Chemical Reactions of Alcohols, Phenols and Ethers

We all have had hard drinks. Yes, it is alcohol. But apart from human consumption it is used in many other applications or to get different compounds. Similar is with phenol and ether. These chemical compounds (alcohol, phenol, and ether) are reacted with some other compounds and converted to some other chemical. So before beating around let's get to the point. Below given reactions will let you see these three chemicals from a different perspective.

What is Alcohol?

Alcohol is an organic compound which contains a hydroxyl functional group attached to a carbon. We get alcohol from alkenes, carbonyl compounds, hydrolysis of alkyl halides, primary amines, alcohol fermentation, and hydrolysis of ethers.

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- Preparation of Phenols
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Reactions of Alcohols

Reaction with Metal

When ethanol reacts with sodium metal (a base) sodium ethoxide and hydrogen gas is produced.

$$2ROH + Na \rightarrow 2RO{+}Na_{-} + H_2$$

Formation of Halides

Halogens such as chlorine or bromine replace the -OH group in an alcohol.

$$ROH + Zn + HCl \rightarrow R\text{-}Cl$$

$$R_2C\text{-}OH \text{ alcohol} + HCl \rightarrow R_2CCl$$

Reaction with HNO_3

There is oxidation, accompanied by gas evolution (slow but progressive) in this reaction.

$$R\text{-}OH + HO\text{-}NO_2 \rightarrow R\text{-}O\text{-}NO_2$$

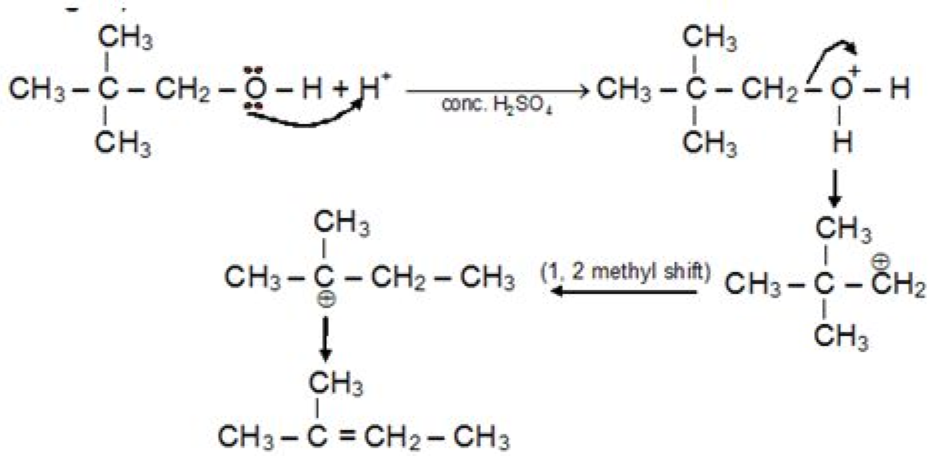
Reaction with Carboxylic Acid (Esterification)

The reaction of the carboxylic acid with an alcohol and an acid catalyst leads to the formation of ester (along with water). This is Fischer esterification.

$$R\text{-}OH + R'\text{-}COOH + H^{+} \leftrightarrow R'\text{-}COOR$$

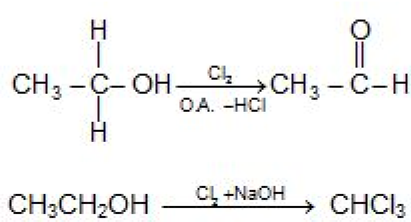
Dehydration of Alcohol

Alcohols dehydrate in an acidic medium. As per the Satyzeff's Rule, intra-molecular dehydration leads to the formation of alkene while intermolecular dehydration forms ether.



Haloform Reaction

Compound that has the CH3CO- group (or compound on oxidation gives CH3CO – group) which is bonded with a C or H, in the presence of halogen and mild alkali gives haloform. CH_3-CH_2-$COCH_2$-CH_3, CH_3-CO-Cl, CH_3COOH will not respond to haloform reaction while CH_3CH_2OH will respond to the haloform reaction.



What is Phenol?

In this chemical compound, a hydroxyl group directly attaches to an aromatic hydrocarbon. Cumene, diazonium salts, etc. form phenols.

Reactions of Phenol

Formation of Ester

Phenyl esters (RCOOAr) do not form directly from RCOOH, but for this acid chlorides or anhydrides react with ArOH in the presence of a strong base.

$(CH_3CO)_2O + C_6H_5OH + NaOH \rightarrow CH_3COOC_6H_5 + CH_3COONa + H_2O$

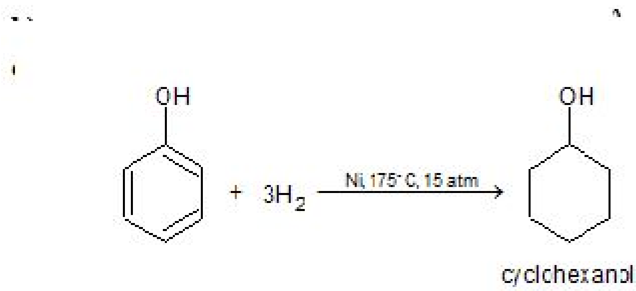
Phenylacetate

$C_6H_5COCl + C_6H_5OH + NaOH \rightarrow C_6H_5COOC_6H_5 + Na^+Cl^- + H_2O$

Phenyl benzoate

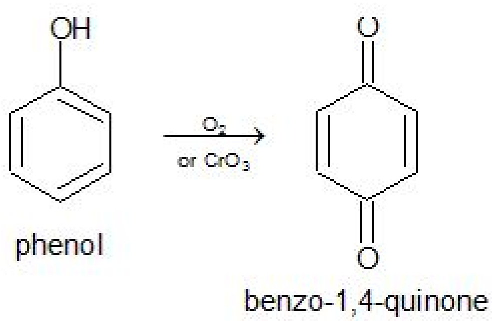
Hydrogenation

Hydrogenation of phenol forms cyclohexanone.



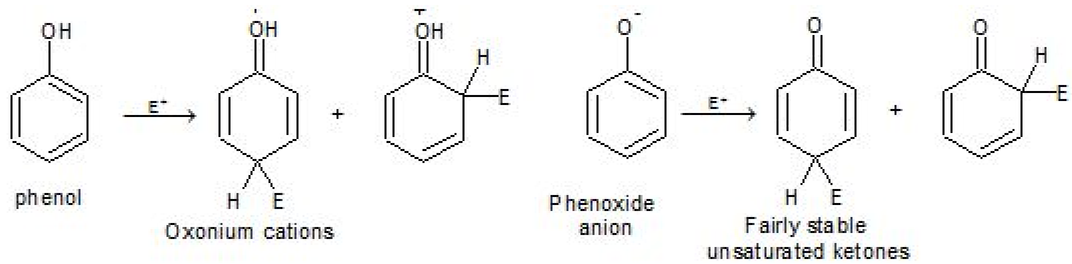
Oxidation of Quinones

Phenols get easily oxidized to para-benzoquinone. This when reduced forms quinones.



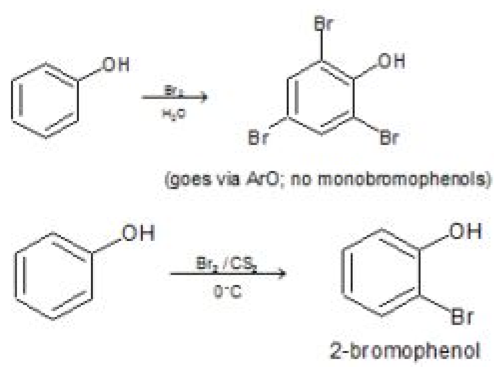
Electrophilic Substitution

The —OH and even the —O(phenoxide) are strongly activating ortho, para – directing. Electrophilic monosubstitution in phenols happens in special mild conditions because they are highly reactive and favors both polysubstitution and oxidation.



Halogenation

There is a formation of monobromophenol, on treating phenols with bromine in the presence of a solvent of low polarity like CHCl3 at low temperature.



What is Ether?

Ether is an organic compound that has an oxygen atom, connected to two alkyl and aryl groups, known as the ether group.

Reactions of Ether

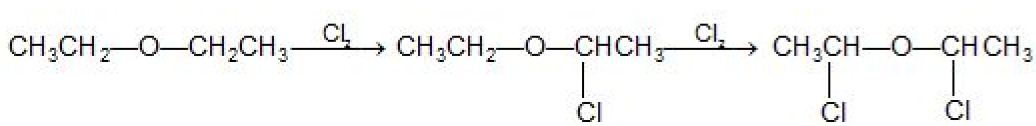
Contact with air

When in contact with air, most aliphatic ethers convert to unstable peroxides slowly. The formation of a red color indicates the presence of peroxides. This color appears when the ether is shaken with an aqueous the solution of ferrous ammonium sulfate and potassium thiocyanate.

$$\text{Peroxide} + Fe^{2+} \rightarrow Fe^{3+} \xrightarrow{SCN^-} \underset{\text{Red}}{Fe(SCN)_n^{(3-n)-}} \quad (n = 1 \text{ to } 6)$$

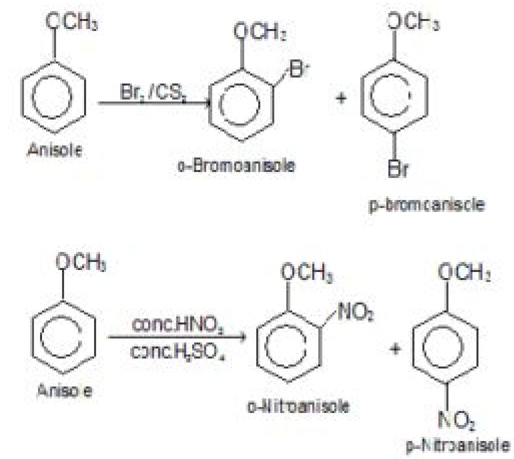
Halogenation of Ether

Halogenation of ether in dark forms halogenated ethers. Halogens replace the hydrogen atom attached to the C atom which is directly linked to the oxygen atom.



Electrophilic Substitution Reaction

The electrophilic substitution reaction activates the aromatic ring in the same way as in phenol. This is due to the presence of the alkoxy group (−OR) in aromatic ethers activates.



Solved Question For You

Q. What is the difference between alcohol and ether?

Answer: The hydroxyl group of phenol directly bonds to a carbon atom of an aromatic ring, whereas in alcohols, the hydroxyl group attaches to a saturated carbon atom.

Chemical Reactions of Ethers

Are you aware of the chemical reactions of ethers? We have looked at the chemical properties of ethers, but are they all similar to their chemical reactions? If we ask you about the chemical reactions of ether, would you be able to identify those for us? Well, in this chapter, we will look at the different chemical reactions of ether and understand the behaviour of ethers better.

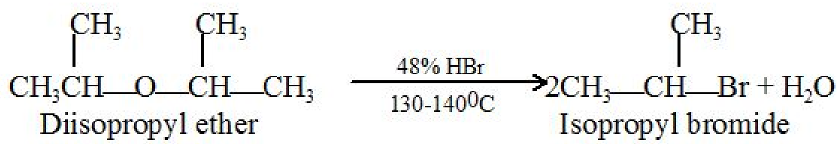
Reactions of Ether

Ethers are relatively unreactive compounds. The ether linkage is quite stable towards bases, oxidizing agents, and reducing agents. Therefore, we must remember that with respect to the ether linkage, ethers undergo just one kind of reaction. It is cleavage by acids :

$$R\text{-}O\text{-}R' + HX \rightarrow R\text{-}X + R'\text{-}OH\ R'\ ¾X$$

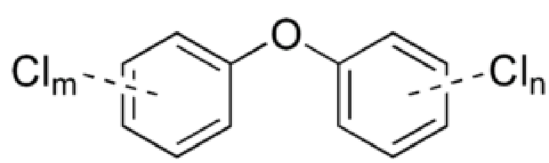
Reactivity of HX : HI > HBr > HCl

Cleavage takes place only under quite extreme conditions, like in concentrated acids (usually HI or HBr) and high temperatures. A dialkyl ether produces, initially, an alkyl halide and an alcohol. This alcohol may react further and form a second mole of alkyl halide. For example :



The oxygen of an ether is basic, similar to the oxygen of an alcohol. The initial reaction between an ether and an acid is no doubt, the formation of the protonated ether. Cleavage, then, involves the nucleophilic attack by a halide ion on this protonated ether, with the displacement of the weakly basic alcohol molecule.

Such a reaction usually occurs much more readily as compared to the displacement of the strongly basic alkoxide ion from the neutral ether.



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1) Reactions of Ether Due to an Alkyl Group

- Combustion: Ethers are highly inflammable and they form extremely explosive mixtures with air giving CO_2 and water.

$$C_2H_5O\ C_2H_5 + 6O_2 \rightarrow 4CO_2 + 5H_2O$$

- Halogenation: The alkyl group undergoes substitution reaction with chlorine or bromine. The resultant product is halogenated ether in absence of sunlight. However, in presence of sunlight, it substitutes all the hydrogen atoms of ethers.

$$CH_3CH_2OCH_2CH_3 \xrightarrow{CI_2, dark} CH_3CHCIOCHCICH_3$$ (α α’-dichloro diethyl ether)

$$CH_3CH_2OCH_2CH_3 \xrightarrow{CI_2, dark} C_2CI_2OC_2CI_5$$ (Perchloro diethyl ether)

2) Reaction of Ether Due to Ethereal Oxygen

Ethers behave as Lewis bases because of the presence of two lone pairs of electrons on the oxygen atom. Therefore, they form salts with strong acids. The oxonium salts are soluble in acid solution. We can facilitate the regeneration of ether by hydrolysis of these salts.

$$\underset{\displaystyle H}{R_2O^+}Cl^- \xrightarrow{H_2O} R_2O + HCl$$

Ethers also form coordination complexes with Lewis acids like BF_3, $AICI_3$, RMgX etc. Therefore, we can derive the fact that ethers are very good solvents for Grignard reagents.

3) Formation of Peroxides

Ethers form peroxide linkage with oxygen when we expose them to air or ozonized oxygen in presence of sunlight or ultraviolet light. These peroxides are highly poisonous in nature. They are oily liquids and decompose violently even at low concentrations. Therefore, we must ensure never to evaporate esters to dryness. It might lead to explosive reactions.

Besides this, we must also check the purity of ether before its use as an anaesthetic agent. An impure ether (having peroxide linkage) gives red colour when shaken with ferrous ammonium sulphate and potassium thiocyanate. This could prove to be lethal for the patients on whom we try anaesthesia.

$$\text{Peroxide} + Fe^{+2} \rightarrow Fe^{+3} \xrightarrow{CNS} \underset{\text{red}}{Fe(CNS)_3}$$

On mixing with KI solution, it liberates I_2 which turns starch paper blue.

$$\text{Peroxide} + KI \rightarrow I_2 \xrightarrow[\text{paper}]{starch} \text{Blue}$$

We can make these ethers free from peroxide linkages by distilling them with highly concentrated sulphuric acid, H_2SO_4. Also, we can check for the peroxide formation by adding a little amount of Cu_2O to the ether.

4) Reactions of Ether Involving Cleavage of Carbon-Oxygen Bond

- Action of dil. H_2SO_4 : Ethers, on heating with dilute H_2SO_4 , under high pressure, hydrolyse to corresponding alcohols.
- Action of Conc. H_2SO_4 : Ethers, on warming with conc. H_2SO_4 , give alkyl hydrogen sulphate.

$$R\text{-}OR + \text{conc. } H_2SO_4 \rightarrow 2R\ HSO_4$$

$$R\text{-}OR' + \text{conc. } H_2SO_4 \rightarrow RHSO_4 + R'HSO_4$$

- Action of HI:

The products that we get during the action of HI on ethers depend mainly upon the temperature in which we carry out the reaction.

$$R\text{-}OR + HI \xrightarrow{cold} R\text{-}OH + RI$$

$$R\text{-}OR' + HI \xrightarrow{cold} R'\text{-}OH + RI$$

Note: In case of a mixed ether, halogen atom attaches itself to the simpler alkyl group.

$$CH_3OC_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$$

$$R\text{-}R + HI \xrightarrow{hot} 2RI + H_2O$$

We would observe similar reactions with HCI, HBr & the reactivity order is HI > HBr > HCI.

- Action of PCI_5 : In the presence of heat, we get the following reaction:

$$R\text{-}O\text{-}R + PCI_5 \xrightarrow{\Delta} 2RCI + POCI_3$$

- Action of Acetyl chloride or Acetic anhydride :

$$R—O—R + CH_3COCl \xrightarrow[AlCl_3]{ZnCl_2\ or} RCl + CH_3COOR$$

$$R—O—R + (CH_3CO)_2O \xrightarrow{AlCl_3} 2CH_3COOR$$

- Dehydration of Ethers:

$$C_2H_5OC_2H_5 \xrightarrow[350^oC]{Al_2O_3} 2CH_2{=}CH_2 + H_2O$$

- Action of Carbon Monoxide :

$$C_2H_5OC_2H_5, + CO \xrightarrow[500\ atm]{BF_3, 150^0 C} C_2H_5COOC_2H_5$$

$$ROR + CO \rightarrow RCOOR$$

Solved Example for You

Q: Write down a few uses of ethers.

Ans: We commonly use ethers as:

- General anaesthetic agent.

- As a refrigerant. This is because it produces cooling on evaporation.
- A solvent for oils, fats, resins, Grignard reagent etc.
- For providing inert & moisture free medium for reactions e.g. Wurtz reaction.

Alcohol, Phenol, and Ether – Classification, Types, Videos

Alcohol, Phenol, and Ether are classes of organic compounds. These compounds have huge applications in industries for domestic purposes. When hydroxyl (-OH) group bonds with saturated carbon atom we get Alcohol. And dehydration of alcohol forms Ether. Monohydric, Dihydric, and Trihydric are three types of alcohols, based on the hydroxyl group. In this chapter, we will talk about the types of alcohol, ether, and phenol. We will look at their classification and also cover a few examples.

Alcohol, Phenol, and Ether

These three are classes of organic compounds having a wide usage in a broad range of industries as well as for domestic purposes. But, what are they?

- Alcohol is the product we get when a saturated carbon atom bonds to a hydroxyl (-OH) group.
- Phenol is what we get when the -OH group replaces the hydrogen atom in benzene.

- Ether is the product that we get when an oxygen atom bonds to two alkyl or aryl groups.

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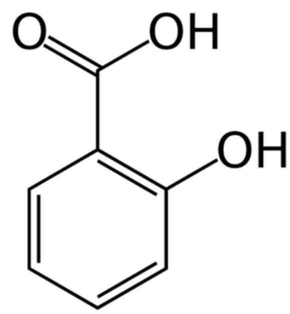
In the below section, we will discuss the various classifications of these organic compounds, alcohol, phenol, and ether.



Types of Alcohol

Based on the total number of hydroxyl groups present, there are three types of alcohol. They are:

- Monohydric alcohols: These contain one -OH group. For example, CH_3CH_2-OH
- Dihydric alcohols: These contain two -OH groups. For example, 1,2-Ethandiol.
- Trihydric alcohols: These have three -OH groups. For example 1,2,3-Propantriol.

However, this is not the only method of classification for alcohols. There is another method by which we can classify alcohols. Depending on the number of carbon atoms which are directly attached to the carbon that is bonded to the -OH group, we can classify alcohols into three types:

- Primary alcohol: One carbon atom directly attaches to the -OH group.
- Secondary alcohol: Two carbon atoms are directly attached to the -OH group.
- Tertiary alcohol: Three carbon atoms are directly attached to the -OH group.

Preparation of Alcohol

1. Hydrolysis of Alkyl Halides
2. Oxymercuration and Demercuration of Alkanes
3. Preparation of Alcohols from Grignard Reagent
4. Reduction of Carbonyl Compounds
5. Reduction of Acids to Alcohols

Learn more about methods for Preparation of Alcohol here in detail.

Classification of Phenol

Depending on the number of hydroxyl groups attached, we can classify phenols into three main types:

- Monohydric phenols: These phenols contain one -OH group.
- Dihydric phenols: They contain two -OH groups. They could be either ortho-, meta- or para- derivative.
- Trihydric phenols: They contain three -OH groups.

Preparation of Phenol

1. Haloarenes
2. Benzene Sulphonic Acid
3. Diazonium Salts
4. Cumene

Learn more about methods for Preparation of Phenol in detail here.

Classification of Ether

Depending on the type of the alkyl or aryl groups attached to the oxygen atom in ether, we can classify ethers into the following two types:

- Symmetrical ether: Also known as the simple ether, they have the same alkyl or the aryl group attached to either side of the oxygen atoms. Examples are CH_3OCH_3, $C_2H_5OC_2H_5$, etc.
- Unsymmetrical ether: Also known as the mixed either, they have different alkyl or the aryl group attached to either side of the oxygen atoms. Examples are $CH_3OC_2H_5$, $C_2H_5OC_6H_5$, etc.

Preparation of Ether

1. Dehydration of Alcohols
2. Williamson Synthesis

Learn more about methods for Preparation of Ether in detail here.

Solved Example for You

Q: Write down the physical properties of phenols.

Ans:

- Phenol is a colourless, toxic, corrosive, needle-shaped solid. It liquifies due to high hygroscopic nature.

- Phenol is less soluble in water, but it dissolves properly in organic solvents.
- Simplest phenols, because of hydrogen bonding have quite high boiling points.
- o-nitrophenol is volatile and also less soluble in water because of intramolecular hydrogen bonding

Nomenclature

There are reasons how each one of us got our names. Isn't it? Similarly, there are reasons behind how alcohol, phenol and ethers got their name. Are you familiar with the nomenclature of these organic compounds? Well, let's find out! In this chapter, we will look at the nomenclature of alcohol, phenols and ethers. We will cover the IUPAC rules and see a few examples for the same. Let us start with the nomenclature of alcohols.

Nomenclature of Alcohols

We know alcohols are of three major classes. They are:

- Monohydric Alcohol
- Dihydric Alcohol
- Trihydric Alcohol

We will now discuss the nomenclature of these alcohols.

1) Monohydric Alcohol

Monohydric alcohols have the general formula $C_nH_{2n+1}OH$ where n = 1, 2, etc. We can also represent them as R-OH where R describes an alkyl group. There are three systems for the nomenclature of Monohydric Alcohol.

- Common System: In this system, we name the monohydric alcohols as Alkyl Alcohol. We get their names by adding the name alcohol after the name of the alkyl group present in the molecule. Example: The compound CH_3-OH has one methyl group with an alcohol group. Hence, we call it Methyl Alcohol.
- Carbinol System: In this system, methyl alcohol (CH_3OH) gets the name Carbinol while other alcohols get their names as alkyl or aryl derivatives of carbinol. Example: CH_3-CH_2-OH is methylcarbinol and CH_3-CH_2-CH_2-OH is Ethylcarbinol.
- IUPAC System: In IUPAC nomenclature, we term the alcohols as Alkanols. We get the name of any alcohol by replacing the last 'e' from the name of the corresponding alkane by the suffix '–ol'. Then, we select the longest carbon chain containing the OH group as the parent chain. We, then, number the longest chain in such a way that the carbon atom carrying the OH group gets the smaller number. After. this, we show the

position of the substituents by suitable numbers allotted to their respective carbon atom.

Example: The compound CH_3-OH is Methyl Alcohol but in the IUPAC, we call it as Methanol. Here, we replace the last 'e' of the methane by 'ol' which indicates the presence of an alcohol group. In the naming of the Cyclic monohydric alcohols prefix, 'cyclo' is used in writing the common or the IUPAC names of the straight chain alcohols.

2) Dihydric Alcohol

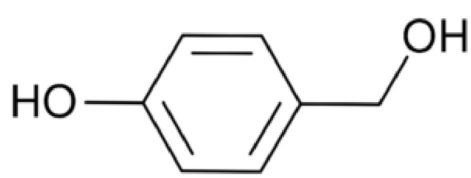
Dihydric alcohols have the general formula of $(CH_2)_n(OH)_2$, where n= 2,3,4…. etc. Because of their sweet taste, we refer to them as Glycols. Depending upon the relative position of the two hydroxyl group, we can classify them as α, β, ϒ…..ω-glycols, etc. Let us look at the system of their nomenclature.

- Common System: In common system, we name the α- glycols by adding the word Glycol after the name of the alkene. In contrast β, ϒ … ω – glycols get their names as the corresponding polymethylene glycols. Example:

$HO\text{-}CH_2CH_2CH_2\text{-}OH$ — Trimethylene glycol (A β-glycol)

$HO\text{-}CH_2CH_2CH_2CH_2CH_2\text{-}OH$ — pentamethylene glycol

- IUPAC system: In this system, we name the glycols as Diols and their class name is Alkanediols. We use Arabic numerals to indicate the two hydroxyl group positions.



3) Trihydric Alcohol

The general formula of trihydric alcohols is $(CH_2)_n(OH)_3$ where n = 3, 4, 5 …etc. In this system, we do not have any general rule of nomenclature. So, there is only one IUPAC rule. In this IUPAC system of trihydric alcohol, we call them as Alakanetriols. We use Arabic numerals to indicate the position of the OH group.

Nomenclature of Phenols

The simplest derivative of benzene is Phenol. It is the common name as well as an accepted IUPAC name. Both in the common and in the IUPAC system, we name the substituted phenols as the derivatives of phenols.

In the common system, we indicate the substituent position present on the benzene ring with respect to –OH group by adding the prefix such as ortho (o-) for 1:2, meta (m-) for 1,3 and para (p-) for 1,4.

However, in the IUPAC system, we use Arabic numerals to indicate the position of the substituent w.r.t –OH group. The carbon carrying the OH group gets the number 1. The phenols having a carbonyl group such as aldehyde, ketonic, carboxyl or an ester group get their names as hydroxyl derivatives of the parent aromatic compound.

Nomenclature of Ethers

- Common System: We get the common names of ethers by naming the two alkyl or aryl groups linked to the oxygen atom as separate words in alphabetical order and adding the word ether. In case of symmetrical ethers, we use the prefix di before the name of the alkyl or the aryl group.
- IUPAC system: In the IUPAC system, ethers are Alkoxyalkanes. The ethereal oxygen is taken with the smaller alkyl group and forms a part of the alkoxy group. On the other hand, the larger alkyl group is taken to be the part of the alkane.

Solved Example for You

Q: How do we name dihydric and trihydric phenols according to the IUPAC system?

Ans: In the IUPAC system, di-, Tri- and polyhydric phenols get the names of Hydroxyl Derivatives of Benzene.

Physical Properties of Alcohols, Phenols and Ethers

Now that we know quite a bit about alcohols and ethers and phenols, how many of you know about the physical properties of alcohol? You may ask why it is important? Well, we need to the know the physical properties of these organic compounds to be able to use them for our benefit. Imagine how would it be if alcohol weren't miscible in water?

Therefore, in this chapter, we will look at the concept of physical properties of alcohols, phenols and ethers, one after the other. By the end of this chapter, you will be in a better position to know about the basic properties of these compounds.

Physical Properties of Alcohol

Alcohols are organic compounds where a hydroxyl group replaces the hydrogen atom of an aliphatic carbon. Thus, an alcohol molecule consists of two parts. The first one has the alkyl group and the other has the hydroxyl group.

They have a sweet odour and exhibit a unique set of physical and chemical properties. The presence of hydroxyl group is the main factor in determining the properties of alcohol. Let us now look at some of the prominent physical properties of alcohol.

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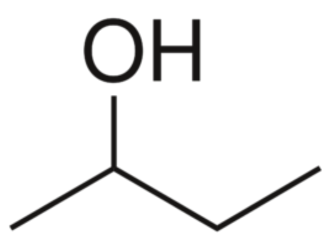
1) The Boiling Point of Alcohols

Alcohols generally have higher boiling points as compared to other hydrocarbons having equal molecular masses. We can attribute this to the presence of intermolecular hydrogen bonding between hydroxyl groups of alcohol molecules. In addition to this, the boiling point of alcohols increases with increase in the number of carbon atoms in the aliphatic carbon chain.

2) The Solubility of Alcohols

The hydroxyl group decides the solubility of alcohol in water. The hydroxyl group in alcohol takes part in the formation of intermolecular hydrogen bonding. Thus, hydrogen bonds between water and alcohol molecules make alcohol soluble in water. The solubility of alcohol decreases with the increase in the size of the alkyl group because of the hydrophobic nature of the alkyl group.



3) The Acidity of Alcohols

Alcohols react with active metals such as sodium, potassium etc. and form the corresponding alkoxide. These reactions of alcohols are indicative of 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. This is due to the fact that it increases the electron density of the oxygen atom. Thus, primary alcohols are generally more acidic.

Phenols and Their Physical Properties

Phenols are the organic compounds that have a benzene ring bonded to a hydroxyl group. We also name them as carbolic acids. They exhibit unique physical and chemical properties that are mainly due to the presence of a hydroxyl group. Let us discuss some of the important physical properties of phenols in the section below.

1) The Boiling Point of Phenols

Phenols generally have higher boiling points in comparison to other hydrocarbons with equal molecular masses. The main reason behind this is the presence of intermolecular hydrogen bonding between hydroxyl groups of phenol molecules. In general, the boiling point of phenols increases with increase in the number of carbon atoms.

2) The Solubility of Phenols

The hydroxyl group determines the solubility of phenol in water. The hydroxyl group in phenol is responsible for the formation of intermolecular hydrogen bonding. Thus, hydrogen bonds form between water and phenol molecules which make phenol soluble in water.

3) The Acidity of Phenols

Phenols react with active metals such as sodium, potassium etc. and give the corresponding phenoxide. These reactions of phenols indicate its acidic nature. In phenol, the sp^2 hybridized carbon of the benzene ring attached directly to the hydroxyl group acts as an electron withdrawing group.

Thus, it decreases the electron density of oxygen. Due to the delocalization of negative charge in the benzene ring, phenoxide ions are more stable than alkoxide ions. Therefore, we can say phenols are more acidic than alcohols.

Ethers and Their Physical Properties

Ether is an organic compound that has an oxygen atom bonded to two similar or different alkyl or aryl groups. The general formula for ethers can be R-O-R, R-O-Ar or Ar-O-Ar. Here, the term R points towards an alkyl group and Ar stands for an aryl group. Ethers exhibit a wide range of physical and chemical properties. physical properties of ethers are:

- An ether molecule has a net dipole moment. This dipole moment is mainly due to the polarity of C-O bonds.
- The boiling point of ethers is comparable to the alkanes. However, it is much lower than that of alcohols of comparable molecular mass despite the polarity of the C-O bond. The miscibility of ethers with water is on the same lines as that of alcohols.
- Ether molecules are miscible in water.

Solved Example for You

Q: Why are ethers soluble or miscible in water?

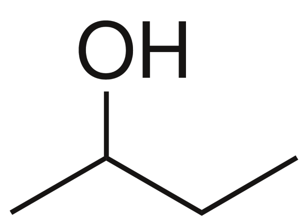
Ans: Like alcohols, the oxygen atom of ethers is capable of forming hydrogen bonds with a water molecule. Therefore, ethers are soluble in water.

Preparation of Alcohols

You are probably very well versed with the concept and term ‘alcohol’. It is not just what you see people drinking! It is a very common organic compound that finds large-scale practical applications. However, are you aware of the various methods for the preparation of alcohols? In this chapter, we will look at the various industrial methods of preparation of alcohols.

Preparation of Alcohols

There are various methods and ways to prepare alcohols in industries and laboratories. Let’s learn about these one-by-one below.



1) Hydrolysis of Alkyl Halides

This is a nucleophilic substitution reaction. The method is not a very effective one. This is because it has as olefins as by-products. ion.

$$R\text{-}X + KOH_{aq} \rightarrow R\text{-}OH$$

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2) Oxymercuration and Demercuration of Alkanes

Alkenes react with mercuric acetate in presence of H_2O and tetrahydrofuran to give alkyl mercury compounds. This is one of the most common types of methods to prepare alcohols.

3) Preparation of Alcohols from Grignard Reagent

We can obtain the three types of monohydric alcohols (primary, secondary and tertiary alcohols) by using Grignard reagents and carbonyl compounds. The addition of RMgX on carbonyl compounds, along with hydrolysis gives us alcohols. The Grignard reagent is basically an organometallic compound. Let us look at this reaction in greater detail as it is a very important reaction.

When we allow a solution of an alkyl halide in dry ethyl ether, $(C_2H_5)O$ to stand overturnings of metallic magnesium, we witness a vigorous reaction. We can see that the solution turns cloud and begins to boil. The magnesium metal gradually disappears. The resulting solution is the Grignard reagent.

$$CH_3I \quad + \quad Mg \quad \overset{Ether}{\rightarrow} \quad CH_3MgI$$

$$H_3CH_2Br + Mg \quad \overset{Ether}{\rightarrow} \quad CH_3CH_2MgBr$$

Ethyl bromide Ethylmagnesium bromide

The Grignard reagent has the general formula R MgX, and the general name alkyl magnesium halide.

More about Grignard Reagent

The Grignard reagent is highly reactive. It reacts with numerous inorganic compounds including water, carbon dioxide, and oxygen, and with most kinds of organic compounds. It is interesting to note that an alkane is such a weak acid that Grignard reagent can displace it by compounds that we might ordinarily consider to be very weak acids themselves, or possibly not acids at all.

Grignard Synthesis of Alcohols

What class of alcohol we obtain from a Grignard synthesis depends upon the type of carbonyl compound that we use in the reaction: formaldehyde, HCHO, yields primary alcohols. On the other hand, aldehydes yield secondary alcohols while ketones, R_2CO, yield tertiary alcohols.

How do we get this? It is simple. The number of hydrogens attached to the carbonyl carbon defines the carbonyl compound as formaldehyde, higher aldehyde or ketone. The carbonyl carbon is the one that finally bears the –OH group in the product; here the number of hydrogen defines the alcohol as primary, secondary, or tertiary.

4) Reduction of Carbonyl Compounds

We can also get alcohols by the reduction of aldehydes and ketones. We can reduce aldehydes to primary alcohols and ketones to secondary alcohols. This process can take place by the catalytic hydrogenation or by the use of chemical reducing agents like lithium aluminium hydride, $LiAlH_4$.

Such reduction techniques find an important place in the preparation of certain alcohols that are less available than the corresponding carbonyl compounds. What we must note here is that Sodium borohydride, $NaBH_4$, does not reduce carbon-carbon double bonds, not even those conjugated with carbonyl groups.

5) Reduction of Acids to Alcohols

Lithium aluminium hydride, $LiAlH_4$, is one of the few reagents that can reduce an acid to an alcohol.

$$4RCOOH + 3LiAlH_4 \rightarrow 4RCH_2OH \qquad 1^{o} alcohol$$

Because of the excellent yields it gives, $LiAlH_4$ is a common ingredient in the laboratory for the reduction of not only acids but many other classes of compounds.

6) Other Methods of Preparation of Alcohols

- By the Action of Nitrous Acid on Primary Amines

$$R\text{-}NH_2 + HNO_2 \rightarrow R\text{-}OH + N_2 + H_2O$$

However, under similar conditions, CH_3NH_2 gives $CH_3\text{-}O\text{-}N{=}O$ or CH_3OCH_3

$$CH_3NH_2 + 2HNO_2 \rightarrow CH_3\text{-}O\text{-}N{=}O + 2H_2O + N_2$$

$$\text{OR } 2CH_3NH_2 + 2HNO_2 \rightarrow CH_3OCH_3 + 2N_2 + 3H_2O$$

- By Fermentation

Fermentation is the slow decomposition of complex organic compounds into simpler organic compounds by the activity of enzymes. Enzymes are complex, nitrogenous (proteins), non-living macromolecules of high molecular weight. We usually get these enzymes from living organisms.

This process is usually followed by the evolution of gases like CO_2 & CH_4. They release a lot of energy and are exothermic in nature. The alcoholic fermentation involves the conversion of sugar into ethyl alcohol by yeast.

Solved Example for You

Q: What are the favourable conditions for fermentation?

Ans: To facilitate fermentation, we must carry out the following:

- Maintain the optimum temperature range for fermentation at 25-30^{o}C. At higher temperatures, the enzymes could coagulate.
- We need to add certain inorganic substances like $(NH_4)_2SO_4$, or phosphates etc as a food for the ferment cells.
- We must keep the concentration of the fermentation solution very diluted.
- Make sure that the substances like boric acid, mercury slats etc. should not be present as they retard fermentation.
- We must ensure proper aeration during the process of fermentation.

Physical Properties of Ethers

Do you think you have read enough about ethers? Well, what do you know about this class of organic compounds? In this chapter, we will cover, not only ether definition but also the various chemical and physical properties of ethers. To start with, how many of you remember what ethers are?

What are Ethers?

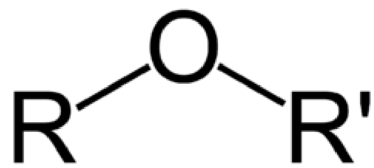
Ethers are a class of organic compounds that have an oxygen atom attached to two same or different alkyl or aryl groups. We can write down the general formula for ethers as R-O-R, R-O-Ar or Ar-O-Ar.

From our knowledge of organic nomenclature, we know that in the above formula, R represents an alkyl group and Ar represents an aryl group. We can classify these compounds into two main types or categories. This categorisation depends on the substituent groups attached to the compound. Accordingly, we can classify them into

- Symmetrical ether: It has two identical groups attached to the oxygen atom.

- Asymmetrical ether: It has two different groups attached to the oxygen atom.

Ethers exhibit a wide range of physical and chemical properties. Let us now discuss some of the physical and chemical properties of ethers.



Physical Properties of Ethers

- An ether molecule has a net dipole moment. We can attribute this to the polarity of C-O bonds.
- The boiling point of ethers is comparable to the alkanes. However, it is much lower compared to that of alcohols of comparable molecular mass. This is despite the fact of the polarity of the C-O bond.
- The miscibility of ethers with water resembles those of alcohols.

- Ether molecules are miscible in water. We can attribute this to the fact that like alcohols, the oxygen atom of ether can also form hydrogen bonds with a water molecule.

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Chemical Properties of Ethers

Ethers generally undergo chemical reactions in two ways. We will talk about them in the below section.

- Cleavage of C-O bond: Ethers are generally very unreactive in nature. When we add an excess of hydrogen halide to the ether, cleavage of C-O bond takes place. It leads to the formation of alkyl halides. The order of reactivity is as follows:

$$HI > HBr > HCl$$

$$R\text{-}O\text{-}R + HX \rightarrow RX + R\text{-}OH$$

- Electrophilic substitution: The alkoxy group in ether activates the aromatic ring at ortho and para positions for electrophilic substitution. Common electrophilic substitution reactions are halogenation, Friedel Craft's reaction etc.
- Halogenation reaction of ethers: Aromatic ethers undergo halogenation, for example, bromination, when we add a halogen in the presence or absence of a catalyst.
- Friedel Craft's reaction of ethers: Aromatic ethers undergo Friedel Craft's reaction for example addition of alkyl or acyl

group when we introduce it to an alkyl or acyl halide in the presence of a Lewis acid as catalyst.

Let us also study about the preparation of Ethers.

Solved Example for You

Q: What are the uses of ethers?

Ans: The common uses of ethers include:

- We use dimethyl ether as a refrigerant and as a solvent at low temperature.
- Diethyl ether is a common ingredient as an anaesthesia in surgery.
- Diethyl ether is common as a solvent for oils, gums, resins etc.
- We use phenyl ether as a heat transfer medium because of its high boiling point.

Preparation of Ethers

You have probably come across a variety of organic compounds in your organic chemistry section. So, we are quite confident that you know about the ether family. Do you know what ethers are? Do you know the various methods for preparation of ethers?

Well, if the answer to these questions is 'No', then you really need to go through this chapter once! We have created a brief summary for you to understand all about ethers and their methods of preparation. We will start with what ethers are.

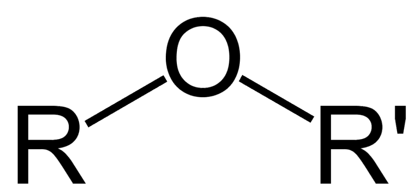
What are Ethers?

Ethers are the organic compounds containing an oxygen atom bonded to two same or different alkyl or aryl groups. We can write the general formula for ethers as R-O-R, R-O-Ar or Ar-O-Ar. As we already know from the chapter of nomenclature, R represents an alkyl group and Ar represents an aryl group.

We can classify these into two categories on the basis of substituent group attached: symmetrical ethers and asymmetrical ethers. The former ether is when we have two identical groups attached to the oxygen atom. On the other hand, an asymmetrical ether is when we have two different groups attached to the oxygen atom.

Preparation of Ethers

These days, with the advancement in technology, we can synthesise ethers in industries in a number of ways. Let us now look at some of the most common industrial methods of preparation of ethers.



Source: Wikipedia

1) Preparation of Ethers by Dehydration of Alcohols

In the presence of protic acids (sulphuric acid), alcohols undergo dehydration to produce alkenes and ethers under different conditions. For example: in the presence of sulphuric acid, dehydration of ethanol at 443 K yields ethene. On the other hand, it yields ethoxyethane at 413 K. This is an ideal method of preparation for primary alcohols.

The preparation of ethers by dehydration of an alcohol is a nucleophilic substitution reaction. There are two major roles of the alcohol that we find in this reaction. One is that the alcohol molecule can act as the substrate while the other is that it acts as a nucleophile. It can follow either SN_1 or SN_2 mechanism.

The choice of mechanism is dependent on whether the protonated alcohol loses water before or simultaneously upon the attack of a second alcohol molecule. Generally, we will find that the secondary and tertiary alcohols follow S_N1 mechanism. While on the other hand, the primary alcohols follow SN_2 mechanism.

2) Preparations of Ethers by Williamson Synthesis

Williamson synthesis is an important method for the preparation of symmetrical and asymmetrical ethers in laboratories. In this method, we carry out a reaction of an alkyl halide with sodium alkoxide which leads to the formation of ether. The reaction generally follows SN_2 mechanism for primary alcohol.

As we know alkoxides are strong bases and they can react with alkyl halides. Thus, they take part in elimination reactions. Williamson synthesis exhibits higher productivity in case of primary alkyl halides.

Solved Example for You

Q: Why do ethers have a dipole nature?

Ans: Ethers have a tetrahedral geometry i.e., oxygen is sp_3 hybridized. The C— O—C angle in ethers is 110°. Due to the greater electronegativity of oxygen than carbon, the C—O bonds are slightly polar and are inclined to each other at an angle of 110° This is what results in ethers having a net dipole moment.

Preparation of Phenols

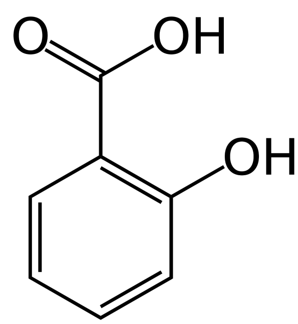
While studying organic chemistry, you have come across the term 'phenol' many times. Haven't you? So, what are phenols? In this chapter, we will look at the preparation of phenols and how we can get them on a large scale requirement. We will study the various methods and reactions that we must carry out in order to obtain phenols. However, before we proceed, let us take a quick look at what phenols are. Can you tell us what phenols are?

What is a Phenol?

Phenols are the organic compounds that have a benzene ring bonded to a hydroxyl group. We also know them by the name of carbolic acids. They are weak acids and generally form phenoxide ions by losing one positive hydrogen ion (H^+) from hydroxyl group.

In earlier days, people were able to synthesise phenol from coal tar. It was a very complex and lengthy process. It had a lot of risks associated with it as well. Nowadays, with advancements in technologies, however, certain new methods have come up for the preparation of phenols in laboratories.

In laboratories, chemists primarily synthesise and derive phenol from benzene derivatives. In this chapter, we will look at some of the ways in which we can produce phenols commercially in laboratories.



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1) Preparation of Phenols from Haloarenes

Chlorobenzene is an example of haloarenes. We can obtain chlorobenzene by the monosubstitution of a benzene ring. When chlorobenzene fuses with sodium hydroxide at 623K and 320 atm, we obtain sodium phenoxide. Finally, sodium phenoxide on acidification gives phenols.

2) Preparation of Phenols from Benzene Sulphonic Acid

We can obtain Benzenesulphonic from benzene by reacting it with oleum. Benzenesulphonic acid, thus formed, is treated with molten sodium hydroxide at high temperature. This process leads to the formation of sodium phenoxide. Finally, sodium phenoxide on acidification gives phenols.

3) Preparation of Phenols from Diazonium Salts

When we treat an aromatic primary amine with nitrous ($NaNO_2$ + HCl) acid at 273 – 278 K, we can easily obtain diazonium salts. These diazonium salts are highly reactive in nature. Upon warming with water, these diazonium salts finally hydrolyse to phenols. We can also obtain phenols from diazonium salts by treating it with dilute acids.

4) Preparation of Phenols from Cumene

Cumene is an organic compound that we can obtain by the Friedel-Crafts alkylation of benzene with propylene. Upon oxidation of cumene (isopropylbenzene) in presence of air, we obtain cumene hydroperoxide.

Upon further treatment of cumene hydroperoxide with dilute acid, we get the phenols. We also produce acetone as one of the by-products of this reaction in large quantities. Hence, phenols prepared by these methods need purifications.

Solved Example for You

Q: Write down the physical properties of phenols.

Ans: The physical properties of phenol are:

- Phenols are usually colourless, toxic, corrosive, needle-shaped solids.
- They can soon liquify due to their highly hygroscopic nature.

- Phenol is less soluble in water but readily soluble in organic solvents.
- Simplest phenols, because of hydrogen bonding have quite high boiling points.
- o-nitrophenol is volatile and also less soluble in water because of intramolecular hydrogen bonding

Some Commercially Important Alcohols

Do you think all alcoholic compounds are bad? We always have that conception that alcohol is bad. Well, we must understand that not all alcoholic compounds are harmful or bad. We will now look at the importance of some of the alcohols that we produce commercially. In this chapter, we will look at their properties and uses and also take a brief look at how we prepare those.

Alcoholic Compounds

There are many alcoholic compounds that are very useful in industries and day to day life. Let's see what these compounds are.

Methanol

Originally, methanol needed the burning of wood chips in the presence of absolutely no air. In this process, few carbohydrates of wood broke to give methanol vapours. These need condensation to give the liquid form. That is why we also know it as wood alcohol.

Commercially, we can synthesise methanol by a catalytic reaction of carbon monoxide (CO) with hydrogen gas (H_2) under high temperature and pressure. We generate this mixture of carbon monoxide and hydrogen by the partial burning of coal in the presence of water. By carefully regulating the amount of water added, we can get the correct ratio of carbon monoxide to hydrogen.

Properties of Methanol

- Methanol has excellent properties as a polar organic solvent.
- It finds a common use as an industrial solvent.
- It is more toxic than ethanol. You must know that it could cause blindness or death if you inhale or ingest it in large amounts.

- Methanol has a high octane rating and a low emission of pollutants. This makes it ideal for many vehicles.

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- Preparation of Phenols

Ethanol

Ethanol or ethyl alcohol is common since old times. People produced it by the fermentation of fruit juices. They stored the fermented juice in a sealed container to drink throughout the winter.

Many different compounds can provide the sugars and starches that break down into simpler compounds during fermentation. Ethanol is also famous as the 'grain alcohol' because it is often made from grains, such as corn (maize), wheat, rye, and barley.

We first boil the grain in water to produce the mash. This is then incubated with malt (sprouted barley) to yield the wort. Malt provides an enzyme (diastase) that converts starches in the grain to the sugar maltose. We then incubate the wort with brewer's yeast, which secretes the enzyme maltase to convert maltose to glucose.

It also gives the enzyme zymase to convert glucose to ethanol. Two of the six carbon atoms in glucose oxidise to give carbon dioxide (CO_2); this oxidation provides energy to the yeast cells.

Fermentation yields a solution that is only about 12–15 percent alcohol because higher concentrations are toxic to the yeast cells. We can distil this solution to raise the ethanol content to as high as 95 percent. Fermentation is a relatively expensive method of making ethanol. Industrially, therefore, we produce ethanol by the high-temperature catalytic addition of water to ethylene (C_2H_4).

Application of Ethanol

Ethanol is an excellent motor fuel with a high octane rating and low emission. However, we can use it as a fuel in peculiar systems that withstand the alcohol's tendency to dissolve plastic parts. We can use solutions of 10 percent ethanol in gasoline (gasohol) in most cars without any adjustments. Today, ethanol fuels are typically made from natural products, such as corn or sugar.

Isopropyl Alcohol

We produce Isopropyl alcohol (2-propanol) by the indirect hydration of propylene(CH_2CHCH_3). It finds a common use in industries asana industrial solvent and as a rubbing alcohol that we apply to the skin. Although isopropyl alcohol is more toxic than ethanol, it has less of a drying effect on the skin.

Ethylene glycol

The name 'ethylene glycol' literally means "the glycol made from ethylene". Its systematic name is ethane-1,2-diol. We use ethylene glycol commonly as an automotive antifreeze and as an ingredient in hydraulic fluids, printing inks, and paint solvents. We also use it as a reagent in making polyesters, explosives, alkyd resins, and synthetic waxes.

Glycerol

Glycerol (also called glycerine) is a sweet syrupy substance with three alcoholic hydroxyl groups. Its systematic name is propane-1,2,3-triol. The first time, chemists were able to obtain Glycerol as a by-product of soap manufacture, through the saponification (hydrolysis in the base) of fats.

We can obtain about 25 kg (60 pounds) of glycerol with each ton of soap. We can also get it by fermentation from molasses and sugar. During World War II, large quantities of glycerol were needed for the production of glyceryl trinitrate (nitroglycerin); this need was met by synthetic glycerol made from propylene, $CH_2{=}CH{-}CH_3$.

Solved Example for You

Q: Mention some uses of glycerol.

Ans: We can use glycerol for making nitroglycerin, which is the primary explosive in dynamite and blasting gelatin. Nitroglycerin is also common as a coronary vasodilator (a drug that relaxes and expands blood vessels) for symptomatic relief of chest pain caused by poor circulation to the heart.

Glycerol also finds use as a solvent, moisturizing agent, plasticizer, antifreeze, and water-soluble lubricant. We can find it in a wide variety of products, including foods, soaps, cosmetics, printing inks, hydraulic fluids, and pharmaceuticals.