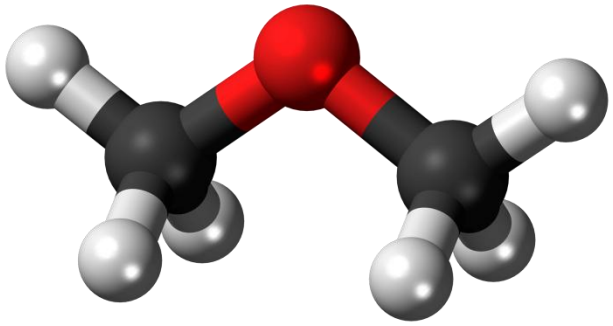
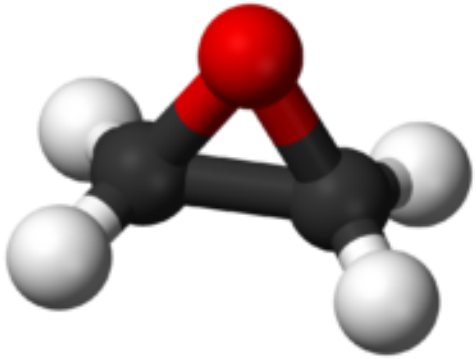
جامعة الملك سعود
King Saud University

Ethers & Epoxides

Chapter 5





Dr. Seham ALTERARY

Chapter's out line

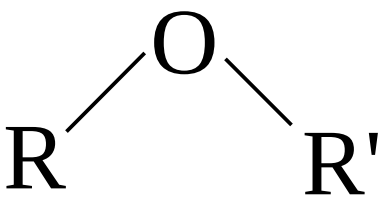
Ethers

- 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.

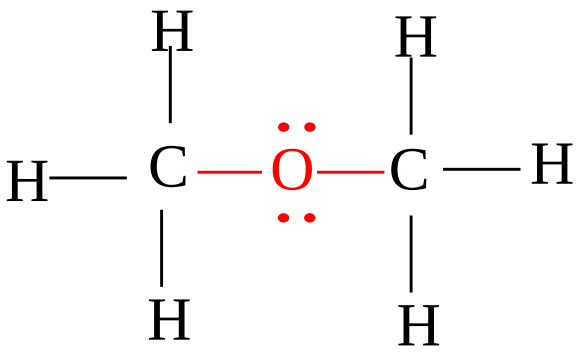
Definition



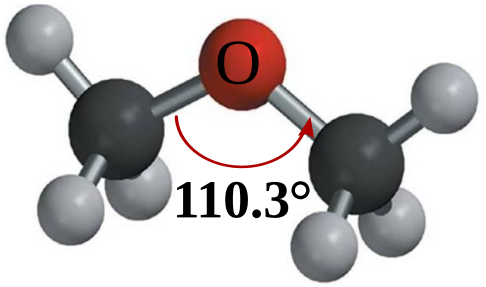
Ether is a class of organic compounds that contain an ether group — (an oxygen atom connected to two alkyl or aryl groups) — of general formula R–O–R.

- 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



Lewis structure



Ball and stick model

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:

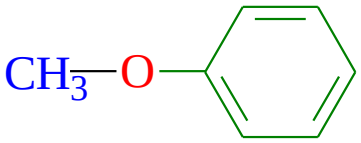
$$CH_3CH_2CH_2CH_2-O-CH_3$$

Butylmethylether

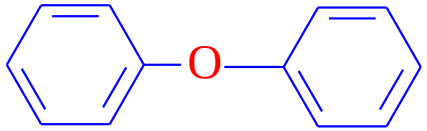
(II) *Aromatic Ethers*

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

Examples:



Methyl phenylether



$C_6H_5-O-C_6H_5$

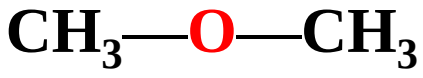
Diphenylether

Types of Ethers

1- Simple Ethers or Symmetrical Ethers

If **R'** are the same the ethers are called "simple ethers"

Examples

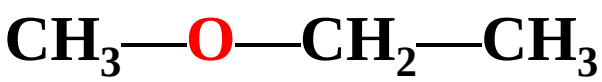


Dimethyl ether

Diethyl ether

2- Mixed Ethers or Unsymmetrical Ethers

Examples



Ethylmethyl ether

Nomenclature: A. Common Names.

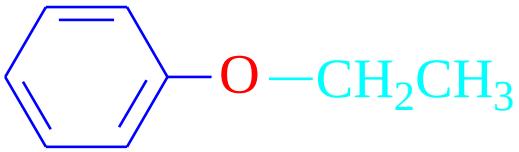
✓In the Common system the ethers are named **according to *the alkyl group bonded to the oxygen atoms***.

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

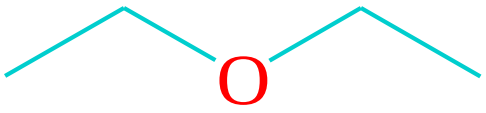
Examples

CH_3 - **O** - C_2H_5

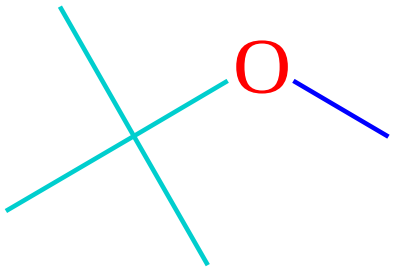
Ethyl methyl ether



Ethyl phenyl ether



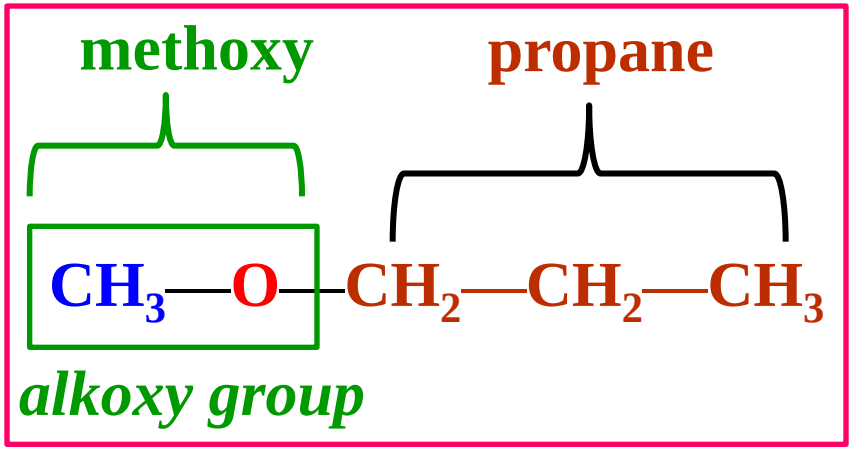
Diethylether



Tert-butylmethyl 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.***

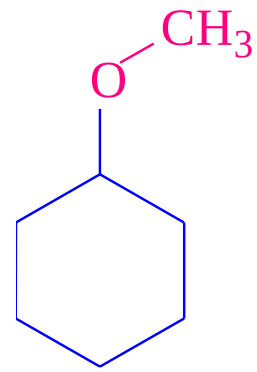
✓**Numbering the longer alkane gives**

1-methoxypropane.

Alkyl Group	Name	Alkoxy Group	Name
CH_3-	Methyl	CH_3O-	Methoxy
CH_3CH_2-	Ethyl	CH_3CH_2O-	Ethoxy
$(CH_3)_2CH$-	Isopropyl	$(CH_3)_2CHO$-	Isopropoxy
$(CH_3)_3C$-	tert-Butyl	$(CH_3)_3CO$-	tert-Butoxy
C_6H_5-	Phenyl	C_6H_5O-	Phenoxy

Examples

(a)



Methoxy cylohexane

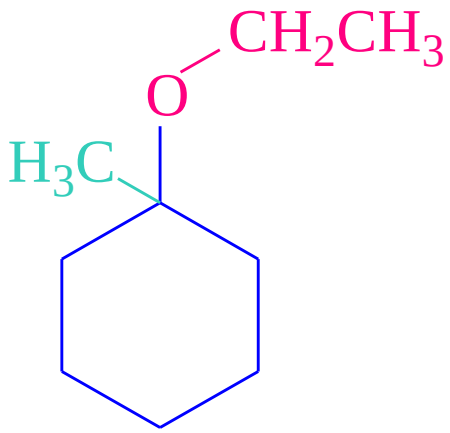
(b) $CH_3CHCH_2-O-CH_3$ (CH3 on C2; numbering 3 2 1)

1-Methoxy-2-methyl propane

(c) $CH_3CH_2CH_2-O-CH_2CH_2CH_2CH_3$ (numbering 1 2 3 4)

Propoxy butane

(d)

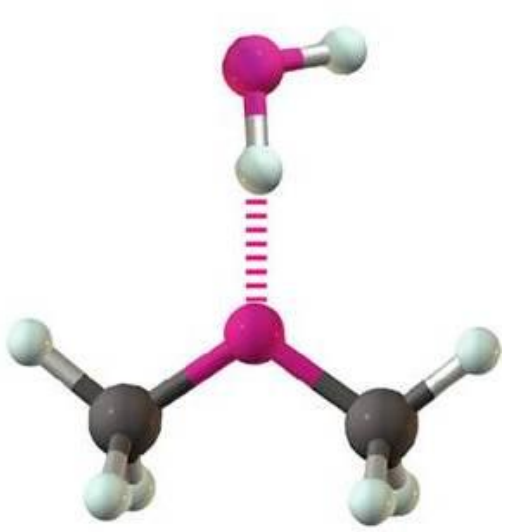


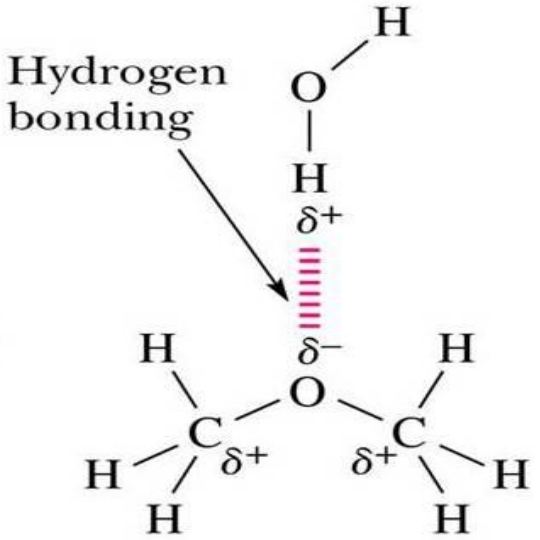
1-Ethoxy-1-methyl Cyclohexane

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.





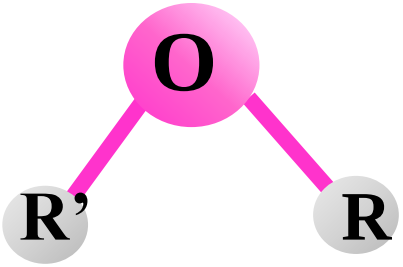
Ethers can form hydrogen bonds with water molecules

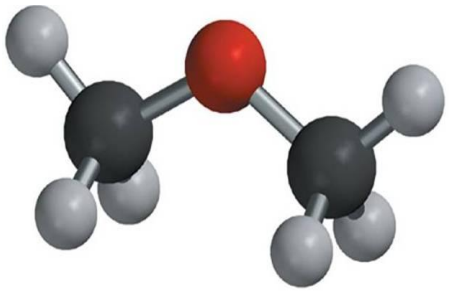
• The solubility decreases with increase in the number of carbon atoms.

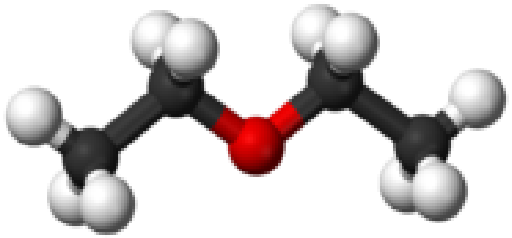
• The relative increase in the hydrocarbon portion of the molecule decreases the tendency of H-bond formation.

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***.

$CH_3CH_2CH_2CH_3$	$CH_3-O-CH_2CH_3$	$CH_3CH_2CH_2OH$
Butane	Methoxyethane	1-Propanol
(butane)	(ethyl methyl ether)	(Propyl alcohol)
M.W. = 58	M.W. = 60	M.W. = 60
b.p. = - 0.5°C	b.p. = 7.9 °C	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

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

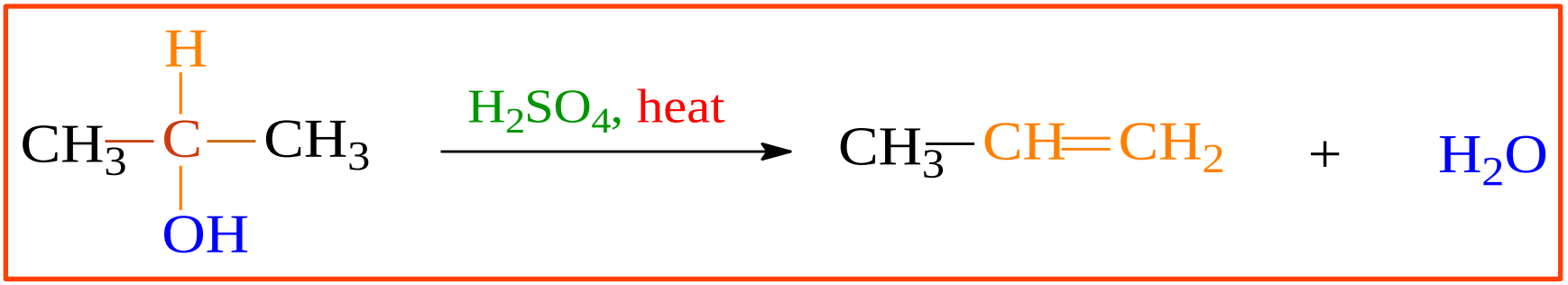
Examples

$$2\ CH_3OH \xrightarrow[140°C]{H_2SO_4} CH_3-O-CH_3 + H_2O$$

$$2\ CH_3CH_2OH \xrightarrow[140°C]{H_2SO_4} CH_3CH_2-O-CH_2CH_3 + H_2O$$

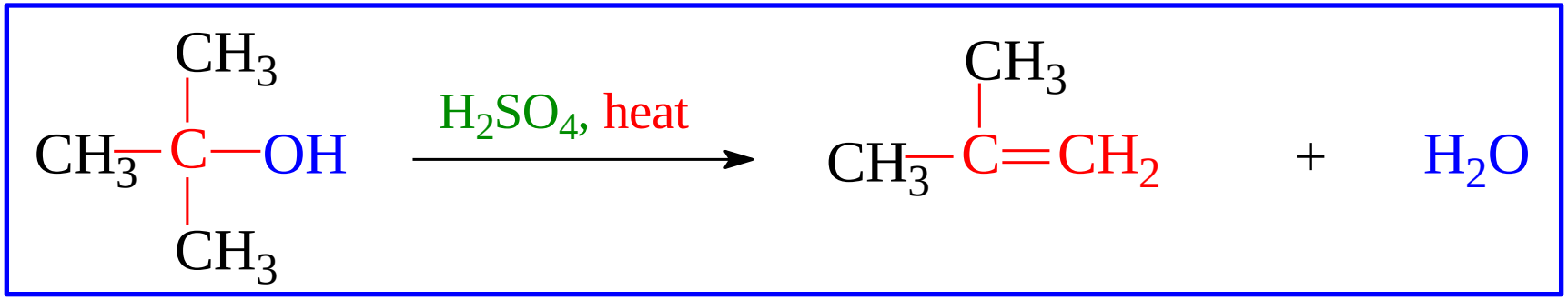
Note: The dehydration of 2° and 3° alcohol is unsuccessful to get ethers as alkenes are formed easily.

2°, *Sec*-alcohol **, (No ether is formed)**



Isopropyl alcohol ***propene***

3°, *t*-alcohol **, (No ether is formed)**



Tert-Butyl alcohol ***Iso-Butylene***

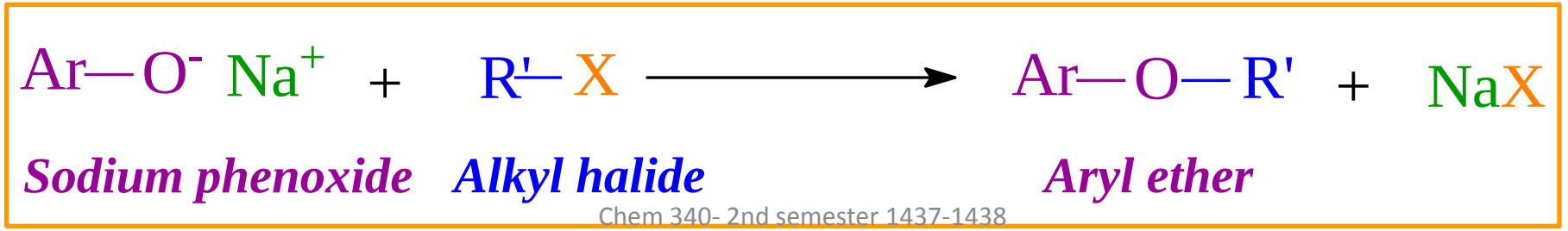
B- Williamson Synthesis.

The reaction of a sodium alkoxide; RONa or a sodium phenoxide; 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.

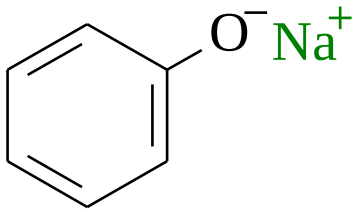
- The reaction involves ***nucleophilic substitution*** of an **alkoxide ion** for a **halide ion**.

General Equations

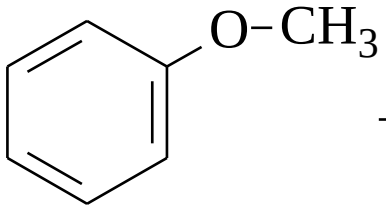


Examples

$$CH_3CH_2Br + CH_3CH_2\bar{O}\,Na^+ \longrightarrow CH_3CH_2O{-}CH_2CH_3 + NaBr$$



$$+ \quad CH_3I \longrightarrow$$



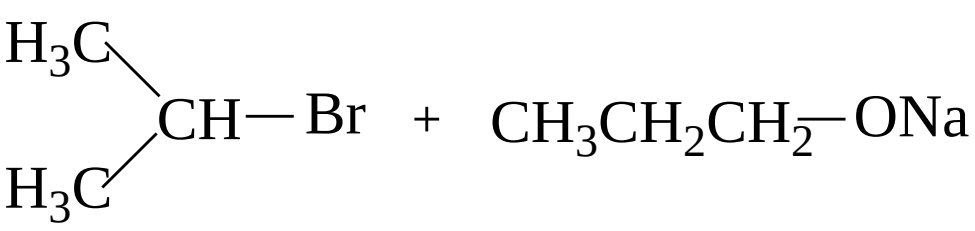
$$+ \quad NaI$$

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.

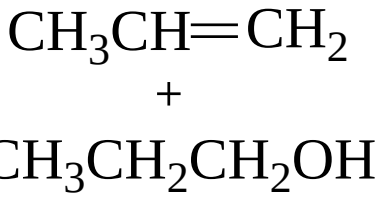
Examples

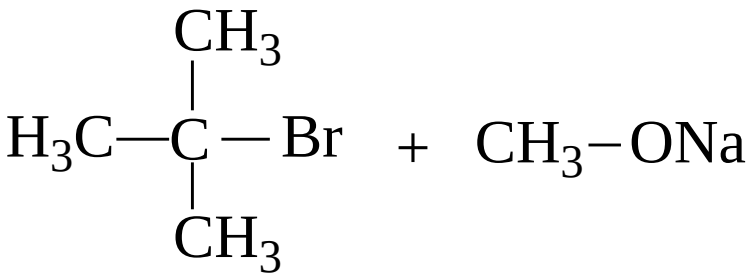


2° alkyl halide

No Ether Product

An Alkene Product

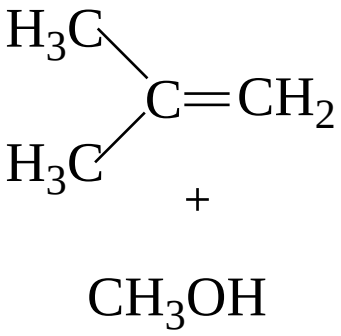




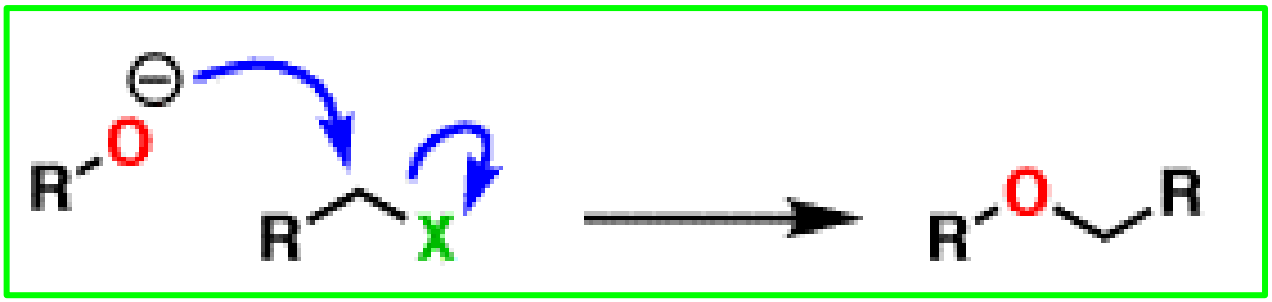
3° alkyl halide

No Ether Product

An Alkene Product



The Willamson Ether Synthesis Reaction Mechanism



Alkoxide nucleophile

Primary or methyl alkyl halide

Ether

Bond Formed	Bond Broken
C-O	C-X

Note that

- ✓The reaction follow S_N2 pathway.
- ✓Best for methyl and primary alkylhalides.
- ✓X may be (Cl, Br, I or any good living group).
- ✓Solvents is usually the conjugate acid of the alkoxide.

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 Acids

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

Reactivity: HI > HBr >> HCl

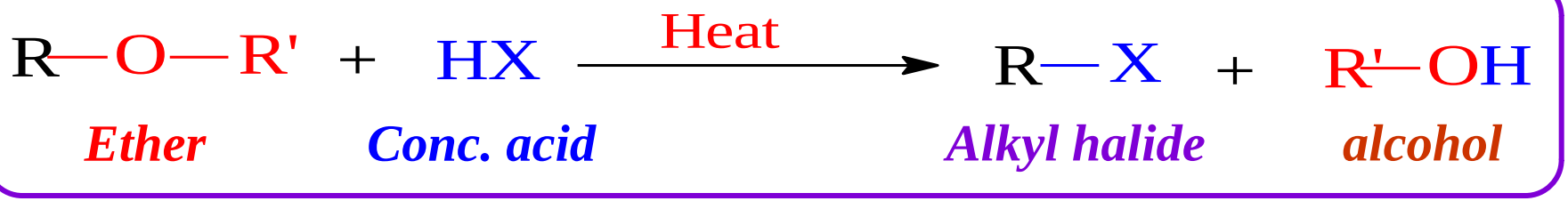
Note that

Cleavage by concentrated HCl is ***less effective***, primarily because **Cl^-** is a **weaker** ***nucleophile*** in water **than** either **I^-** or **Br^-** .

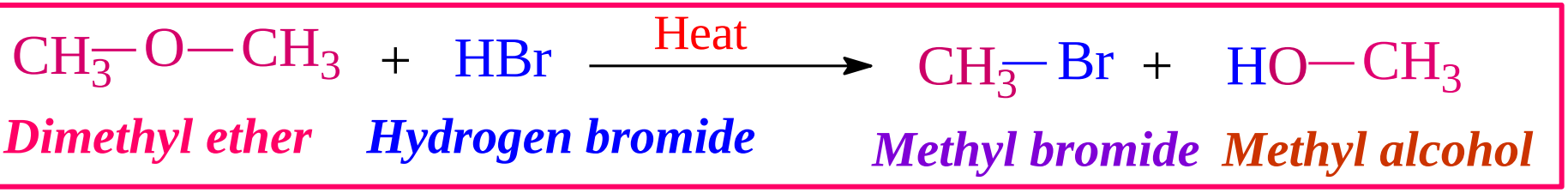
Cleavage of ***Ethers*** by HI or HBr

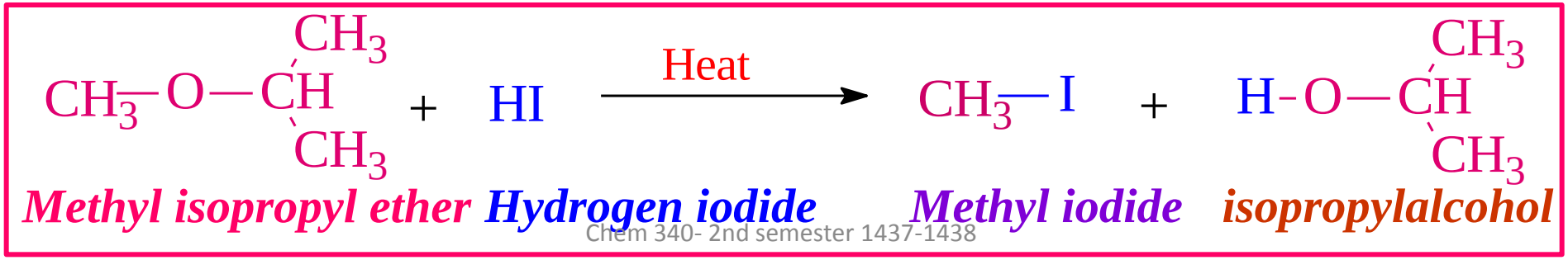
- Ethers are cleaved by HX to an alcohol and a haloalkane.
- Cleavage requires both a strong acid and a good nucleophile.

General Equation



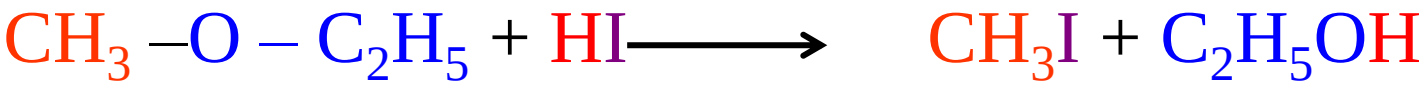
Specific Example



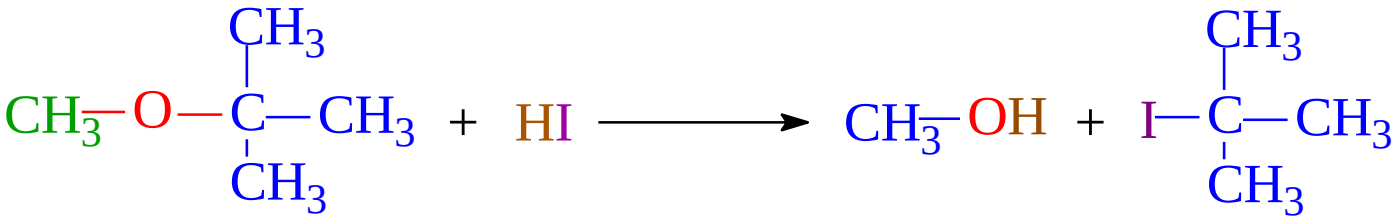


Point of cleavage:

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



(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.

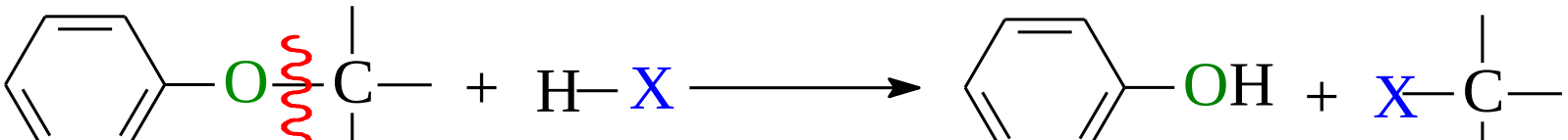
Example

Diethyl ether ***Excess Hydrogen bromide*** ***Ethyl bromide***

(iii) In case of **phenolic ether** the cleavage occurs with the formation of phenol and alkyl halide.

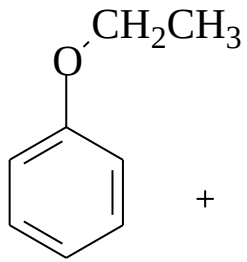
✓Alkyl aryl ethers are cleaved at the alkyl oxygen bond due to the **low reactivity** of aryl oxygen bond.

General Equation

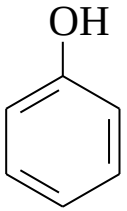


Example

(a)



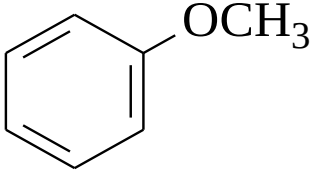
+ HBr $\xrightarrow{H_2O,\ Heat}$



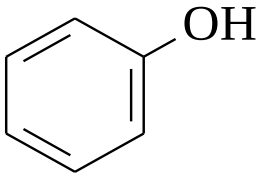
+ CH_3CH_2Br

Ethyl phenyl ether ***phenol*** ***Ethyl bromide***

(b)



+ HI $\xrightarrow{H_2O/Heat}$

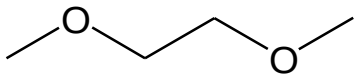


+ CH_3I

Methyl phenyl ether ***phenol*** ***Methyl Iodide***

Home Work

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



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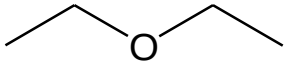
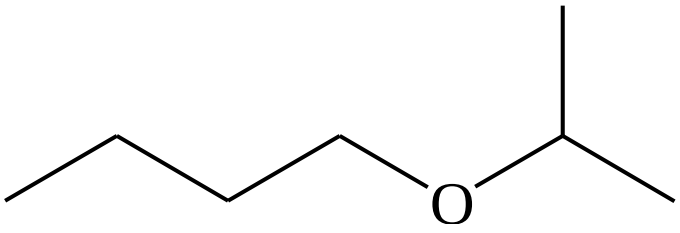


2

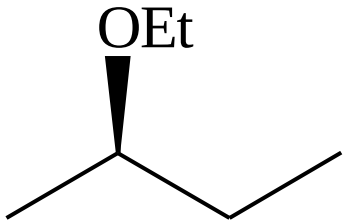
3

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

a)



b)

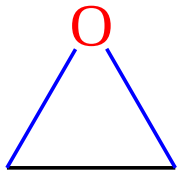


Definition

Epoxides

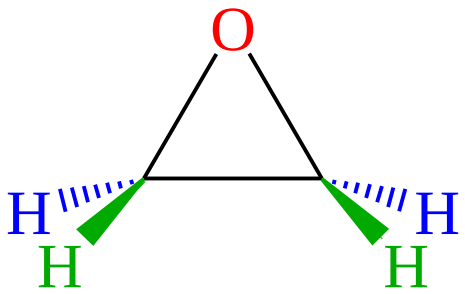
Epoxides or Cyclic ethers

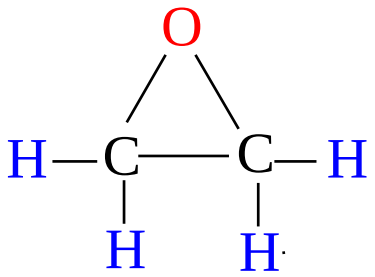
An epoxide



- 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**.





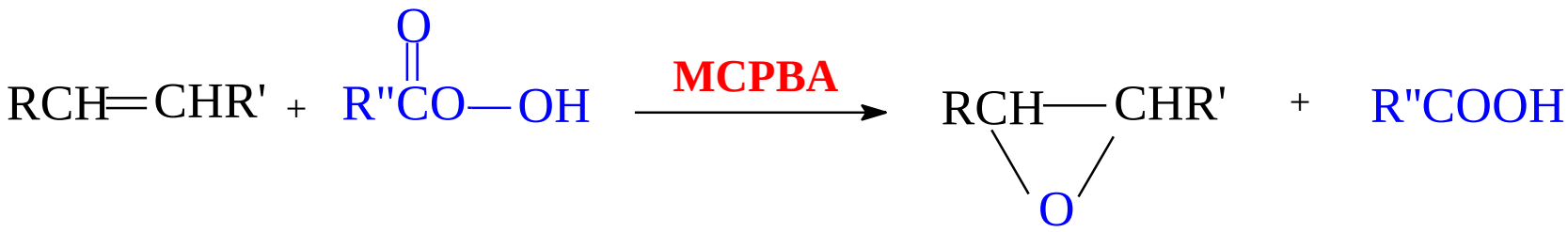
Ethylene oxide

General methods of preparation of Epoxides

Peroxide Epoxidation

Epoxides are often prepared from reacting with organic peroxy acids ("peracids") ex; $CH_3C(O)OOH$ in a process called ***epoxidation***.

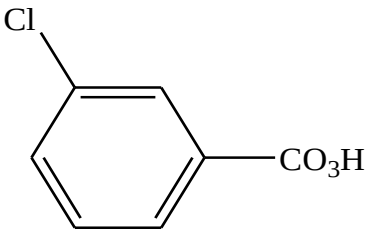
General equation



Peroxy acid ***Epoxide***

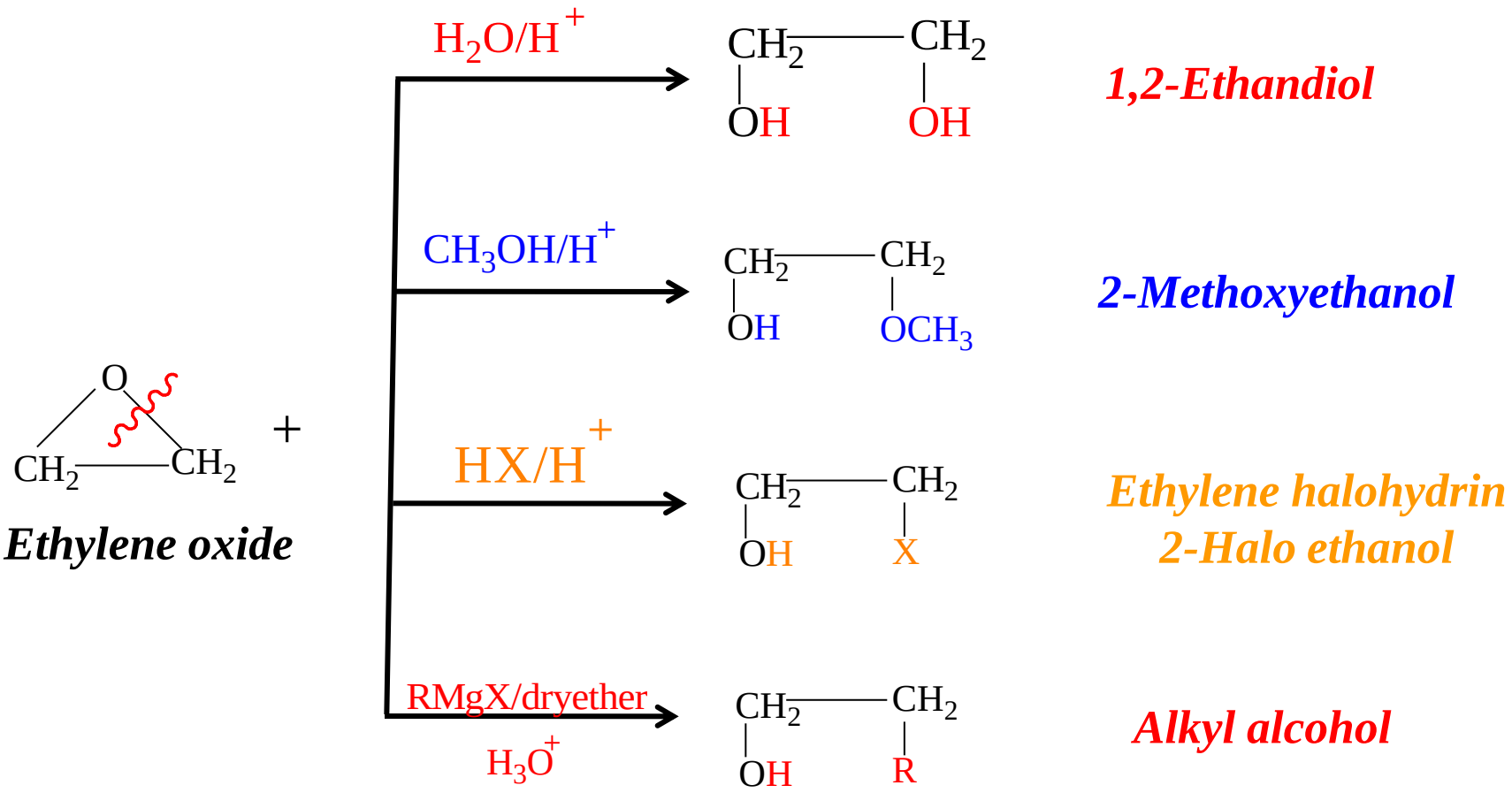
Note that:

MCPBA=



***m*-Chloroperoxybenzoic acid**

Reaction of Epoxides.



Home Work

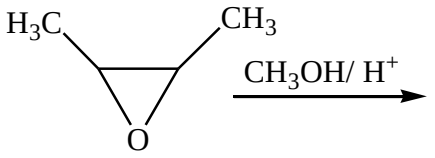
Q.1 Choose the correct answer:

1- The reaction of two moles of HI with dimethylether gives:

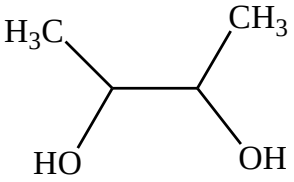
- Ethyl iodide and ethanol
- Two moles of methyl iodide
- Two moles of ethanol
- Two moles of ethyl iodide

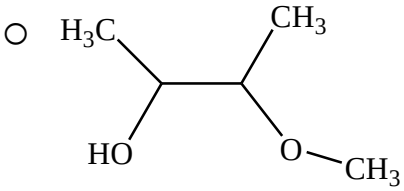
2- The compound with highest boiling point is:

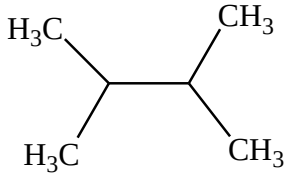
- Ethanol
- Dimethyl ether
- Ethane
- Cloroform

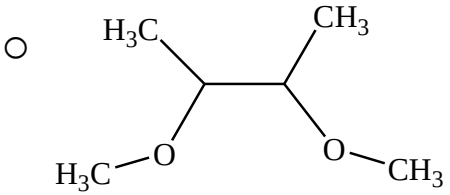
3- The product of the following reaction 

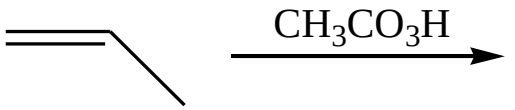
is:

○ 

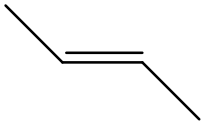
○ 

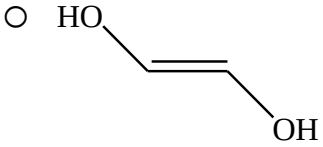
○ 

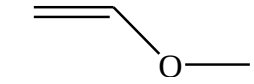
○ 

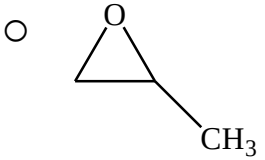
4- The major product of the following reaction 

is:

○ 

○ 

○ 

○ 


Thank You!