

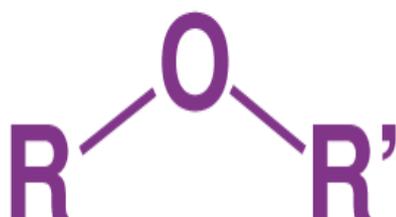
B.Sc Semester – IV MJC – 6(T) Organic Chemistry

Unit – I Alcohols, Phenols , Ethers and Epoxides

What Are Ethers?

Ethers are a class of organic compounds that mostly contain an ether group wherein the oxygen atom is bonded to two alkyl or aryl groups. The word Ether has been derived from the Latin word 'aether' which means 'to ignite'. At room temperature and under a high-pressure, ethers are usually flammable. The general formula of ether is given as R-O-R, R-O-R', R-O-Ar or Ar-O-Ar where R represents an alkyl group and Ar represents an aryl group.

We generally come across this topic in organic chemistry, and it is also a widely covered topic in biochemistry where we find common linkages between carbohydrates and lignin. Meanwhile, if we look at the structure of ethers they basically feature bent C-O-C linkages.



The above figure represents the general structure of an ether. You can see that ether is mainly characterised by an oxygen atom that is bonded to two alkyl or aryl groups, represented here by R and R'. The substituents can be the same or different.

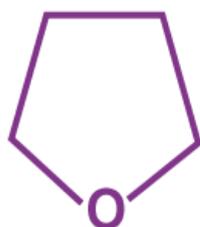
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Examples Of Ethers

Below we have given a few ethers examples.

1. $\text{CH}_3 - \text{O} - \text{CH}_3$ (Dimethyl ether)
2. $(\text{CH}_3)_2\text{CH} - \text{O} - \text{CH}(\text{CH}_3)_2$ (Diisopropyl ether)
3. Cyclic ethers such as
 $\text{C}_6\text{H}_5 - \text{O} - \text{C}_6\text{H}_5$ (Diphenyl ether)



Tetrahydrofuran (THF)



1,4 dioxane

Physical Properties of Ethers

Dimethyl ether and ethyl methyl ether are both gases at room temperature. Other lower homologues are colourless, pleasant smelling, volatile liquids with a typical ether smell.

- 1) **Dipole moment:** C-O-C bond angle is not 180° , dipole moments of the two C-O bonds do not cancel each other, and thus ethers possess a small net dipole moment.
- 2) **Boiling point:** The boiling points of ether molecules are comparable to that of alkanes but they are very low compared to that of alcohols of comparable molecular mass. This is because of the presence of hydrogen bonding in alcohol.
- 3) **Solubility:** The solubility of ethers with water resembles those of alcohols of comparable molecular mass. Ether molecules are soluble in water. This is because of the fact that like alcohol, oxygen atoms of ether can also form **hydrogen bonds** with a water molecule. Also, solubility decreases with an increase in carbon atoms. This is because the relative increase in hydrocarbon content of the molecule decreases the tendency of H-bond formation.
- 4) **Polarity:** Ether is less polar than esters, alcohols or amines because of the oxygen atom that is unable to participate in hydrogen bonding due to the presence of bulky alkyl groups on both sides of the oxygen atom. but ether is more polar than alkenes.

5) **Hybridization:** In ethers, the oxygen atom is sp^3 hybridized with a bond angle of 109.5° .

Classification of Ethers

Ethers can be classified into two broad categories based on the substituent group attached to its oxygen atom: symmetrical ethers and asymmetrical (or unsymmetrical) ethers.



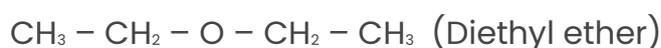
Symmetrical



Unsymmetrical

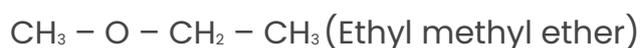
Symmetrical ethers are those ethers where two identical groups are attached to the oxygen atom

Example:



Asymmetrical ethers are those where two different groups are attached to the oxygen atom.

Example:



Their structure is similar to that of the structure of the alcohol. Interestingly, the structures of both ether and alcohol are similar to the structure of water molecules. This is because, in alcohol, one hydrogen atom of a water molecule is replaced by an alkyl group, and in the case of ethers both hydrogen atoms of water molecules are replaced by an alkyl or aryl group.

Note: Ether does not possess a hydroxyl group, unlike alcohols and phenols.

Nomenclature of Ethers

Ethers are named simply by the names of two alkyl/aryl groups bonded to oxygen and add the word 'ether'. Those alkyl groups are listed in alphabetical order.

For example, *t*-butyl methyl ether, ethyl methyl ether

If only one alkyl/aryl group is shown in the name of a particular ether, it implies two identical groups, as in ethyl ether for diethyl ether. Naming for

ethers adopted by IUPAC uses a more complex group as the root name, with the oxygen atom and the smaller group named as an alkoxy substituent. Thus, in IUPAC systems, ethers are alkoxy alkanes.

Example: ethoxyethane (diethyl ether), methoxy ethane (methyl ethyl ether), 2-methoxy-2-methylpropane (methyl tert-butyl ether), phenoxy benzene (diphenyl ether).

This IUPAC nomenclature is very useful for naming compounds with additional functional groups because these functional groups can be described by the root name.

Rules for Naming the Ether Using IUPAC Name

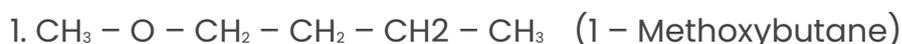
Rule 1: Select the longest carbon chain as the base chain and give the base name.

Rule 2: Change the name of the other hydrocarbon group ends with 'yl' change into 'oxy'.

Example: Methyl becomes methoxy and ethyl becomes an ethoxy group.

Rule 3: Alkoxy name is placed with a locator number in front of the base chain name.

Example:



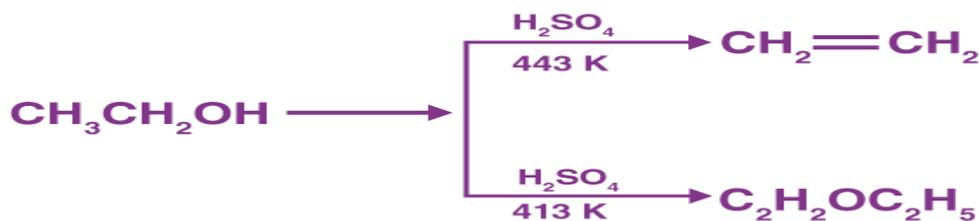
Preparation Of Ethers

Ethers can be prepared or synthesized in a number of ways. The most common industrial methods for preparing ethers are:

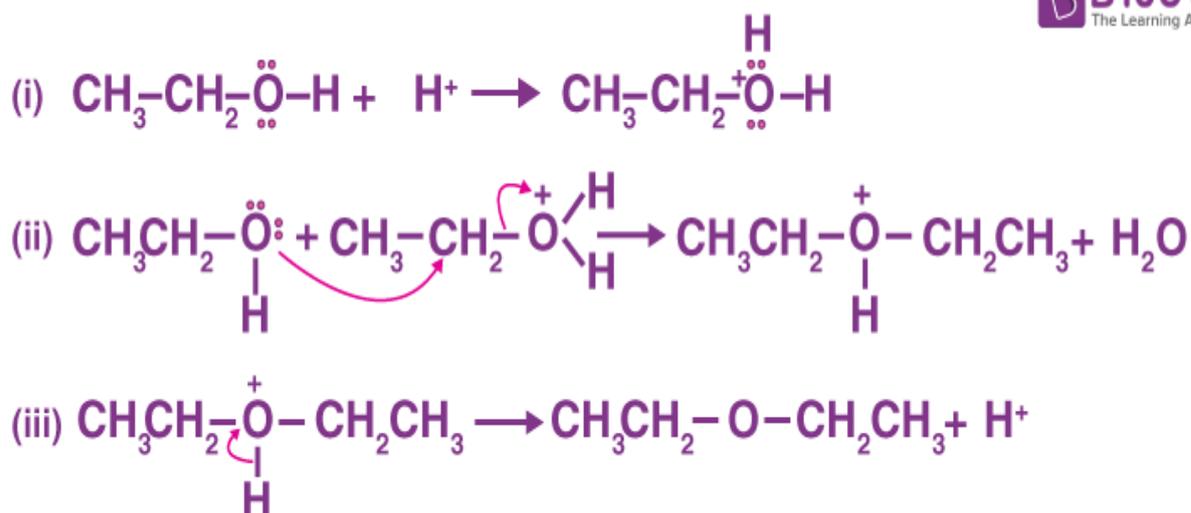
Dehydration of Alcohols

Alcohol undergoes dehydration in the presence of protic acids (sulphuric acid, phosphoric acid) to produce alkenes and ethers under different conditions. The formation of the reaction product depends on the reaction conditions.

For example, ethanol is dehydrated to ethene at 443K in the presence of sulphuric acid. On the other hand, ethanol yields ethoxyethane in the presence of sulphuric acid at 413K.



The formation of ethers by dehydration of an alcohol is a nucleophilic bimolecular reaction. That is, here the alcohol acts as a **nucleophile** which means it involves the attack of an alcohol molecule on a protonated alcohol as shown below.



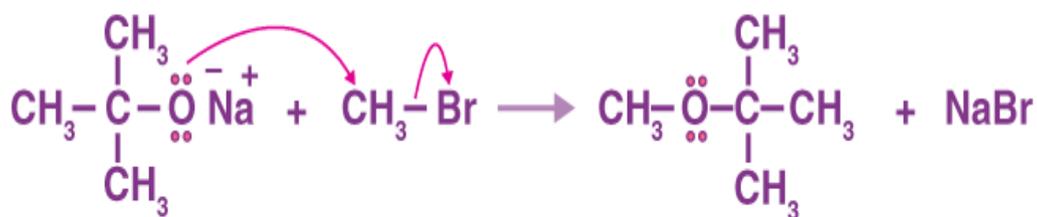
This method is used for the preparation of ethers having primary alkyl groups. To synthesize ethers in this way, the alkyl group should be unhindered and must be kept at a low temperature or else the reaction will give rise to alkenes.

Read More: [Electrophiles and Nucleophiles](#)

Williamson Synthesis

This is an important method for the preparation of symmetrical and asymmetrical ethers in laboratories. In Williamson synthesis, an alkyl halide is made to react with sodium alkoxide which leads to the formation of ether.

Example:



This reaction involves an S_N2 attack of an alkoxide ion on an alkyl halide. We know that alkoxides are very strong bases and they react steadily with alkyl halides, and thus they take part in elimination reactions.

In the case of primary alkyl halides, Williamson synthesis shows higher productivity.

Alkyl Halide with Dry Silver Oxide

When alkyl halide is treated with dry silver oxide, ether is produced



Ether Chemical Reactions

Of all the functional groups, ethers are the least reactive ones. Ether bonds are quite stable towards bases, oxidizing agents and reducing agents. But on the other hand, ethers undergo cleavage by reaction with acids. The prominent chemical reactions of ethers are as follows;

Cleavage of C-o Bonds in Ethers

Cleavage of C-O bonds in ether takes place in excess hydrogen halide (which are acidic) under extreme conditions like in concentrated acids (usually HBr and HI) and high temperatures.

For example, the reaction of dialkyl ether produces, initially, an alkyl halide and alcohol. This alcohol further reacts with halide to form a second mole of alkyl halide and water.

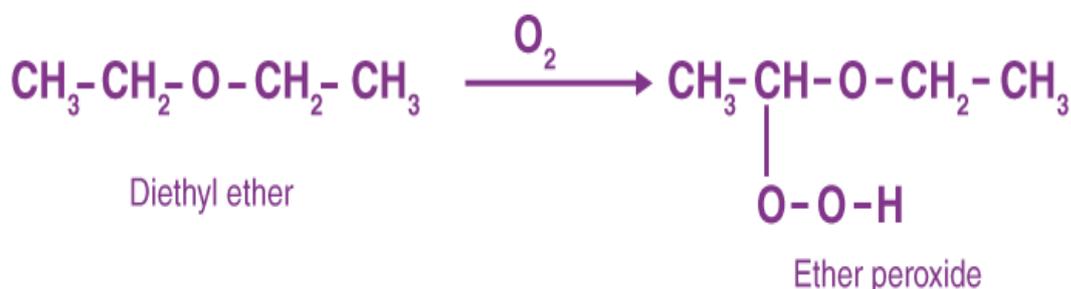


Reactivity of RX: $HI > HBr > HCl$

It is known that the oxygen atom of ether is basic, similar to the oxygen atom of alcohol. Thus, the initial reaction between ether and halide produces a protonated ether. The nucleophilic attack of halide ion on this protonated ether leads to cleavage of C-O bond.

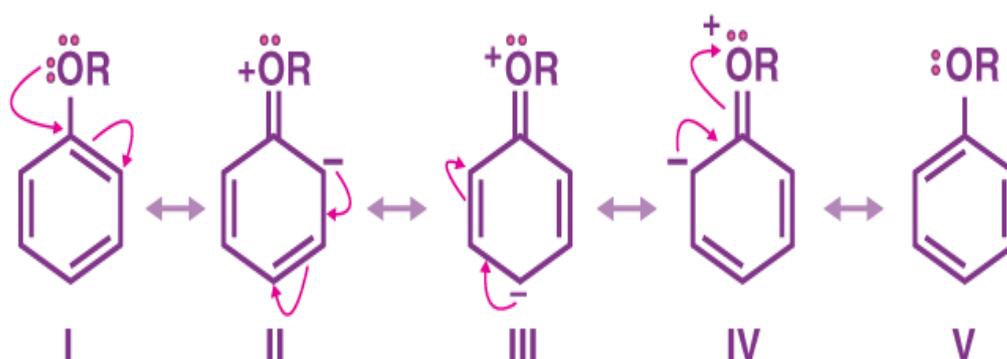
Formation of Peroxides

When ether is exposed to air in the presence of UV light or sunlight, peroxide linkage will be formed.



Electrophilic Substitution Reaction

Aromatic ethers activate their aromatic ring towards **electrophilic substitution reaction** just like in phenol because of the presence of alkoxy groups (-OR). This alkoxy group is *ortho* and *para* directing. In the case of aryl ethers, the lone pair of oxygen is involved in resonance with the benzene ring, and increases electron density in the ring at ortho and para positions. This, in turn, facilitates the attack of electrophile at ortho and para positions.

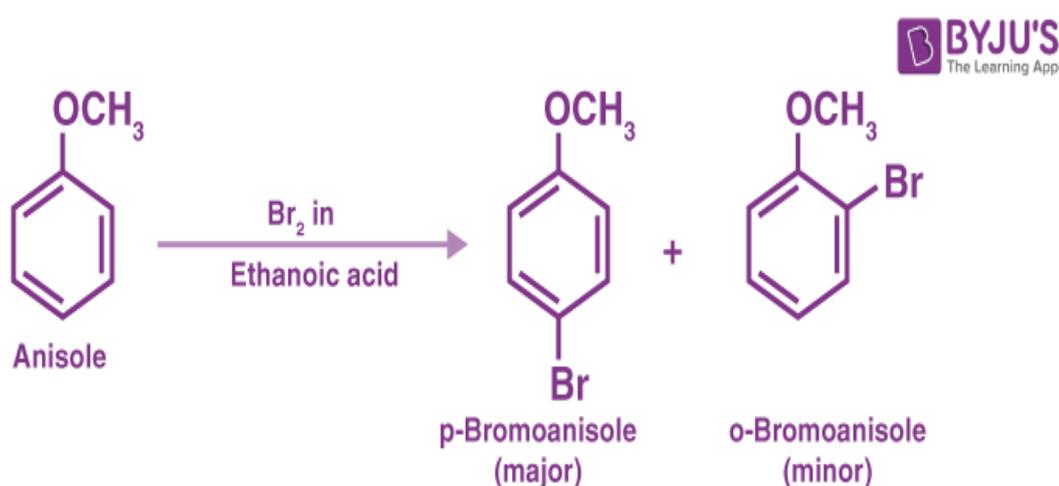


Some of the different types of electrophilic substitution reactions include:

1) Halogenation

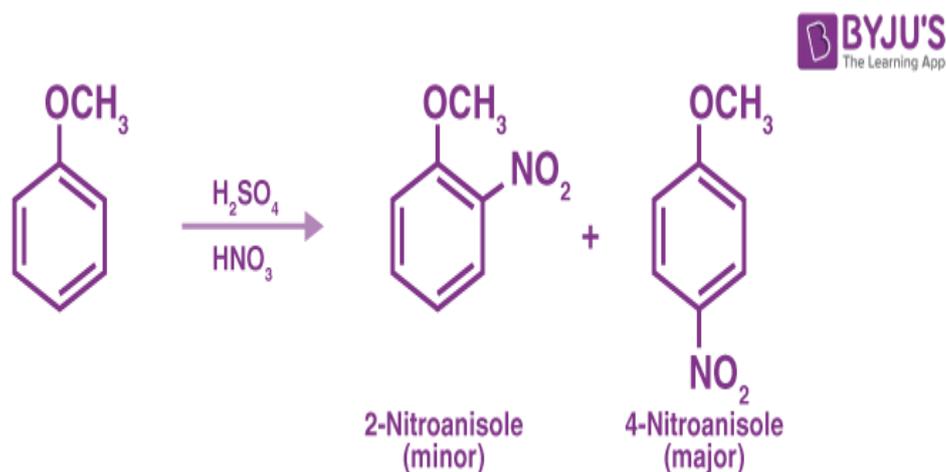
Alkyl groups undergo a substitution reaction with halides such as chlorine and bromine. This reaction yields halogenated ether in the absence of sunlight. In the presence of sunlight, it constitutes all the hydrogen atoms of ethers. In the benzene ring, phenyl alkyl ethers undergo usual **halogenation**. Example: anisole undergoes bromination with bromine

in ethanoic acid even in the absence of iron (III) bromide catalyst. This occurs because of the activation of the benzene ring by the methoxy group. Para isomer is obtained in 90% yield.



2) Nitration

The nitration of anisole is an electrophilic substitution reaction. Whenever anisole is nitrated with a mixture of concentrated nitric (HNO_3) and sulphuric (H_2SO_4) acids, it yields a mixture of ortho-Nitroanisole and para-Nitroanisole (major).

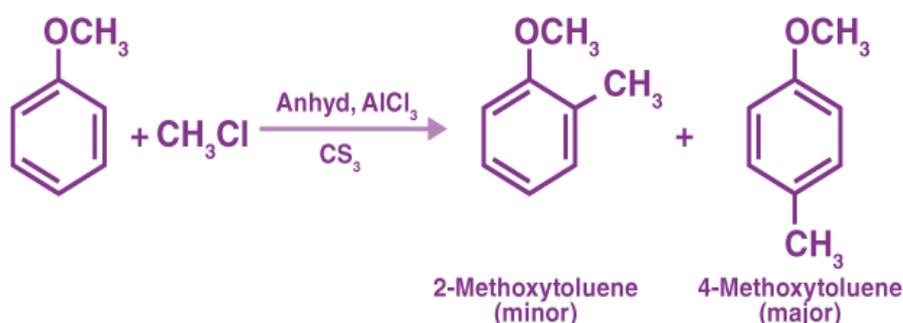


3) Friedel-Crafts Reaction

These are a couple of reactions created by Charles Friedel and James Crafts in 1877 to attach substituents to aromatic rings. These reactions are of two types:

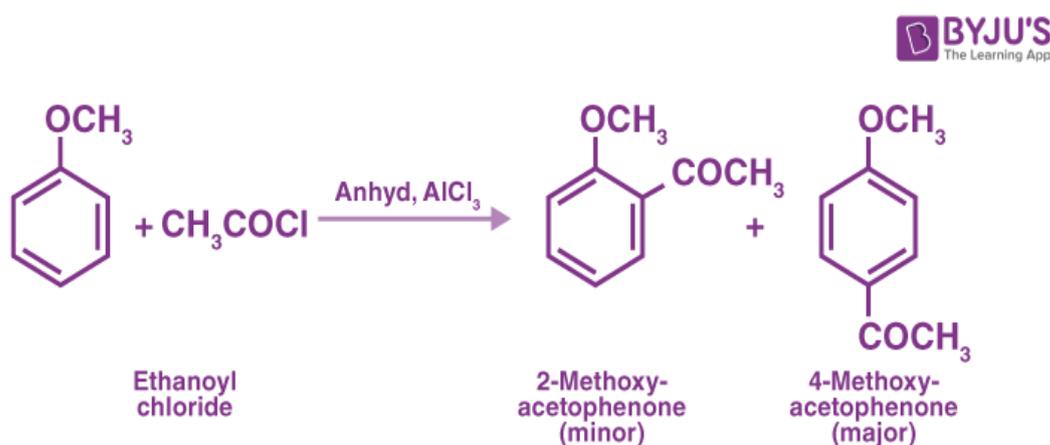
- Friedel-Crafts Alkylation Reaction:

Friedel-Crafts alkylation involves the alkylation of anisole with alkyl chloride and anhydrous aluminium chloride (a Lewis acid) as a catalyst.



- Friedel-Crafts Acylation:

This reaction involves the acylation of anisole with an acyl chloride in the presence of anhydrous aluminium chloride as a catalyst.



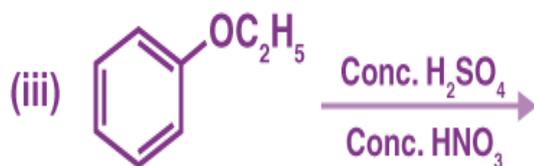
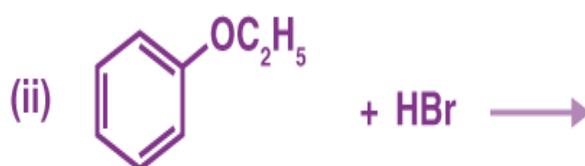
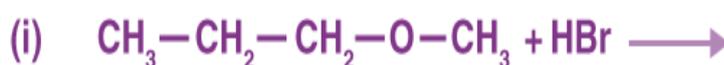
Both these reactions follow the electrophilic substitution reaction. To be precise, in both these reactions, the alkyl and acyl groups are introduced at ortho and para positions by reaction with an alkyl halide and acyl halide in the presence of anhydrous aluminium chloride.

Uses of Ether

- Dimethyl ether is used as a refrigerant and as a solvent at low temperatures.
- Diethyl ether is a common ingredient in anaesthesia used in surgeries.
- Ether is used along with petrol as a motor fuel.
- Diethyl ether is a common solvent for oils, gums, resins, etc.
- Phenyl ether can be used as a heat transfer medium because of its high boiling point.

Practice Questions

1. Why is the C-O-C bond in dimethyl ether 111.7°?
2. Alcohol has a higher boiling point than ethers of comparable molecular masses. Why?
3. Phenyl methyl ether reacts with HI to form phenol and iodomethane and not iodobenzene and methanol. Why?
4. An ether A ($C_5H_{12}O$), when heated with excess of hot concentrated HI, produced two alkyl halides which on hydrolysis forms compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.
5. Deduce the products of the following reactions:



6. Write the reactions of Williamson synthesis of 2-ethoxy-3-methyl pentane starting from ethanol and 3-methyl pentane-2-ol.