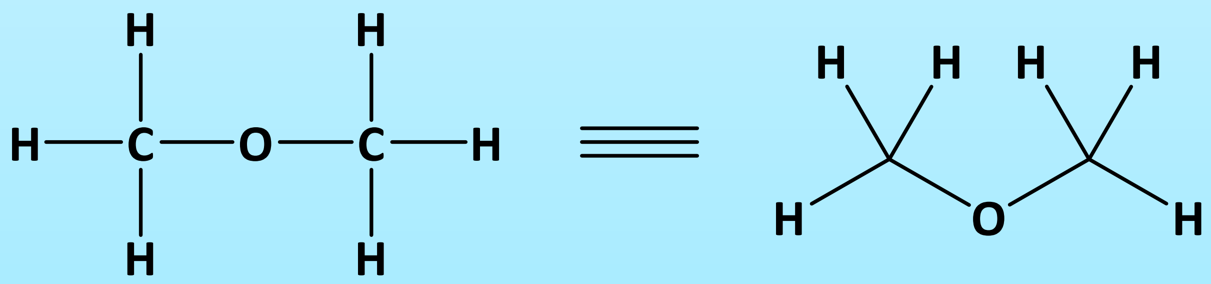
Ethers

Ethers

- **Ethers are compounds that are characterized by its functional group, i.e. an oxygen atom bonded to two carbon atoms**
- **An example of this is dimethyl ether, the simplest ether known and as shown below**

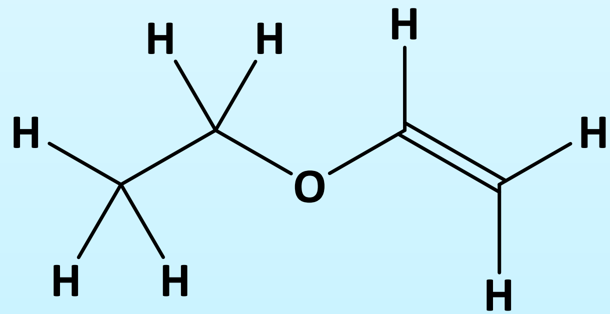


≡ $CH_3\text{-}O\text{-}CH_3$

Ethers

- **In this compound, the oxygen atom is sp^3 hybridized and two of its hybrid orbitals form sigma bonds with an sp^3 hybrid orbital of each of the carbon atoms**
- **The other two sp^3 hybridized orbitals of the oxygen atom each contain non-bonding electron pairs**
- **Another example of an ether is ethyl vinyl ether – structure shown below**

Ethers



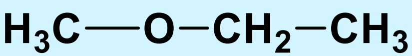
$\equiv$ CH_3CH_2-O-CH=CH2

- **Here the sp^3 hybridized orbitals of the oxygen atom are bonded to an *sp^3* hybridized orbital of one carbon atom and an *sp^2* hybridized orbital of the other carbon atom**
- **As seen from these two examples, the carbon atoms that are attached to the oxygen atom in an ether can be *sp^1*, *sp^2* or *sp^3* hybridized**

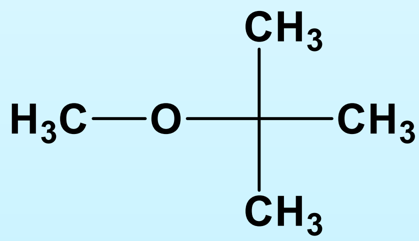
Nomenclature of ethers

- **In the IUPAC naming system, ether are named by selecting the longest chain as the parent alkane and naming the –OR group attached to it as the *alkoxy group***
- **The old (common) names of ether were derived by listing the alkyl groups attached to the oxygen in alphabetical order and then adding the word “ether” at the end**
- **The following are some examples:**

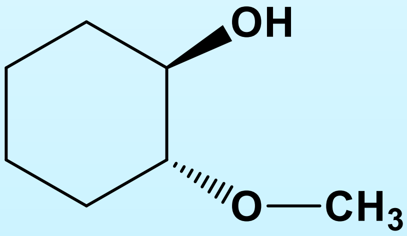
Nomenclature of ethers



Methoxyethane
(ethyl methyl ether)



2-Methoxy-2-methylpropane
(methyl *tert*-butyl ether)



trans-2-methoxycyclohexanol

- **Ether are also found in the form of cyclic compounds where the oxygen atom is part of the ring system**
- **It is because of their presence in the ring that chemists refer to these compounds as heterocyclics**

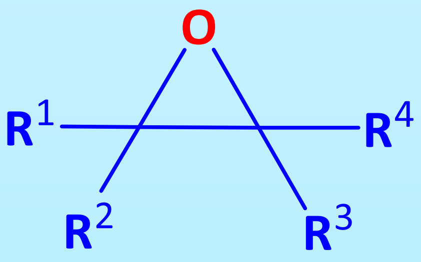
Reaction of ethers

- Ethers, [i.e. R–O–R], resemble alkanes in that they are resistant to chemical reactions
- They do not react with oxidizing agents (such as $KMnO_4$, $K_2Cr_2O_7$)
- They are not affected by most acids or bases at moderate temperatures
- It is because of their good solvent properties as well as their general inertness to chemical reactions that ethers are widely employed as solvents in which reactions are carried out

Reaction of ethers

Epoxides

- An epoxide is a cyclic ether in which the oxygen atom is part of a three-membered ring

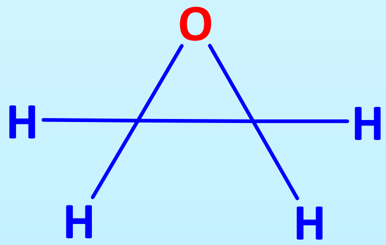


Functional group of an epoxide

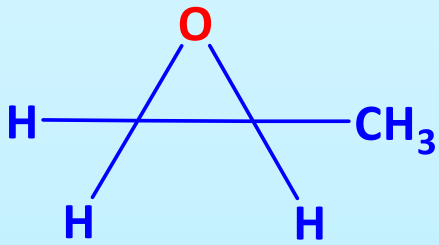
- Although classed as an ether, they are quite reactive when compared to other ethers…

Reaction of ethers

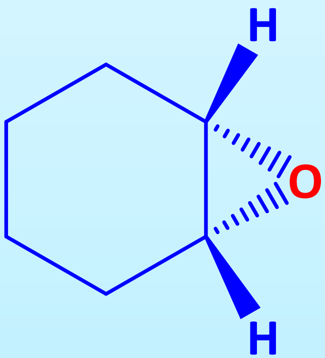
- **Examples of these include:**



ethylene oxide



propylene oxide

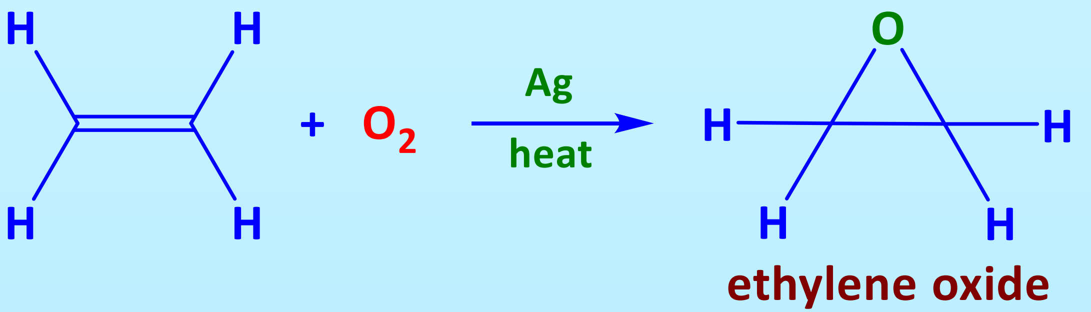


1,2-epoxycyclohexane

- **Common names of epoxides are derived by giving the common name of the alkene from which the epoxide might have been derived followed by the word 'oxide': e.g. ethylene oxide**

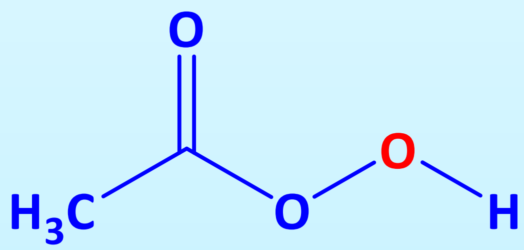
Synthesis of ethers

- Ethylene oxide is prepared by passing a mixture of ethene and air (or oxygen) over a silver catalyst – an industrial process



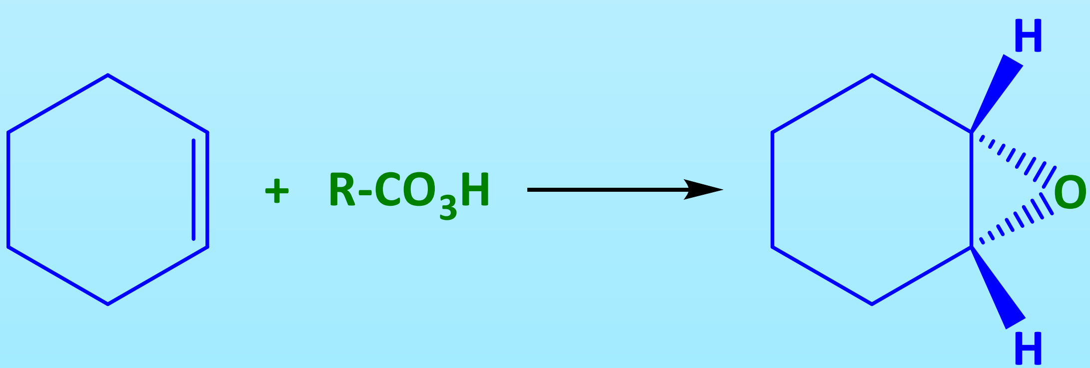
- The most common laboratory method for the synthesis of epoxides from alkenes is oxidation with a peroxycarboxylic acid, R-CO_3H, such as peroxyacetic acid

Synthesis of ethers



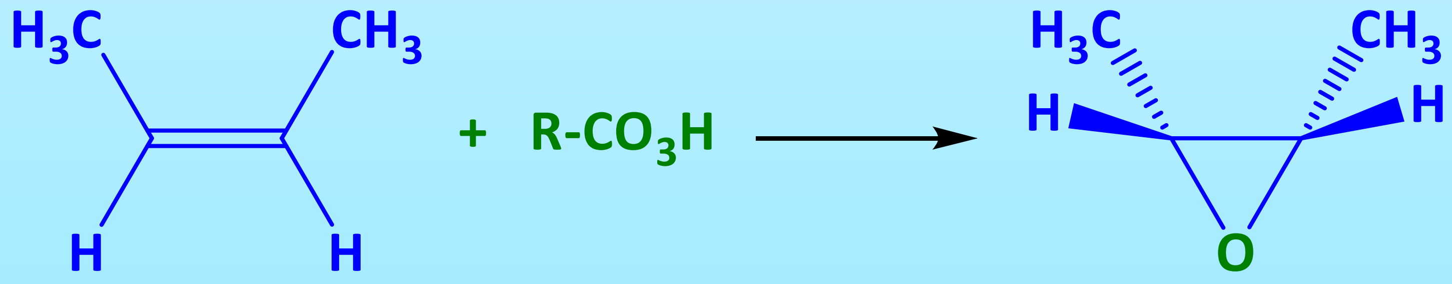
peroxyacetic acid
(peracetic acid)

- **Cyclohexene when treated with peroxy-carboxylic acid will produce the epoxide, 1,2-epoxycyclohexane or cyclohexene oxide**



Synthesis of ethers

- Epoxidation occurs in a very stereospecific way in which the oxygen is delivered from one side only
- An example can be seen in the epoxidation of *cis*-2-butene where *cis*-2-butene oxide is forms



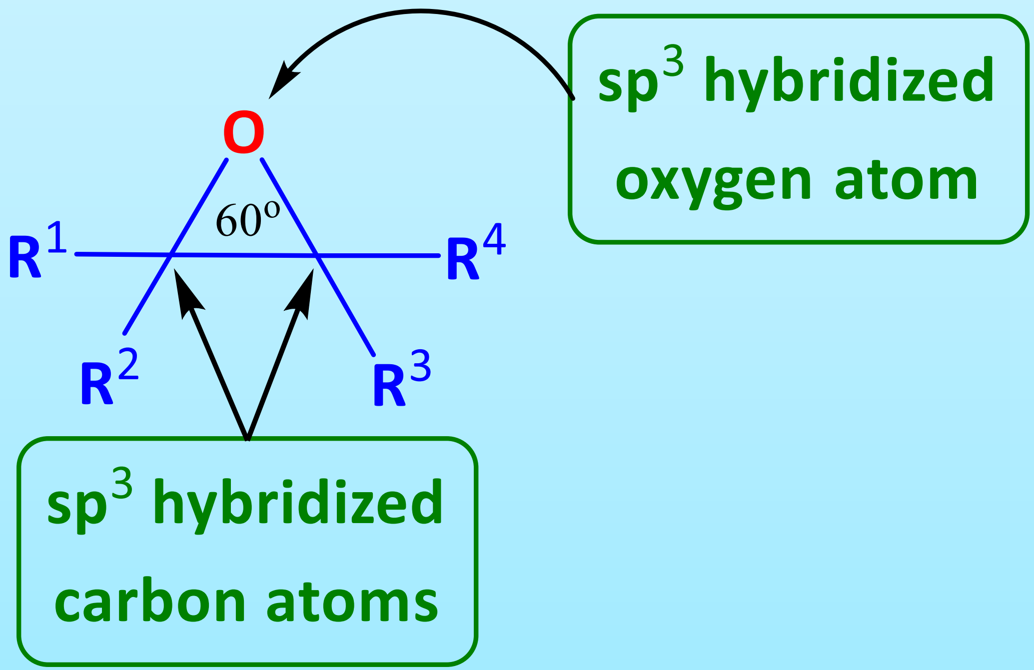
Synthesis of ethers

Acid-catalysed ring opening of epoxides

- **Ethers as shown earlier are very inert towards chemical reactions because of their structure**
- **The epoxides however are very reactive and this is primarily due to the nature of the molecule**
- **The two carbon atoms and the oxygen in an epoxide are all sp^3 hybridized and as such should have a bond angle of about 109.5^{o}**

Synthesis of ethers

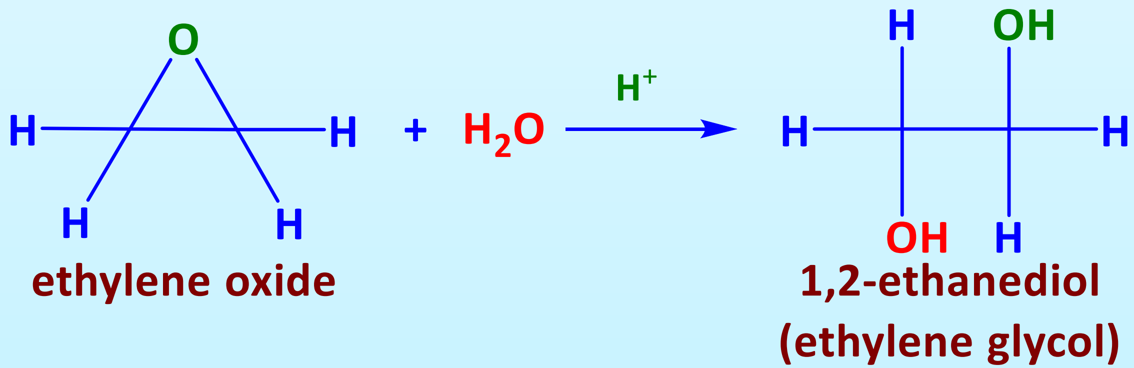
- In a three-membered epoxide ring, this bond angle is around 60º and as such, the ring is experiencing great strain



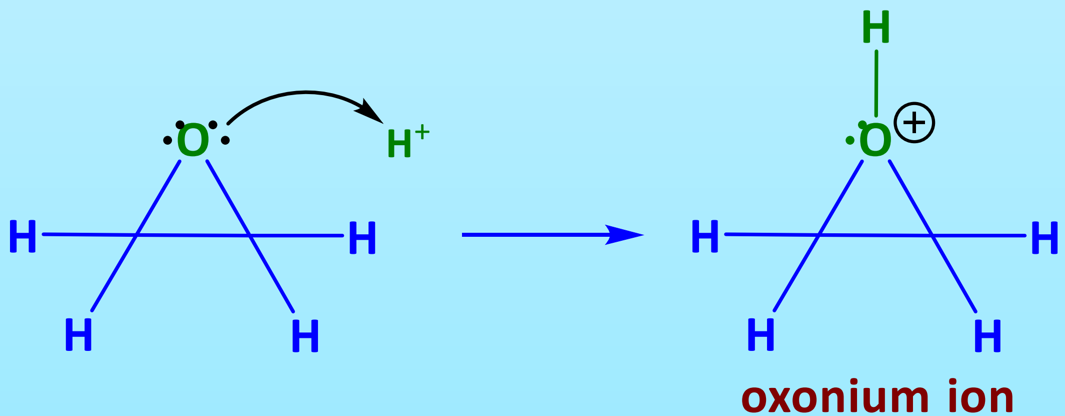
Synthesis of ethers

- It is because of this ring strain that epoxide undergo ring-opening reactions with a variety of reagents
- In the presence of an acid catalyst like perchloric acids, epoxides are hydrolyzed to glycols
- An example of this is the acid-catalyzed hydrolysis of ethylene oxide to yield 1,2-ethanediol

Synthesis of ethers

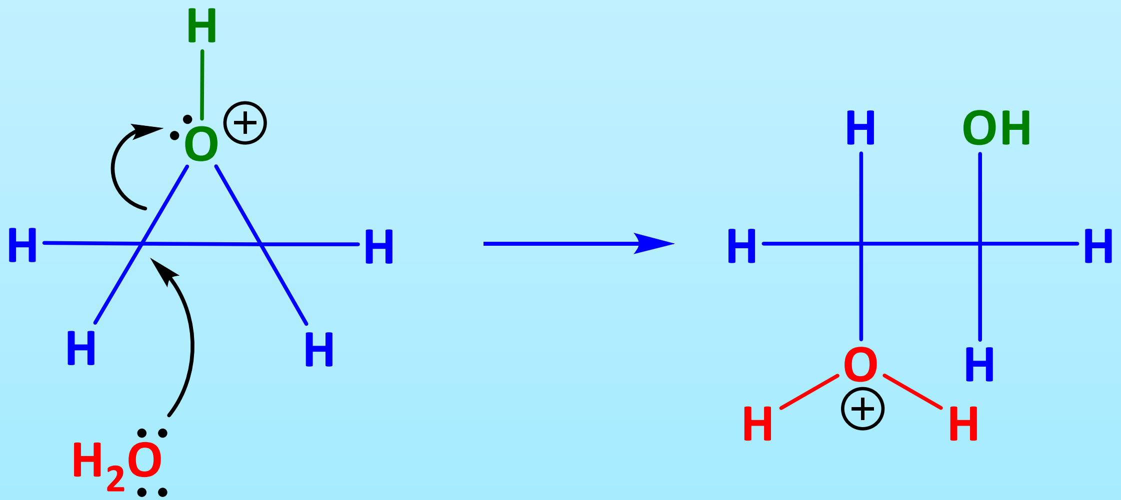


- **Under acidic conditions, the oxygen atom of the epoxide is protonated to form the oxonium ion intermediate**



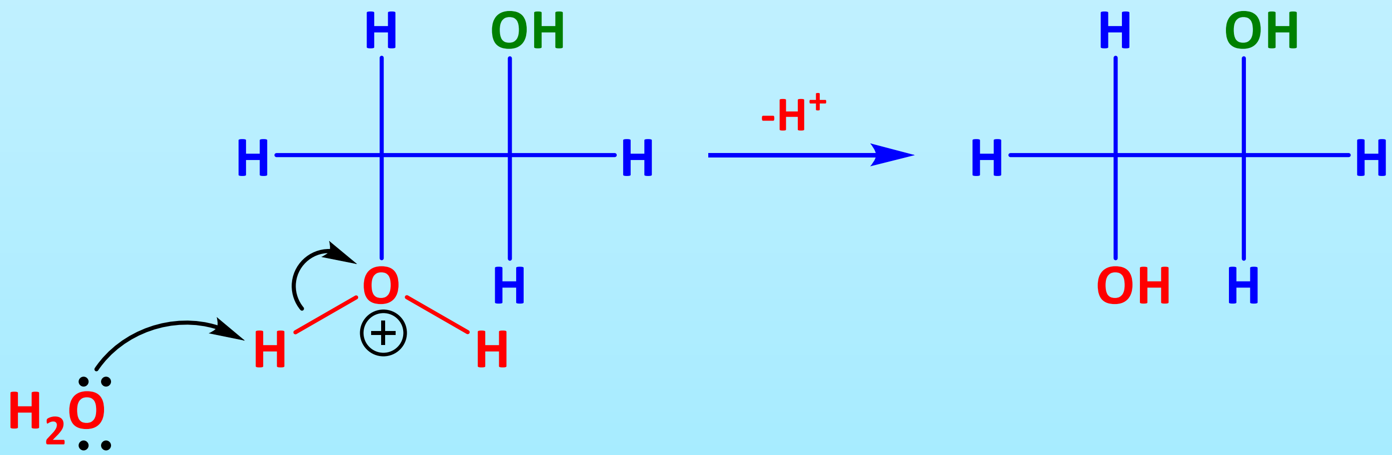
Synthesis of ethers

- **The oxonium ion intermediate is then attacked by water from the opposite side to the oxonium ion bridge, which results in the ring opening**



Synthesis of ethers

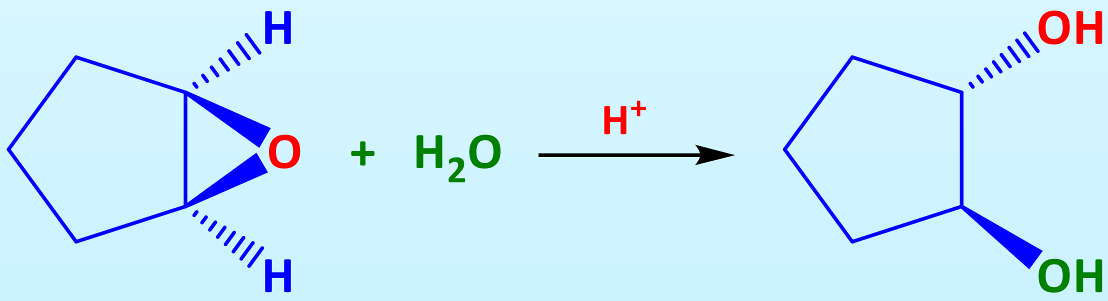
- **The final step simply involves the proton transfer to the solvent, which results in the glycol formation plus the regeneration of the acid-catalyst**



Synthesis of ethers

- As important aspect of this reaction is that the attack of the protonated epoxide occurs from the opposite side to the leaving group
- This means that the incoming nucleophile will attack in an *anti* fashion
- Consequently, when 1,2-epoxycyclopentane is hydrolyzed, the product obtained is *trans*-cyclopentanediol

Synthesis of ethers

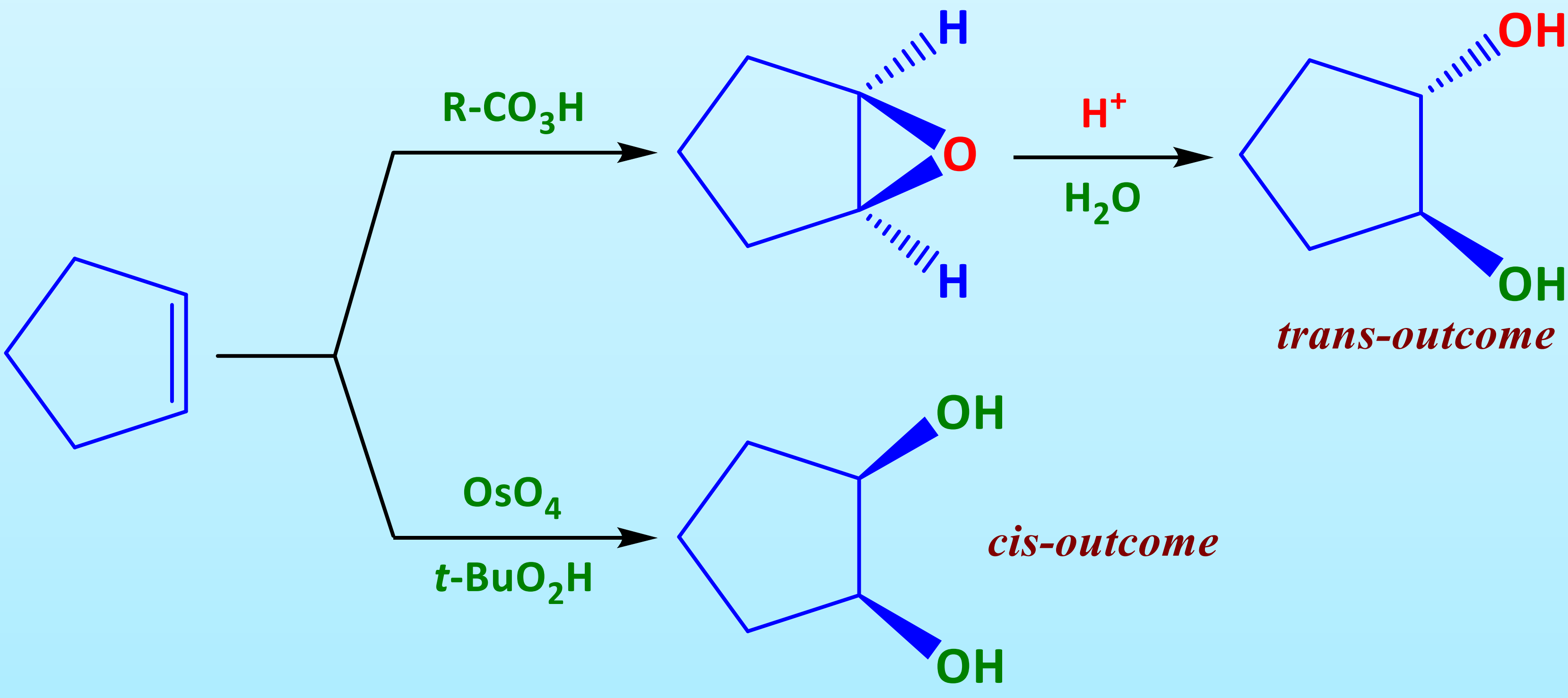


- Lets us at this point compare the stereochemistry of the glycol formation by acid-catalyzed hydrolysis of an epoxide with that formed by the oxidation of an alkene with OsO_4 or $KMnO_4$
- Each reaction sequence is stereoselective but giving different isomers

Synthesis of ethers

- The acid-catalyzed hydrolysis of an epoxide yields a *trans*-product while the oxidation reaction yields a *cis*-product
- This difference in the outcome of the reaction can therefore be cleverly utilized to achieve the desired product
- Thus cyclopentene can be converted to the desired glycol by the proper choice of reagents as shown below

Synthesis of ethers

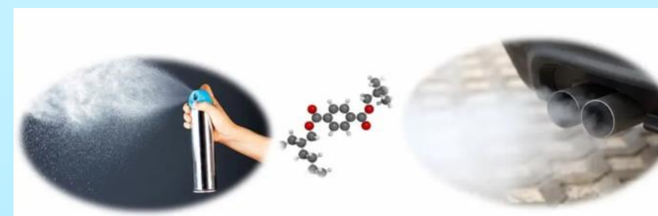


Industrial Applications of Ethers

- **Ethers have a wide variety of industrial uses**
- **Their commercial value is recognized in the following industries: rubber, plastics, paints and coatings, refrigeration, medicine, dentistry, petroleum, chemical, perfume, cosmetics, toiletries, and food**
- **The more volatile ethers have been used as liquid refrigerants, general anesthetics, commercial solvents, primers for gasoline engines, fuel additives, and rocket propellants**

Industrial Applications of Ethers

- A denaturant for several alcohol formulas, a starting fuel for diesel engines, and an entrainer for ethanol dehydration
- It is used abundantly for the military production of smokeless powder.



Industrial Applications of Ethers

- In the pharmaceutical industry, ethers are used as solvents, suspending agents, flavourings for oral drugs, and dental products
- They are used to increase viscosity, as penetrants and wetting agents, and as antioxidants and stabilizers