

12. ETHERS

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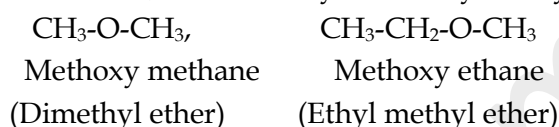
Learning outcomes

After the lesson, learners should be able to:

- ✓ Describe the nomenclature, classification and isomerism of ethers.
- ✓ Describe the preparation of aliphatic and aromatic ethers from Williamson's synthesis.
- ✓ Describe the physical properties of ethers.
- ✓ Explain the chemical properties of ethoxyethane with HI, Conc. HCl, Conc. H₂SO₄, air and Cl₂
- ✓ State important uses of ethers.

Introduction

Ethers are organic compounds in which an oxygen atom is bonded to two alkyl or aryl groups. They possess a general structure R-O-R', where R may be an alkyl or aryl group. E.g.,



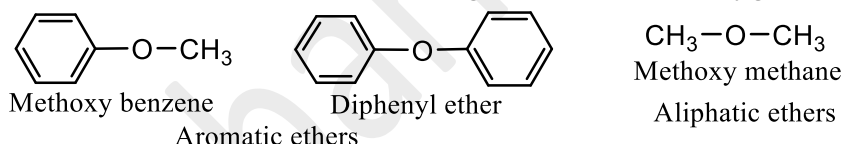
Classification

Ethers can be classified as **simple (symmetrical)** and **mixed (unsymmetrical)** ethers depending upon the nature of the alkyl or aryl groups. If R=R', it is called a simple ether, and if R≠R', it is called a mixed ether. E.g.,

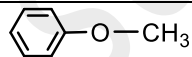
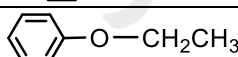
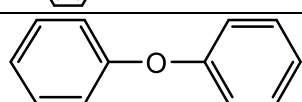


Ethers can also be classified as aliphatic or aromatic depending on the groups attached to the O atom.

- **Aliphatic ether:** both groups are alkyl groups.
- **Aromatic ether:** at least one group attached to oxygen is an aryl group. e.g.,



Aromatic ethers

Formula	IUPAC name	Common name
	methoxybenzene	methyl phenyl ether or anisole
	ethoxybenzene	ethyl phenyl ether or phenetole
	phenoxybenzene	diphenyl ether

Nomenclature

The IUPAC names of ethers are written according to general IUPAC rules and follow the general form **alkoxyalkane**.

Choose the longer carbon chain as the parent alkane. The shorter group attached through oxygen is named as an alkoxy group.

For example:



- longer group = propane
- shorter group + O = methoxy
- name = **1-methoxypropane**

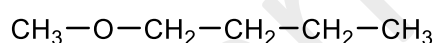
The common names of simple and mixed ethers take the general form **dialkyl ether** and **alkyl alkyl ether (listed in alphabetical order)**, respectively.

Structure	IUPAC name	Common name
$\text{CH}_3\text{-O-CH}_3$	Methoxymethane	Dimethyl ether
$\text{CH}_3\text{CH}_2\text{-O-CH}_3$	Methoxyethane	Ethyl methyl ether
$\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$	Ethoxyethane	Diethyl ether
$\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{CH}_3$	1-methoxypropane	Methyl n-propyl ether
$\begin{array}{c} \text{CH}_3\text{-CH-O-CH}_3 \\ \\ \text{CH}_3 \end{array}$	2-methoxypropane	Isopropyl methyl ether

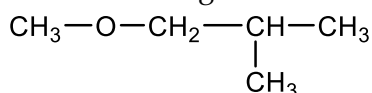
Isomerism

Chain isomerism

Chain isomers have the same molecular formula but different arrangements of the carbon chain. E.g., the molecular formula $\text{C}_5\text{H}_{12}\text{O}$ can represent the following two ethers.



1-methoxybutane



1-methoxy-2-methylpropane

Functional isomerism

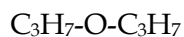
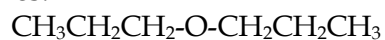
(refer to 10. alcohols chapter)

Metamerism

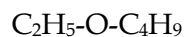
Like ketones and secondary amines, ethers also show metamerism.

Isomers that differ in the distribution of carbon atoms (alkyl groups) on either side of the functional group are called metamers.

Examples:



1-propoxypropane



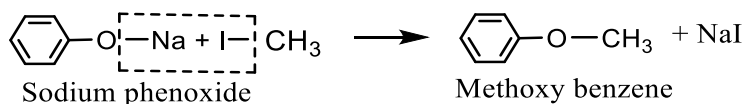
1-ethoxybutane

Preparations

1. **From Haloalkanes (Williamson's etherification process)** (studied in properties of Haloalkanes already)

2. **Preparation of methoxybenzene (anisole) by Williamson's synthesis**

In Williamson synthesis, an alkoxide or phenoxide ion reacts with a suitable alkyl halide to form an ether.



Williamson synthesis works best with primary alkyl halides because secondary and tertiary alkyl halides can undergo elimination reactions

Physical Properties

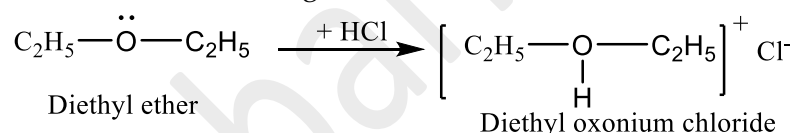
1. **Lower ethers** such as dimethyl ether are **gases** at room temperature, while most **higher ethers** are **colourless, volatile liquids with characteristic odours**.
2. Boiling points of ethers are **lower than those of alcohols and carboxylic acids** with comparable molecular masses. Because ether molecules cannot form hydrogen bonds with one another.
3. They are generally **highly flammable**.
4. They are **slightly soluble in water** but generally **soluble in alcohol and other organic solvents**.

Chemical Properties

[A] Reaction due to ethereal oxygen

1. **Reaction with cold concentrated HCl and H₂SO₄** (*formation of oxonium salt*)

Ethers react with strong acids to form oxonium salts.



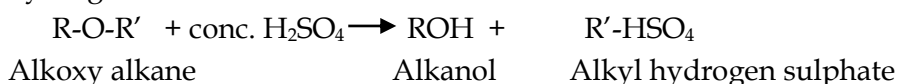
The salt is stable at low temperatures in a strongly acidic solution. On dilution with water, the oxonium salt decomposes back to ether and acid.

Why are ethers Lewis bases?

The oxygen atom has two lone pairs of electrons that can be donated to a proton or other electron-deficient species.

2. **Reaction with hot concentrated H₂SO₄**

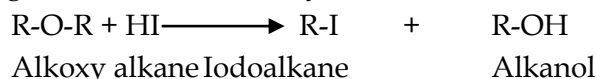
On heating with concentrated H₂SO₄, ethers can undergo cleavage to form an alcohol and an alkyl hydrogen sulfate.



[B] Reaction involving cleavage of C-O bond

3. Reaction with HI

When ethers are heated with conc. halogen acids (especially HI and HBr), the C-O bond is cleaved, yielding an alcohol and an alkyl halide.



If hydroiodic acid is in excess, the alcohol produced also gets converted into an Iodoalkane.

When anisole is heated with HI, cleavage occurs at the alkyl-oxygen bond, giving phenol and methyl iodide **NOT methanol and iodobenzene**.

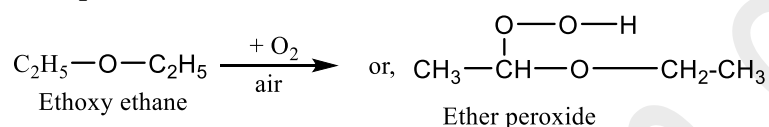
 **Why does HI cleave anisole on the alkyl side?**

Because $\text{S}_{\text{N}}2$ attack occurs at the alkyl carbon, whereas the aryl C-O bond is not readily cleaved by $\text{S}_{\text{N}}2$

[C] Reactions involving alkyl group

4. Reaction with Air

When exposed to air for a long time in light, the oxygen in the air slowly reacts with the ether to form peroxides.



Explosion Hazard & Prevention

Ether peroxides are thermally unstable and explosive! Distilling old samples of ethers containing accumulated peroxides can cause severe explosions.

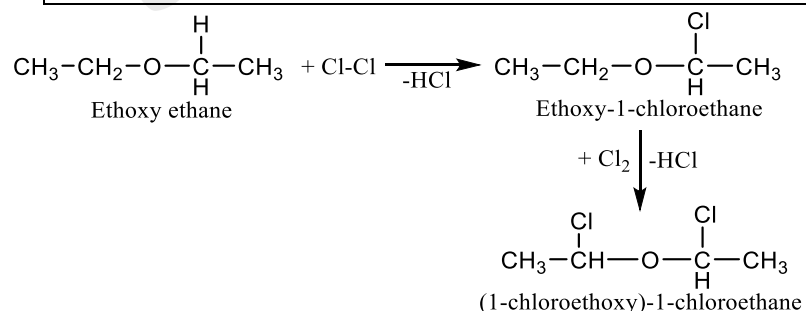
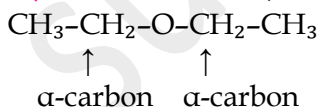
Prevention: Keeping iron wire or ferrous salts in the bottle prevents peroxide formation because atmospheric oxygen combines preferentially with iron:



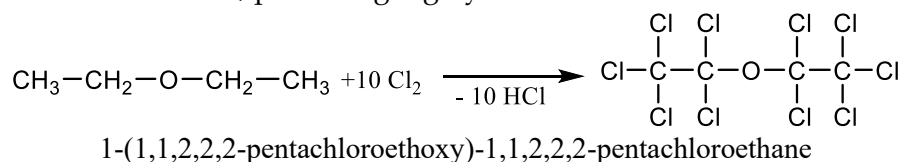
5. Reaction with Cl_2

When ether is chlorinated **in the absence of sunlight**, substitution by halogen preferably takes place at the α position.

 Remember: here, α -carbon = carbon directly attached to oxygen.

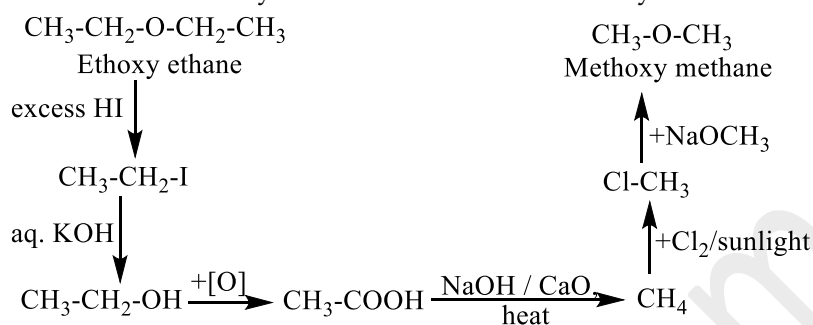


★ Higher-level concept: In the presence of sunlight and excess chlorine, further chlorination can occur, producing highly chlorinated derivatives.



Worked Example

1. How is Ethoxyethane converted to Methoxymethane?



Uses of Ethoxyethane

- As a solvent for oils, resins, petroleum products, etc.
- Solvent for the extraction of compounds in labs and industries
- As a solvent/reaction medium, e.g., in preparation of Grignard's reagent, Wurtz reaction, etc.
- Historically used as a general anaesthetic, but is no longer used as safer anaesthetics are available.

Uses of Anisole

- For making perfumes
- In pharmaceuticals.
- Starting material for organic synthesis.

Quick Revision Summary

- Definition & Formula: Ethers possess the general formula $R-O-R'$.
- Acyclic saturated monohydric alcohols and ethers can have the same general molecular formula, $C_nH_{2n+2}O$, and therefore can be functional isomers.
- **Isomerism:** Ethers may show chain isomerism, functional isomerism and metamerism
- Classification: Divided into symmetrical ($R=R'$) and unsymmetrical ($R \neq R'$) as well as aliphatic and aromatic ethers.
- Nomenclature: Systematically named as Alkoxyalkanes (smaller group = alkoxy, larger group = alkane).
- Preparation: Williamson's synthesis ($R-X + R'-ONa \rightarrow R-O-R' + NaX$) is an important method for preparing simple, mixed, and aromatic ethers such as Anisole.
- Physical Properties: Lower boiling points than alcohols due to the absence of hydrogen bonding. Highly volatile and flammable.
- Chemical Reactions:
 - Oxygen lone pairs form oxonium salts with cold, conc. acids.
 - C-O bond cleavage occurs with HI (hot) to form alkyl iodides.
 - Anisole + HI produces Phenol and Methyl Iodide.
 - Prolonged exposure to air forms explosive peroxides (prevented with iron wire).
 - Chlorination yields substituted halo-ethers depending on dark vs. light conditions.

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