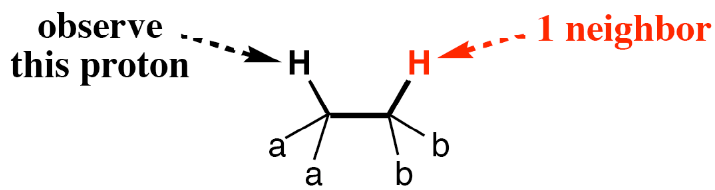
Spin-Spin Splitting: Why Does It Happen?

Origin of spin–spin splitting

The magnetic field of the neighboring protons adds or subtracts from the applied magnetic field - so changing the total magnetic field at an observed proton



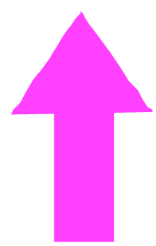
Total magnetic field at **H** (observed) = Applied field + effect of **H** (neighbor)

*The magnetic field due the **H** (neighbor) can be either with the applied field...*

Total magnetic field at **H** (observed) =  + 

applied magnetic field

...or it can be against the applied field

Total magnetic field at **H** (observed) =  + 

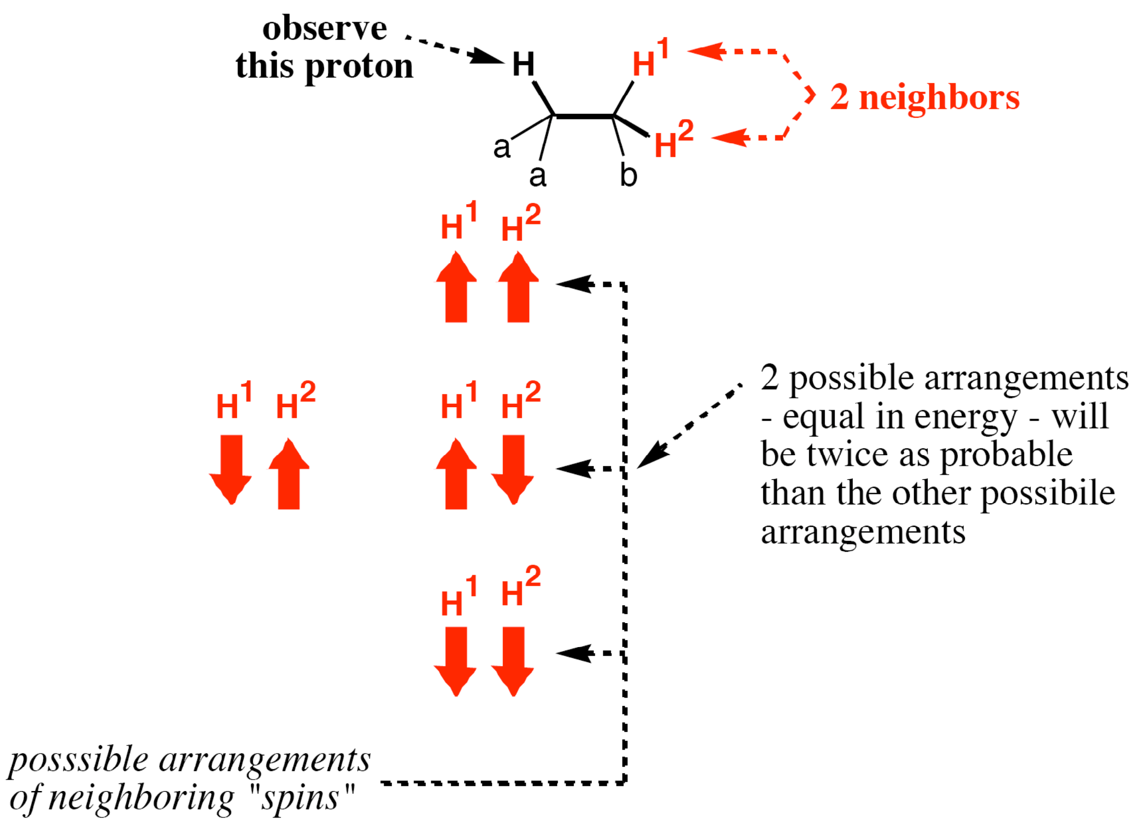
applied magnetic field

posssible arrangements of neighboring "spin"

- **These two possibilities have different energies - so there are 2 lines**
- **Each is equally probable - so the intensity of the lines is equal**

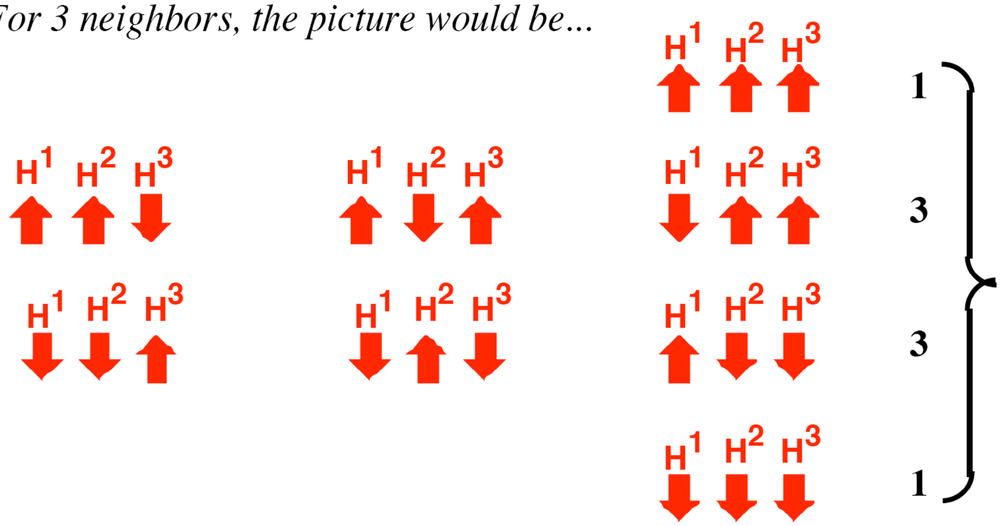
Reading: Section 13.4

Spin-Spin Splitting: More Than One Neighbor



- **These three possibilities have different energies - so there are 3 lines**
- **Probabilities 1:2:1 - so the intensity of the lines is 1:2:1**

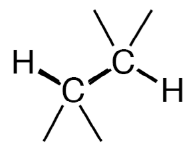
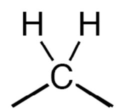
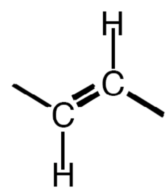
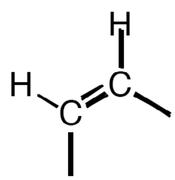
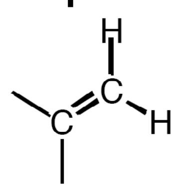
For 3 neighbors, the picture would be...



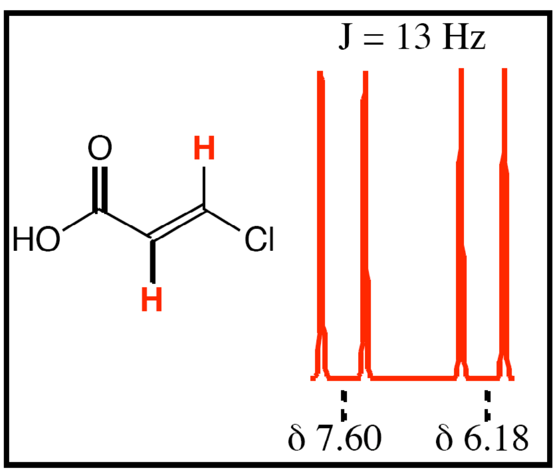
Reading: Section 13.4

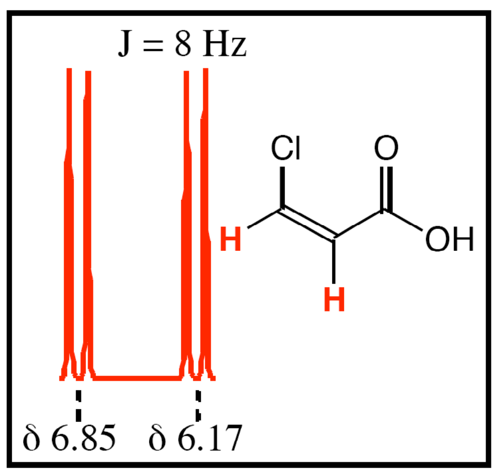
Spin-Spin Splitting: The Coupling Constant

Some typical values for coupling constants (J values)

Type of coupling	Typical structure	Range of coupling constant	Notes
vicinal		6 - 8 Hz	most common type of coupling
geminal		0 - 22 Hz	*only* observed when the two hydrogens are *chemically nonequivalent*
trans-alkene		11 - 18 Hz	
cis-alkene		6 - 14 Hz	
vinyl geminal		0 - 3 Hz	

Example:

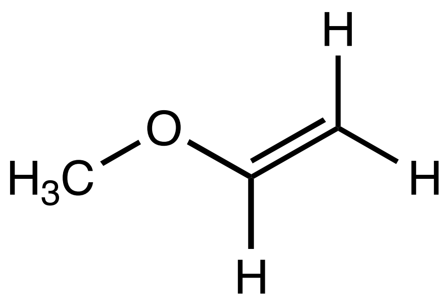




Reading: Section 13.4

Spin-Spin Splitting: More Complex Splitting Patterns

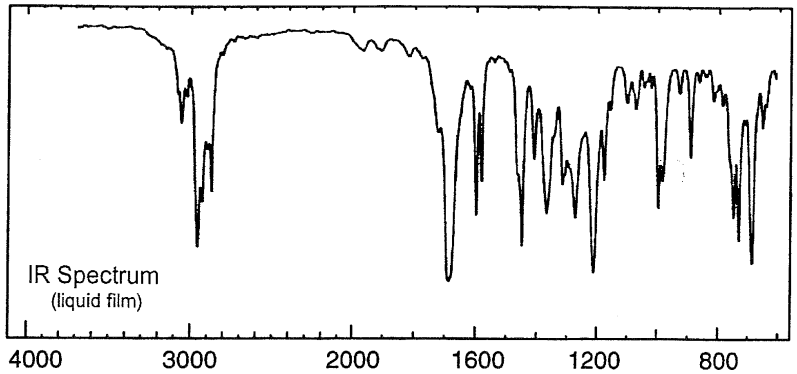
- Predict the NMR spectrum of the following molecule:



Reading: Section 13.5

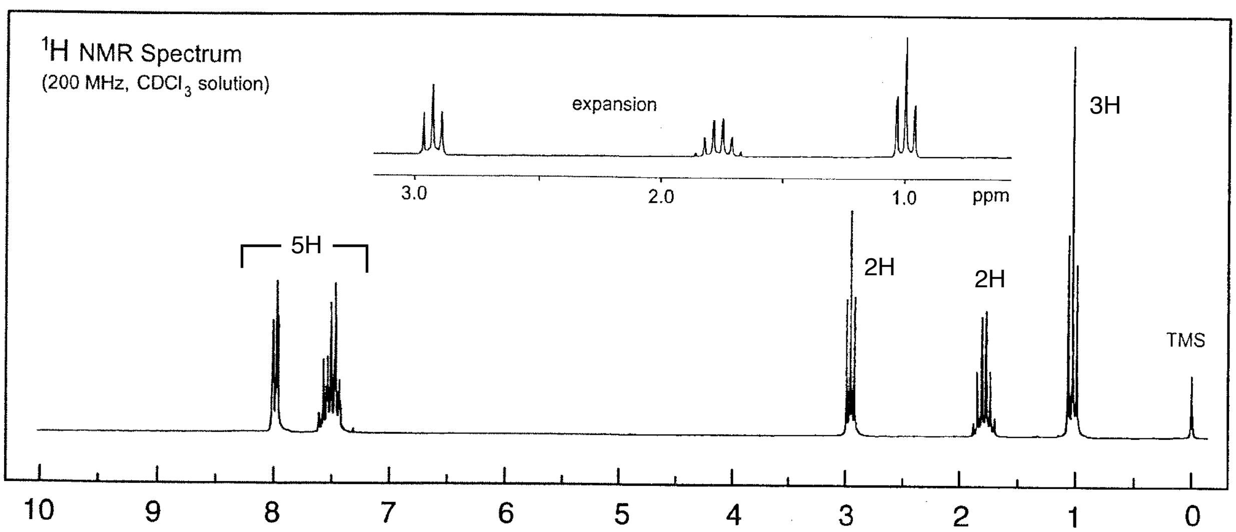
Chemistry S-20 3 Name:

3. You have just synthesized a new compound, and the following spectroscopic data is obtained:
   - From the mass spectrum, you deduce that the molecular formula is $\mathbf{C_{10}H_{12}O}$.
   - The infrared spectrum is:



From the infrared spectrum, what functional groups are **definitely present:**	From the infrared spectrum, what functional groups are **definitely absent:**

   - The proton NMR spectrum is:

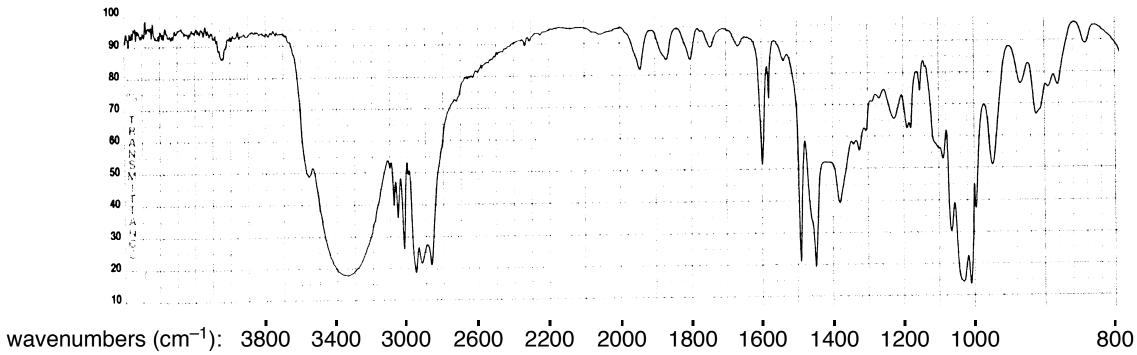


Draw your **best choice** for the structure of this molecule in the box below.

_______ / 14

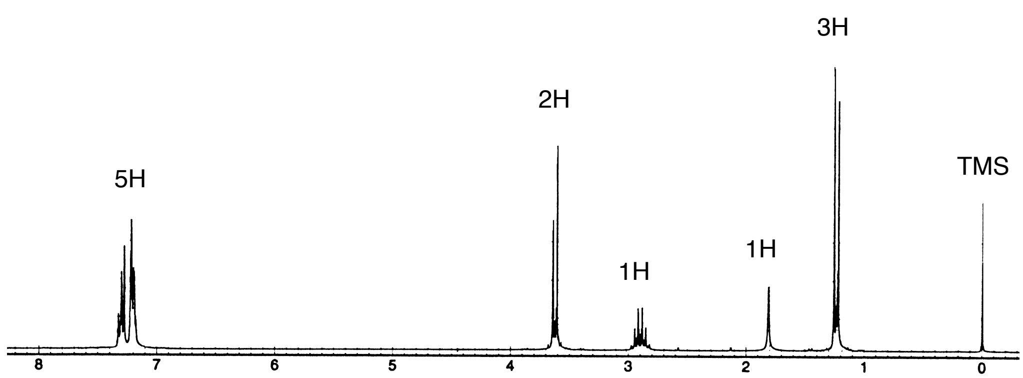
Chemistry S-20 **3** Name:

3. You have just synthesized a new compound, and the following spectroscopic data is obtained:
   - From the mass spectrum, you deduce that the molecular formula is $\mathbf{C_9H_{12}O}$.
   - The infrared spectrum is:



From the infrared spectrum, what functional groups are **definitely present:**	From the infrared spectrum, what functional groups are **definitely absent:**

- The proton NMR spectrum is:



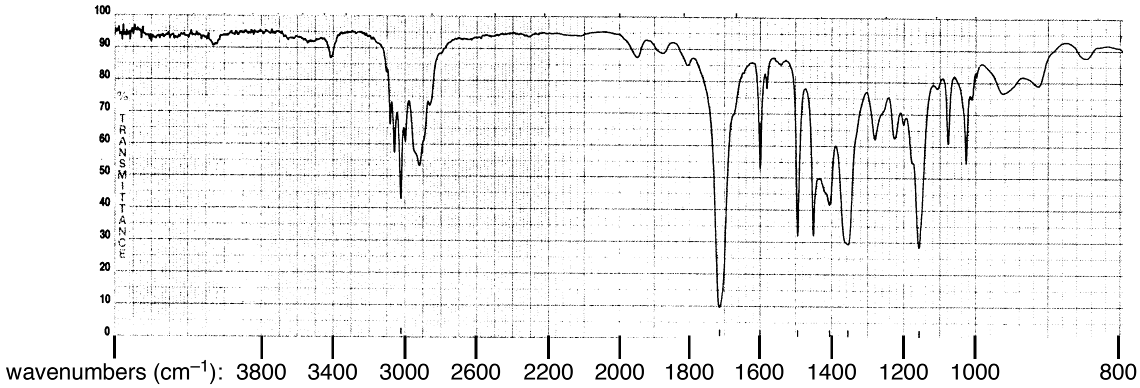
Draw your **best choice** for the structure of this molecule in the box below.

_______ / 14

Test Yourself Now!

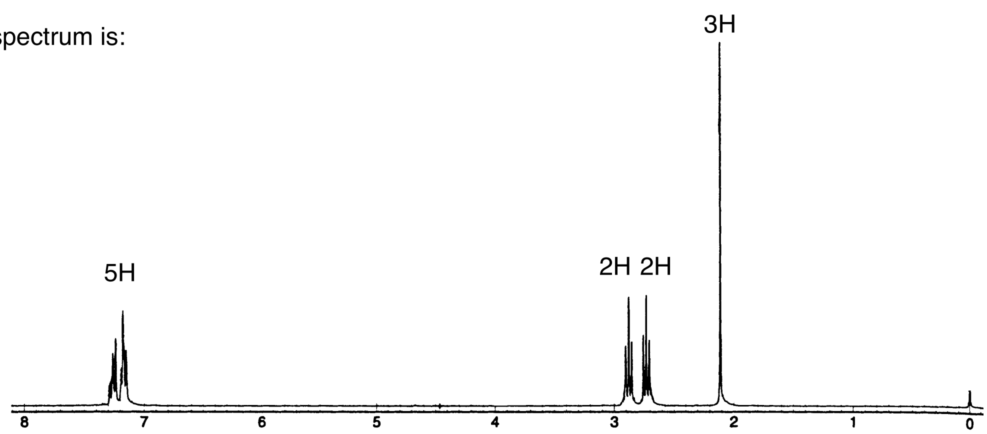
You have just synthesized a new compound, and the following spectroscopic data is obtained:

- From the mass spectrum, you deduce that the molecular formula is **$C_{10}H_{12}O$**.
- The infrared spectrum is:



From the infrared spectrum, what functional groups are **definitely present:**	From the infrared spectrum, what functional groups are **definitely absent:**

- The proton NMR spectrum is:

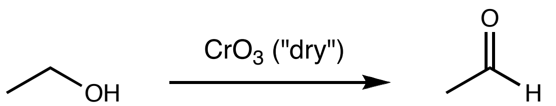


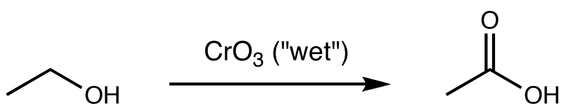
Draw your **best choice** for the structure of this molecule in the space below:

Oxidation of Alcohols

- Alcohols can be oxidized with various oxidizing agents. The most common are various derivatives of CrO_3. We can make the following general observations:

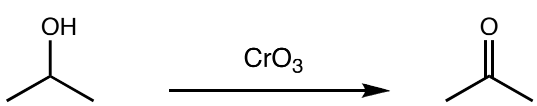
For **primary** alcohols:



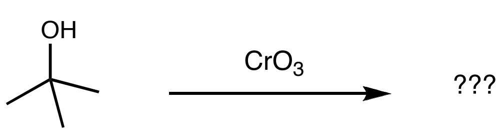


(Where else have you seen an "option" for forming aldehydes versus forming carboxylic acids?)

For **secondary** alcohols:



What do you think will happen for **tertiary** alcohols?

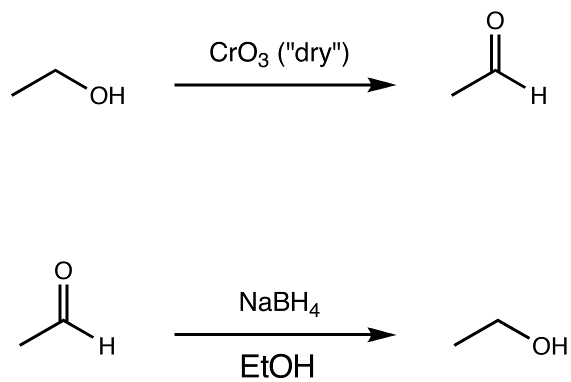


Reading: Sections 10.5 and 10.6

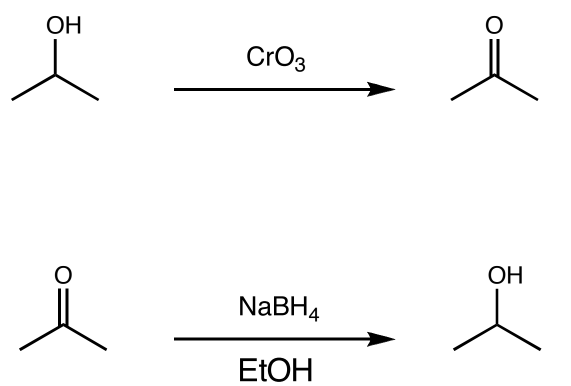
Reduction of Aldehydes and Ketones

- Aldehydes and ketones can be **reduced** to alcohols using $NaBH_4$. We will not discuss the mechanism of this reaction at this point; you should simply be aware that this reaction gives exactly the reverse of the oxidation reactions discussed above:

Interconversion of **primary** alcohols and **aldehydes**:



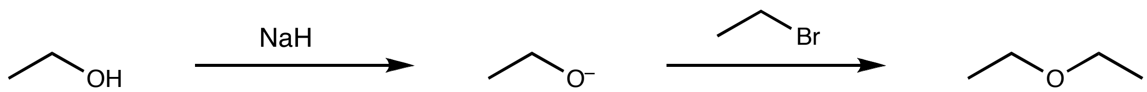
Interconversion of **secondary** alcohols and **ketones**:

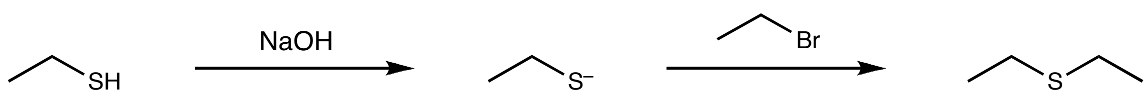


Reading: Section 19.8 (no, that’s not a typo!)

Thiols vs. Alcohols: Similarities

- The following reactions show some of the similarities between thiols and alcohols. Can you draw curved-arrow mechanisms for each step?





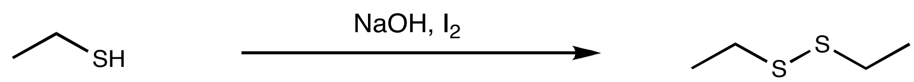
- Compare alkoxides with thiolates. Which will be better nucleophiles, and why?

Reading: Section 11.1

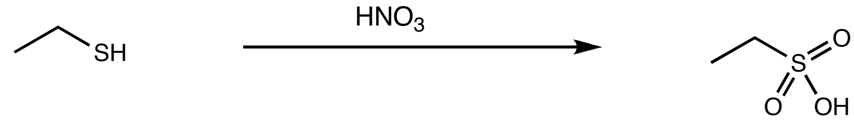
Thiols vs. Alcohols: Differences

- Oxidation of thiols proceeds quite differently from oxidation of alcohols. In particular, it is the *sulfur* that is oxidized, rather than the carbon.

- Draw a curved-arrow mechanism for the following oxidation of thiols to disulfides:



- Vigorous oxidation of thiols yields sulfonic acids. (No need to know the mechanism)

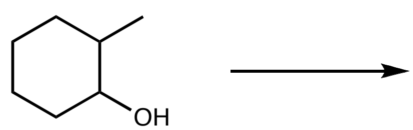


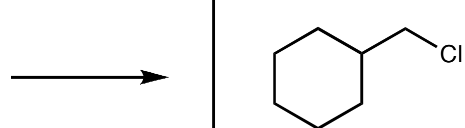
Reading: Section 10.9

Putting It Together: Synthesis

- Propose a synthetic route to the following desired product from the indicated starting material. All of the carbon atoms from the starting material must end up in your product.

Starting Material:

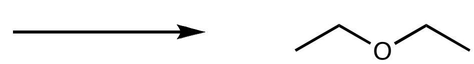




Desired Product

Test Yourself Now!

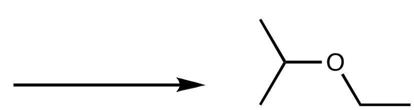
Using only **alcohols** as starting materials, synthesize the following product:



Synthesis of Ethers 1: Williamson Ether Synthesis

- You already know all of the routes for synthesizing ethers! Let's take a look at the following problem:

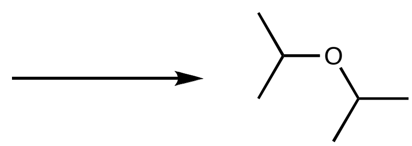
Using **only alcohols** as starting materials, synthesize the following ether:



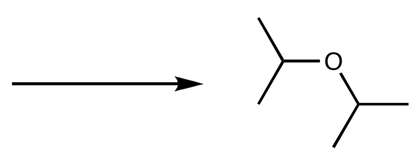
Reading: Section 11.1

Synthesis of Ethers 2: Alkoxymercuration-Reduction

- What would happen if you tried a "Williamson" route to synthesize the following ether?



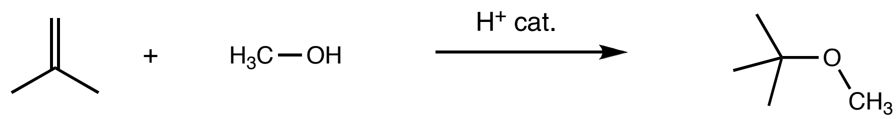
- Is there another way to synthesize that ether? Use only **alcohols** as starting materials.

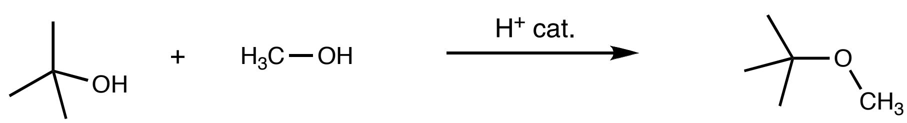


Reading: Section 11.1

Synthesis of Ethers 3: Routes Involving Carbocations

- Write complete curved-arrow mechanisms for the following reactions, each of which produces the ether MTBE (methyl-*tert*-butyl ether), which has been used as a gasoline additive:

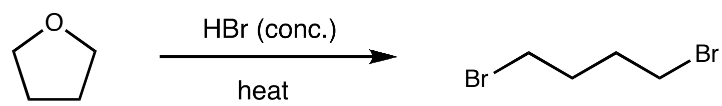


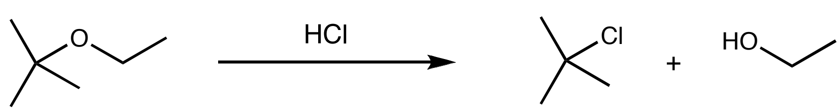


Reading: Section 11.1

Cleavage of Ethers

- Ethers are generally inert under most reaction conditions; they are often used as solvents. However, ethers can be cleaved under certain conditions. Draw curved-arrow mechanisms for the following reactions:

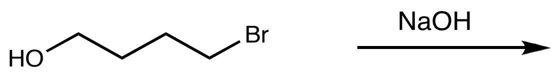




Reading: Section 11.3

Cyclic Ethers and Epoxides

- Draw a curved-arrow mechanism and predict the product of the following reactions:

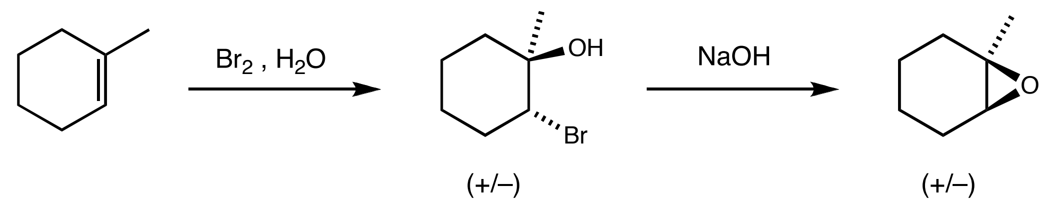


- The three-membered cyclic ether is given the special name **epoxide**. Why might this epoxide exhibit reactivity different from that of the 5-membered ring above?

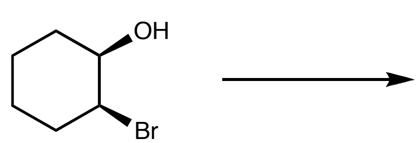
Reading: Section 11.2

Synthesis of Epoxides With Halohydrins

- Provide complete curved-arrow mechanisms for each step in the following transformation. Be sure to pay attention to stereochemistry!



- Explain why the following halohydrin *cannot* be transformed into an epoxide:



Reading: Section 11.2