12. Ethers

🎯 Learning outcomes

After the lesson, learners should be able to:

- ✓ Describe the nomenclature, classification and isomerism of ethers.
- ✓ Show the preparation of aliphatic and aromatic ethers from Williamson's synthesis.
- ✓ State physical properties of ethers.
- ✓ Explain the chemical properties of ethoxyethane with HI, Conc. HCl, Conc. H_2SO_4, air and Cl_2
- ✓ State important uses of ethers.

Introduction

Ethers are a class of organic compounds characterised by an oxygen atom 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.,

CH_3-O-CH_3,	CH_3-CH_2-O-CH_3
Methoxy methane	Methoxy ethane
(Dimethyl ether)	(Ethyl methyl ether)

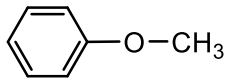
These can be considered the derivatives of alkanes with one -H substituted by –OR group.

Classification

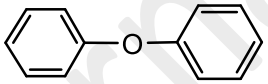
Ethers can be classified as **simple (symmetrical)** and **mixed (unsymmetrical)** ethers depending upon the nature of the alkyl or aryl groups. If R=R′, it's called a simple ether, and if R≠ R', it's called a mixed ether. E.g.,

CH_3CH_2-O-CH_2CH_3,	CH_3CH_2-O-$CH_2CH_2CH_3$
Ethoxy ethane	1-ethoxy propane
(Simple ether)	(Mixed ether)

Ethers can also be classified as aliphatic and aromatic ethers depending upon the R. e.g.,



Methoxy benzene



Diphenyl ether

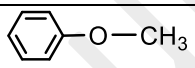
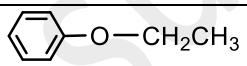
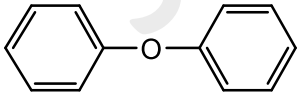
Aromatic ethers

$CH_3—O—CH_3$

Methoxy methane

Aliphatic ethers

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 the ethers are written by general rules of IUPAC, which take the general form **Alkoxy alkane**.

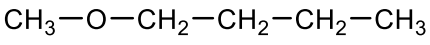
The common names of simple and mixed ethers take the general form **Dialkyl ether** and **Alkyl alkyl ether (listed in alphabetical order),** respectively.

Structure	IUPAC name	Common name
CH_3-O-CH_3	Methoxymethane	Dimethyl ether
CH_3CH_2-O-CH_3	Methoxyethane	Ethyl methyl ether
CH_3CH_2-O-CH_2CH_3	Ethoxyethane	Diethyl ether
CH_3-O-$CH_2CH_2CH_3$	1-methoxypropane	Methyl n-propyl ether
CH_3-CH(-CH_3)-O-CH_3	2-methoxypropane	Isopropyl methyl ether

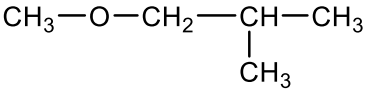
Isomerism

Chain isomerism

Isomers that differ only in chain are called chain isomers. E.g., $C_5H_{12}O$



1-methoxybutane



1-methoxy-2-methylpropane

Functional isomerism

Ethers show functional isomerism with alcohols.

E.g. CH_3CH_2OH CH_3-O-CH_3 (C_2H_6O)
Ethanol Methoxy methane;

$CH_3CH_2CH_2OH$ CH_3CH_2-O-CH_3 (C_3H_8O)
Propan-1-ol Methoxy ethane etc.

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:

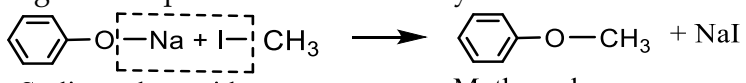
$CH_3CH_2CH_2$-O-$CH_2CH_2CH_3$ CH_3CH_2-O-$CH_2CH_2CH_2CH_3$
1-propoxypropane 1-ethoxybutane

Preparations

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

2. **Preparation of Methoxybenzene (Anisole)** By Williamson's synthesis

This method is generally used for the preparation of aromatic ethers. Alkyl aryl ethers are prepared by reacting sodium phenoxide with an alkyl halide.



Sodium phenoxide Methoxy benzene

Physical Properties

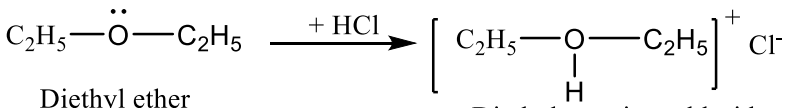
1. **Dimethyl ether and ethyl methyl ether are gases,** but others are **colourless, volatile liquids** with a **pleasant odour**.
2. Boiling points of ethers are **lower than alcohols and carboxylic acids** with comparable molecular masses.
3. They are generally **highly inflammable**.
4. They are **sparingly soluble in water** but more **soluble in alcohol and other organic solvents**.

Chemical Properties

[A] Reaction due to ethereal oxygen

1. Action with cold conc. HCl and H_2SO_4 *(formation of oxonium salt)*

Since ethers can behave as **weak Lewis bases**, they dissolve in cold and conc. Mineral acids to form oxonium salt.



Diethyl ether — Diethyl oxonium chloride

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.

2. Action with Conc. H_2SO_4

When heated with hot and conc. H_2SO_4, alcohol and alkyl hydrogen sulphate are formed.

$$R\text{-}O\text{-}R + \text{conc. } H_2SO_4 \longrightarrow ROH + R\text{-}HSO_4$$

Alkoxy alkane — Alkanol — Alkyl hydrogen sulphate

[B] Reaction involving cleavage of C-O bond

3. Action with HI

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

$$R\text{-}O\text{-}R + HI \longrightarrow R\text{-}I + R\text{-}OH$$

Alkoxy alkane — Iodoalkane — Alkanol

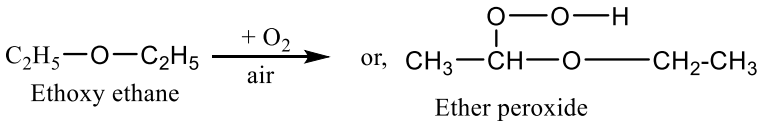
If hydroiodic acid is in excess, the alcohol produced also gets converted into an Iodoalkane.

When anisole is heated with HI, the products are always phenol and methyl iodide, *NOT methanol and iodobenzene.*

[C] Reactions involving alkyl group

3. Action with Air

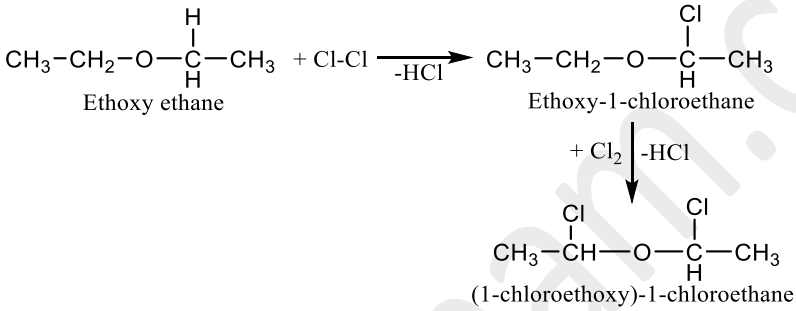
When exposed to air for a long time in light, the oxygen of air slowly reacts with the ether to form peroxides.



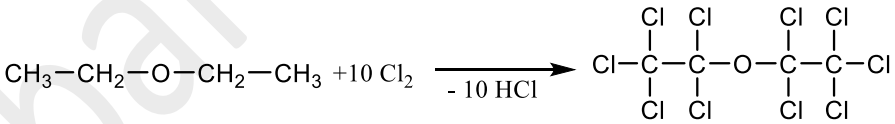
> ⚠ **Explosion Hazard & Prevention**
>
> Ether peroxides are thermally unstable and explosive! Distilling old samples of ethers containing accumulated peroxides can cause severe explosions.
>
> Prevention: Keeping iron wire or ferrous salts in the bottle prevents peroxide formation because atmospheric oxygen combines preferentially with iron:
>
> $2\,Fe + O_2 \longrightarrow 2FeO$

4. Action with Cl_2

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



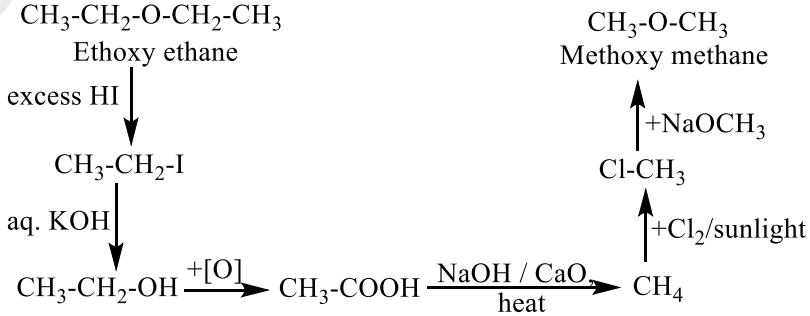
But if the reaction is carried out **in the presence of sunlight** and excess chlorine, all the hydrogen atoms are substituted.



1-(1,1,2,2,2-pentachloroethoxy)-1,1,2,2,2-pentachloroethane

Worked Example

1. How is Ethoxyethane converted to Methoxymethane?



Uses of Ethoxyethane

- As solvent (for oils, resins, petroleum, etc.)
- Solvent for the extraction of compounds in labs and industries
- As a reaction medium, e.g., in preparation of Grignard's reagent, Wurtz reaction, etc.
- As an anaesthetic (historical use)
- As a coolant.

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'. They are functional isomers of monohydric alcohols ($C_nH_{2n+2}O$).

• Classification: Divided into symmetrical (R=R') and unsymmetrical (R≠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 –→ R–O–R' + NaX) is the standard method for preparing simple, mixed, and aromatic ethers (like Anisole).

• Physical Properties: Lower boiling points than alcohols due to absence of hydrogen bonding. Highly volatile and inflammable.

• 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.

*** ... *** https://subarnam.com.np/