

Ethers Notes:

READS



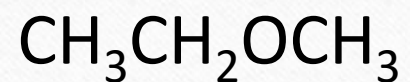
Organic Chemistry I

Ethers (R-O-R)

In contrast to alcohols with their rich chemical reactivity, ethers (compounds containing a C—O—C unit) undergo relatively **few** chemical reactions. This **lack** of reactivity of ethers makes them valuable as **solvents** in a number of synthetically important transformations. In this lecture; the conditions in which an ether linkage acts as a functional group will be explained, as well as the methods by which ethers are prepared.

NOMENCLATURE OF ETHERS

- Ethers are named, in **substitutive IUPAC** nomenclature, as alkoxy derivatives of alkanes.
- **Functional class IUPAC** names of ethers are derived by listing the two alkyl groups in the general structure ROR' in alphabetical order as separate words, and then adding the word “**ether**” at the end. When both alkyl groups are the same, the prefix di- precedes the name of the alkyl group.



Substitutive

IUPAC name: Ethoxyethane

Methoxyethane

1-Chloro-3-ethoxypropane

Functional class

IUPAC name: Diethyl ether

Ethyl methyl ether

3-Chloropropyl ethyl ether

- ❖ Ethers are described as **symmetrical** or **unsymmetrical** depending on whether the two groups bonded to oxygen are the same or different. Unsymmetrical ethers are also called **mixed ethers**. Diethyl ether is a symmetrical ether; ethyl methyl ether is an unsymmetrical ether
- ❖ Many substances have more than one ether linkage. For example the diethers 1,2-dimethoxyethane commonly used as a solvent.



1,2-Dimethoxyethane

PHYSICAL PROPERTIES OF ETHERS:

By comparing the physical properties of ethers with alkanes and alcohols: with respect to boiling point, ethers resemble alkanes more than alcohols. With respect to solubility in water the reverse is true; ethers resemble alcohols more than alkanes.

	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ Diethyl ether	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ Pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ Butanol
Boiling point:	35°C	36°C	117°C
Solubility in water:	7.5 g/100 mL	Insoluble	9 g/100 mL

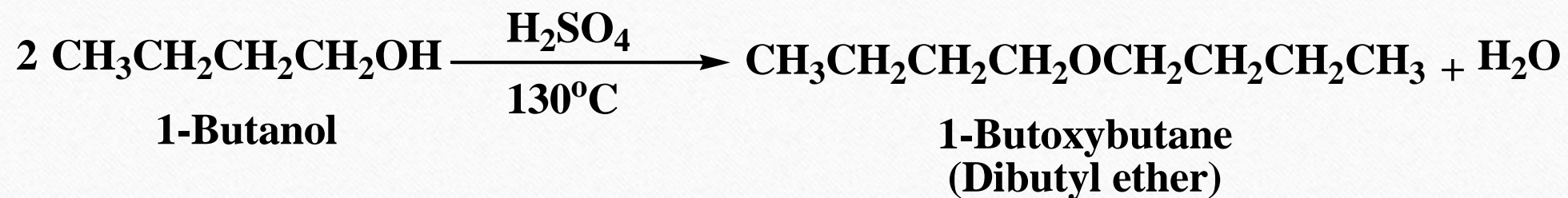
In general, the boiling points of alcohols are unusually high because of hydrogen bonding. Attractive forces in the liquid phases of ethers and alkanes, which lack —OH groups and cannot form intermolecular hydrogen bonds, are much weaker, and their boiling points lower.

However, the presence of an oxygen atom permits ethers to participate in hydrogen bonds to water molecules. These attractive forces cause ethers to dissolve in water to approximately the same extent as comparably constituted alcohols. Alkanes cannot engage in hydrogen bonding to water.

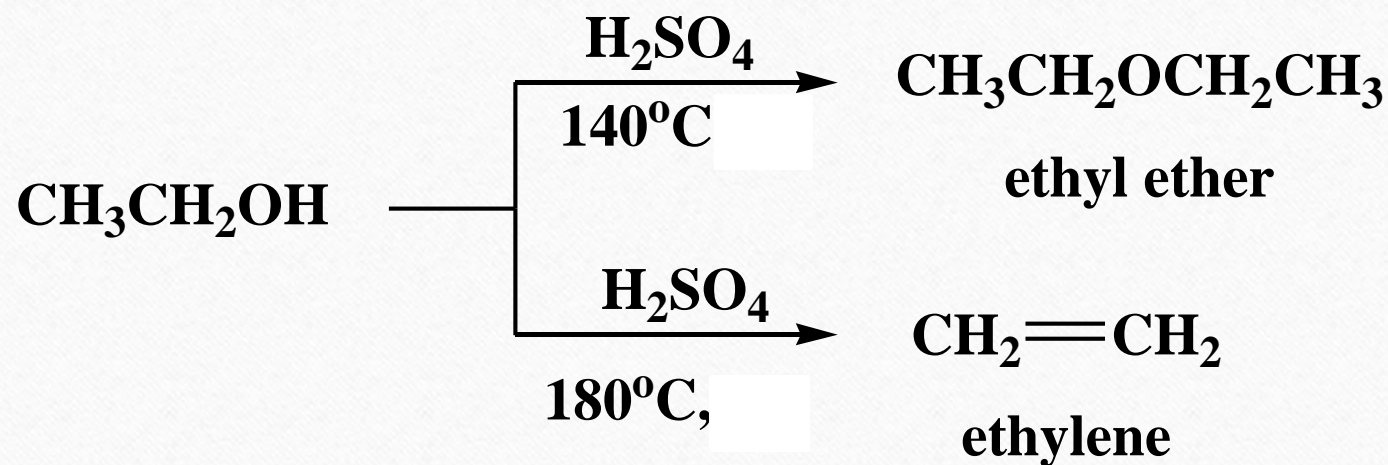
PREPARATION OF ETHERS

I-From Alcohols:

Because they are widely used as solvents, many simple dialkyl ethers are commercially available. Diethyl ether and dibutyl ether, for example, are prepared by acid-catalyzed condensation of the corresponding alcohols:

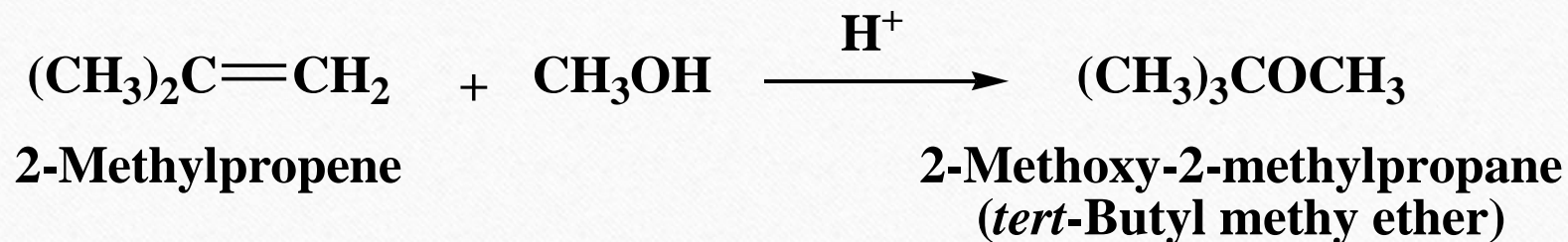


In general, this method is limited to the preparation of symmetrical ethers in which both alkyl groups are primary. For example isopropyl alcohol, is readily available at low cost and gives high yields of diisopropyl ether $(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2$ by this method on an industrial scale. Dehydration to ethers rather than to alkenes is controlled by choice of the reaction conditions. For example, ethyl ether is the predominant product of dehydration of ethanol at 140°C ; while ethylene is the major product at 180°C :



II- Synthesis of *tert*-Butyl ethers by alkylation of alcohols

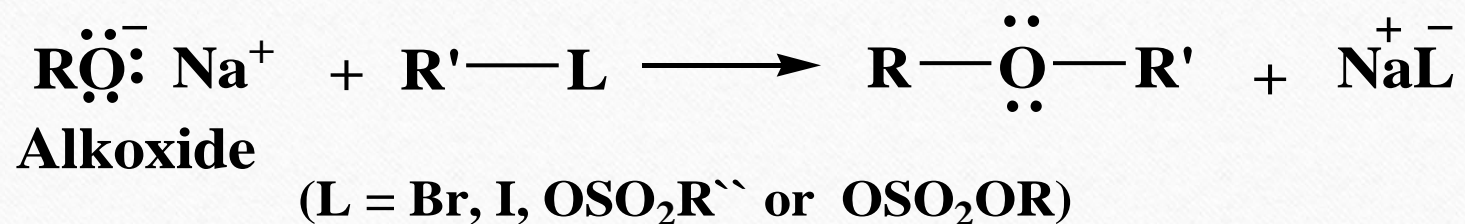
tert-Butyl methyl ether can be prepared in by the acid-catalyzed addition of methanol to 2-methylpropene:



Small amounts of *tert*-butyl methyl ether are added to gasoline as an octane booster. This method is used often to “protect” the hydroxy group of a 1° alcohol while another reaction is carried out on some part of the molecule. The protecting *tert*-butyl group can be removed easily by treating the ether with dilute aqueous acid. (Ethers are often used as protecting groups, because ethers are remarkably stable under a wide variety of reaction conditions, including oxidative and basic conditions.)

III- The Williamson Ether Synthesis

The Williamson ether synthesis is an example of a nucleophilic substitution reaction. The nucleophile is an **alkoxide anion** which displaces a halide ion, typically chloride or bromide, from a **primary haloalkane**. This synthesis is a versatile procedure for preparing symmetrical and unsymmetrical ethers. The method consists of an S_N2 reaction of sodium (or potassium) alkoxide with alkyl halide, alkyl sulphonate or alkyl sulphate.



Sodium and potassium alkoxides are prepared by reaction of an alcohol with the appropriate metal. An example of Williamson synthesis is the synthesis of butyl ethyl ether:



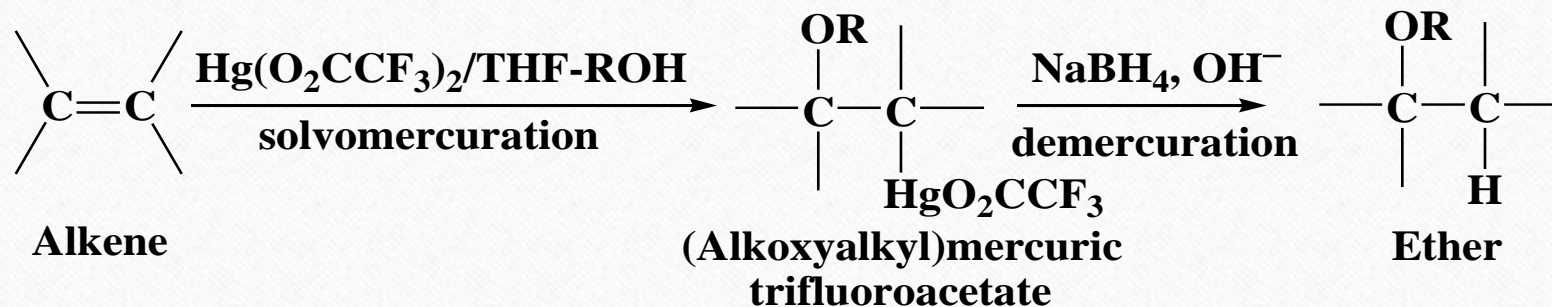
Although the Williamson ether synthesis is a general method for the laboratory production of ethers, there are some limitations to its use. Since the alkoxide ion is a strong base, their use is limited to primary unhindered alkylating agents. Otherwise, elimination competes strongly with the nucleophilic substitution for the reactant molecules.

IV-Solvomercuration-Demercuration:

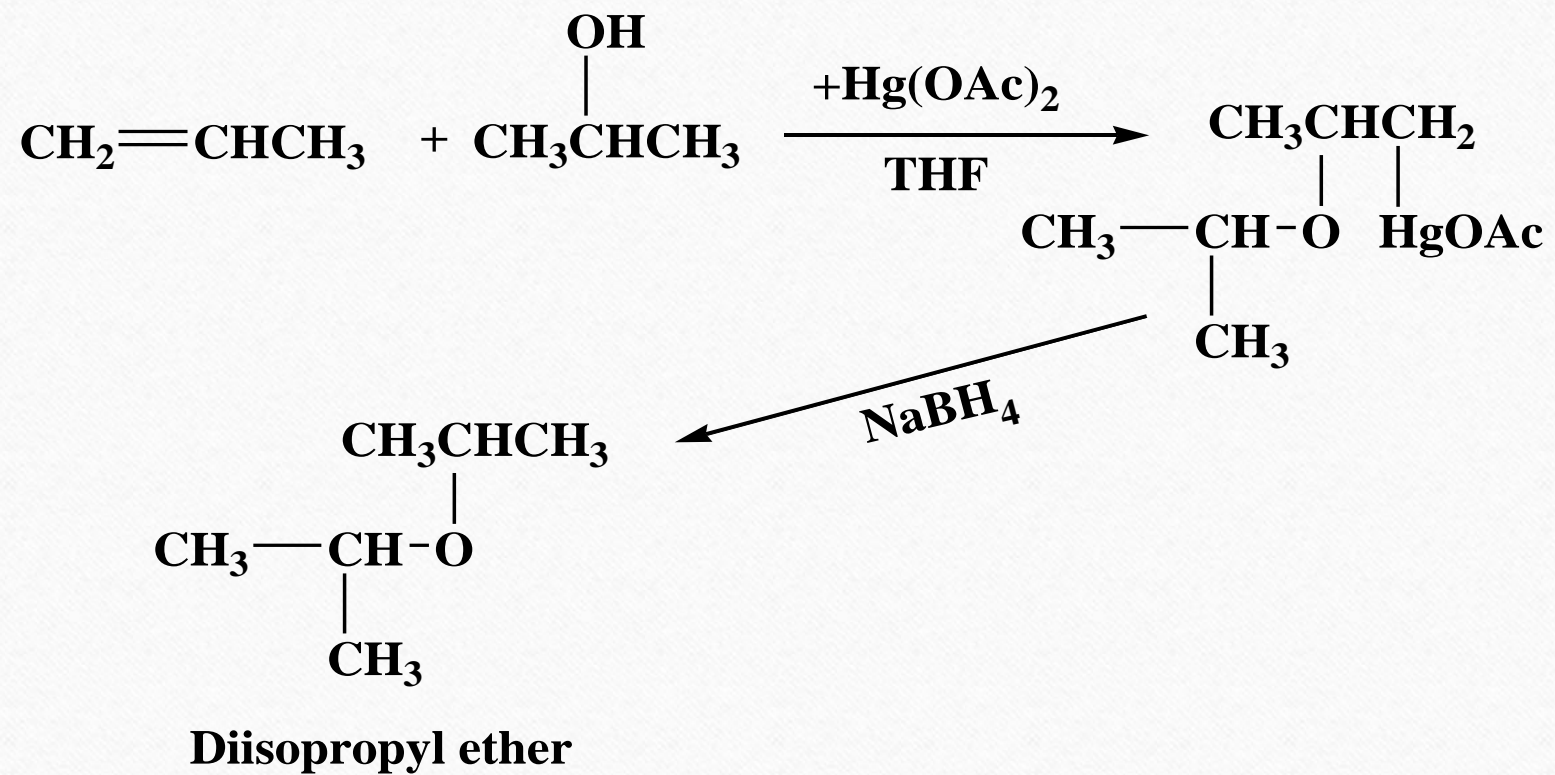
(Alkoxy-Mercuration-Demercuration)

As seen under preparation of alcohols; water can be added to alkenes to produce alcohols by treating them first with mercuric acetate or mercuric trifluoroacetate in THF/water, and then with Sodium Borohydride. This process is known as oxymercuration-demercuration.

If an alcohol is used as the solvent in the first step, instead THF/water, the product is an ether resulting from formal addition of the alcohol to the alkene and the process is called: “Solvomercuration-Demercuration” .



For example the preparation of diisopropyl ether:



V- Preparation of Methyl Ethers by Methylation of Alcohols:

Alcohol react with diazomethane in presence of Lewis acid as a catalyst to give methyl ethers.



