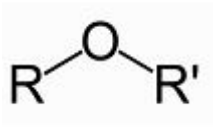
Extension 19: Preparation and properties of ethers

1. Prerequisites

The key ideas required to understand this section are:

Topic	Book page
Functional groups	341
Nucleophilic substitution	370

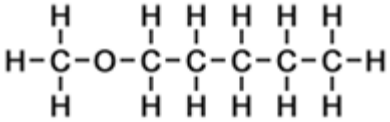
Ethers contain an oxygen atom connected to two alkyl or aryl groups, they can be represented as R–O–R′, R–O–Ar or Ar–O–Ar where R and Ar represent the alkyl or aryl groups.



The most common is diethyl ether, often referred to simply as "ether". It is a colourless, highly volatile flammable liquid which is commonly used as a solvent in laboratories. It was used as an anaesthetic until non-flammable drugs, such as halothane, were developed.

2. Nomenclature of ethers

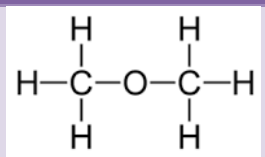
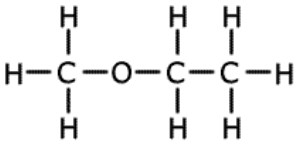
The older nomenclature of ethers (which is still commonly used) names the different alkyl/aryl groups attached to the oxygen atom in alphabetical order then adding the word ether. For example methyl pentyl ether is:

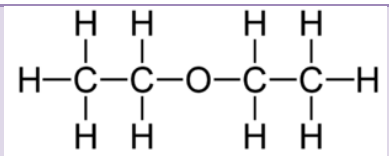
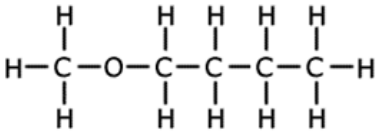
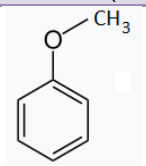


If the oxygen atom is attached to the same group on either side, they are named by adding "di" before the alkyl/aryl groups attached to the oxygen atom. For example, CH_3OCH_3 is dimethyl ether. More modern IUPAC nomenclature of ethers follows different guidelines. The group containing more carbon atoms is chosen as the parent hydrocarbon. The group attached to the oxygen atom is named with a prefix "oxy". So the molecule illustrated above would be 1-methoxypentane.

The table below illustrates some ethers with their common and IUPAC names:

Table 2 Common and IUPAC names of ethers

Ether	*Common name*	*IUPAC name*
 (C_2H_6O)	dimethyl ether	methoxymethane
 (C_3H_8O)	ethyl methyl ether	methoxyethane

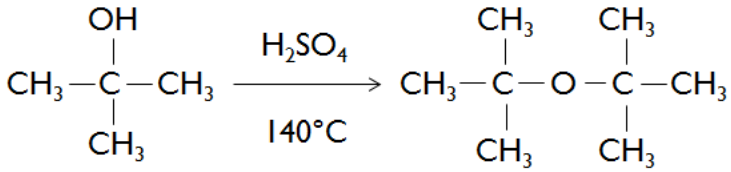
 ($C_4H_{10}O$)	diethylether	ethoxythane
 ($C_5H_{12}O$)	butyl methyl ether	1-methoxybutane
 A cyclic ether (C_4H_8O)	tetrahydrofuran (THF)	oxolane
 (C_7H_8O)	anisole	methoxybenzene

Dimethyl ether and ethyl methyl ether are gases at room temperature. The other lower ethers are colourless, volatile liquids with a typical ether smell (difficult to describe, but distinctive). They are volatile because although the molecules have a net dipole (the C-O bond is polar and the molecule is V-shaped), the polarity is weak and the molecules cannot hydrogen bond with each other.

3. Synthesis of ethers

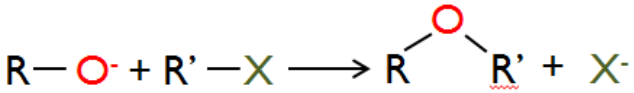
The sulfuric acid process

Sulfuric acid dehydrates alcohols to produce alkenes and ethers under different temperatures As an example: in the presence of sulfuric acid, dehydration of ethanol at 170°C yields ethene whereas it yields ethoxyethane at 140°C. This method is used to make sterically hindered symmetrical ethers.



Williamson ether synthesis

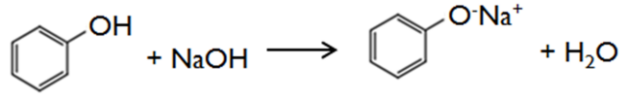
This is the reaction of an alkoxide anion with an alkyl halide and can give symmetrical or unsymmetrical ethers, depending on the reactants.



EXAMPLE 1

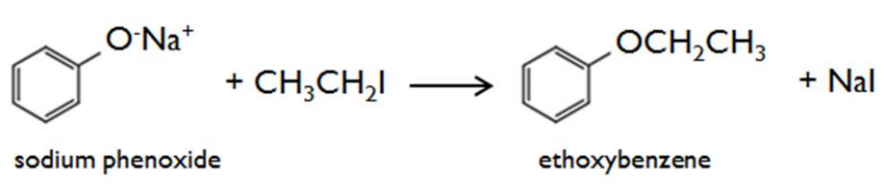
As an example:

(i) The reaction proceeds in two stages:



Sodium hydroxide reacts as a base, to remove a proton and make the phenoxide ion.

(ii)



The phenoxide ion then undergoes a nucleophilic substitution reaction with the iodoalkane to form an unsymmetrical ether.

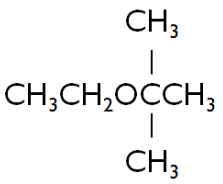
4. Chemical properties of ethers

Ethers are unreactive as compared with alcohols. They are not easily attacked, for example, by dilute acids or metallic sodium under ordinary conditions. This is one of the reasons why they are used widely as solvents.

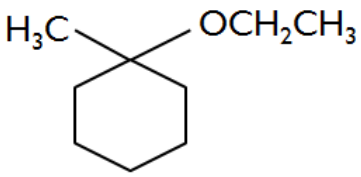
Revision questions

1. Can you give IUPAC names to the following:

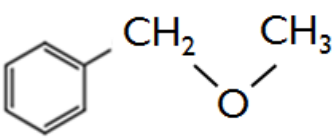
(i)



(ii)

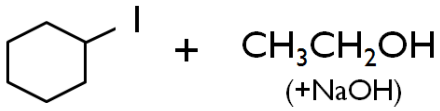


(iii)

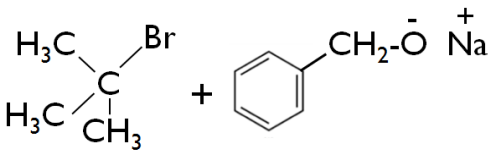


2. What would be the structural formula of the product of the following reactions through the Williamson ether synthesis?

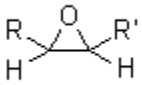
(i)



(ii)



3. An epoxide is a cyclic ether with 3 atoms on its ring (2 carbons and 1 oxygen). For example:



Which one do you think is more reactive – a straight chain ether or an epoxide? Explain your answer.

4. Ethers cannot hydrogen bond with each other. Can they hydrogen bond with water?

Answers

1.

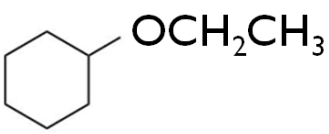
(i) 2-ethoxy-2-methylpropane

(ii) 1-ethoxy-1-methylcyclohexane

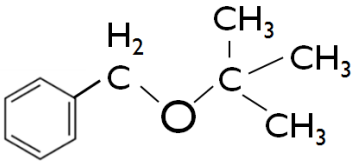
(iii) phenylmethoxymethane

2.

(i)



(ii)



3. The epoxide. Epoxides are very reactive because of the ring strains. They tend to react with other compounds to open the ring in order to become more stable.

4. In aqueous solutions, provided the ether is not too sterically crowded, the ether molecules can form hydrogen bonds with the water molecules. Water has hydrogen that can bond with ether oxygen atoms, but the bonds are weaker. Dimethyl ether is the most soluble – the oxygen atom is least sterically hindered.