

Learning Guide for Chapter 16 - Ethers and Epoxides

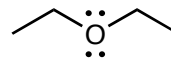
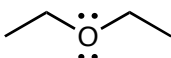
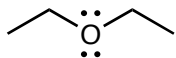
- I. Introduction to ethers, sulfides, and epoxides
- II. Nomenclature of ethers
- III. Synthesis of ethers and sulfides
- IV. Reactions of ethers and sulfides
- V. Synthesis of epoxides
- VI. Reactions of epoxides
- VII. Review of reactions

I. Introduction to ethers, epoxides, and thioethers

Definition and examples of ethers and thioethers

Describe an ether functional group:

How is an ether different from an ester or anhydride?



What is the most common ether? What is it used for?

What ether is used as an additive in gasoline? Why? Why has its use declined?

What does a thioether look like? What else are they called?

What do thioethers often smell like?

What thioether did we use in the reaction of alkenes with ozone?

Classifications of Ethers

Draw an example of each of the following:

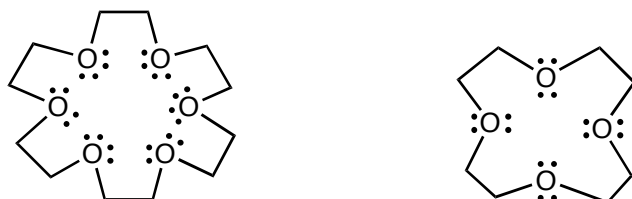
alkyl ether

aryl ether

cyclic ether

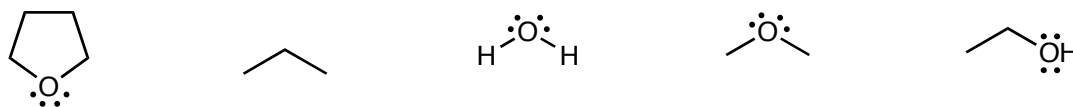
epoxide

What are crown ethers useful for?



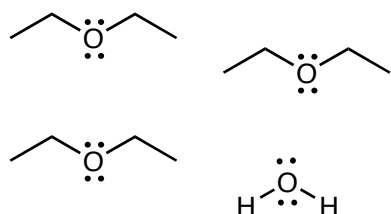
Physical Properties of Ethers

Put the following compounds in order of their boiling points.

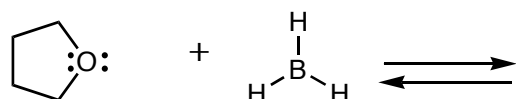


Why are ethers good solvents?

Can ethers undergo hydrogen bonding with each other? What about with water?

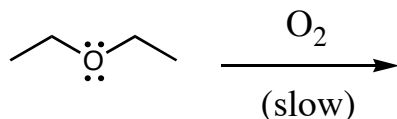


How can ethers stabilize electron deficient compounds?



Are ethers flammable?

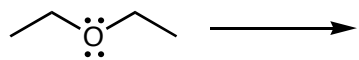
What can happen when ethers are exposed to air for a long time?



Reactivity of Ethers and Thioethers

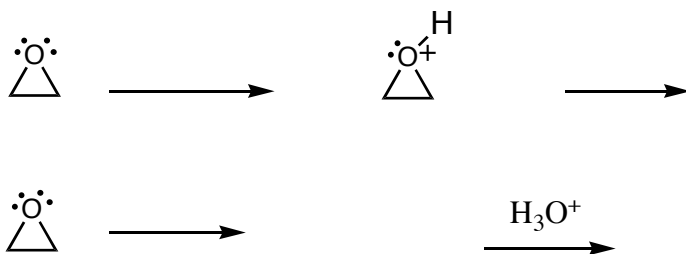
Which of the following will ethers react with?

acids bases nucleophiles electrophiles oxidizing agents reducing agents



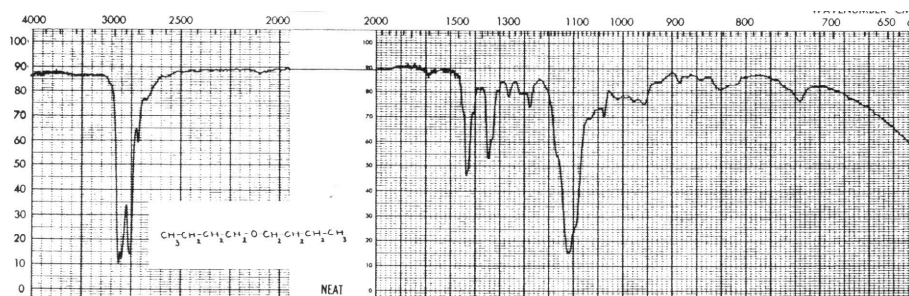
Which of the following will epoxides react with?

acids bases nucleophiles electrophiles



IR Spectra of Ethers

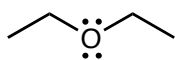
What band do ethers have that alkanes don't?



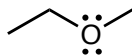
What other compounds have this band? How can they be distinguished from ethers?

NMR Spectra of Ethers

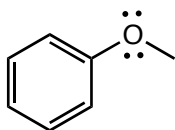
What chemical shift are the H's next to the O in an ether?



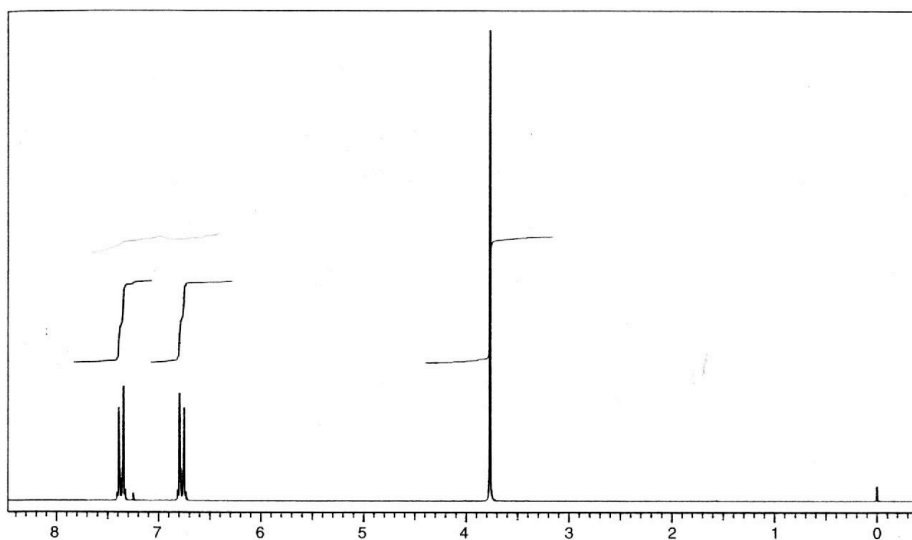
How will the spectra of a symmetrical ether and a nonsymmetrical ether be different?



What will happen with an aryl ether?



Deduce the structure of the compound which gave the following spectrum.



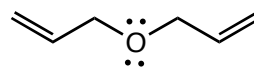
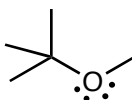
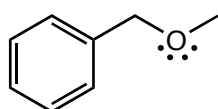
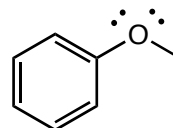
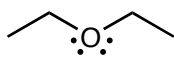
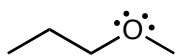
C_7H_7BrO

II. Nomenclature of ethers

Common names

How are common names for ethers constructed?

Give common names for the following ethers.

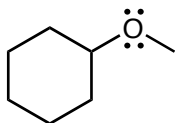
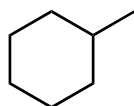


IUPAC names

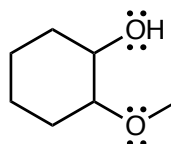
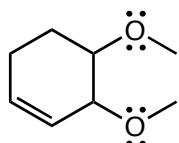
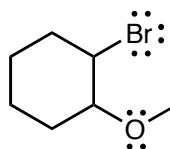
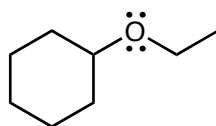
Are ethers principle groups?

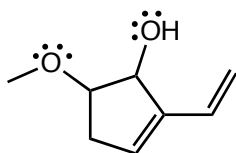
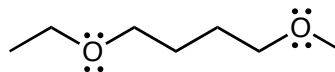
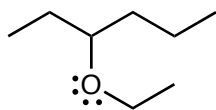
What part of the ether is considered a substituent?

How are ether substituents named?



Name the following compounds.





Draw structures for the following:

1-ethoxypropane

1-butoxy-1-ethanol

4-propoxy-1-butene

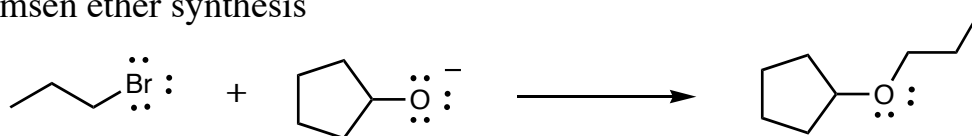
1,3-dimethoxypropane

1,1-dimethoxy-3-bromocyclopentane

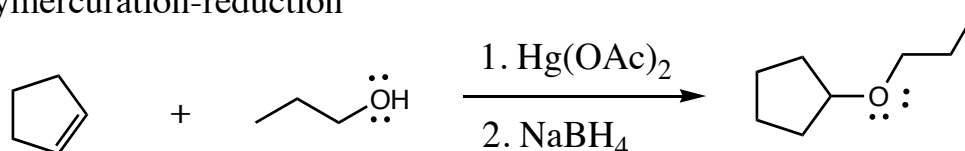
III. Synthesis of ethers and sulfides

What starting materials and reagents are needed for each of the methods of ether synthesis?

Williamson ether synthesis

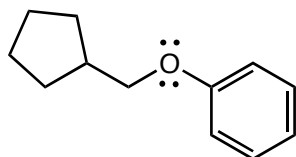


alkoxymercuration-reduction



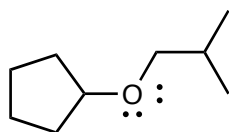
What is the main limitation of the Williamsen ether synthesis?

Synthesize the following ether by the Williamsen ether synthesis.

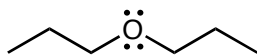


What is the main limitation of the alkoxymercuration-reduction reaction?

Synthesize the following ether by alkoxymercuration-reduction.

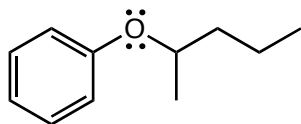


Synthesize the following ethers by either the Williamsen ether synthesis or alkoxymercuration-reduction. Explain why the other won't work!



Williamsen

alkoxymercuration-
reduction



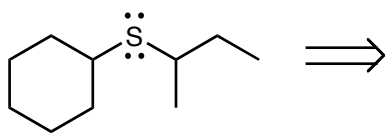
Williamsen

alkoxymercuration-
reduction

Which of these methods works for synthesis of sulfides?

What effect does the lower acidity of thiolate ions have?

Synthesize the following sulfide.

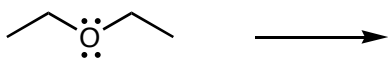


IV. Reactions of ethers and sulfides

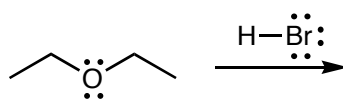
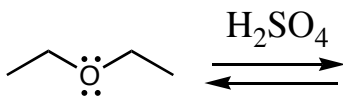
Reactions of Ethers

Are ethers highly reactive, or highly unreactive functional groups?

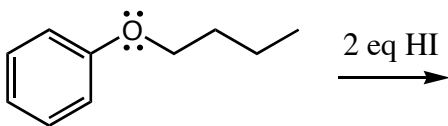
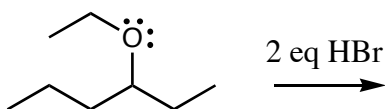
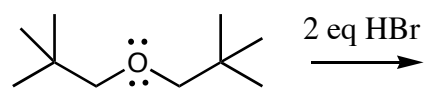
What kind of reagents do ethers react with?



Which of the following will give a new product?



What products would the following ethers give?

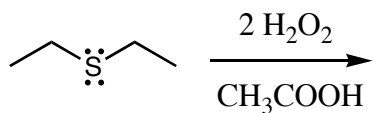
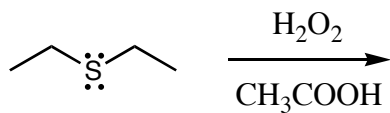


Is this a good way to make alkyl halides?

Reactions of Sulfides

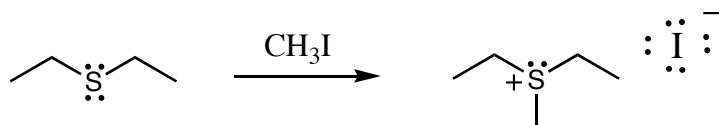
What reaction can sulfides undergo that ethers cannot?

What can they be oxidized to?



Which is a better nucleophile, S or O?

What happens when a sulfide acts as a nucleophile towards an alkyl halide?



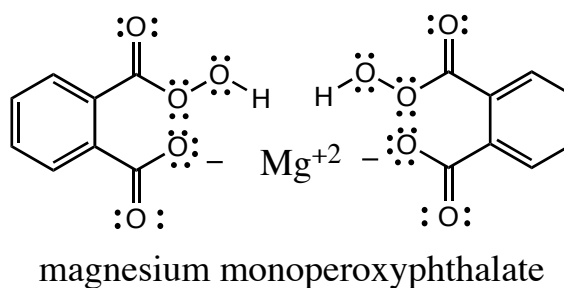
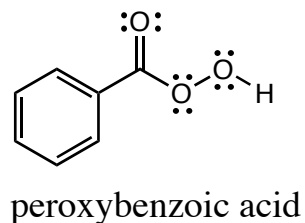
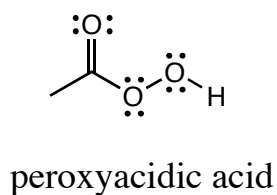
V. Synthesis of Epoxides

What are the two ways in which epoxides may be formed?

Epoxidation of alkenes

What do peroxyacids look like?

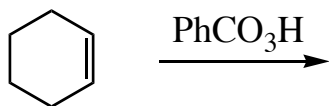
Which of the following peroxy acids are soluble in water or alcohols? Which in low polarity solvents? How are they abbreviated?

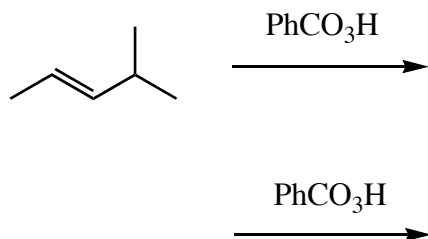


Write a reaction of an alkene with a peroxy acid to form an epoxide.

What gets oxidized and reduced in the reaction above?

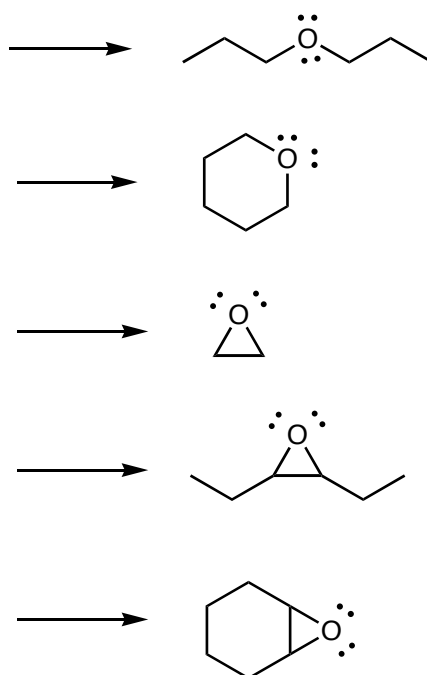
What stereochemistry does this reaction have? Why?



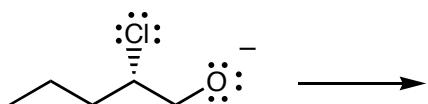


Cyclization of halohydrins

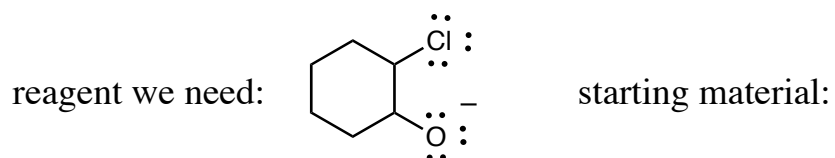
We have seen how alkoxides react with alkyl halides to form ethers in the Williamson ether synthesis. How could this be used to make an epoxide?



What is the stereochemistry of this reaction? Why?

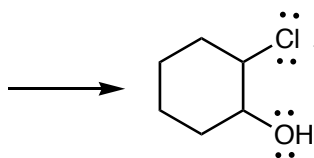


What does the starting material look like before the H is removed to make the alkoxide?
 What is this functional group called?



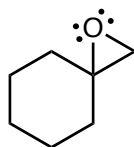
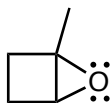
Write the entire reaction starting with the neutral starting material.

Where do halohydrins come from?



So, how are the two epoxide syntheses related?

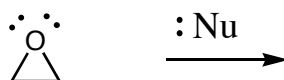
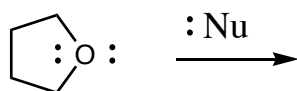
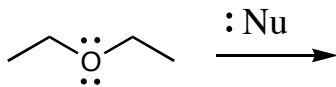
Show two ways each of the following epoxides could be formed from an alkene.



VI. Reactions of Epoxides

Reaction of epoxides with strong nucleophiles

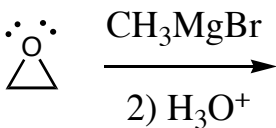
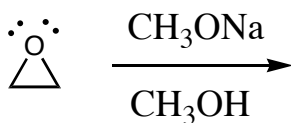
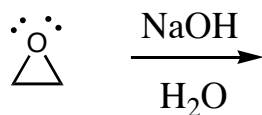
Why are epoxides good electrophiles, while ethers are not?



How do their energy diagrams compare?

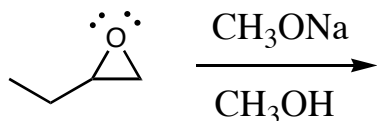
What needs to happen to complete the reaction?

What product is formed when each of the following nucleophiles is reacted with ethylene oxide? What is the proton source in each case?



What other nucleophiles would attack epoxides?

If the epoxide is not equally substituted, which side will be attacked?



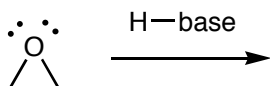
Write the two possible products.

How could we figure out which will be formed?

Knowing the answer, how can we make sense of it?

Reactions of protonated epoxides with weak nucleophiles

How can an epoxide react with an acid?

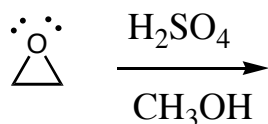
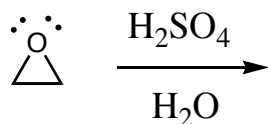


Which is a better electrophile, a neutral epoxide or a protonated one? Which requires a stronger nucleophile?

—

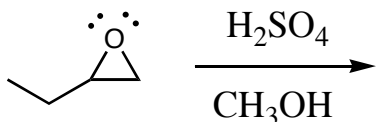
What kinds of weak nucleophiles would work?

Show how a protonated epoxide would form, then react with water or an alcohol. What product is formed?



What do you notice about the acid?

If the epoxide is not equally substituted, which side will be attacked?



Write the two possible products.

How could we figure out which will be formed?

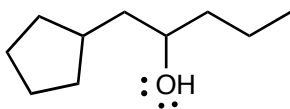
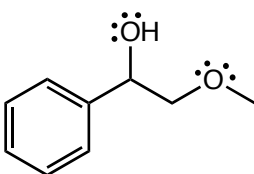
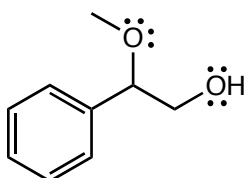
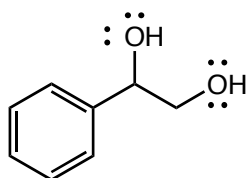
Knowing the answer, how can we make sense of it?

Synthesis using epoxides

What kinds of products can be made using epoxides?

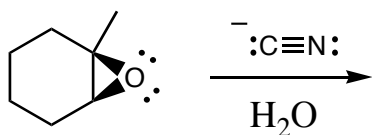
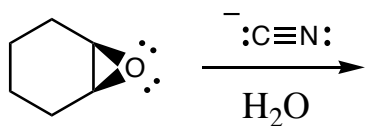
What steps should you take when designing a synthesis using an epoxide?

What reaction could be used to form the following products?



Stereochemistry of epoxide reactions

What is the stereochemistry of the addition of the Nu to an epoxide?



Compare the stereochemistry of the following reactions.

