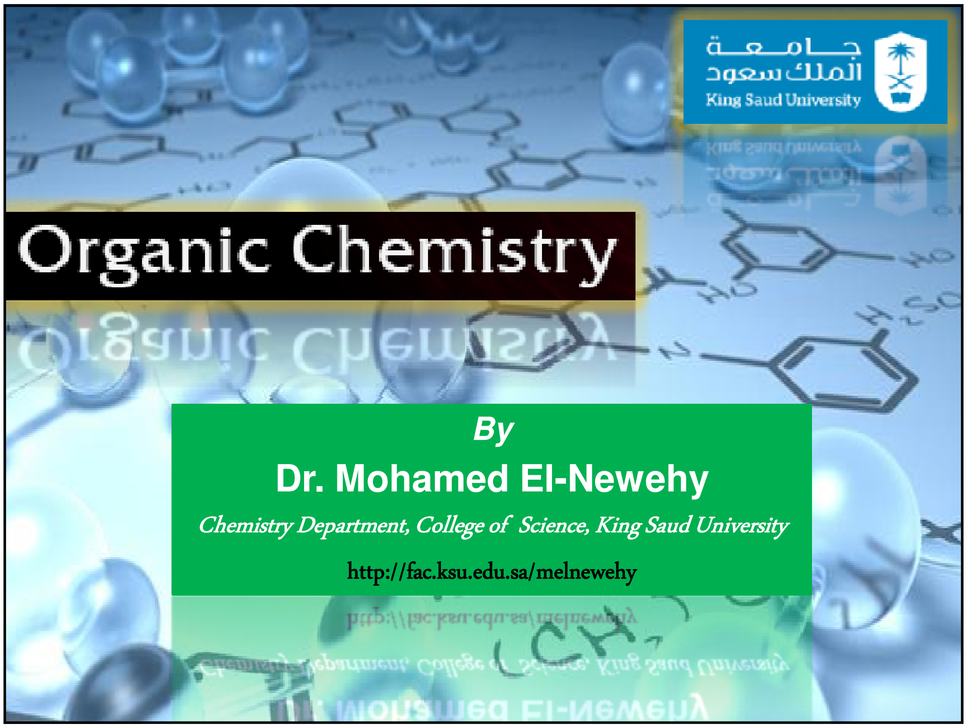
جامعة
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Organic Chemistry
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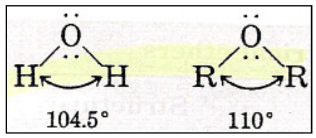
Ethers

Structure of Ethers

- All ethers are compounds in which two organic groups are connected to a single oxygen atom.
- The general formula for an ether is R-O-R', where R and R' may be identical or different, and they may be alkyl or aryl groups

R—O—R, Ar—O—R, or Ar—O—Ar

- The geometry of simple ethers is similar to that of water.



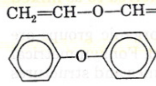
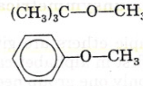
- The ether is classified as

- **Symmetrical ethers;**
  When the organic groups attached to the oxygen are identical.
- **Unsymmetrical ethers (mixed ethers);**
  When the organic groups attached to the oxygen are different.

Nomenclature of Ethers

- Common Names

Ethers are usually named by giving the name of each alkyl or aryl group, in alphabetical order, followed by the word *ether.*

Methyl ether	$CH_3—O—CH_3$	Ethyl methyl ether	$CH_3—O—CH_2CH_3$
Ethyl ether	$CH_3CH_2—O—CH_2CH_3$	Ethyl-*n*-propyl ether	$CH_3CH_2—O—CH_2CH_2CH_3$
Vinyl ether	$CH_2{=}CH—O—CH{=}CH_2$	*t*-Butyl methyl ether	$(CH_3)_3C—O—CH_3$
Phenyl ether		Methyl phenyl ether (anisole)	

- IUPAC system

For ethers with more complex structures, it may be necessary to name the -OR group as an alkoxy group. In the IUPAC system, the smaller alkoxy group is named as a substituent.

$CH_3CH_2CH_2CHCH_3$ with OCH_3 on C-2	$CH_3CH_2CH_2CHCH_2CH_3$ with OCH_2CH_3 on C-3	$H_3CO—CH_2CH_2OH$
2-Methoxypentane	3-Ethoxyhexane	2-Methoxyethanol

Physical Properties of Ethers

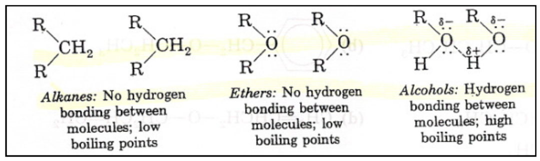
- Physical State

- Ethers are colorless compounds with characteristic, relatively pleasant odors.

- Boiling Points

- *They have lower boiling points (bp,s) than alcohols with an equal number of carbon atoms.*
- In fact, an ether has nearly the same bp as the corresponding hydrocarbon in which a -CH_2- group replaces the ether's oxygen.

  Because of their structures (no O-H bonds), ether molecules cannot form hydrogen bonds with one another.



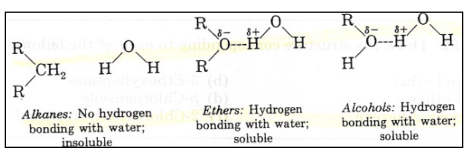
Compound	Formula	bp	mol wt	Water solubility (g/100 mL, 20°C)
1-butanol	$CH_3CH_2CH_2CH_2OH$	118°C	74	7.9
diethyl ether	$CH_3CH_2—O—CH_2CH_3$	35°C	74	7.5
pentane	$CH_3CH_2—CH_2—CH_2CH_3$	36°C	72	0.03

Physical Properties of Ethers

- Solubility

- Low-molecular-weight ethers, such as dimethyl ether, are quite soluble in water.

  Ether molecules can form hydrogen bonds to water.



Structure	Name	Mol wt	Bp (°C)	Solubility in H_2O at 20°C
$CH_3CH_2CH_3$	propane	44	−42	insoluble
CH_3OCH_3	methyl ether	46	−24	soluble
CH_3CH_2OH	ethanol	46	78	soluble
$CH_3CH_2CH_2CH_3$	*n*-butane	58	−0.5	insoluble
$CH_3CH_2OCH_3$	ethyl methyl ether	60	8	soluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	soluble
$CH_3(CH_2)_3CH_3$	*n*-pentane	72	35	insoluble
$CH_3CH_2OCH_2CH_3$	ethyl ether	74	36	7.5 g/100 g
$CH_3(CH_2)_2CH_2OH$	1-butanol	74	118	7.9 g/100 g
$CH_3(CH_2)_5CH_3$	*n*-heptane	100	98	insoluble
$CH_3(CH_2)_2O(CH_2)_2CH_3$	*n*-propyl ether	102	91	0.2 g/100 g
$CH_3(CH_2)_4CH_2OH$	1-hexanol	102	157	0.6 g/100 g

Preparation of Ethers

- There are *two general methods* for synthesizing ethers.

1) Dehydration of alcohols

It is used commercially and in the laboratory to make certain symmetrical ethers.

2) Williamson synthesis

General laboratory method used to prepare all kinds of ethers, symmetrical and unsymmetrical.

Preparation of Ethers

1) Dehydration of alcohols

- It takes place in the presence of acid catalysts (H_2SO_4, H_3PO_4) (*intermolecular reaction*).

$$R{-}OH + H{-}OR \xrightarrow[\text{heat}]{H^+} R{-}O{-}R + H_2O$$

- Example:
  The most important commercial ether is diethyl ether. It is prepared from ethanol and sulfuric acid.

$$\underset{\text{ethanol}}{CH_3CH_2OH + HOCH_2CH_3} \xrightarrow[140°C]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3} + H_2O$$

Preparation of Ethers

Scope and Limitations

- When ethyl alcohol is dehydrated by sulfuric acid at 180° C, the dominant product is ethylene.

$$\underset{\text{Ethyl alcohol}}{\underset{|\quad\ \ |}{CH_2CH_2}\atop{H\quad OH}} \xrightarrow[180°C]{H_2SO_4} \underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O$$

- To prepare ethyl ether

- Dissolve ethyl alcohol in sulfuric acid at ambient temperature.
- Heat the solution to 140°C while adding more alcohol.

$$\underset{\text{Ethyl alcohol}}{2\ CH_3CH_2OH} \xrightarrow[140°C]{H_2SO_4} \underset{\text{Ethyl ether}}{CH_3CH_2{-}O{-}CH_2CH_3} + H_2O$$

Preparation of Ethers

1) Williamson synthesis

- **This method has two steps;**

  1) An alcohol is converted to its alkoxide by treatment with a reactive metal (sodium or potassium).

$$2\ ROH + 2\ Na \longrightarrow 2\ RO^-Na^+ + H_2$$

  2) Displacement is carried out between the alkoxide and an alkyl halide.

$$RO^-Na^+ + R'{-}X \longrightarrow ROR' + Na^+X^-$$

- To obtain the best yields of mixed dialkyl ethers, we select a 1° rather than a 2°or 3°alkyl halide and react it with a sodium alkoxide
- To prepare an alkyl aryl ether, we must be careful not to pick a combination in which one of the reagents has a halogen directly attached to an aromatic ring.

Preparation of Ethers

1) Williamson synthesis

- Example 1

Preparation of *t*-butyl methyl ether, $(CH_3)_3C\text{-}O\text{-}CH_3$.

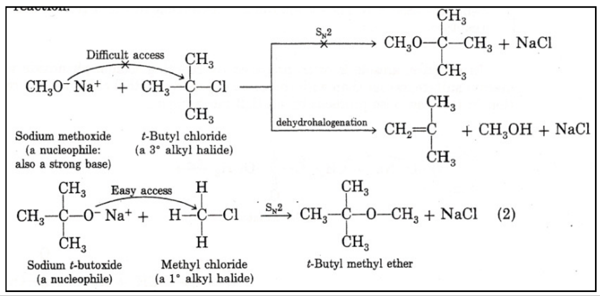
- In theory, this could be done by either of two reactions.

1. You could react sodium methoxide, $CH_3O^-Na^+$, with *t*-butyl chloride, $(CH_3)_3C\text{-}Cl$.

   This combination leads to dehydrohalogenation to an alkene, an elimination reaction.

2. You could react sodium *t*-butoxide, $(CH_3)_3C\text{-}O^-Na^+$, with methyl chloride, CH_3Cl.

   This route gives the desired ether by substitution.



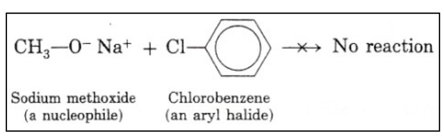
Preparation of Ethers

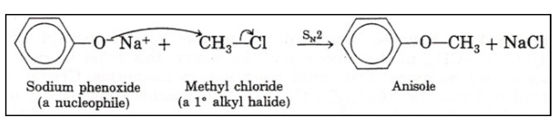
1) Williamson synthesis

- Example 2

Assume you need to synthesize methyl phenyl ether (anisole), $CH_3\text{-}O\text{-}C_6H_5$, by the Williamson method.

- *In theory, you could obtain anisole in either of two ways.*





Reactions of Ethers

- Ethers are quite stable compounds.

- The ether linkage does not react with bases, reducing agents, oxidizing agents, or active metals.

- Ethers react only under strongly acidic conditions.

Cleavage of Ethers by Hot Concentrated Acids

- When ethers are heated in concentrated acid solutions, the ether linkage is broken.

$$CH_3CH_2{-}\ddot{\underset{..}{O}}{-}CH_2CH_3 + \underset{\text{(conc)}}{\mathbf{HI}} \xrightarrow[\text{heat}]{} CH_3CH_2OH + CH_3CH_2I$$

- The acids most often used in this reaction are HI, HBr, and HCl.

- **If an *excess of acid* is present, the alcohol initially produced is converted into an alkyl halide by the reaction.**

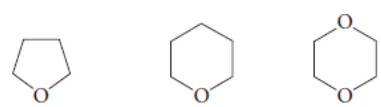
$$R{-}OH + HX \longrightarrow RX + H_2O$$

For example,

$$CH_3CH_2{-}O{-}CH_2CH_3 + \underset{\text{(conc)}}{2\,HBr} \xrightarrow[\text{heat}]{} 2\,CH_3CH_2Br + H_2O$$

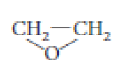
Cyclic Ethers

- Cyclic ethers whose rings are larger than the three-membered epoxides are known.
- The most common are five- or six-membered rings.



tetrahydrofuran tetrahydropyran 1,4-dioxane

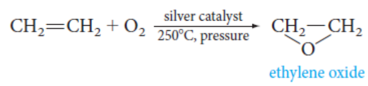
- Epoxides are cyclic ethers in which the ether oxygen is part of a three membered ring.



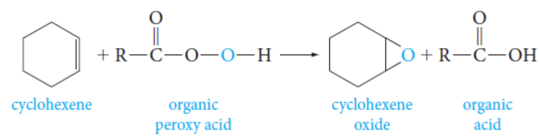
ethylene oxide

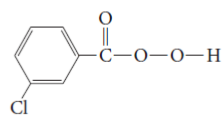
Cyclic Ethers

- The most important commercial epoxide is ethylene oxide, produced by the silver-catalyzed air oxidation of ethylene.



- Other epoxides are usually prepared by the reaction of an alkene with an organic peracid.





m-chloroperbenzoic acid,

Cyclic Ethers

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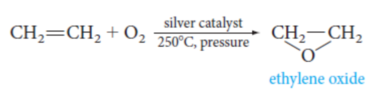

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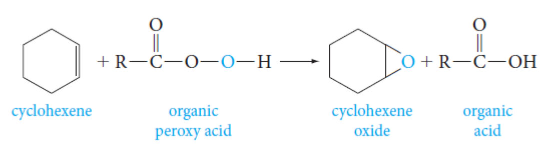
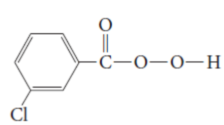


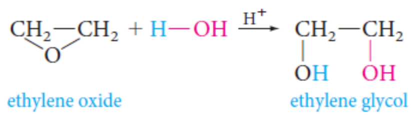


m-chloroperbenzoic acid,

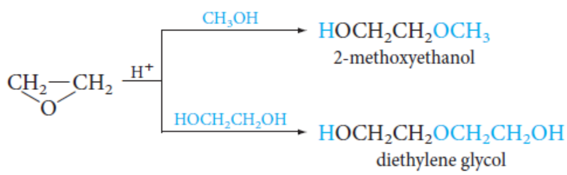
Reactions of Cyclic Ethers (Ring Opening)

- Because of the **strain in the three-membered ring**, epoxides are much more reactive than ordinary ethers and give products in which the ring has opened.

1) **Reaction with water,** they undergo acid-catalyzed ring opening to give glycols.

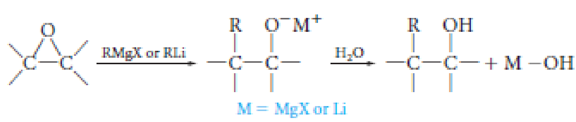


2) **Reaction with alcohols,** they undergo acid-catalyzed ring opening to give glycols.

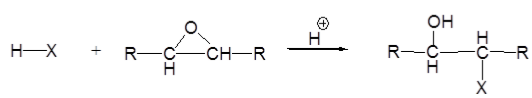


Reactions of Cyclic Ethers (Ring Opening)

3) **Reaction with Grignard's reagent,** they undergo acid-catalyzed ring opening to give alcohols.



4) **Reaction with HX,** they undergo acid-catalyzed ring opening to give glycols.



5) **Reaction with amines,** they undergo acid-catalyzed ring opening to give glycols.