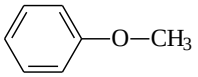
ETHERS

• A class of organic compounds which contain an ether group, an oxygen atom connected to two (substituted) alkyl or aryl groups

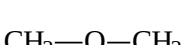
•Formula R-O-R where R is alkyl or aryl.

•Ethers can be symmetrical (i.e. have similar groups separated by the oxygen atom) or unsymmetrical

•Examples:



Methyl Phenyl Ether



Dimethyl ether

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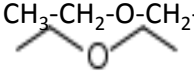
Primary, secondary, and tertiary ethers

- The terms *"primary ether"*, *"secondary ether"*, and *"tertiary ether"* are occasionally used and refer to the carbon atom next to the ether oxygen.
- In a *primary ether* this carbon is connected to only one other carbon as in diethyl ether

CH_3-CH_2-O-CH_2-CH_3.



Primary Ether

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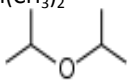
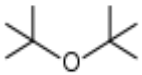
Primary, secondary, and tertiary ethers

- An example of a *secondary ether* is diisopropyl ether $(CH_3)_2CH$-O-$CH(CH_3)_2$



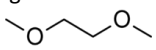
Secondary Ether

- An example of a *tertiary ether* is di-tert-butyl ether $(CH_3)_3C$-O-$C(CH_3)_3$.



Tertiary Ether

- Polyethers are compounds with more than one ether group, e.g.



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IUPAC Names

- To name ethers in IUPAC:
  - Identify the longest chain or largest ring (R^1 or R^2 as the parent compound.
  - Number the parent carbon skeleton to give the carbon connected to the ether Oxygen the lower possible number.
  - Name the OR substituent group as "alkoxy" = alk[yl] →-alk + oxy (from oxygen). Thus, methoxy is CH_3O- ; ethoxy is CH_3CH_2O- ; propoxy is $CH_3CH_2CH_2O$- , and so on.

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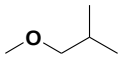
- Ethers are named using the general formula *"alkoxyalkane"*, for example CH_3-CH_2-O-CH_3 is methoxyethane.
- If the ether is part of a more complex molecule, it is described as an alkoxy substituent, so -OCH_3 would be considered a *"methoxy-"* group.
- Examples:

Methoxy-ethane

1-Methoxy-propane



1-Methoxy-2-methyl-propane

2-Methoxy-propane

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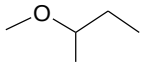
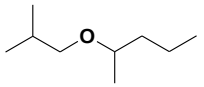
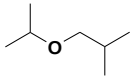
IUPAC names of Ethers



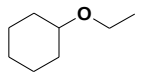
2-Methoxy-butane



2-Isobutoxy-pentane



1-Isopropoxy-2-methyl-propane



Ethoxy-cyclohexane

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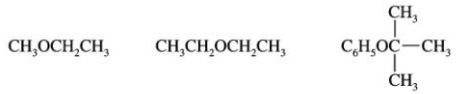
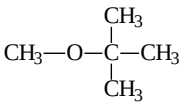
Common Names of Ethers

- Common names: name the groups bonded to oxygen in alphabetical order followed by the word ether.
- I.e. Alkyl alkyl ether e.g. *"ethyl methyl ether"*.
- Symmetrical: use dialkyl, or just alkyl.



Ethyl methyl ether | **Diethyl ether** | ***tert*-Butyl phenyl ether**



***t*-butyl methyl ether or methyl *t*-butyl ether**

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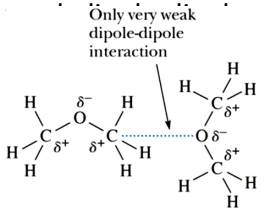
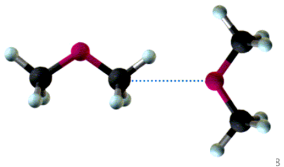
Physical Properties

- Ether molecules cannot form hydrogen bonds among each other, resulting in a relatively low boiling point comparable to that of the analogous alcohols.
- Although ethers are polar compounds, only





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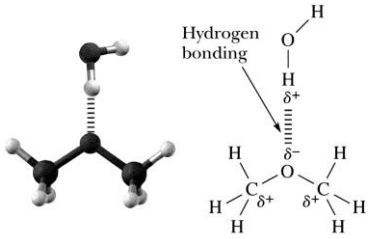
Physical Properties

Boiling points of ethers are:

- lower than alcohols of comparable MW.
- close to those of hydrocarbons of comparable MW

Ethers are hydrogen bond acceptors.

- They are more soluble in H_2O than hydrocarbons.
- Diethyl ether and 1-butanol have solubilities of about 8 g per 100 mL in water



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Boiling Points

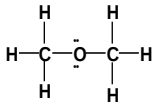
Ethers have similar to alkanes of comparable molecular weight. Note that alcohols are hydrogen-bonded giving them much higher boiling points.

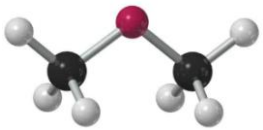
Comparison of the Boiling Points of Ethers, Alkanes, and Alcohols of Similar Molecular Weights

Compound	*Formula*	*MW*	*bp (°C)*
water	H_2O	18	100
ethanol	$CH_3CH_2—OH$	46	78
dimethyl ether	$CH_3—O—CH_3$	46	−25
propane	$CH_3CH_2CH_3$	44	−42
n-butanol	$CH_3CH_2CH_2CH_2—OH$	74	118
tetrahydrofuran		72	66
diethyl ether	$CH_3CH_2—O—CH_2CH_3$	74	35
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36

Structure and Polarity

- Bent molecular geometry
- Oxygen is sp^3 hybridized
- Tetrahedral angle
  - In dialkyl ethers, oxygen is sp^3 hybridized with bond angles of approximately 109.5°.
  - In dimethyl ether, the C-O-C bond angle is 110.3°.





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Solubility of Ethers

Structural Formula	Name	Molecular Weight	bp (°C)	Solubility in Water
CH_3CH_2OH	Ethanol	46	78	Infinite
CH_3OCH_3	Dimethyl ether	46	−24	7.8 g/100 g
$CH_3CH_2CH_2CH_2OH$	1-Butanol	74	117	7.4 g/100 g
$CH_3CH_2OCH_2CH_3$	Diethyl ether	74	35	8.0 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	1,4-Butanediol	90	230	Infinite
$CH_3CH_2CH_2CH_2CH_2OH$	1-Pentanol	88	138	2.3 g/100 g
$CH_3OCH_2CH_2OCH_3$	Ethylene glycol dimethyl ether	90	84	Infinite
$CH_3CH_2CH_2CH_2OCH_3$	Butyl methyl ether	88	71	Slight

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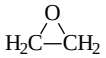
Cyclic Ethers

- These ethers have some special names:
- Epoxides (oxiranes) 
- Oxetanes 
- Furans 
- Oxolanes 
- Pyrans 
- Oxanes 
- Dioxanes 

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Crown Ethers

- Crown ether: A cyclic polyether derived from ethylene glycol
- These ethers are called "crown ethers" due to their shape. They are based on repeating -$\mathbf{OCH_2CH_2}$- units, derived from ethylene glycol $\mathbf{HOCH_2CH_2OH}$
- These compounds are important co-solvents.
- The *interior* of the cavity is *water like*, whereas the *exterior* is *hydrocarbon like*.
- So a metal ion inside the cavity can be "carried" into an organic solvent.

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Crown Ethers

- This allows ionic systems such as KF to be dissolved in organic solvents and used as reagents where the metal ion is in a complex, but the anion is unsolvated and therefore quite reactive.
- Varying the size of the crown ether varies the cavity size and some metal ions fit better than others.

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Crown Ethers

- The parent name is crown, preceded by a number describing the size of the ring and followed by the number of oxygen atoms in the ring.
- The usual “shorthand” designation of crown ethers is m-crown-n where
  - m = total number of atoms and
  - n = number of hetero-atoms (usually oxygen) in the ring.
  - E.g. 12-crown-4, 15-crown-5, 18-crown-6

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Crown Ethers

- The outstanding characteristic of crown ethers is their ability to incorporate inorganic cations in their cavity;
- the extent and specificity of this ability depends on the size of the cavity;
- the extent and specificity of this ability depends on the size of the cavity and of the cation.
- As an example, 15-crown-5 is highly specific for sodium,
- 18-crown-6 is highly specific for potassium ion.

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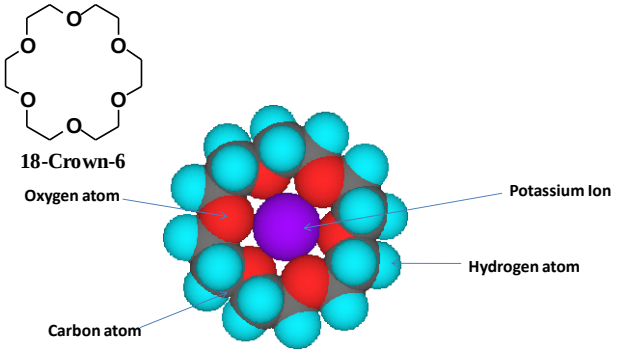
Crown ethers ….

- The diameter of the cavity created by the repeating oxygen atoms is comparable to the diameter of alkali metal cations.
  - 18-crown-6 provides very effective solvation for K^+



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Important ethers used in the industry

Ethylene oxide

- It is the smallest cyclic ether and is mainly used as an intermediate in the production of ethylene glycol and other chemicals. It is also used to sterilize medical supplies and spices.

Dimethyl ether

- An aerosol spray propellant, It is useful as a solvent (in liquefied form), multi-purpose fuel, refrigerant, aerosol spray propellant, medium for chemical reactions, and a blowing agent for foam..

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Important ethers used in the industry

Diethyl ether

- A common low boiling solvent (b.p. 34.6°C), and an early anaesthetic.

Dimethoxyethane (DME)

- It is a good solvent and a higher boiling (b.p. 85°C) alternative to diethyl ether and tetrahydrofuran. It is often used in organometallic chemistry and is the low-viscosity component of the solvent for electrolytes in lithium batteries.

Tetrahydrofuran (THF)

- This cyclic ether is one of the most polar simple ethers used as a solvent. It is also used to degrease metal parts.

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Important ethers used in the industry

Polyethylene glycol (PEG)

- A linear polyether, e.g. used in cosmetics and pharmaceuticals. This nontoxic, water-soluble polymer is the basis for a number of laxatives and skin creams, and is a dispersant in various toothpastes.
- It prolongs the medicinal effect of protein medications, when the proteins are attached to it.
- In woodworking, it can be used to replace some of the water content in wood, to prevent the wood from warping or shrinking when dried.

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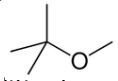
Important ethers used in the industry

MTBE (**M**ethyl **t**ert-**B**utyl **E**ther or IUPAC name: 2-methoxy-2-methylpropane)



- MTBE is an additive to gasoline that improves the octane rating of gasoline . If 15% MTBE is added to gasoline the rating goes up by 5 points! MTBE is called an oxygenate because it adds oxygen to the combustion reaction with gasoline making it a cleaner burning reaction.
- Due to its solubility in water, MTBE has gotten into the water table and has caused some concern.
- At present, it is being phased out and alternatives are being investigated.

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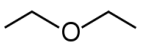
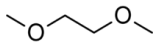
Structures of some important ethers



Diethyl Ether

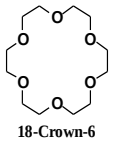
Dimethyl Ether

Ethylene Oxide



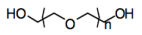
Dimethoxy Ethane

Dioxane



18-Crown-6

An example of
A crown ether



Polyethylene glycol

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