

Ethers

Nomenclature, Properties, Synthesis and Reactions

Dr. Sapna Gupta

Ether Functional Group

An **ether** has two organic groups (alkyl, aryl, or vinyl) bonded to the same oxygen atom, R-O-R'. Ethers can be in chains as well as in cyclic structures.

Oxygen is single bonded to carbons, it is sp^3 hybridized thus the bond angle is 109° giving ethers a bent shape.

Just like thiols (R-S-H), *sulfides* (R-S-R') are sulfur (for oxygen) analogues of and ethers.



109°



109°

Nomenclature: Ethers

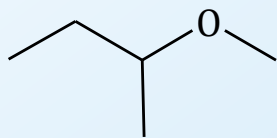
Common names: Alkyl groups bonded on either side of oxygen are named in alphabetical order followed by the word **ether**.

Smallest ether is CH_3OCH_3 dimethyl ether.

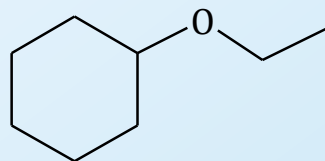
$\text{CH}_3\text{CH}_2\text{OCH}_3$ ethyl methyl ether (substituents should be named alphabetically).

$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ diethyl ether.

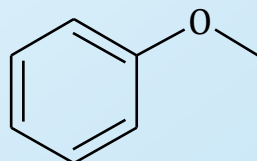
For larger ethers or ether groups: identify the longest carbon chain as the base/parent name. The small ether group are called “alkoxy” substituent: methoxy, ethoxy etc. Some compounds can have two names and both can be acceptable. Alkoxy groups have no priority over any other substituent in case of branching start numbering closest to any substituent.



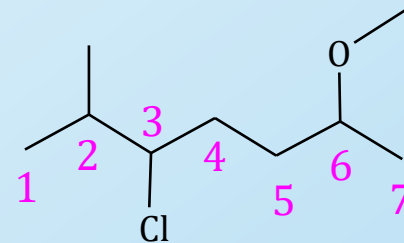
2-methoxy butane
OR sec-butylmethyl
ether



ethoxy cyclohexane
OR
cyclohexyl ethyl ether



methyl phenyl
ether

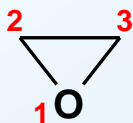


3-chloro-6-methoxy-
2-methyl heptane

Cyclic Ethers

Although cyclic ethers have IUPAC names, their common names are more widely used.

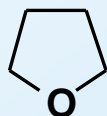
IUPAC: prefix **ox-** shows oxygen in the ring. The suffixes **-irane**, **-etane**, **-olane**, and **-ane** show three, four, five, and six atoms in a saturated ring.



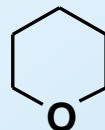
Oxirane
(epoxide)



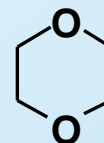
oxetane



oxolane
Tetrahydrofuran



oxane



1,4-dioxane

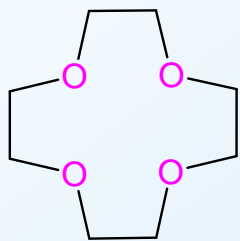
Physical Properties of Ethers

1. Boiling Points: Ethers have low boiling points since their intermolecular force is the weak dipole moment. Their boiling point is lower than alcohols of corresponding molecular weight (MW). (due to lack of H-Bonding) and higher than alkanes.
2. Solubility in water: Due to lack of hydrogen bonding they have low solubility in water. As the MW increases solubility in water decreases.
3. Density: They are lower in density than water.
4. Odor: Have a sweet odor.

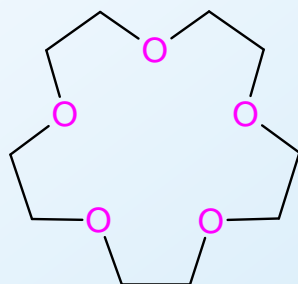
Compound	Formula	MW g/mol	Bpt °C	Dipole moment
Water	H ₂ O	18	100	1.9
Ethanol	CH ₃ CH ₂ OH	46	78	1.7
Dimethyl ether	CH ₃ OCH ₃	46	-25	1.3
Propane	CH ₃ CH ₂ CH ₃	44	-42	0.1
Diethyl ether	CH ₃ CH ₂ OCH ₂ CH ₃	74	35	1.6
1-butanol	CH ₃ CH ₂ CH ₂ CH ₂ OH	74	118	1.7

Applications of Ethers

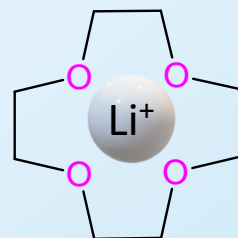
- **Solvent:** This is by far the most common use of ethers. They are more nonpolar than alcohols and can dissolve more nonpolar compounds. Tetrahydrofuran is a very common lab solvent – it has a higher boiling point so reactions can be carried out at higher temperatures.
- **Crown Ethers:** used to trap metals (chelating agents). Can also be used as phase transfer catalyst.



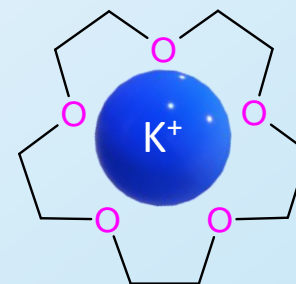
12-crown-4



18-crown-6



solvates Li^+ ion

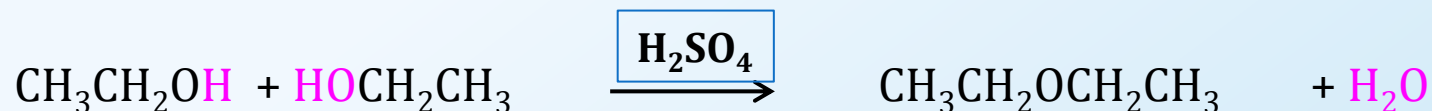


solvates K^+ ion

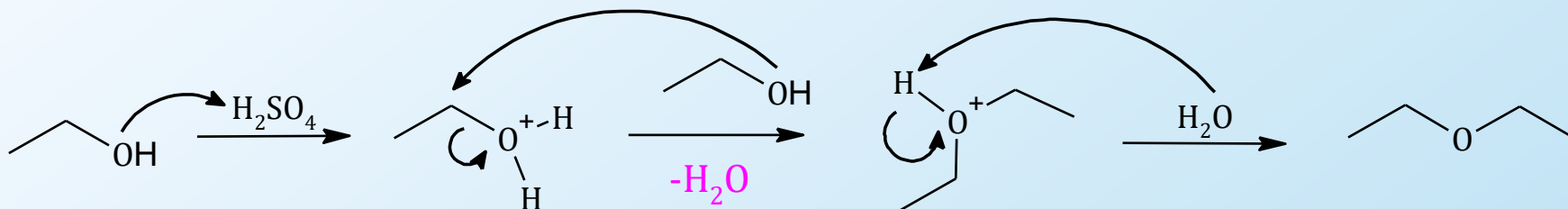
- **Anesthetic Agents:** Diethyl ether was used first as an anesthetic agent in the 1840s. It is still used presently, but it does cause side effects.
- **Epoxy Ethers:** These are polymers of epoxy ethers used as coating agents on metals to protect from weathering.

Ether Synthesis 1 - Bimolecular Dehydration

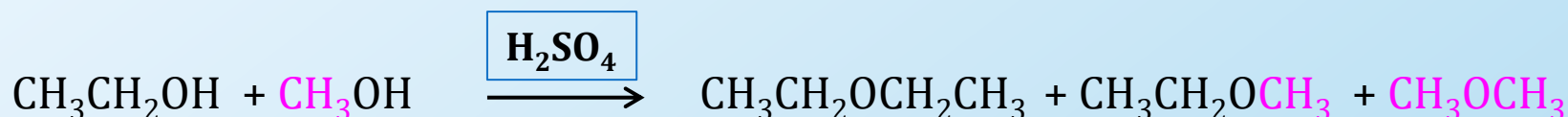
- 1) Bimolecular Dehydration: Industrial method, not good lab synthesis. If temperature is too high, then an alkene forms (elimination occurs).



Mechanism involves protonation from the acid and then a $\text{S}_{\text{N}}2$ substitution with the second molecule of alcohol as nucleophile. The final step is deprotonation of oxonium ion to give the ether.

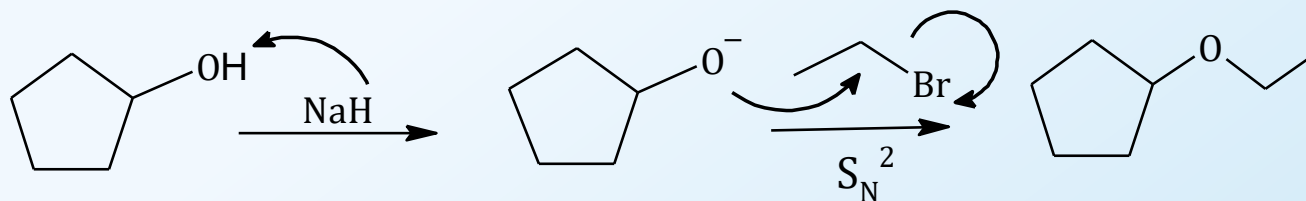


This is a good way to make symmetrical ether (the two alkyl groups on either side of oxygen are same); however, this is not good for asymmetric ethers as it can result in a mixture.

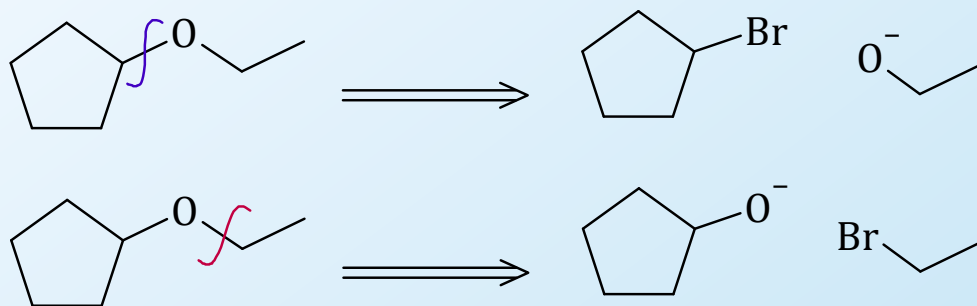


Ether Synthesis 2 – Williamson Synthesis -1

2) Williamson Synthesis: This synthesis is more efficient in making asymmetric ethers. An alkoxide ion is added to a 1° alkyl bromide (or tosylate) and reaction occurs via S_N2 mechanism.



Retrosynthesis of ethers using Williamson synthesis. Cleave the oxygen to form the alkoxide and alkyl halide. In the example below, both cleavages will work equally well as there is no steric hinderance or a bulky nucleophile.

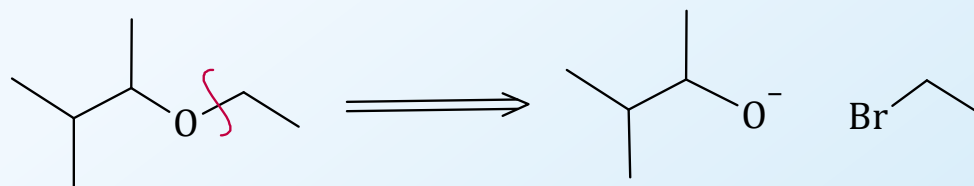


In some retrosynthesis, it is possible that in addition to substitution of alkyl halide and alkoxide to give ether, there might be elimination reaction to give alkene also. See next slide for such an example.

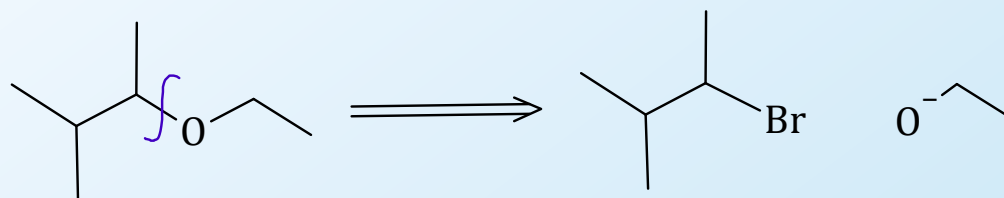
Ether Synthesis - 2 - Williamson Synthesis -2

In the retrosynthesis below, the two fragments are quite different and here it is possible to get an E2 product also.

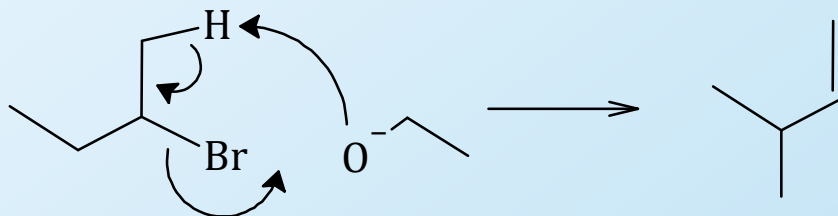
Retro 1



Retro 2

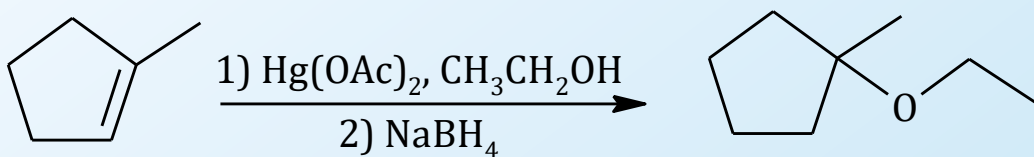
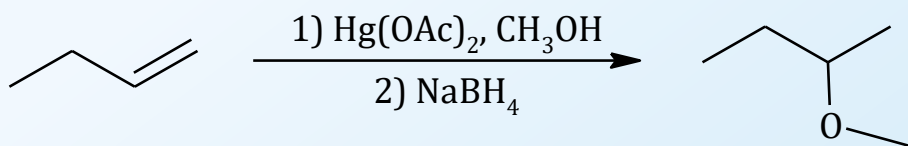


Retrosynthesis 2 may also give E2 product because the halide is secondary and sterically hindered for S_N2 reaction.



Ether Synthesis – 3 – Alkoxymercuration

3) Alkoxymercuration-Demercuration: This is another excellent way to make asymmetric ethers. The addition of the alkoxy group is Markovnikov addition.

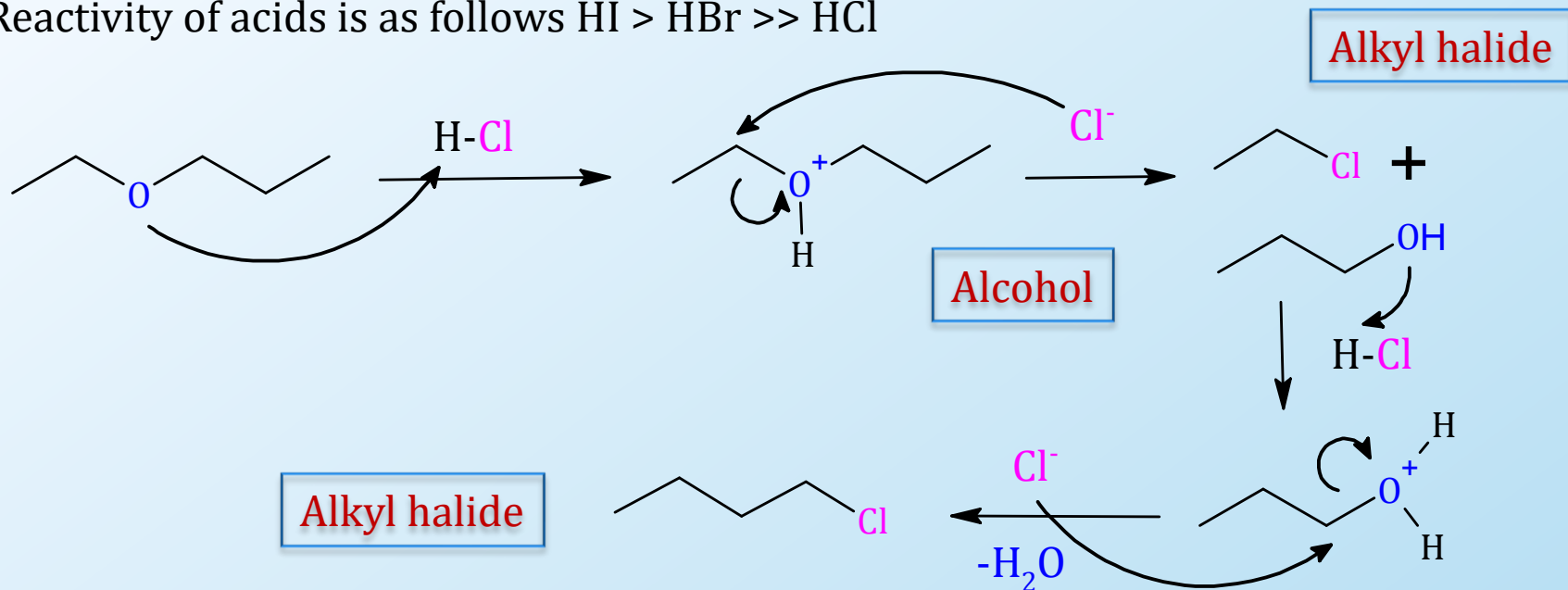


Reaction of Ethers - Acidic Cleavage

Ethers are unreactive toward base, but in presence of haloacids the ether is the Lewis base and becomes protonated which can undergo substitution reactions with strong acids generating an alcohol and alkyl halide.

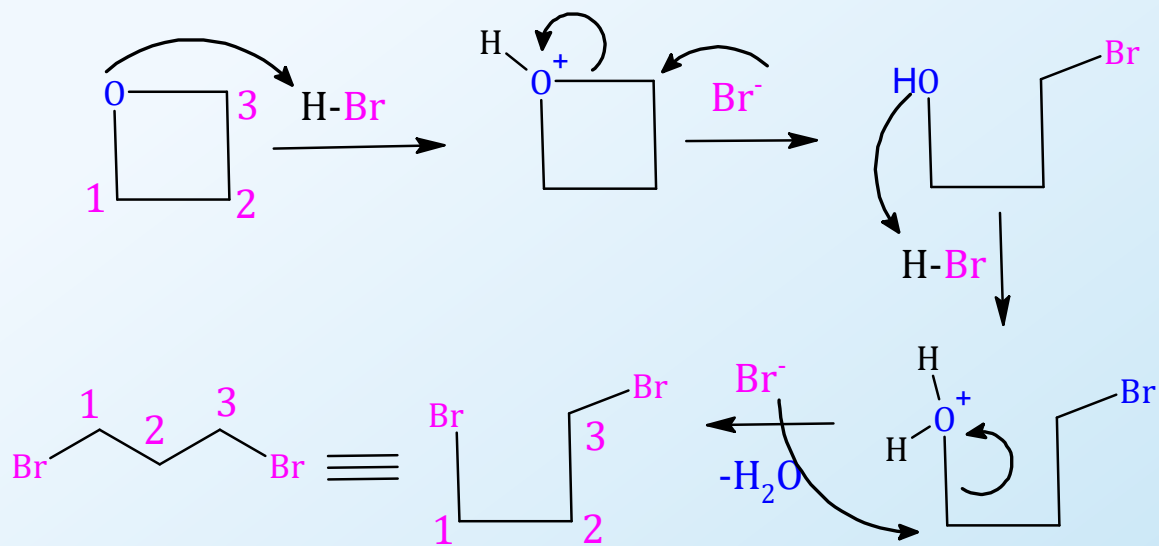
The alcohol generate can now undergo a typical S_N2 reaction to give an alkyl halide with haloacids. The alcohol is protonated, becomes a leaving group, and is substituted by a halide. Once ether is treated with haloacid, the reaction will occur twice to make two alkyl halides.

Reactivity of acids is as follows $HI > HBr \gg HCl$



Another Acid Cleavage Example

This example is the acidic cleavage of a cyclic ether. In this case you still get two halides but not two molecules since the cleavage will give a long alkyl group.



Key Concepts

- Ethers – Nomenclature
- Physical properties
- Synthesis
 - Dehydration of alcohol
 - Williamson synthesis
 - Oxymercuration
- Reactions (Acidic Cleavage)