

10. ALCOHOLS- CONTENTS

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Learning outcomes

After completing the chapter, the students should be able to:

- ✓ Describe the nomenclature, isomerism, and classification of monohydric alcohols.
- ✓ Distinguish primary, secondary, and tertiary alcohols by Victor Meyer's Method.
- ✓ Explain the preparation of monohydric alcohols from haloalkanes, primary amines, and esters.
- ✓ Describe the industrial preparation of alcohol from: the oxo process, hydroboration-oxidation of ethene & fermentation of sugar.
- ✓ Define absolute alcohol, power alcohol, denatured alcohol (methylated spirit), rectified spirit, and alcoholic beverage.
- ✓ State physical properties of monohydric alcohols.
- ✓ Explain the chemical properties of monohydric alcohols
 - reactions with HX, PX_3 , PCl_5 , and $SOCl_2$.
 - Action with reactive metals like Na, K, and Li.
 - Dehydration of alcohols.
 - Oxidation of primary, secondary, and tertiary alcohols with oxidising agents like acidified $KMnO_4$ or $K_2Cr_2O_7$.
 - Catalytic dehydrogenation of 1° and 2° alcohol and dehydration of 3° alcohol,
 - Esterification reaction and test of ethanol.

Introduction, Classification, Nomenclature & Isomerism

 Step into any pharmacy, and you'll find a bottle of 'spirit' for cleaning small cuts. Check the label on a hand sanitiser and 'ethyl alcohol' or 'isopropyl alcohol' is usually right there near the top. Petrol pumps in several countries now sell fuel blended with alcohol. Behind every one of these everyday items is one small but powerful group of atoms – the hydroxyl ($-OH$) group – attached to a carbon chain. Welcome to the chemistry of alcohols!

 Compounds having 1, 2, 3, and many $-OH$ groups are called monohydric, dihydric, trihydric, and polyhydric alcohols, respectively.

Ethane-1,2-diol is dihydric, and glycerol is a trihydric alcohol. Carbohydrates can be considered as examples of polyhydric alcohols.

Monohydric alcohols

Monohydric alcohols can further be classified into primary, secondary, and tertiary alcohols depending upon the carbon atom to which the $-OH$ group is bonded.

 **Quick Trick:** Count the carbons attached to the $-OH$ carbon.

- 1 carbon $\rightarrow$ Primary (1°)
- 2 carbons $\rightarrow$ Secondary (2°)
- 3 carbons $\rightarrow$ Tertiary (3°)

Structure	IUPAC name	Common name	Class
CH_3-OH	methanol	methyl alcohol	1°
CH_3-CH_2-OH	ethanol	ethyl alcohol	1°
$CH_3CH_2CH_2OH$	propan-1-ol	n-propyl alcohol	1°
$\begin{array}{c} CH_3-CH-CH_3 \\ \\ OH \end{array}$	propan-2-ol	isopropyl alcohol	2°
$CH_3CH_2CH_2CH_2OH$	butan-1-ol	n-butyl alcohol	1°

$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{OH} \end{array}$	butan-2-ol	sec-butyl alcohol	2°
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{OH} \end{array}$	2-methylpropan-1-ol	iso-butyl alcohol	1°
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{OH} \end{array}$	2-methylpropan-2-ol	tert-butyl alcohol	3°

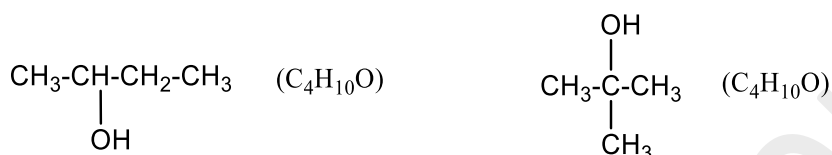
Structural isomerism

a. Chain isomers:

Same molecular formula, different carbon chain arrangement.

Occurs in alcohols with 4 or more carbons.

e.g. butan-2-ol and 2-methylpropan-2-ol.



b. Position isomers:

Occurs when the **-OH group is at different positions** on the same carbon chain.

e.g. propan-1-ol and propan-2-ol.



c. Functional isomers

Alcohols and ethers with the same molecular formula are functional isomers.

E.g. $\text{CH}_3\text{CH}_2\text{OH}$ $\text{CH}_3-\text{O}-\text{CH}_3$ $(\text{C}_2\text{H}_6\text{O})$
ethanol methoxymethane;

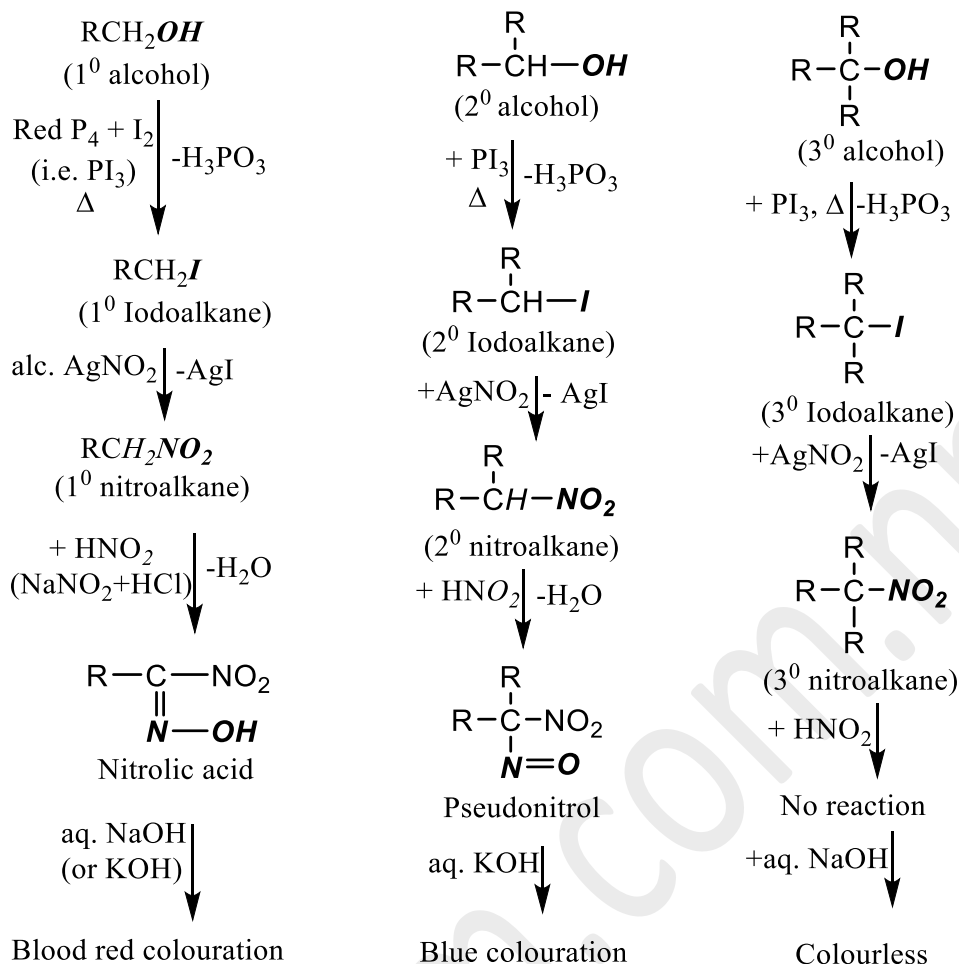
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_3$ $(\text{C}_3\text{H}_8\text{O})$
propan-1-ol methoxyethane etc.

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ $\text{H}_3\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ $(\text{C}_4\text{H}_{10}\text{O})$
 $(\text{C}_4\text{H}_{10}\text{O})$ Butan-1-ol 1-methoxypropane

Victor-Meyer Method for distinguishing of 1°, 2° and 3° alcohols

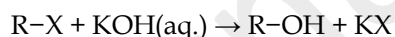
This classic method involves three steps:

- Conversion to iodoalkane**
alcohol + $\text{PI}_3 \rightarrow$ iodoalkane
- Conversion to nitroalkane**
iodoalkane + alcoholic $\text{AgNO}_2 \rightarrow$ nitroalkane
- Treatment with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) followed by aqueous alkali**
 - **Red colour** is given by the primary alcohol
 - **Blue colour** is given by the secondary alcohol
 - The tertiary alcohol gives a colourless solution.



General Methods of Preparation

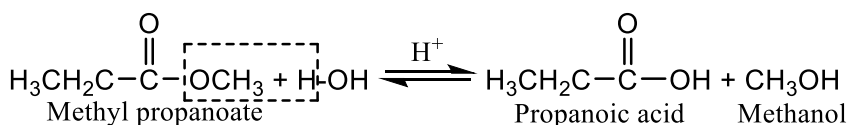
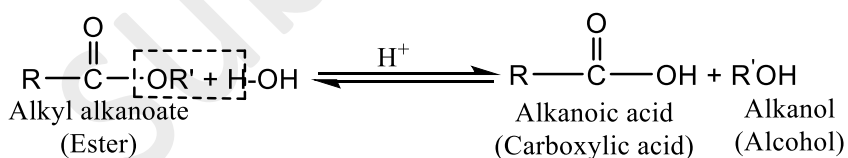
1. From Haloalkane (studied in substitution reactions of [haloalkanes](#))



2. From Esters (By hydrolysis in acidic/alkaline medium and reduction)

a. Acidic hydrolysis

Esterification is the reaction of an alcohol with a carboxylic acid to form an ester and water. The reverse reaction is ester hydrolysis.

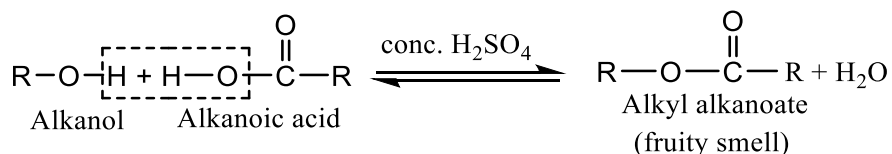


Being a reversible reaction, the equilibrium could be reached by starting from either direction. The reverse of the above reaction is called the esterification reaction/test.

Ester hydrolysis	$\text{RCOOR}' + \text{H}_2\text{O} \rightleftharpoons \text{RCOOH} + \text{R}'\text{OH}$
Esterification	$\text{RCOOH} + \text{R}'\text{OH} \rightleftharpoons \text{RCOOR}' + \text{H}_2\text{O}$

Reaction of alcohols with carboxylic acids - Esterification (test of alcohol)

When a mixture of alcohol and carboxylic acid is heated in the presence of a calculated amount of conc. H_2SO_4 , an ester is formed. The ester has a characteristic fruity smell. Hence, this reaction is used as a test for both alcohol and carboxylic acid functional groups.

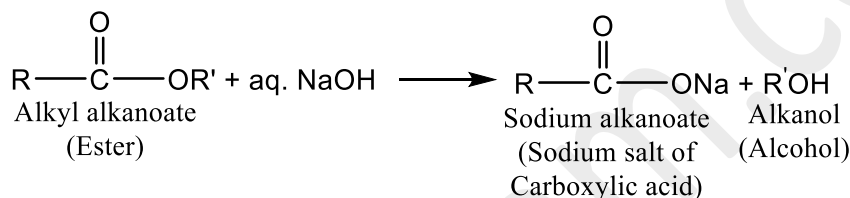


Concentrated H_2SO_4 acts as an acid catalyst. The reaction is reversible, so removing water or using an excess of one reactant can increase the yield of ester.

Real Life Connection

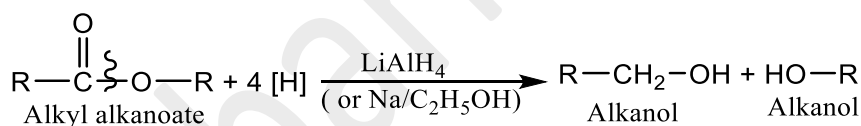
That unmistakable fruity smell is no coincidence. Many natural fruit flavours – banana, pineapple, apple – are esters, and this same reaction is used to manufacture artificial flavourings, perfumes, etc.

b. Hydrolysis in basic medium



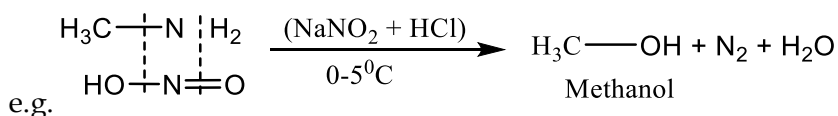
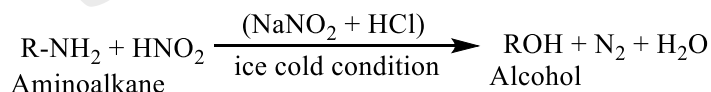
Basic hydrolysis of esters is called **saponification**; it produces an alcohol and the sodium salt of the carboxylic acid. When fatty esters are hydrolysed, the salts formed are soaps.

c. Reduction by $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ or LiAlH_4



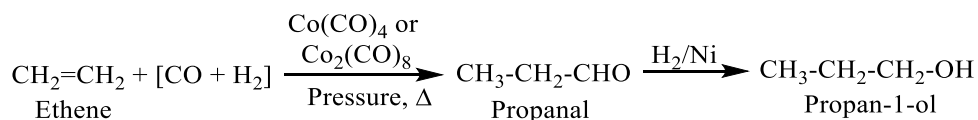
3. From Primary amines (by reaction with nitrous acid)

Primary amines react with nitrous acid (prepared in situ by reacting sodium nitrite with hydrochloric acid) in ice-cold conditions, resulting in alcohols.



1. Oxo process

Alkenes react with carbon monoxide and hydrogen in the presence of octacarbonyldicobalt or cobalt tetracarbonyl at high temperatures and pressure to produce aldehydes. Aldehydes can be changed into alcohols by hydrogenation.



2. Fermentation of sugar

Fermentation is the enzyme-catalysed **anaerobic** conversion of sugars and starches into ethanol and carbon dioxide by yeast.

Anaerobic means it takes place in the absence of oxygen.

Enzymes- biological catalysts

Beyond the distilleries, fermentation is a cornerstone of Nepalese traditional food science, utilised in the artisanal production of local beverages and preserved foods like pickles.

Primary Feedstocks for Alcohol Production

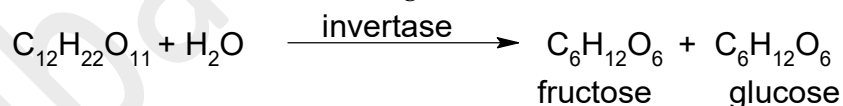
In industrial and laboratory settings, two main raw materials serve as the carbon source for fermentation:

1. Molasses (The Sugar Route)

Molasses is the concentrated, dark, viscous byproduct of the sugar refining process, remaining after the crystallisation of sugarcane juice. It is rich in **sucrose** $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, a disaccharide that serves as the starting point for ethanol synthesis.

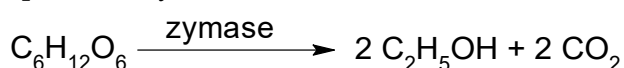
The Biochemical Pathway:

- **Hydrolysis:** The enzyme **invertase** (derived from yeast) catalyses the hydrolysis of sucrose into its constituent monosaccharides: glucose and fructose.



Fermentation of Glucose and Fructose

The monosaccharides are then converted into ethanol and carbon dioxide by the enzyme **zymase** present in yeast.



Starch (The Complex Carbohydrate Route)

Starch is a polysaccharide abundant in grains, fruits, and vegetables. To produce ethanol, starch must undergo a systematic enzymatic breakdown:

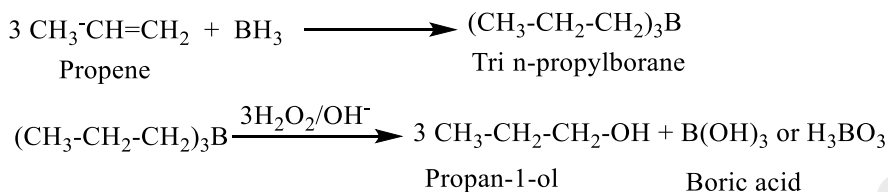
- **Saccharification: Diastase** (found in germinating barley) first converts starch into the disaccharide **maltose**.
- **Hydrolysis: Maltase** then breaks down maltose into **glucose**.
- **Fermentation:** Finally, **zymase** converts the glucose into ethyl alcohol (ethanol).

Key Concepts for revision:

Term	Definition/Function
Fermentation	An enzyme-catalysed, anaerobic breakdown of organic substances into simpler products.
Zymase	The specific enzyme complex that converts glucose into ethanol and CO ₂ .
Invertase	The enzyme that breaks down sucrose into glucose and fructose.

3. Hydroboration-oxidation of Ethene (Alkene) ⚡

Alkenes can be treated with diborane ((BH₃)₂ or B₂H₆) followed by treatment with alkaline hydrogen peroxide to yield 1^o alcohols.



Hydroboration-oxidation gives an alcohol by anti-Markovnikov addition of water.

[Practice the hydroboration-oxidation of **ethene**]

Absolute alcohol, methylated spirit, rectified spirit: alcoholic beverages

- Pure (~100%) and anhydrous ethyl alcohol is called **absolute alcohol**.
- **Rectified spirit** is the 95% pure alcohol containing 5% water.
- Undrinkable ethyl alcohol containing poisonous substances, especially methyl alcohol, is called **denatured alcohol** or **methylated spirit**.
- **Alcoholic beverages** are liquors for drinking purposes. They contain ethanol, water, colouring materials, and flavouring materials. They may be distilled (e.g., vodka, gin, whisky, brandy) or undistilled (e.g., beer, wine).
- **Methanol** was historically called **wood alcohol** because it was once obtained by destructive distillation of wood.
- **Power alcohol** — a blend of ethanol (about 20%) with petrol, used as an engine fuel

Physical Properties

1. State:

- The lower members of alcohols are usually colourless liquids.
- They have a characteristic alcoholic or spirit-like smell.
- As the carbon chain becomes longer, alcohols eventually become waxy or solid.

2. Solubility:

- Alcohols are more soluble in water than corresponding alkanes, haloalkanes, and ethers of similar molecular mass.
- This is because the alcohol molecule has a polar **–OH group**, and it forms hydrogen bonds with water molecules.
- As the number of carbon atoms increases, the solubility of alcohols decreases.

- As the alkyl group becomes larger, the non-polar part of the molecule becomes more significant, so water solubility decreases.

3. Boiling and melting points:

- Alcohols have higher boiling points and melting points than corresponding ethers and haloalkanes of similar molecular mass.
- This is due to their greater polarity and the formation of **intermolecular hydrogen bonds** between alcohol molecules.
- In a homologous series, the boiling point generally increases as molecular mass increases.
- This is because the van der Waals forces between molecules become stronger with increasing molecular mass.
- For isomeric alcohols, boiling points decrease as branching increases.
- This is because branching reduces the surface area of the molecule.
- Therefore, the order of boiling point is generally $1^\circ > 2^\circ > 3^\circ$.

Chemical properties

[A] Reaction involving the cleavage of the O-H bond

1. Action with active metals like Li, Na, K (acidic nature of alcohol)

When alcohols are treated with active metals such as Na, K, Mg, etc., they liberate hydrogen with the formation of metal alkoxides. This shows the acidic nature of alcohol. E.g.,



However, alcohols are weak acids, weaker than water. They neither turn litmus red nor neutralise even strong alkali or aq. alkali solutions.

[B] Reaction involving cleavage of C-O bond (Nucleophilic Substitution rxn)

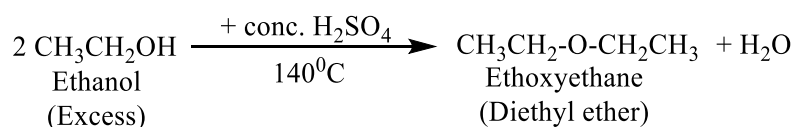
1. Reaction with HX, PX_3 , PCl_5 , $SOCl_2$ (studied in preparations of [haloalkanes](#))

[C] Other Reactions

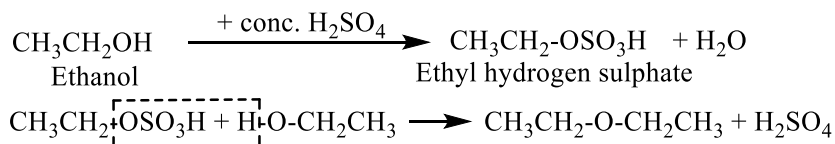
1. Dehydration of alcohols 🔥

Alcohols can be dehydrated under different conditions with concentrated sulphuric acid, producing Ether or Alkene.

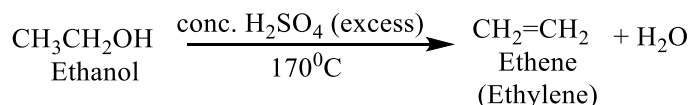
- a. When an excess amount of ethyl alcohol is heated with conc. H_2SO_4 as a dehydrating agent at about 140°C , ethyl alcohol undergoes intermolecular dehydration to give diethyl ether.



This reaction is supposed to occur in the following two steps.



b. When the calculated amount of ethyl alcohol is heated with an excess of conc. H_2SO_4 at about 170°C , intramolecular dehydration results in Ethene.

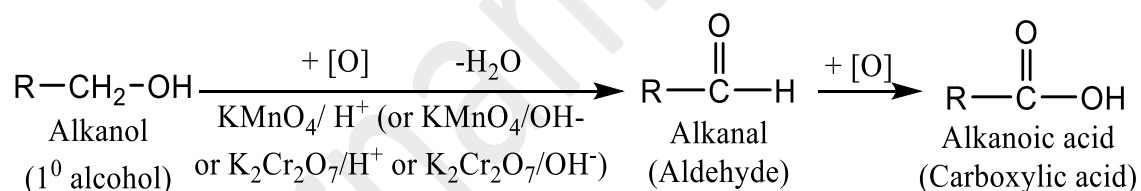


Ethyl alcohol can undergo intermolecular dehydration to give diethyl ether by passing its vapour over heated alumina at a temperature of about 250°C .

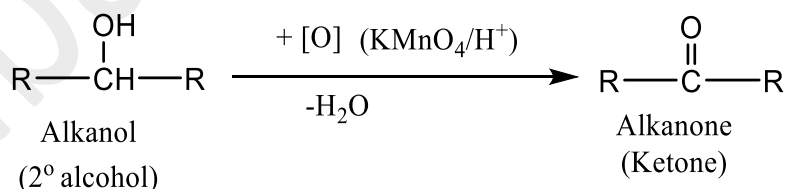
Ethyl alcohol can undergo intramolecular dehydration to give ethene by passing its vapours over heated alumina (Al_2O_3) at a temperature of about 350°C .

2. Oxidation of primary, secondary, and tertiary alcohols

1^o alcohol: Primary alcohols can be oxidised into aldehydes; the reaction does not stop there, and the aldehydes are further oxidised into carboxylic acids. The number of carbon atoms in the main skeleton does not change. Different oxidising agents, such as alkaline or acidified potassium permanganate, sodium dichromate, and potassium dichromate, can be used.

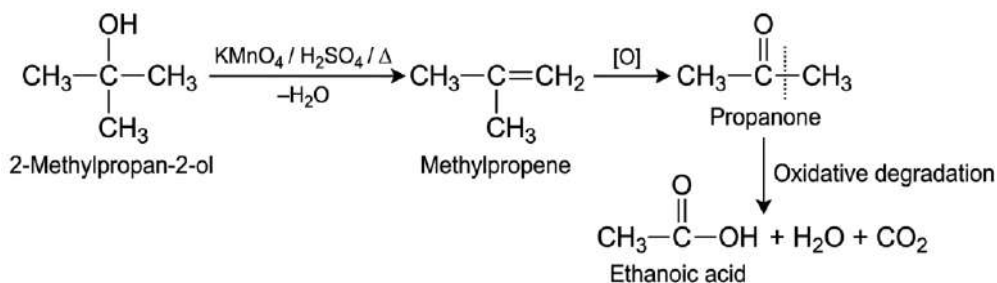


2^o alcohol: Secondary alcohols are oxidised into ketones with the same number of carbon atoms.



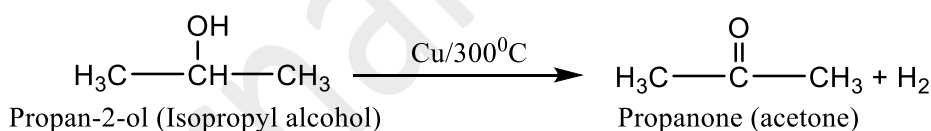
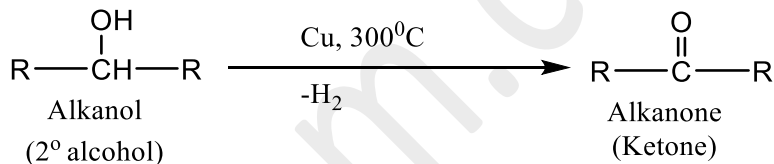
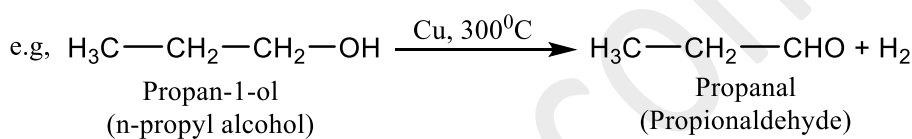
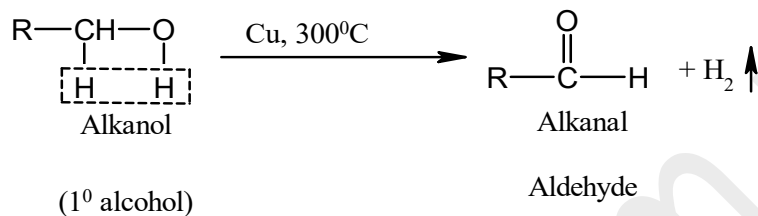
The ketones are not further oxidised easily.

3^o alcohol: Tertiary alcohols are quite resistant to oxidation under normal conditions. But when oxidation is carried out under drastic acidic conditions with a strong oxidising agent like KMnO_4 and conc. H_2SO_4 , tertiary alcohol first undergoes dehydration into alkenes. The alkene formed is then oxidised to a ketone, which is finally oxidised to a carboxylic acid with a lesser number of carbon atoms. e.g.



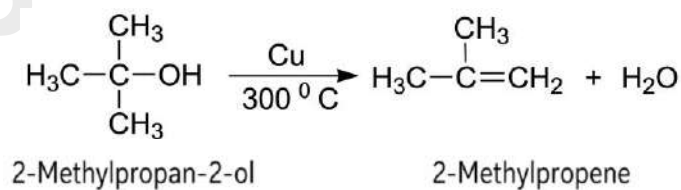
3. Catalytic dehydrogenation of alcohols

Primary and secondary alcohols undergo dehydrogenation to give aldehydes and ketones, respectively, in the presence of Cu at 300 °C.



This process is also called **dehydrogenation**.

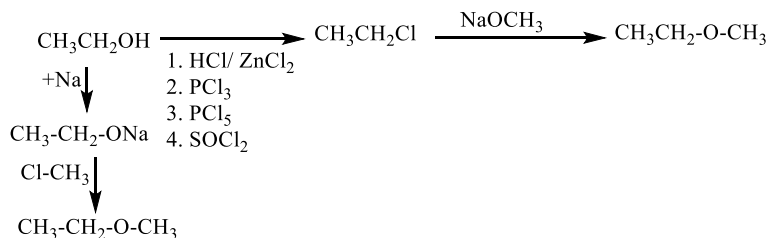
When a tertiary alcohol is passed over a red-hot copper tube, it is dehydrated to an alkene.



Some Conversion questions with Hints

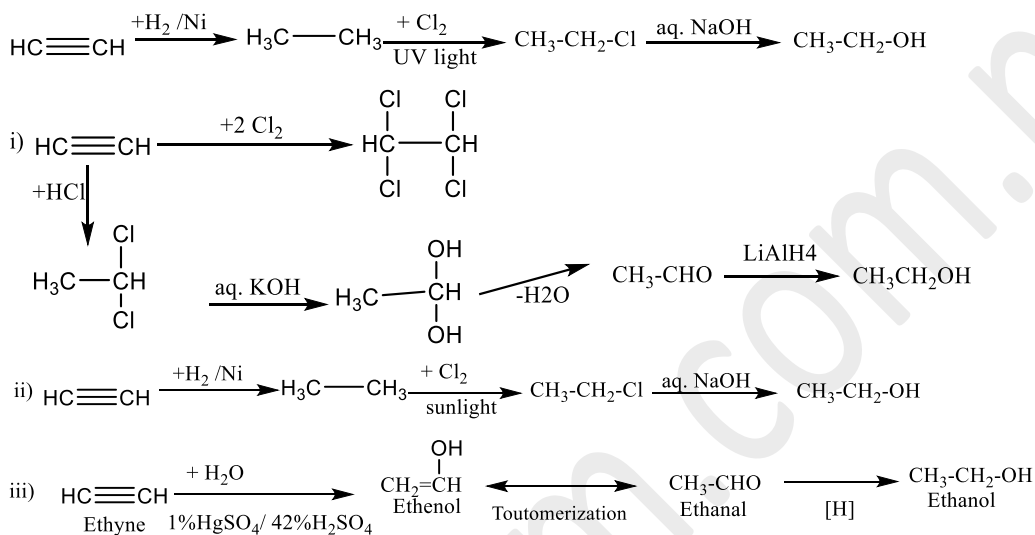
1. How would you obtain Methoxyethane from Ethanol?

1



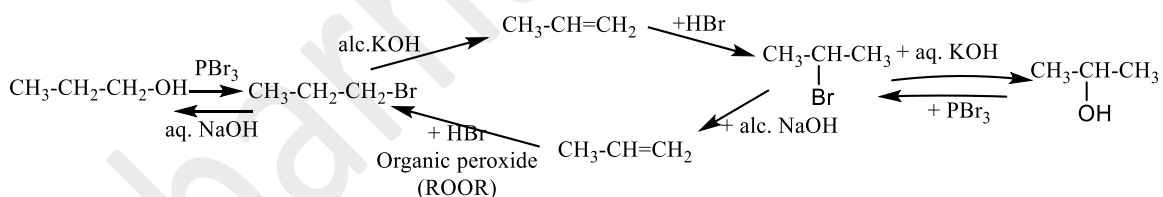
2. How is Ethanol prepared from Ethyne?

1



3. Write down the isomers of monohydric alcohols from $\text{C}_3\text{H}_8\text{O}$ and give their IUPAC names. How would you convert one isomer into another and vice versa?

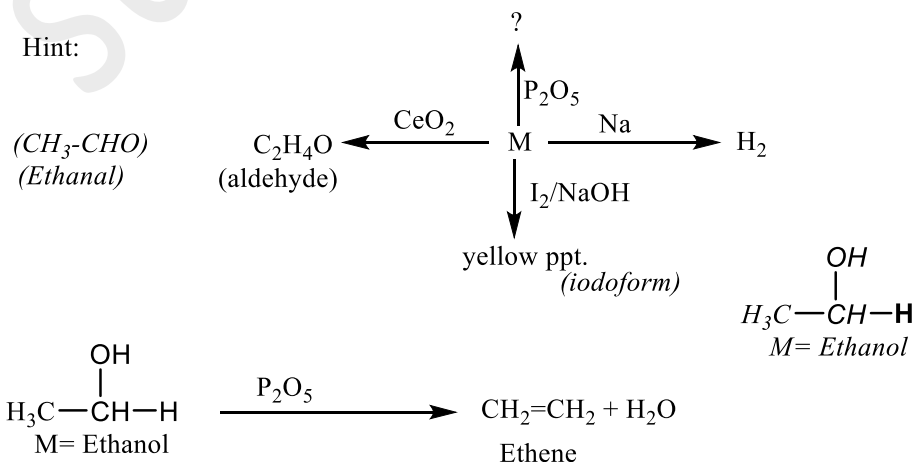
3



4. An organic compound M gives H_2 gas with sodium metal. On treatment with alkaline iodine, it gives a yellow ppt, and on oxidation with CeO_2 forms an aldehyde ($\text{C}_2\text{H}_4\text{O}$). Name the compound M and write the reactions involved. What happens when M is heated with P_2O_5 ?

5

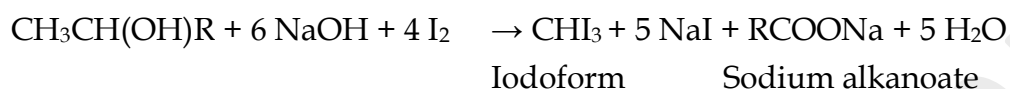
Hint:



1. Esterification test (studied in chemical properties-esterification reaction)

2. Iodoform test (test for $\text{CH}_3-\overset{\text{OH}}{\underset{|}{\text{CH}}}-$ group)

Alcohols having the $\text{CH}_3\text{CH}(\text{OH})-$ group respond to this test. When alcohols having the above-mentioned group are treated with I_2 and aq. alkali (NaOH), iodoform forms, a yellow crystalline precipitate with a characteristic hospital smell.



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Quick Revision

- Monohydric alcohols ($\text{R}-\text{OH}$) are 1° , 2° or 3° depending on the carbon holding $-\text{OH}$
- Victor-Meyer's test tells them apart by colour: red (1°), blue (2°), colourless (3°)
- Made from haloalkanes, esters (hydrolysis/reduction) and primary amines; industrially, by the Oxo process, hydroboration-oxidation, and fermentation
- Absolute alcohol is 100% pure; rectified spirit is ~95%; denatured alcohol has poison added to make it undrinkable; power alcohol is an ethanol-petrol fuel blend
- Lower alcohols mix freely with water and boil at relatively high temperatures – both thanks to hydrogen bonding
- Alcohols react with active metals (acidic nature), dehydrate to an ether or an alkene depending on temperature, and oxidise in a fixed order: $1^\circ \rightarrow$ aldehyde $\rightarrow$ carboxylic acid; $2^\circ \rightarrow$ ketone; 3° resists, or breaks apart under force
- Over hot copper, 1° and 2° alcohols dehydrogenate (lose H_2); 3° alcohols dehydrate (lose H_2O)
- Ethanol is confirmed by the esterification test (fruity smell) and the iodoform test (yellow precipitate)

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