CHEMISTRY PROJECT

ALCOHOL, PHENOL
& ETHER

ACKNOWLEDGEMENT

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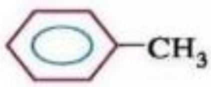
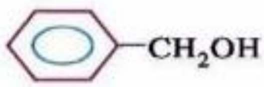
Introduction:

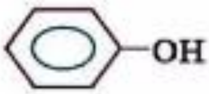
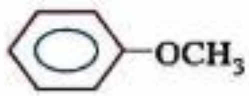
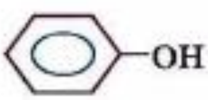
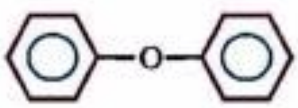
When the hydrogen atom attached to saturated carbon of hydrocarbon, is substituted by hydroxyl group (-OH) then alcohol is formed.

E. g.,

Hydrocarbon	Alcohol
CH_4	CH_3OH
	
$H_2C{=}CHCH_3$	$H_2C{=}CHCH_2OH$
$HC{\equiv}C{-}CH_3$	$HC{\equiv}C{-}CH_2OH$

Thus, the general formula of alcohol is R-OH; where R = alkyl group or alkenyl or alkynyl or aryalkyl group. If the hydrogen atom attached to the carbon atom of an aromatic, is substituted by hydroxyl group then phenol is formed.

Thus, the general formula of phenol is Ar-OH; where Ar= aryl group. If the hydrogen atom of hydroxyl group of alcohol or phenol, is substituted by alkyl or alkenyl or alkynyl or aryl group then ether is formed.

Alcohol/Phenol	Ether
CH_3OH	CH_3OCH_3
$H_2C{=}CHCH_2OH$	$H_2C{=}CHCH_2OCH_3$
$HC{\equiv}CCH_2OH$	$HC{\equiv}CCH_2OCH_3$
	
	

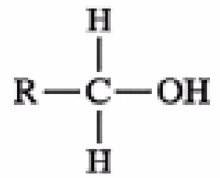
Thus, the general formula of ether is R_1/Ar_1 -O-R_2/Ar_2 where R_1 and R_2 = alkyl or alkenyl or alkynyl group and Ar_1 and Ar_2= aryl group.

Alcohols and ethers have same general formula $C_nH_{2n+2}O$ but due to different functional groups, they are called functional group isomers. For example, ethanol and methoxymethane have same molecular formula C_2H_6O but their structural formula CH_3CH_2OH and CH_3OCH_3 possess different functional groups.

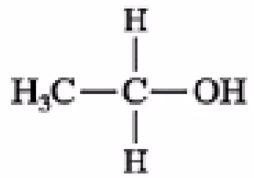
ALCOHOLS:
Classification of Alcohols:

The classification of alcohols is carried out in three types depending on the carbon which has been attached to the hydroxyl group in structure of alcohol, viz (1) Primary (1^0) alcohol, (2) Secondary (2^0) alcohol and (3) Tertiary ($3^{0)}$ alcohol.

(1) Primary (1^0) alcohol: Alcohol, in which the hydroxyl group is attached to primary carbon is called primary (1^0) alcohol.



Primary (1^0) alcohol.



Primary (1^0) alcohol.

(2) Secondary (2^0) alcohol: Alcohol, in which the hydroxyl group is attached to secondary carbon is called secondary (2^0) alcohol.

Secondary (2^0) alcohol. Secondary (2^0) alcohol.

Tertiary (3^0) alcohol. Tertiary (3^0) alcohol.

(3) Tertiary (3^0) alcohol: Alcohol, in which the hydroxyl group is attached to tertiary carbon is called tertiary (3^0) alcohol.

<u>Preparation of Alcohol:</u>

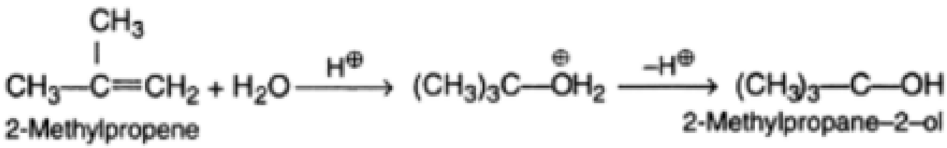
1. Hydration of Halides:

Alkyl halides when boiled with an aqueous solution of an alkali hydroxide give alcohol through nucleophilic substitution mechanism.

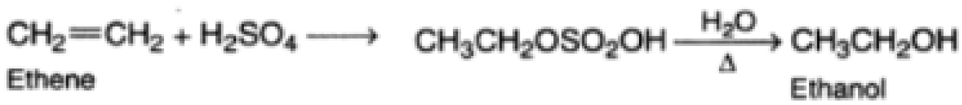
R-X + KOH → R-OH + KX

This general procedure produces primary and secondary alcohols. Glycerol can be synthesized from propylene by a series of reactions including the hydrolysis of a halide as one step in the process.

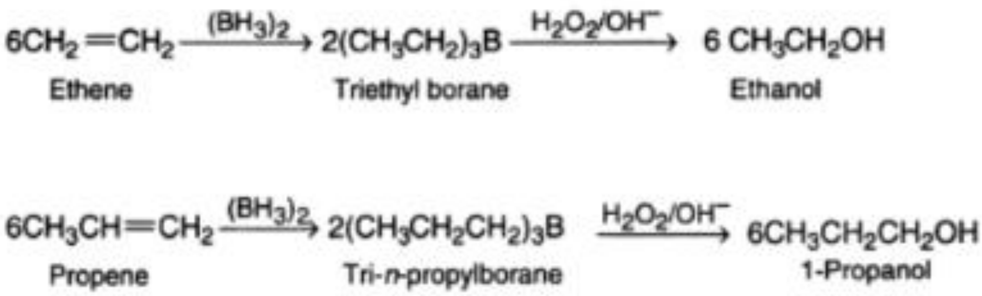
2. Hydration of Alkenes:
Direct hydration takes place by adding water in the presence of a catalyst.



Indirect hydration is achieved by the addition of sulphuric acid to alkane followed by hydrolysis of the alkyl hydrogen sulfate.



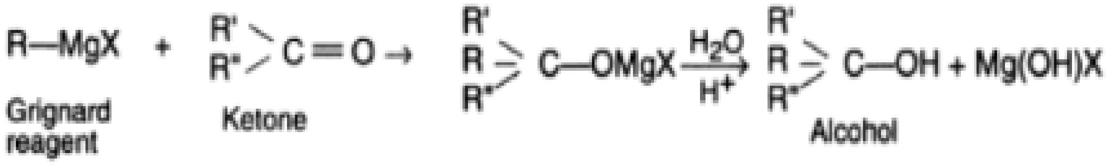
3. Hydroboration of Alkenes:
Alkenes, when treated with diborane, give alkyl boranes, R3B. Alkylboranes on oxidation with alkaline hydrogen peroxide give alcohol.



It is significant to note that this method always leads to anti-Markovnikov's addition of water to alkenes.

4. Grignard Synthesis:

All three types of alcohol (primary, secondary and tertiary) can be prepared from the Grignard reagents by interaction with suitable carbonyl compounds.



The reaction of the Grignard reagent with formaldehyde leads to primary alcohols, that with aldehydes other than formaldehyde yield secondary alcohols and that with ketones give tertiary alcohols.

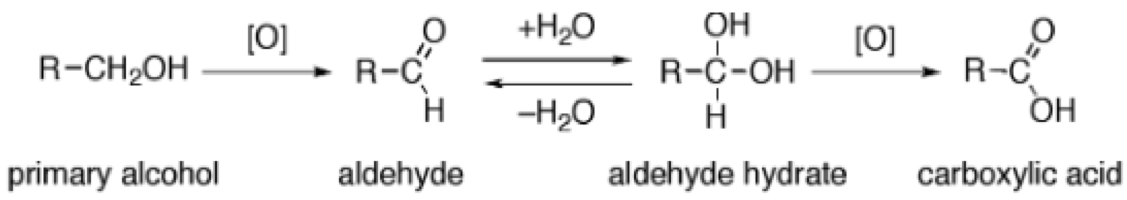
Properties of Alcohol:

1. Acidic Nature of Alcohol:

Alcohols react with active metals such as sodium, potassium etc. to form the corresponding alkoxide. These reactions of alcohols indicate their acidic nature. The acidic nature of alcohol is due to the polarity of –OH bond. The acidity of alcohols decreases when an electron-donating group is attached to the hydroxyl group as it increases the electron density on the oxygen atom. Thus, primary alcohols are generally more acidic than secondary and tertiary alcohols.

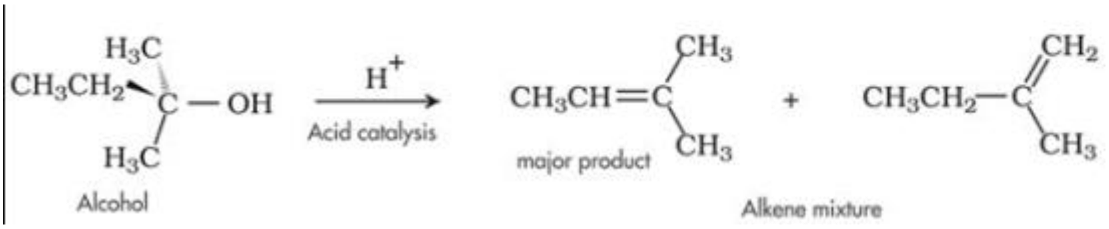
2. Oxidation of Alcohol:

Alcohols undergo oxidation in the presence of an oxidizing agent to produce aldehydes and ketones which upon further oxidation give carboxylic acids.



3. Dehydration of Alcohol

Upon treatment with protic acids, alcohols undergo dehydration (removal of a molecule of water) to form alkenes.



4. Esterification: When alcohol reacts with a carboxylic acid in the presence of a catalyst, it results in the formation of a sweet-smelling compound called an ester.

<u>Uses of Alcohols:</u>

- The alcohol in alcoholic drinks is ethanol.

- Alcohol is used as high-efficiency fuel. It gives carbon dioxide and water when it burns.
- It is also used to make vinegar.
- It is used as an antiseptic, dressing for wounds, and antidote for snake bites. It is also used as a mild sedative.
- Alcohol is a common cough remedy ingredient that can be found in most cough syrups.
- Since alcohol has antifungal and antibacterial properties, it is used in disinfectants.
- To eliminate microbial contamination, alcohol is used as a cleaning agent in hospitals, medical facilities, and laboratories.
- Ethanol, Methanol, and Isopropanol are solvents used in analytical chemistry processes, such as chromatography analysis.
- Some of the commonly used alcohols are methanol, ethanol, propanol and butanol.

Lucas Test:

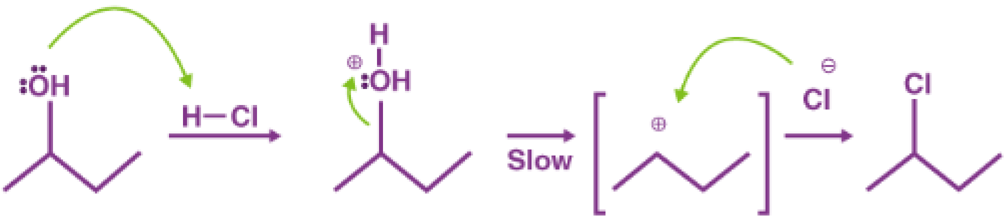
The mechanism followed in this reaction is an SN1 nucleophilic substitution. It can be broken down into the following two steps.

Step 1

The OH group belonging to the alcohol is protonated by hydrochloric acid. Now, since chlorine is a stronger nucleophile than water, it replaces the resulting water molecule attached to the carbon. This leads to the formation of a carbocation.

Step 2

The chloride anion now attacks the carbocation and forms an alkyl chloride. This alkyl chloride is insoluble and hence turns the solution turbid. The net mechanism of the Lucas test can be illustrated as follows.

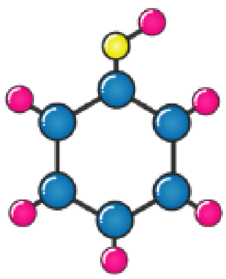


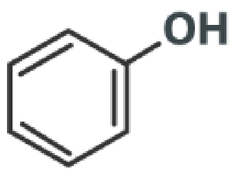
Thus, the primary, secondary, and tertiary alcohols can be differentiated based on the rate at which they turn the solution turbid when reacted with the Lucas reagent.

Primary Alcohol	The solution remains colourless unless it is subjected to heat. The solution forms an oily layer when heated. Example: 1-Pentanol.
Secondary Alcohol	The solution turns turbid and forms an oily layer in three to five minutes (varies based on the solubility). Example: 2-Pentanol.
Tertiary Alcohol	The solution turns turbid and forms an oily layer immediately. Example: 2-methyl-2-butanol.

PHENOL:

Phenol is an aromatic compound. The chemical formula of this organic compound is C6H6O. Phenol is also known as Carbolic acid.





Preperation of Phenol

1. From sulphonic acids (by alkali fusion of sodium benzene sulphonate)

The first commercial process for the synthesis of phenol. Sodium benzene sulphonate is fused with sodium hydroxide at 573K to produce sodium phenoxide, which upon acidification yields phenol.

$$\underset{\text{Sodium benzenesulphonate}}{C_6H_5SO_3Na} + 2\,NaOH \xrightarrow{573\text{ K}} \underset{\text{Sodium phenoxide}}{C_6H_5ONa} + Na_2SO_3 + H_2O$$

$$\underset{\text{Sodium phenoxide}}{2C_6H_5ONa} + 2\,HCl \longrightarrow \underset{\text{Phenol}}{2C_6H_5OH} + 2\,NaCl$$

2. From diazonium salts (by the hydrolysis of diazonium salt – laboratory method)

When a diazonium salt solution is steam distilled or is added to boiling dil.H2SO4, it forms phenol.

$$Ar\overset{+}{N_2}\overset{-}{X} + H_2O \xrightarrow[H_2SO_4]{\text{Warming}} Ar{-}OH + N_2 + HX$$

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl + H_2O} \xrightarrow[H_2SO_4]{\Delta} \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

3. From Cumene

Cumene is an organic compound obtained by Friedel-Crafts alkylation of benzene with propylene. Upon oxidation of cumene (isopropylbenzene) in the presence of air, cumene hydroperoxide is obtained. Upon further treatment of cumene hydroperoxide with dilute acid, phenols are obtained. Acetone is also produced as one of the by-products of this reaction in large quantities. Hence, phenols prepared by these methods need purifications.

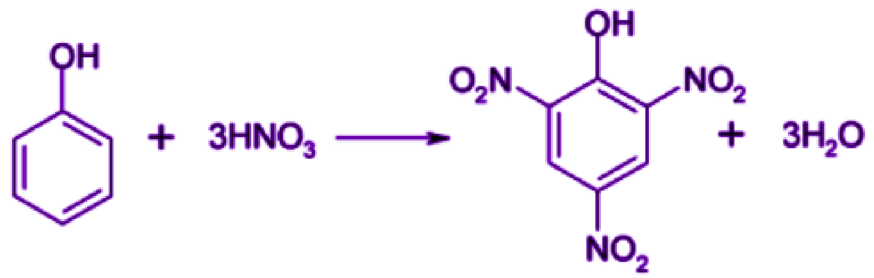
Chemical Properties

1. Acidic character of Phenols

Phenols react with active metals such as sodium, potassium, etc. to form the corresponding phenoxide. These reactions of phenols indicate its acidic nature. In phenol, the sp2 hybridized carbon of the benzene ring attached directly to the hydroxyl group acts as an electron-withdrawing group. Thus, it decreases the electron density on oxygen.

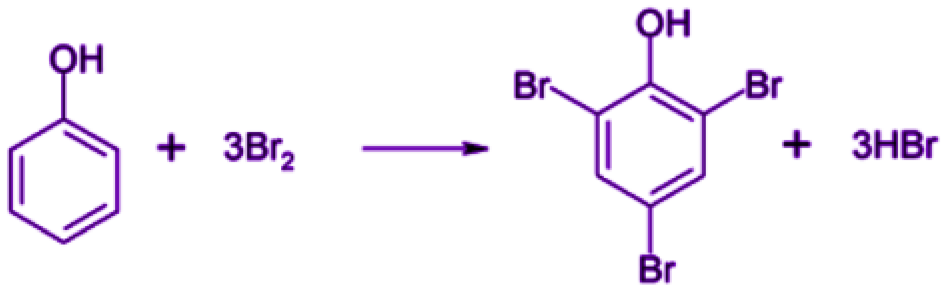
Due to the delocalization of negative charge in the benzene ring, phenoxide ions are more stable than alkoxide ions. As a result, phenols are more acidic than alcohols.

2. Nitration of Phenols



When phenol is treated with concentrated nitric acid, the nitration results in the formation of 2, 4, 6-trinitrophenol (commonly called picric acid).

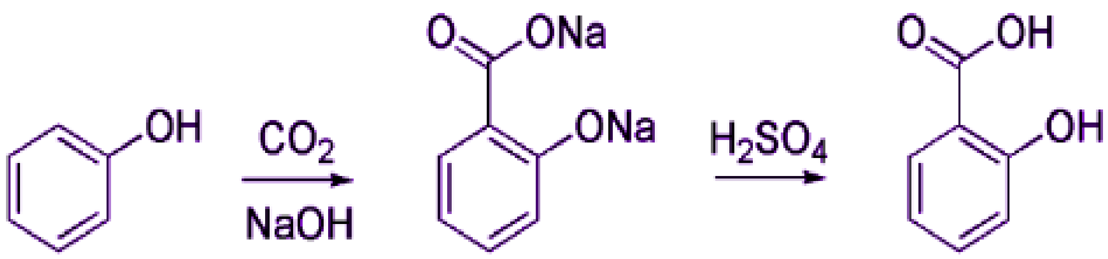
3. Halogenation of Phenols



When phenol is treated with bromine water, a white precipitate of 2, 4, 6-tribromophenol is formed.

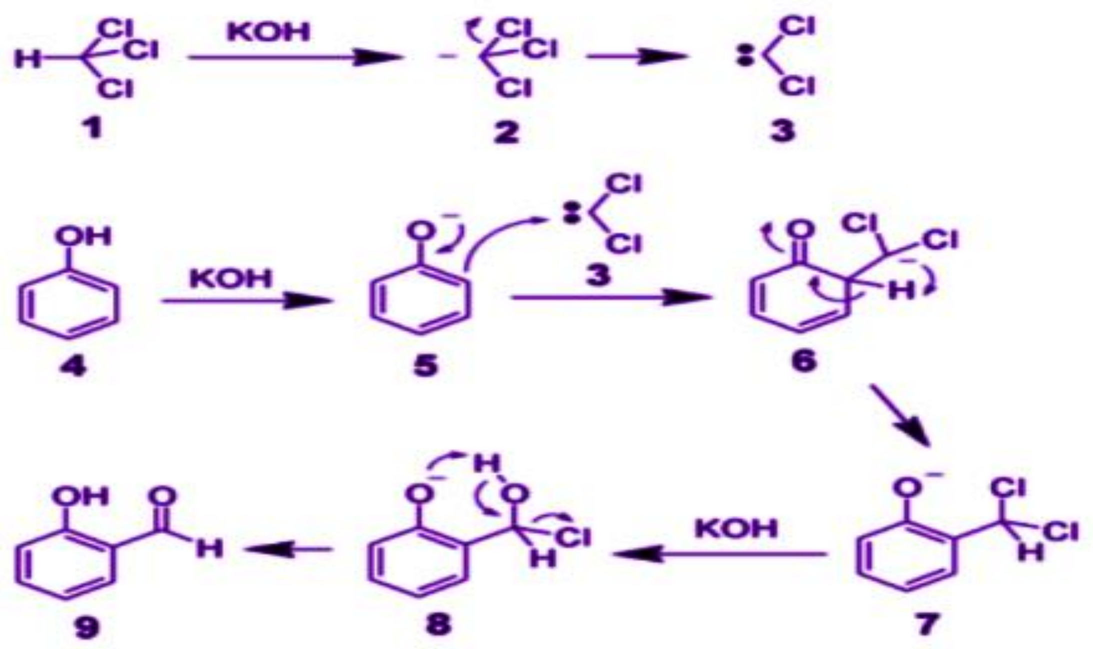
4. Kolbe's Reaction

When phenol is treated with sodium hydroxide, phenoxide ion is formed. This phenoxide ion formed is highly reactive towards electrophilic substitution reactions. Upon treatment with a weak electrophile (carbon dioxide), it undergoes electrophilic substitution reaction to form Ortho-hydroxybenzoic acid. This reaction is popularly known as Kolbe's reaction.



5. Reimer-Tiemann Reaction

When phenol is treated with chloroform in the presence of sodium hydroxide, an aldehyde group is formed at the ortho position of the benzene ring. This reaction is popularly known as the Reimer-Tiemann reaction.



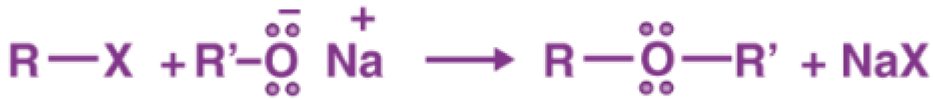
ETHER:

A molecule with an oxygen atom linked to two alkyl groups is known as ether. Ethers are colourless liquids with a sweet odour that are liquid at room temperature. Diethyl ether is the most common form of ether, which is highly flammable and was one of the first anaesthetics used in surgery.

Preparation of Ethers:

By Williamson Synthesis:

In laboratories, Williamson's synthesis is an important method for preparing symmetrical and asymmetrical ethers. An alkyl halide is reacted with sodium alkoxide in this technique, resulting in the creation of ether. For primary alcohol, the reaction follows the SN2 mechanism.



Physical And Chemical Properties Of Ether:

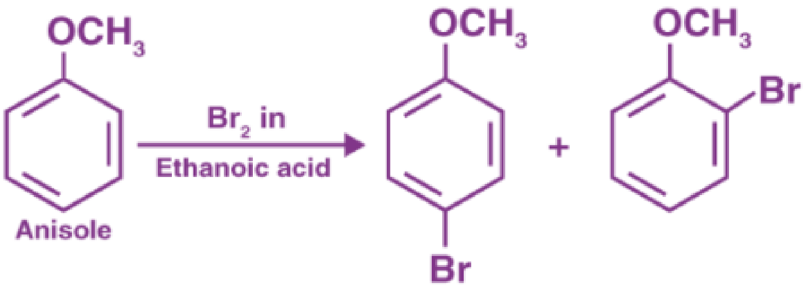
Symmetrical ether (when two identical groups are connected to the oxygen atom) and Asymmetrical ether (when two different groups are attached to the oxygen atom) are the two types of ethers (when two different groups are attached to the oxygen atom). Ethers have a diverse set of physical and chemical characteristics.

Physical Properties Of Ether:

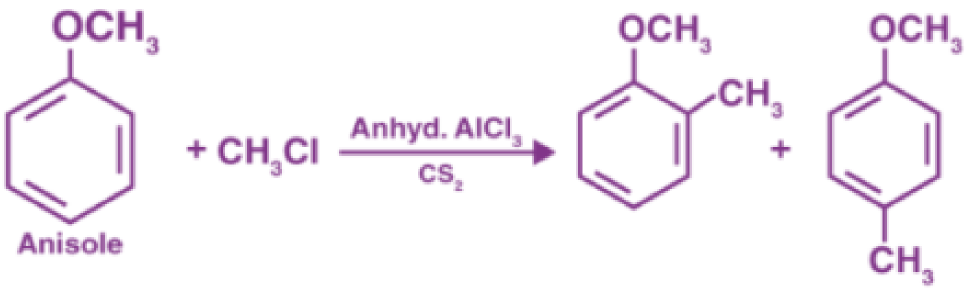
A net dipole moment exists in an ether molecule. The polarity of C-O bonds is to blame for this.
Ethers have a boiling point similar to that of alkanes. However, when compared to alcohols of comparable molecular mass, it is far lower. Despite the polarity of the C-O bond, this is the case.
The water miscibility of ethers is similar to that of alcohols.
In water, ether molecules are miscible. This is due to the fact that the oxygen atom of ether, like that of alcohols, may form hydrogen bonds with a water molecule.

Chemical Properties Of Ether:

Halogenation of Ethers:
When aromatic ethers are exposed to halogen in the presence or absence of a catalyst, they undergo halogenation, such as bromination.



Friedel Crafts Reaction of Ethers:
Friedel Crafts reaction, for example, adds an alkyl or acyl group to aromatic ethers when they react with an alkyl or acyl halide in the presence of a Lewis acid as a catalyst.



Uses of Ethers:

- Ethers are chemical substances that are extremely flammable. They're employed in medicine, laboratories, our daily lives, and a variety of other applications. Let's take a closer look at how they're used.

- They’re usually used in surgeries as an anaesthetic. Because ethers are volatile liquids, they release vapours that patients inhale or are given intravenously. They cause individuals to lose consciousness before surgery.
- Antiseptics were also made from ethers. Ether was used to sanitise patients’ wounds and save them from dangerous illnesses during World War II. They are still used as antiseptics.
- Because of their olfactory and organoleptic qualities, ethers are frequently employed in the perfumery and scent business. Fruit-based meals and beverages, sweets, fruit jams, yoghurts, ice cream, chewing gum, and some pharmaceutical treatments all contain them.