Ethers & Epoxides

Chapter 5

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Chem 340- 2nd semester 1437-1438
Chapter’s out line

Ethers

Definition; General formula; Classification and Types

Nomenclature
- Common Names.
- IUPAC Naming.

Physical Properties

General methods of preparation of ethers
A- Dehydration of Alcohols.
B- Williamson Synthesis.

Reactions of ethers

Cyclic Ethers; “Epoxides”

Definition

IUPAC Naming

General methods of preparation of Epoxides

Reaction of Epoxides.
Definition

Ether is a class of organic compounds that contain an ether group — (an oxygen atom connected to two alkyl or aryl groups) — of general formula \( R-O-R' \).

- The functional group of an ether is an oxygen atom bonded to two carbon atoms.
- In dialkyl ethers, the oxygen is \( sp^3 \) hybridized with bond angles of approximately 109.5°.

For the simplest ether, Dimethyl ether

The C-O-C bond angle is 110.3°
Classification of Ethers

(I) Aliphatic Ethers

Aliphatic ethers are those in which R and R' are both alkyl groups.

Example:

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}_-\text{CH}_3
\]

Butylmethylether

(II) Aromatic Ethers

Aromatic ethers are those in which either one or both R and R' are aryl groups.

Examples:

\[
\begin{align*}
\text{CH}_3\text{-O-} & \quad \text{C}_6\text{H}_5\text{-O-} \quad \text{C}_6\text{H}_5 \\
\text{Methyl phenylether} & \quad \text{Diphenylether}
\end{align*}
\]
Types of Ethers

1- Simple Ethers or Symmetrical Ethers

If $R'$ are the same the ethers are called “simple ethers”

Examples

- $\text{CH}_3\text{-O-CH}_3$  \hspace{1cm} $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$

  Dimethyl ether  \hspace{1cm}  Diethyl ether

2- Mixed Ethers or Unsymmetrical Ethers

Examples

- $\text{CH}_3\text{-O-CH}_2\text{-CH}_3$

  Ethylmethyl ether
Nomenclature: A. Common Names.

✓ In the Common system the ethers are named according to the alkyl group bonded to the oxygen atoms.

✓ The two-alkyl groups bonded to the functional group (-O-) are written alphabetically followed by the word ether.

**Examples**

- **CH\(_3\) - O - C\(_2\)H\(_5\)**
  - Ethyl methyl ether

- **\(\text{C}_6\text{H}_4\) - O - CH\(_2\)CH\(_3\)**
  - Ethyl phenyl ether

- **\(\text{O} - \text{C} - \text{H}_2\text{CH}_3\)**
  - Diethyl ether

- **\(\text{O} - \text{C} - \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\)**
  - Tert-butyl methyl ether
B. IUPAC System For Ethers

- The names for ethers are based on the alkane name of the longest chain attached to the oxygen.
- The shorter alkyl group and the oxygen are named as an alkoxy group attached to the longer alkane.

They are named as alkoxyalkanes.

✓ Numbering the longer alkane gives 1-methoxypropane.

<table>
<thead>
<tr>
<th>Alkyl Group</th>
<th>Name</th>
<th>Alkoxy Group</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃-</td>
<td>Methyl</td>
<td>CH₃O-</td>
<td>Methoxy</td>
</tr>
<tr>
<td>CH₃CH₂-</td>
<td>Ethyl</td>
<td>CH₃CH₂O-</td>
<td>Ethoxy</td>
</tr>
<tr>
<td>(CH₃)₂CH-</td>
<td>Isopropyl</td>
<td>(CH₃)₂CHO-</td>
<td>Isopropoxy</td>
</tr>
<tr>
<td>(CH₃)₃C-</td>
<td>tert-Butyl</td>
<td>(CH₃)₃CO-</td>
<td>tert-Butoxy</td>
</tr>
<tr>
<td>C₆H₅-</td>
<td>Phenyl</td>
<td>C₆H₅O-</td>
<td>Phenoxy</td>
</tr>
</tbody>
</table>
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Examples

(a) Methoxy cyclohexane

(b) 1-Methoxy-2-methyl propane

(c) Propoxy butane

(d) 1-Ethoxy-1-methyl Cyclohexane
Physical Properties

1. Solubility of Ethers

- Ethers containing up to 3 carbon atoms are soluble in water, due to their hydrogen bond formation with water molecules.

- The solubility decreases with increase in the number of carbon atoms.

- The relative increase in the hydrocarbon portion of the molecule decreases the tendency of H-bond formation.
2. Boiling Points of Ethers

- Ethers have an O atom, but there is no H attached.
- Thus, hydrogen bonds cannot form between ether molecules.

Ether molecules cannot form hydrogen bonds with other ether molecules.

CH₃CH₂CH₂CH₃
- Butane
- (butane)
- M.W. = 58
- b.p. = - 0.5°C

CH₃—O—CH₂CH₃
- Methoxyethane
- (ethyl methyl ether)
- M.W. = 60
- b.p. = 7.9 °C

CH₃CH₂CH₂CH₂OH
- 1-Propanol
- (Propyl alcohol)
- M.W. = 60
- b.p. = 97.2°C
General methods of preparation of ethers

A- Dehydration of Alcohols.

• This method is used for **industrially** preparation for symmetric ethers.

• In the presence of **acid**, two molecules of **an alcohol** may lose water to form an **ether**.

**General Equation**

\[
R'\text{--OH} + R''\text{--OH} \xrightarrow{H^+, \text{heat /}140\degree C} R'\text{--O}--R'' + H_2O
\]

**Examples**

1. \(2 \text{ CH}_3\text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 140\degree C} \text{CH}_3\text{--O--CH}_3 + \text{H}_2\text{O}\)

2. \(2 \text{ CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 140\degree C} \text{CH}_3\text{CH}_2\text{--O--CH}_2\text{CH}_3 + \text{H}_2\text{O}\)
Note: The dehydration of 2° and 3° alcohol is unsuccessful to get ethers as alkenes are formed easily.

2°, Sec-alcohol, (No ether is formed)

\[ \text{Isopropyl alcohol} \rightarrow \text{propene} \]

\[ \text{CH}_3\text{CCH}_3 \xrightarrow{\text{H}_2\text{SO}_4, \text{heat}} \text{CH}_3\text{CCH} = \text{CH}_2 + \text{H}_2\text{O} \]

3°, t-alcohol, (No ether is formed)

\[ \text{Tert-Butyl alcohol} \rightarrow \text{Iso-Butylene} \]

\[ \text{CH}_3\text{CCHOH} \xrightarrow{\text{H}_2\text{SO}_4, \text{heat}} \text{CH}_3\text{CCH} = \text{CH}_2 + \text{H}_2\text{O} \]
B- Williamson Synthesis.

The reaction of a sodium alkoxide; $\text{RONa}$ or a sodium phenoxide; $\text{ArONa}$ with an alkyl halide to form an ether is known as the **Williamson synthesis**.

- It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers.

- The reaction involves *nucleophilic substitution* of an alkoxide ion for a halide ion.

**General Equations**

$$
\text{R—O}^- \ + \ \text{R'}—\text{X} \quad \rightarrow \quad \text{R—O—R'} \ + \ \text{NaX}
$$

*Sodium alkoxide*  *Alkyl halide*  *Alkyl ether*

$$
\text{Ar—O}^- \ + \ \text{R'}—\text{X} \quad \rightarrow \quad \text{Ar—O—R'} \ + \ \text{NaX}
$$

*Sodium phenoxide*  *Alkyl halide*  *Aryl ether*
Examples

\[
\text{CH}_3\text{CH}_2\text{Br} + \text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+ \rightarrow \text{CH}_3\text{CH}_2\text{O}^-\text{CH}_2\text{CH}_3 + \text{NaBr}
\]

\[
\text{O}^-\text{Na}^+ + \text{CH}_3\text{I} \rightarrow \text{O}^-\text{CH}_3 + \text{NaI}
\]

⚠️ Note that

✓ Good results are obtained if the alkyl halide is primary (1°).

✓ If a secondary (2°) or tertiary alkyl halide (3°) is used, an alkene is the only reaction product and no ether is formed.
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**Examples**

2° alkyl halide:

\[ \text{H}_3\text{C}\text{CH} - \text{Br} + \text{CH}_3\text{CH}_2\text{CH}_2\text{-ONa} \rightarrow \text{No Ether Product} \]

3° alkyl halide:

\[ \text{H}_3\text{C}\text{C} - \text{Br} + \text{CH}_3\text{-ONa} \rightarrow \text{An Alkene Product} \]

\[ \text{CH}_3\text{CH} = \text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \]

\[ \text{H}_3\text{C}\text{C} = \text{CH}_2 + \text{CH}_3\text{OH} \]
The Willamson Ether Synthesis Reaction Mechanism

- The reaction follows the $S_{N2}$ pathway.
- Best for methyl and primary alkylhalides.
- Solvents is usually the conjugate acid of the alkoxide.
- Bond formed: C-O
- Bond broken: C-X

Note that

- $X$ may be (Cl, Br, I or any good leaving group).
Reactions of Ethers

- **Ethers** are comparatively stable non-reactive compounds.

- The ether linkage is quite stable towards bases, oxidizing agents, and reducing agents.

- **Ethers** undergo just one kind of basic chemical reaction: cleavage by acids.

### Cleavage of Ethers by Acides

- When ethers are protonated they can undergo substitution reactions with strong acids $\text{HX}$, $X$ could be; I, Br or Cl.

### Reactivity: $\text{HI} > \text{HBr} >> \text{HCl}$

⚠️ **Note that**

Cleavage by concentrated $\text{HCl}$ is less effective, primarily because $\text{Cl}^-$ is a weaker nucleophile in water than either I$^-$ or Br$^-$. 
Cleavage of *Ethers* by HI or HBr

- Ethers are cleaved by HX to an alcohol and a haloalkane.
- Cleavage requires both a strong acid and a good nucleophile.

**General Equation**

\[
R-\overset{\text{O}}{\text{R'}} + \overset{\text{HX}}{\text{H}}_{\text{X}} \overset{\text{Heat}}{\rightarrow} R-\overset{\text{X}}{\text{R'}} + \overset{\text{OH}}{\text{R'}}
\]

*Ether*  \(\overset{\text{Conc. acid}}{\text{HX}}\)  *Alkyl halide*  \(\overset{\text{alcohol}}{\text{R'}}\)

**Specific Example**

- **Dimethyl ether**  + Hydrogen bromide  \(\overset{\text{Heat}}{\rightarrow}\)  Methyl bromide  + Methyl alcohol

- **Methyl isopropyl ether**  + Hydrogen iodide  \(\overset{\text{Heat}}{\rightarrow}\)  Methyl iodide  + isopropyl alcohol
Point of cleavage:

(i) If both the alkyl groups are primary or secondary, the smaller alkyl group gets converted to the alkyl halide predominantly.

\[ \text{CH}_3-\text{O} - \text{C}_2\text{H}_5 + \text{HI} \rightarrow \text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{OH} \]

(ii) If one of the alkyl group is tertiary, the point of cleavage is such that the tertiary alkyl halide is formed as the major product.

Note: If two or more equivalents of acid are used further dehydration can occur on formed alcohols which may react further to form a second mole of alkyl halide.

**Example**

\[ \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + 2 \text{ HBr} \xrightarrow{\text{Heat}} 2 \text{ CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O} \]

*Diethyl ether* *Excess Hydrogen bromide* *Ethyl bromide*
(iii) In case of **phenolic ether** the cleavage occurs with the formation of phenol and alkyl halide.

✓ **Alkyl aryl ethers** are cleaved at the alkyl oxygen bond due to the **low reactivity** of aryl oxygen bond.

**General Equation**

\[
\text{C} - \text{O} + \text{H-X} \rightarrow \text{C} - \text{OH} + \text{X}
\]

\[X = \text{Br} \text{ or } \text{I}\]

**Example**

(a) **Ethyl phenyl ether**

\[
\text{O}^{\text{CH}_2\text{CH}_3} + \text{HBr} \xrightarrow{\text{H}_2\text{O, Heat}} \text{O}^{\text{CH}_2\text{CH}_3} + \text{CH}_3\text{CH}_2\text{Br}
\]

(b) **Methyl phenyl ether**

\[
\text{O}^{\text{OCH}_3} + \text{HI} \xrightarrow{\text{H}_2\text{O/Heat}} \text{O}^{\text{OCH}_3} + \text{CH}_3\text{I}
\]
Home Work

Q1. Arrange the following compounds in order of increasing solubility in water.

1 2 3

Q2. Show the combination of alcohols and haloalkane that can be best used to prepare each ether by Williamson ether synthesis.

a) b)
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**Epoxides**

**Epoxides or Cyclic ethers**

- Epoxides are cyclic ethers in which the ether oxygen is part of a three-membered.

- The simplest and the most important epoxide is ethylene oxide.

![Ethylene oxide](images/ethylene_oxide.png)
General methods of preparation of Epoxides

Peroxide Epoxidation

Epoxides are often prepared from reacting with organic peroxy acids ("peracids") ex; CH₃C(O)OOH in a process called epoxidation.

General equation

\[ RCH=CHR' + R''CO-\text{OH} \xrightarrow{\text{MCPBA}} RCH-\text{CHR}'+ + R''\text{COOH} \]

Peroxy acid

Epoxide

Note that: MCPBA = m-Chloroperoxybenzoic acid
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Reaction of Epoxides.

\[
\text{H}_2\text{O}/\text{H}^+ \quad \rightarrow \quad \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \text{OH} \quad \text{OH} \end{array}
\]

1,2-Ethandiol

\[
\text{CH}_3\text{OH}/\text{H}^+ \quad \rightarrow \quad \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \text{OH} \quad \text{OCH}_3 \end{array}
\]

2-Methoxyethanol

\[
\text{HX}/\text{H}^+ \quad \rightarrow \quad \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \text{OH} \quad \text{X} \end{array}
\]

Ethylene halohydrin

2-Halo ethanol

\[
\text{RMgX/dryether} \quad \rightarrow \quad \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \text{OH} \quad \text{R} \end{array}
\]

Alkyl alcohol
Home Work

Q.1 Choose the correct answer:

1- The reaction of two moles of HI with dimethylether gives:
   o Ethyl iodide and ethanol
   o Two moles of methyl iodide
   o Two moles of ethanol
   o Two moles of ethyl iodide

2- The compound with highest boiling point is:
   o Ethanol
   o Dimethyl ether
   o Ethane
   o Cloroform
3- The product of the following reaction is:

\[
\begin{array}{c}
\text{O} \\
\text{H}_3\text{C} \\
\text{HO} \\
\text{OH} \\
\text{O} \\
\text{H}_3\text{C} \\
\text{HO} \\
\text{O} \\
\text{CH}_3\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{CH}_3 \\
\end{array}
\]

4- The major product of the following reaction is:

\[
\begin{array}{c}
\text{O} \\
\text{H}_3\text{C} \\
\text{HO} \\
\text{O} \\
\text{CH}_3\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{CH}_3 \\
\end{array}
\]

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