the IUPAC name of isopropyl alcohol? **[2018]**

Ans The IUPAC name of isopropyl alcohol is propan-2-ol.



Propan-2-ol

Important Questions

Q.2 Action of nitrous acid on ethyl amine gives **[Textbook]**

(a) C_2H_6 (b) C_2H_5OH
(c) C_2H_5OH and C_2H_4 (d) C_2H_5OH and NH_3

Ans (*b*) Aliphatic primary amines react with nitrous acid to give primary alcohol.

$$NaNO_2 + HCl \xrightarrow{0\text{-}5\,^\circ C} \underset{\text{Nitrous acid}}{HNO_2} + NaCl$$

$$\underset{\text{Ethyl amine}}{CH_2-CH_2-NH_2} + \underset{\substack{\text{Nitrous}\\\text{acid}}}{HNO_2} \xrightarrow{0\text{-}5\,^\circ C} \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2\uparrow + H_2O$$

Q.3 Ethyl alcohol is heated with conc. H_2SO_4. The product formed is

(a) $CH_3COOC_2H_5$ (b) C_2H_6
(c) C_2H_4 (d) C_2H_2

Ans (*c*) When ethyl alcohol is heated with conc. H_2SO_4 it forms ethene (C_2H_4) along with water.

$$\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow[\Delta]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

Q.4 Which one is primary alcohol? **[Textbook]**

(a) Butan-2-ol (b) Propan-2-ol
(c) Butan-1-ol (d) 2, 3-dimethyl hexan-4-ol

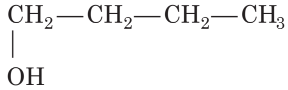
Ans (*c*) Butan-1-ol is primary alcohol because the carbon, which carries the —OH group, is attached with only one alkyl group.

$$\underset{\text{Butan-1-ol}}{CH_3-CH_2-CH_2-CH_2-OH}$$

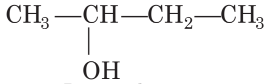
Q.5 How many structural isomers of alcohol with molecular formula C_4H_9OH are possible?

(a) 5 (b) 7 (c) 3 (d) 6

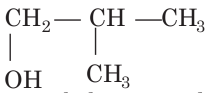
Ans (*b*) Structural isomers of alcohol with molecular formula C_4H_9OH are as follows:

(i) 

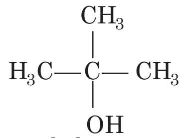
Butan-1-ol

(ii) 

Butan-2-ol

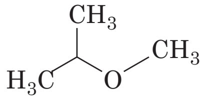
(iii) 

2-methylpropan-1-ol

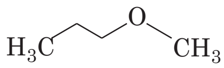
(iv) 

2-methylpropan-2-ol

(v) $\underset{\text{Ethoxyethane}}{H_3C-CH_2-O-CH_2-CH_3}$

(vi) 

2- methoxypropane

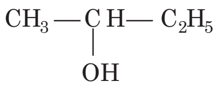
(vii) 

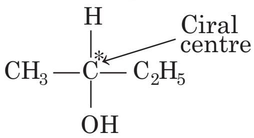
1- methoxypropane

Thus, seven structural isomers are possible.

Q.6 Which of the following compound is optically active? **[Textbook]**

(a) CH_3CH_2OH (b) $CH_2OH \cdot CHOH \cdot CH_2OH$
(c) $CH_3CHOH \cdot C_2H_5$ (d) CCl_2F_2

Ans (*c*)  compound is optically active because of the presence of chiral carbon atom.



Butan-2-ol

Q.7 Which of the following compound is called carbinol?

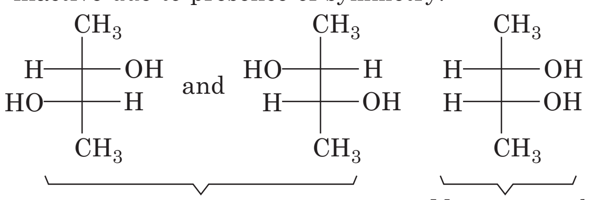
(a) CH_3OH (b) C_2H_3OH
(c) C_3H_7OH (d) $\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>CH-OH$

Ans (*a*) In the carbinol system, the simplest alcohol, i.e. CH_3OH is called carbinol.

Q.8 How many optically active stereoisomers are possible for butan-2, 3-diol? **[Textbook]**

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

Ans (*d*) The number of optically active stereoisomers possible for 2, 3-diol is 2, i.e. *d* and *l* which are optically active. The *meso* compound is optically inactive due to presence of symmetry.



Optically active — *Meso*-compound (optically inactive)

Q.9 Butan-1-ol and butan-2-ol are

(a) chain isomers (b) functional isomers
(c) position isomers (d) optical isomers

Ans (*c*) Butan-1-ol and butan-2-ol are position isomers as they differ in the position of — OH group.

$$\underset{\text{Butan-1-ol}}{CH_3—CH_2—CH_2—OH}; \quad \underset{\text{Butan-2-ol}}{CH_3—\underset{|}{\overset{}{C}}H(OH)—CH_2—CH_3}$$

Q.10 As isomer of ethanol is **[Textbook]**

(a) methanol (b) dimethyl ether
(c) acetone (d) diethyl ether

Ans (*b*) The isomer of ethanol (CH_3CH_2OH) is dimethyl ether ($CH_3—O—CH_3$). This is functional isomer of ethanol.

Q.11 The compound '*B*' formed in the following sequence of reaction is

$$CH_3CH_2CH_2OH \xrightarrow{PCl_5} A \xrightarrow{\text{Alc.KOH}} B$$

(a) propyne (b) propanal (c) propane (d) propene

Ans (*d*) Propan-1-ol reacts with PCl_5 to form the corresponding propyl chlorides (*A*), which reacts with alc. KOH and form propene (*B*).

$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} \xrightarrow{PCl_5} \underset{(A)}{CH_3CH_2CH_2Cl} \xrightarrow{\text{Alc. KOH}} \underset{\substack{\text{Propene}\\(B)}}{CH_3CH{=}CH_2}$$

Q.12 The compound which reacts fastest with Lucas reagent at room temperature is

(a) butan-1-ol (b) butan-2-ol
(c) 2-methyl propan-2-ol (d) 2-methyl propan-1-ol

Ans (*c*) 3°-alcohol reacts fastest with Lucas reagent at room temperature. Hence, 2-methyl propan-2-ol reacts fastest rest of all.

$$H_3C—C(OH)(CH_3)—CH_3 \xrightarrow[\text{and } ZnCl_2]{\text{Conc. HCl}} \text{Turbidity appears immediately.}$$

Q.13 Primary and secondary alcohols on action of reduced copper gives

(a) aldehydes and ketones, respectively
(b) ketones and aldehydes, respectively
(c) only ketones
(d) only aldehydes

Ans (*a*) When the vapours of a primary alcohol is passed over copper heated at 573 K, the corresponding aldehyde is formed. When the vapours of a secondary alcohol is passed over copper heated at 573 K the corresponding ketone is formed.

$$CH_3CH_2OH \xrightarrow[-H_2]{\text{Cu, 300°C,}} \underset{\text{Aldehyde}}{CH_3CH_2CHO}$$

$$(CH_3)_2CH—OH \xrightarrow[-H_2]{\text{Cu, 300°C}} \underset{\text{Ketone}}{CH_3COCH_3}$$

Q.14 Dehydrogenation of 2-butanol gives

(a) 2-butene (b) butan-2-one
(c) butanal (d) None of these

Ans (*b*) Dehydrogenation of butan-2-ol give butanone.

$$\underset{\text{Butan-2-ol}}{CH_3—CH(OH)—CH_2CH_3} \xrightarrow[300°C,\ -H_2]{Cu} \underset{\text{Butan-2-one}}{CH_3—C(=O)—CH_2—CH_3}$$

Q.15 Which of the following compounds is oxidised to prepare methyl ethyl ketone?

(a) Propan-2-ol (b) Butan-1-ol
(c) Butan-2-ol (d) *t*-butyl alcohol

Ans (*c*) Butan-2-ol is oxidised to prepare methyl ethyl ketone.

$$\underset{\text{Butan-2-ol}}{CH_3—CH(OH)—CH_2—CH_3} \xrightarrow{[O]} \underset{\text{Methyl ethyl ketone}}{CH_3—C(=O)—CH_2—CH_3}$$

Q.16 Which of the following gives secondary alcohol?

(a) CH_3COCH_3 (b) CH_3CHO
(c) CH_3COOH (d) $CH_3—O—CH_3$

Ans (*a*) Acetone (CH_3COCH_3) gives secondary alcohol.

$$\underset{\text{(Acetone)}}{(CH_3)_2C{=}O} \xrightarrow{LiAlH_4} \underset{\substack{\text{Propan-2-ol}\\(2°\text{-alcohol})}}{(CH_3)_2CH—OH}$$

Q.17 Fermentation of starch solution to ethyl alcohol does not require

(a) diastase (b) invertase
(c) maltase (d) zymase

Ans (*b*) Fermentation of starch solution to ethyl alcohol does not require invertase. Only sucrose requires invertase.

e.g. $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O + \text{invertase} \longrightarrow 2\,(C_6H_{12}O_6)$

Q.18 The boiling point of ethyl alcohol should be less than

(a) propane (b) dimethyl ether
(c) formic acid (d) None of these

Ans (*c*) The boiling point of ethyl alcohol should be less than formic acid because carboxylic acids have extensive intermolecular H-bonding and H-bonding is a type of intermolecular force. While, extent of H-bonding in alcohol is less than carboxylic acid, hence boiling point of carboxylic acid will be more.

Q.19 The enzyme which can catalyse the conversion of glucose to ethanol is

(a) zymase (b) invertase (c) maltase (d) diastase

Ans (*a*) Zymase is an enzyme complex that catalyses the fermentation of glucose into ethanol and carbon dioxide.

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

Q.20 The reaction between alcohol and carboxylic acid is called

(a) hydrolysis (b) saponification
(c) esterification (d) hydrogenation

Ans (*c*) When a carboxylic acid is treated with an alcohol and an acid catalyst, an ester is formed. This reaction is called esterification.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R\text{—}OH} \longrightarrow \underset{\text{Ester}}{RCOOR} + H_2O$$

Q.21 In CH_3CH_2OH the bond that undergoes heterolytic cleavage most readily is

(a) C—C (b) C—O
(c) C—H (d) O—H

Ans (*d*) Heterolytic fission takes place when two atom differ considerably in their electronegativities, therefore O—H bond will undergo heterolytic fission most readily because of the considerable difference in electronegativities of O-atom and H-atom.

Q.22 Which one of the following is an isomer of diethyl ether?

(a) $(CH_3)_3C\text{—}OH$ (b) $(CH_3)_3CHOH$
(c) C_3H_2OH (d) $(C_2H_5)_2CHOH$

Ans (*a*) Tertiary alcohol is an isomer of diethyl ether because molecular formula of tertiary alcohol and diethyl ether are same ($C_4H_{10}O$).

Q.23 Ethyl alcohol is miscible with water in all proportions. It is because,

(a) it is acidic in nature (b) it dissociates in water
(c) it is basic in nature
(d) it forms hydrogen bonding with water

Ans (*d*) Ethyl alcohol is miscible with water because both water and ethanol are polar in nature and ethanol has — OH groups capable of informing hydrogen bond with water molecule.

Q.24 Hydrochloric acid reacts fastest with

(a) propan-1-ol (b) propan-2-ol
(c) 2-ethyl propan-1-ol (d) 2-methyl propan-2-ol

Ans (*d*) Hydrochloric acid reacts fastest with 2-methyl propan-2-ol, because the order of reactivity of alcohols with halogen acid is 3° > 2° > 1°.

Q.25 A mixture of water and alcohol can be separated by

(a) evaportation (b) decantation
(c) distillation (d) filtration

Ans (*c*) A mixture of water and alcohol can be separated by the process of distillation.

Q.26 Secondary alcohol on oxidation gives,

(a) ketone (b) aldehyde (c) ether (d) hydrocarbon

Ans (*a*) Secondary alcohol on oxidation gives ketone.

$$\underset{\text{(2°-alcohol)}}{R\text{—}\overset{\overset{\large R}{|}}{C}H\text{—}OH} \xrightarrow{K_2Cr_2O_7/\text{Dil. }H_2SO_4} \underset{\text{(Ketone)}}{R\text{—}\underset{\underset{\large O}{\|}}{C}\text{—}R} + H_2O$$

Q.27 Which of the following compounds has the highest boiling point?

(a) $CH_3CH_3CH_3$ (b) CH_3CH_2OH
(c) CH_3Cl (d) $CH_3\text{—}O\text{—}CH_3$

Ans (*b*) Boiling points of alcohol are usually higher in comparison to those of hydrocarbons, ether, haloalkane and haloarenes of comparable molecular masses. This is mainly due to the presence of intermolecular hydrogen bonding in them.

Q.28 What class of compounds have a molecular formula, $C_nH_{2n+2}O$?

Ans Monohydric alcohols have a molecular formula $C_nH_{2n+2}O$.

Q.29 How does metallic sodium react with methyl alcohol?

Ans $2CH_3OH + 2Na \longrightarrow \underset{\text{Sodium methoxide}}{2CH_3ONa} + H_2\uparrow$

Q.30 Methyl alcohol does not give iodoform test, why?

Ans Iodoform reaction is given by a compound containing $CH_3CO\text{—}$ and $\underset{\text{(2°-alcohol)}}{\text{—}\overset{|}{C}H\text{—}OH}$ group. Methyl alcohol, i.e. CH_3OH does not contains $CH_3CO\text{—}$ group and is a primary alcohol does not give iodoform test.

Q.31 Complete the following equation,

$$CH_3CH_2OH + SOCl_2 \longrightarrow \ldots + \ldots + HCl\uparrow$$

Ans $CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2\uparrow + HCl\uparrow$

Q.32 What is the name of the functional group in CH_3CH_2OH?

Ans Alcohol is the functional group present in CH_3CH_2OH.

Q.33 Given, the IUPAC name of a compound which is isomeric with diethyl ether.

Ans The compound isomeric to diethyl ether $CH_3CH_2OCH_2CH_3$ is butan-1-ol ($CH_3CH_2CH_2CH_2OH$)

Q.34 How ethyl alcohol can be converted to acetic acid?

Ans Conversion of ethyl alcohol to acetic acid.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{Alk. } KMnO_4]{[O]} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

Q.35 Ethanol is obtained by ……… reaction of acetaldehyde). (oxidation, reduction, polymerisation)

Ans Reduction

Q.36 What is the IUPAC name of the following compound?

$$\overset{\displaystyle Cl}{\overset{|}{CH_2}}—CH_2—CH_2—OH$$

Ans $\underset{\text{3-chloropropan-1-ol}}{\overset{\displaystyle Cl}{\overset{|}{CH_2}}—CH_2—CH_2—OH}$

2 MARK *Questions*

Important Questions

Q.37 Give equation for the reaction of ethyl bromide with aqueous and alcoholic KOH. Also, given the name of the products.

Ans Reaction of ethyl bromide with *aq*. KOH

$$C_2H_5Br + aq.\ KOH \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KBr$$ **(1)**

Reaction of ethyl bromide with alcoholic KOH

$$C_2H_5Br + \text{alc. } KOH \longrightarrow \underset{\text{Ethene}}{CH_2 = CH_2} + KBr$$ **(1)**

Q.38 Give one chemical test to distinguish between CH_3CH_2OH and CH_3OH.

Ans The iodoform test can be used to distinguish ethanol from methanol CH_3CH_2OH being 2°-alcohol will give positive iodoform test.

$$CH_3—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}—H + 4I_2 + 6OH^{S} \longrightarrow \underset{\text{Iodoform}}{CHI_3(s)\downarrow}$$

$$+ 5I^{S} + 5H_2O + H—\overset{\overset{\displaystyle O}{\|}}{C}—O^{S}$$

While methanol does not give positive iodoform test.

$$CH_3OH + 4I_2 + 6OH^{S} \longrightarrow \text{No reaction.}$$ **(2)**

Q.39 In the preparation of aldehydes from primary alcohol on oxidation, aldehyde is distilled out. Why is it so?

Ans In the preparation of aldehydes from primary alcohol on oxidation, aldehyde is distilled out because otherwise it gets further oxidised to carboxylic acid. **(2)**

Q.40 Complete the following reactions assigning structures of *A*, *B* and *C*

$$CH_3CH_2OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow[H_2O]{H^+} C$$

Ans $CH_3CH_2OH \xrightarrow{PCl_5} \underset{A}{CH_3CH_2Cl} + POCl_3 + HCl$

$$\downarrow KCN$$

$$\underset{(B)}{CH_3CH_2COOH} \xleftarrow[H_2O]{H^+} CH_3CH_2CN$$ **(2)**

Q.41 How many structural isomers of alcohol with molecular formula, C_4H_9OH are possible? Give their IUPAC name. Which one of the isomers is optically active?

Ans Structural isomers of C_4H_9OH alcohol are as follows:

$$\underset{\text{Butan-1-ol}}{CH_3—CH_2—CH_2—CH_2—OH}$$

$$\underset{\text{Butan-2-ol}}{CH_3—CH_2—\underset{\underset{\displaystyle OH}{|}}{C}H—CH_3}, \quad \underset{\text{2-methyl propan-2-ol}}{H_3C—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—OH},$$

$$\underset{\text{2-methyl propan-1-ol}}{HO—CH_2—\underset{\underset{\displaystyle CH_3}{|}}{C}H—CH_3}$$

Butan-2-ol is an optically active isomer. **(2)**

Q.42 Arrange the following in order of their increasing reactivity towards Lucas reagent. Butan-2-ol, 2-methyl propan-2-ol, butan-1-ol.

Ans $\underset{\text{Butan-2-ol}}{CH_3—CH_2—\underset{\underset{\displaystyle OH}{|}}{C}H—CH_3}, \quad \underset{\text{2- methyl propan-2-ol}}{CH_3—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}—CH_3}$

$$\underset{\text{Butan-1-ol}}{CH_3—CH_2—CH_2—CH_2OH}$$ **(1)**

The increasing reactivity order of the above given towards Lucas reagent is shown below:

$$\underset{(1°\text{ alcohol})}{CH_3CH_2CH_2CH_2OH} < \underset{(2°\text{ alcohol})}{CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{C}HCH_3}$$

$$< \underset{(3°\text{ alcohol})}{CH_3—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}—CH_3}$$ **(1)**

Q.43 (i) Write a method of conversion of methyl alcohol to ethyl alcohol. Give equation.

(ii) How will you convert ethyl alcohol to methyl alcohol?

Ans (i) Conversion of methyl alcohol to ethyl alcohol.

$$\underset{\text{Methyl alcohol}}{CH_3OH} + SOCl_2 \longrightarrow CH_3Cl \xrightarrow{KCN}$$

$$CH_3CN \xrightarrow[H_2O]{H^+} CH_3COOH \xrightarrow{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$ **(1)**

(ii) Conversion of ethyl alcohol to methyl alcohol

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} CH_3COOH \xrightarrow{NaOH} CH_3COONa$$

$$\xrightarrow[\Delta]{\text{Soda lime}} CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{AgOH} \underset{\text{Methyl alcohol}}{CH_3OH}$$ **(1)**

Q.44 A neutral liquid A on treatment with Lucas reagent produces a compound B, which upon treatment with alcoholic KOH yields a compound C. The compound C decolourises bromine water and upon ozonolysis forms only methanal. Deduce the structures of A, B and C and explain the reactions.

Ans $$\underset{(A)}{CH_3CH_2OH} \xrightarrow[\text{reagent}]{\text{Lucas}} \underset{(B)}{CH_3CH_2Cl} \xrightarrow{\text{Alc. KOH}} \underset{(C)}{CH_2 = CH_2}$$

(decolourises Br_2 water)

$$\underset{(C)}{CH_2 = CH_2} \xrightarrow{O_3} HCHO$$

According to the given reactions, C is $CH_2 = CH_2$ and B is CH_3CH_2Cl and A is CH_3CH_2OH. **(2)**

Q.45 (i) Identify A, B, C and D in the following sequence of reactions :

$$C_2H_5OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} A \xrightarrow{[O]} B \xrightarrow{NH_3} C \xrightarrow{\text{Heat}} D$$

(ii) Identify A and B in the following reaction :

$$A \xrightarrow[573\text{ K}]{Cu} B \xrightarrow[H_2O/Zn]{O_3} CH_2O + CH_3COCH_3$$

Ans (i) $$C_2H_5OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{(A)}{CH_3CHO} \xrightarrow{[O]} \underset{(B)}{CH_3COOH} \xrightarrow{NH_3} \underset{(C)}{CH_3COO^-NH_4^+} \xrightarrow{\Delta} CH_4(D)$$ **(1)**

(ii) $$\underset{(A)}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3} \xrightarrow[573\text{ K}]{Cu} \underset{(A)}{CH_3-\overset{CH_3}{C}=CH_2} \xrightarrow{O_3,\ H_2O/Zn} HCHO + CH_3COCH_3$$ **(1)**

Q.46 An organic compound $A\ (C_4H_{10}O)$ reacts with HI giving a compound $B(C_4H_9I)$, which on reduction gives n-butane. On oxidation 'A' gives a compound $C(C_4H_8O)$ and then an acid $D(C_4H_8O_2)$.

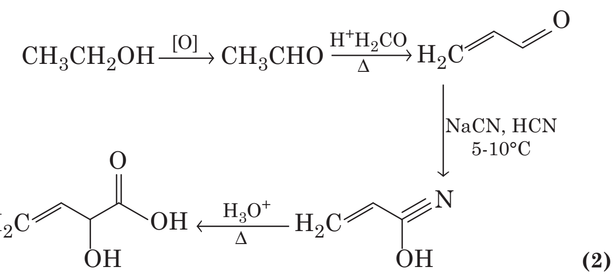
Deduce the structures of A, B, C and D and mention their IUPAC names.

Ans $$\underset{\substack{\text{Butan-1-ol}\\(A)}}{CH_3CH_2CH_2CH_2OH} + HI \longrightarrow \underset{\substack{\text{Butan-1-iodide}\\(B)}}{CH_3CH_2CH_2CH_2I} \xrightarrow{\text{Reduction}} \underset{n\text{-butane}}{CH_3CH_2CH_2CH_3}$$

$$\underset{(A)}{CH_3CH_2CH_2CH_2OH} \xrightarrow{[O]} \underset{\substack{(C)\\\text{Butanal}}}{CH_3CH_2CH_2CHO} \xrightarrow{[O]} \underset{\substack{\text{Butanoic acid}\\(D)}}{CH_3CH_2CH_2COOH}$$ **(2)**

Q.47 How will you convert ethanol to 2-hydroxy but-3-en-1-oic acid?

Ans Ethanol to 2-hydroxy but-3-en-1-oic acid.



(2)

3 MARK *Questions*

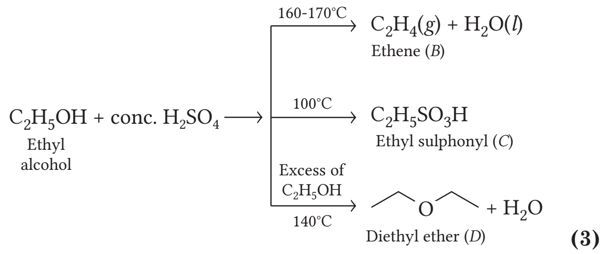
Important Questions

Q.48 Ethyl alcohol (A) reacts with conc. H_2SO_4 at different temperature to give different products B, C and D.

$$A + \text{conc. } H_2SO_4 \begin{cases} \xrightarrow{167\text{-}170^\circ} B \\ \xrightarrow{100^\circ C} C \\ \xrightarrow[140^\circ C]{(\text{Excess of } A)} D \end{cases}$$

Name the compounds B, C and D.

Ans



(3)

Q.49 An organic compound gives hydrogen on reacting with sodium metal. It also gives iodoform test and forms an aldehyde of molecular formula C_2H_4O on oxidation with acidified dichromate. Name the compound and give the equation of these reactions.

Ans Ethanol (CH_3CH_2OH) is the organic compound that gives hydrogen on reacting with sodium metal. It gives positive iodoform test and forms an aldehyde (C_2H_4O) with acidified dichromate

The reactions are as follows:

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3-CH_2-\overset{-}{O}\overset{+}{Na} + H_2\uparrow$$

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CH_3I\downarrow + HCO\overset{-}{O}\overset{+}{Na} + 5H_2O + 5NaI$$

$$CH_3CH_2OH \xrightarrow[KMnO_4]{\text{Acidified}} CH_3CHO$$

(3)

Q.50 How will you convert ethanol to iodoform and chloroform?

Ans **Ethanol to iodoform**

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 3Na_2CO_3 \longrightarrow \underset{\text{Iodoform}}{CHI_3}\downarrow + HCO\overset{-}{O}Na^+$$ **(1½)**

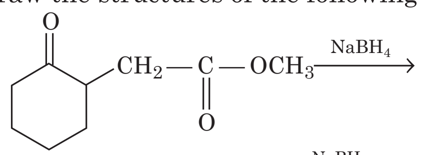
Ethanol to chloroform

$$CH_3CH_2OH \xrightarrow[-2HCl]{Cl_2} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[-3HCl]{3Cl_2} \underset{\text{Chloral}}{Cl_3CCHO}$$

$$Ca(OH)_2 + 2Cl_3C-CHO \longrightarrow (HCOO)_2Ca + \underset{\text{Chloroform}}{2CHCl_3}$$

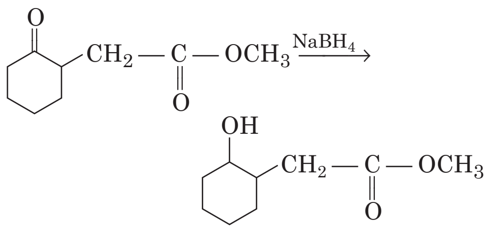
(1½)

Q.51 Draw the structures of the following reactions:

(i) 

(ii) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CHO \xrightarrow{NaBH_4}$

Ans

(i) 

(1)

(ii) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CHO \xrightarrow{NaBH_4}$

$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

(1)

7 MARK *Questions*

Important Questions

Q.52 How would you distinguish between 1°, 2° and 3° alcohols by **[2018]**

(i) oxidation method?

(ii) catalytic dehydrogenation method?

Ans (i) Refer to text on page 229. **(3½)**

(ii) Action of alcohols with heated copper is used to distinguish between primary, secondary and tertiary alcohols. This method is also known as catalytic dehydrogenation method.

When the vapours of a primary or secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed respectively while tertiary alcohols undergo dehydration to form alkenes.

$$\underset{1^\circ\text{ alcohol}}{R-CH_2-OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Aldehyde}}{R-CHO} + H_2\uparrow$$

$$\underset{2^\circ\text{ alcohol}}{\begin{matrix}R\\R'\end{matrix}\!\!>CH-OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!\!>C=O} + H_2\uparrow$$

$$\underset{3^\circ\text{ alcohol}}{CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3} \xrightarrow[573\text{ K}]{Cu} \underset{\text{2-methylpropene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + H_2O$$

(3½)

Q.53 Describe two methods of preparation of alcohol. Write its reaction with PCl_5. How would you prepare methyl alcohol from ethyl alcohol?

Ans **Method of preparation of alcohol**

Refer to text on pages 226 and 227.

Refer to text on page 228, reaction form PCl_5.

Methyl alcohol can be prepared by ethyl alcohol by following method.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{K_2Cr_2O_7,\ H^+} CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow{\text{Heat NaOH+CaO}} CH_4$$

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Aq.\ KOH} \underset{\text{Methyl alcohol}}{CH_3OH}$$

(7)

Chapter Test

1 MARK Questions

- *Choose the correct option*

1 An organic compound 'X' on treatment with acidified $K_2Cr_2O_7$ gives a compound 'Y' which reacts with I_2 and Na_2CO_3 to form tri-iodo methane. The compound 'X' is **[Textbook]**
(a) CH_3OH (b) CH_3COCH_3
(c) CH_3CHO (d) $CH_3CH(OH)CH_3$

2 The compound which does not respond to iodoform test is **[Textbook]**
(a) CH_3OH (b) CH_3CHO
(c) CH_3COCH_3 (d) C_2H_5OH

3 Which of the following compounds has the lowest boiling point?
(a) *n*-butyl alcohol (b) *sec*-butyl alcohol
(c) *tert*-butyl alcohol (d) 2-methyl propan-1-ol

4 Hydrogen bonding is maximum in
(a) ethyl chloride (b) ethanol
(c) diethyl ether (d) triethyl amine

[***Ans.*** **1.** (d), **2.** (a), **3.** (c), **4.** (b)]

5 Which alcohol is present in pyroligneous acid? **[Textbook]**

6 Write the structural formula of butan-2-ol. **[Textbook]**

7 What organic compound is obtained when ethyl bromide reacts with *aq*. NaOH solution?

8 What happens when ethanol is treatd with conc. H_2SO_4 at 443 K?

9 Complete the following equation,
$C_2H_5OH + CH_3COCl \longrightarrow \ldots + \ldots$

[***Ans.*** $CH_3-\overset{\overset{\large O}{||}}{C}-OC_2H_5 + HCl$]

2 MARK Questions

10 (i) How do you distinguish between a primary and secondary alcohol?
(ii) How different classes of alcohols can be tested by Lucas test? **[Textbook]**

11 What happens when acetic acid reacts with ethyl alcohol in presence of conc. H_2SO_4? **[Textbook]**

12 How do you distinguish between primary and secondary alcohol by catalytic dehydrogenation? **[Textbook]**

13 How is maltose converted to ethyl alcohol by fermentation process? **[Textbook]**

14 Write the equations for the oxidation of aliphatic primary, secondary and tertiary alcohols. **[Textbook]**

3 MARK Questions

15 How are the alkanols classified? Give an example of each class with their IUPAC names.

16 There are three unlabelled bottles containing methyl alcohol, ethyl alcohol and diethyl ether. How will you identify each of them?

17 How will you convert methanol to ethanol and *vice-versa*?

18 How many different isomeric alcohols having molecular formula, $C_4H_{10}O$ are possible? Name them. How will you differentiate them?

7 MARK Questions

19 What is fermentation? How is ethanol obtained commercially by fermentation of starch? What happens when ethanol reacts with **[Textbook]**
(i) sodium metal? (ii) copper at 300°C?
(iii) ethanoic acid and? (iv) red phosphorous and I_2?

20 How can you distinguish between primary, secondary and tertiary alcohols by oxidation method? **[Textbook]**

Write the principle of manufacture of ethyl alcohol from starchy materials.

How can you prepare
(i) ethyl alcohol from methyl alcohol?
(ii) methyl alcohol from ethyl alcohol?