

Exam 2 mean:

Last year	74
This year	70



↳ Week 3

first week with

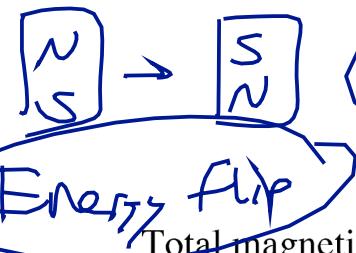
2 labs

time management!

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



observe this proton

H

a a b b

/not protons

$$\text{Total magnetic field at } \mathbf{H} \text{ (observed)} = \text{Applied field} + \text{effect of } \mathbf{H} \text{ (neighbor)}$$

field created by neighbor

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

observe laser field

$$\text{Total magnetic field at } \mathbf{H} \text{ (observed)} =$$

upfield from
"pure" chem. shift



+



neighbor spin up

...or it can be against the applied field

observe smaller field.

$$\text{Total magnetic field at } \mathbf{H} \text{ (observed)} =$$

downfield from
"pure" chem. shift



+

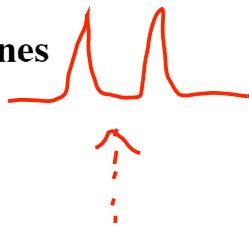


neighbor spin down

See

possible 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



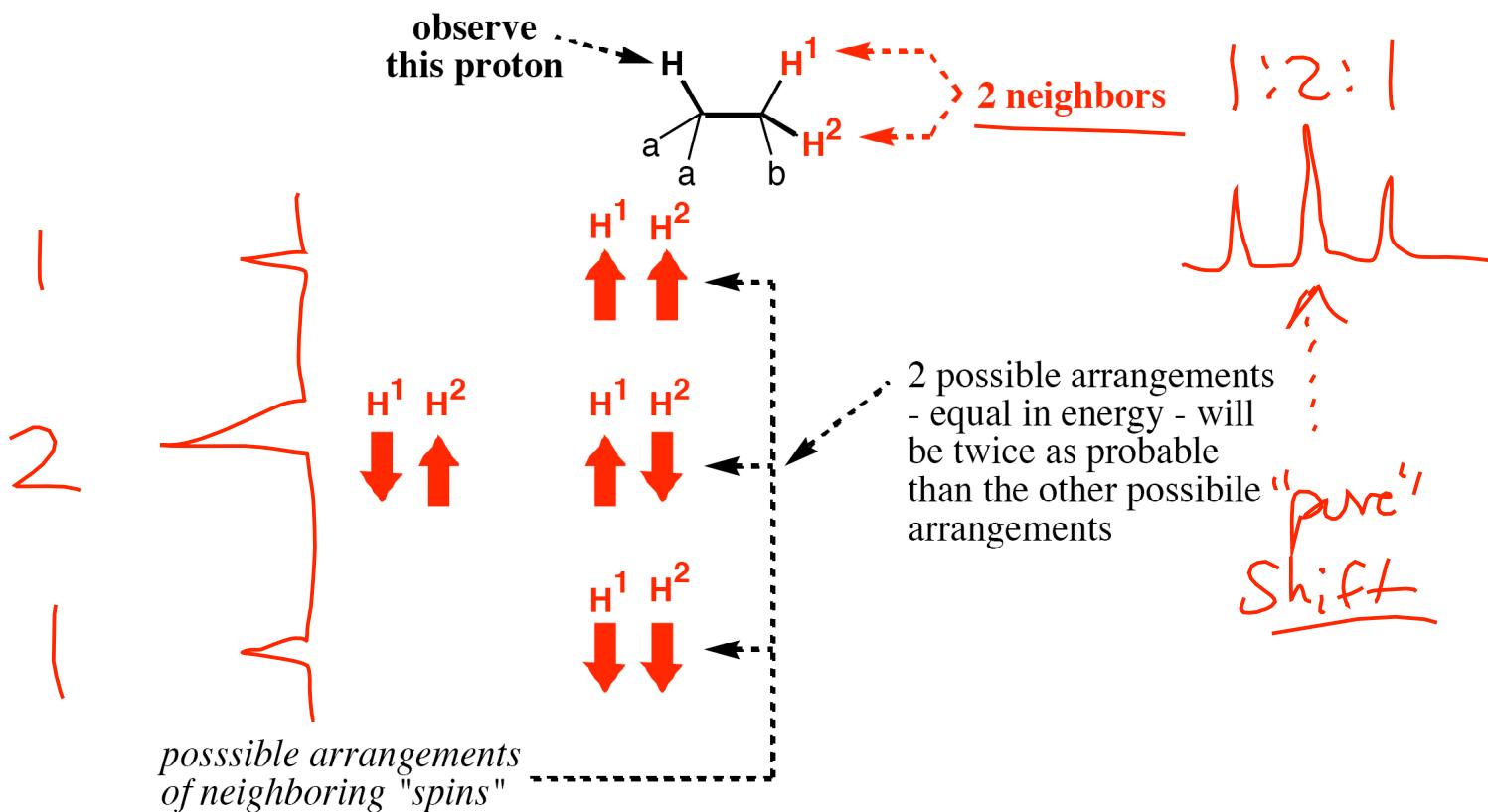
Chemical Shift

With no neighbor (from applied field alone)

Reading: Section 13.4

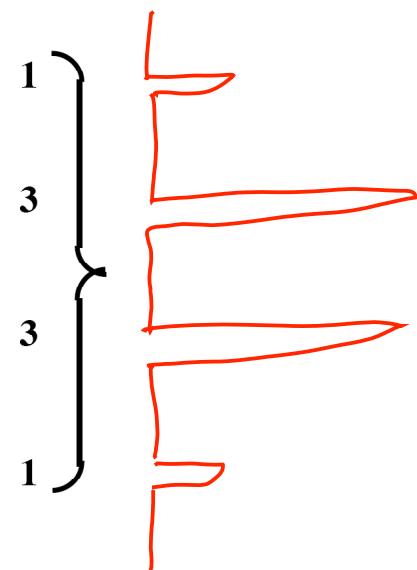
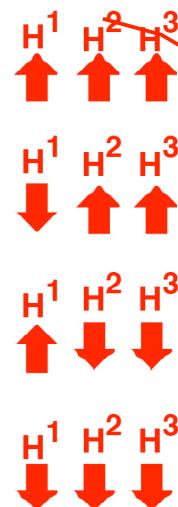
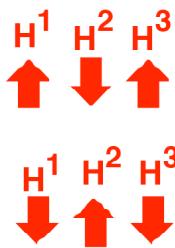
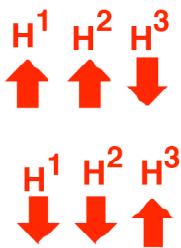
2 identical neighbors

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...



Quartet

Reading: Section 13.4

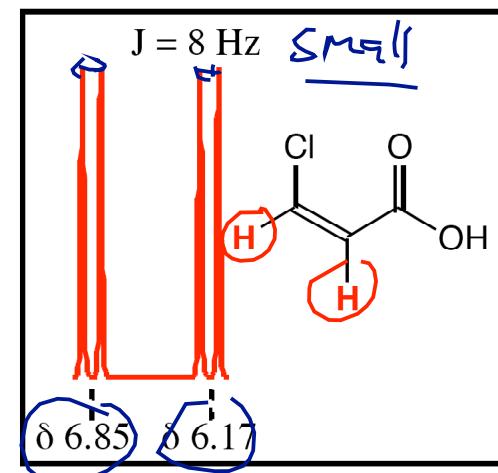
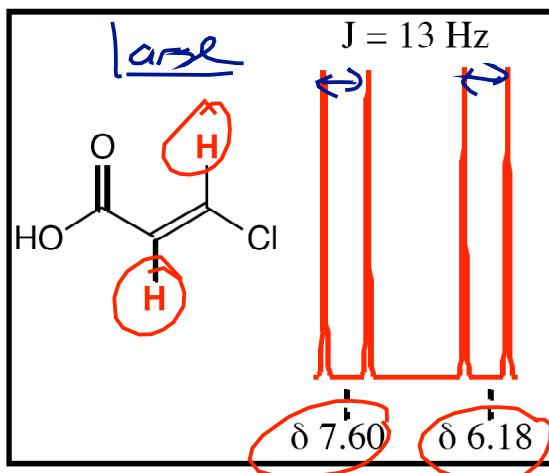
J value
distance between peaks

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	large coupling
cis-alkene		6 - 14 Hz	smaller coupling
vinyl geminal		0 - 3 Hz	smallest coupling

Example:



H
 $\text{C}=\text{C}$
 $\text{O}_\text{C}-\text{H}$
Antiperiplanar

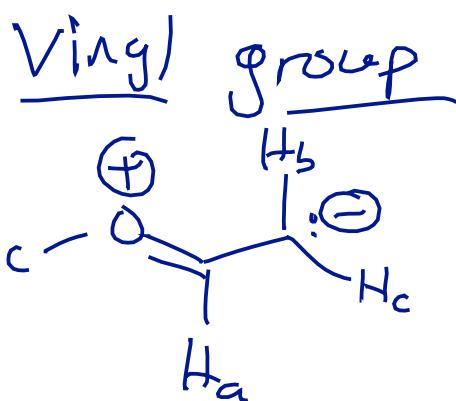
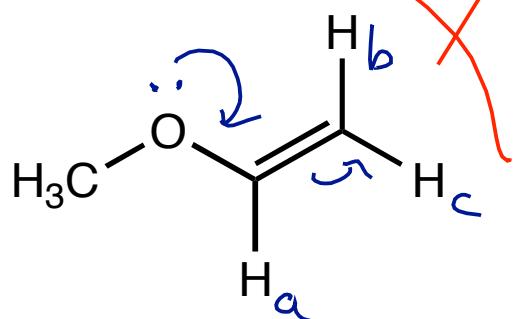
Reading: Section 13.4

Magnetic coupling happens due to ^{145}O orbital overlap.

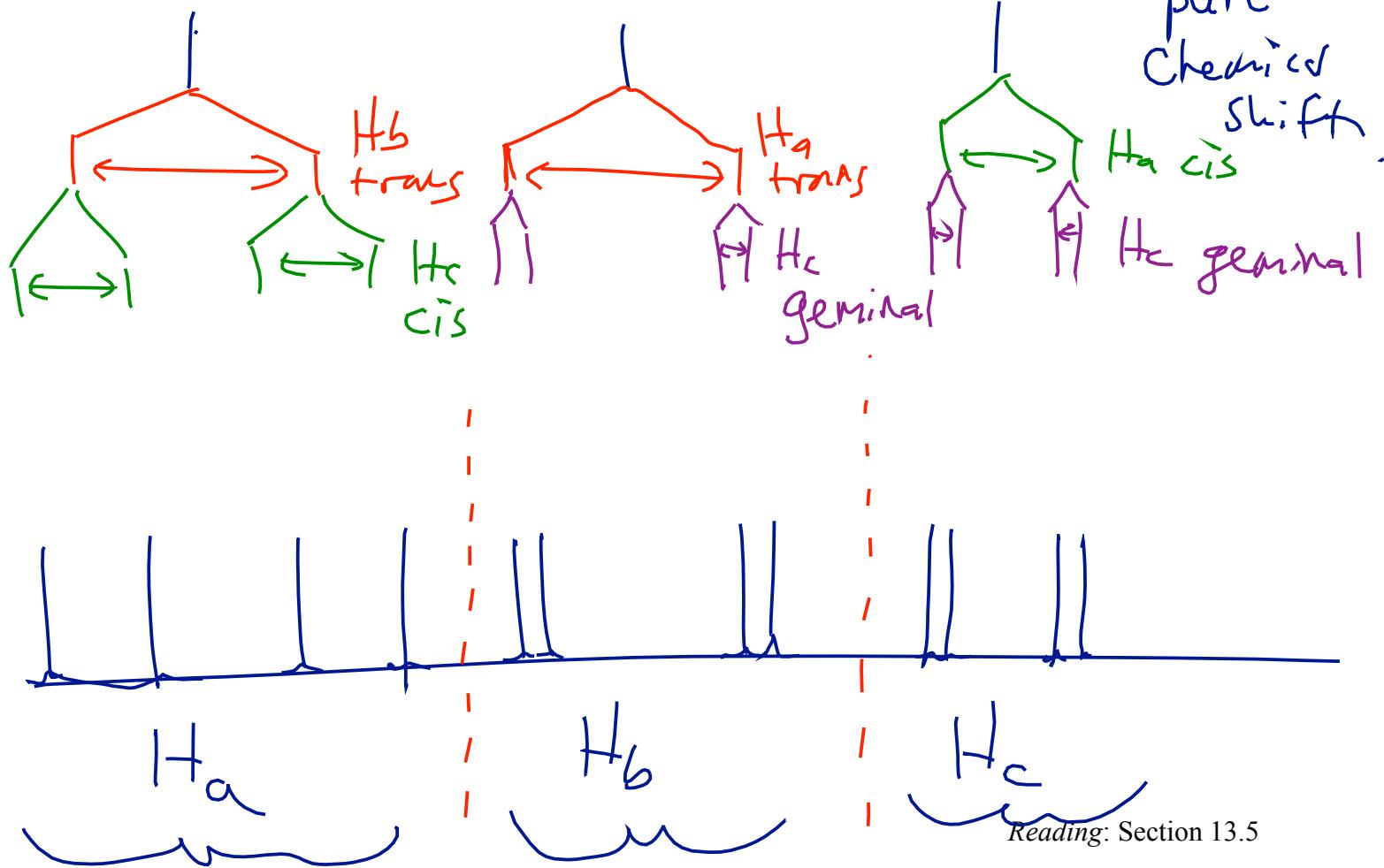
diastereosteric

Spin-Spin Splitting: More Complex Splitting Patterns

- Predict the NMR spectrum of the following molecule:

 H_a H_b H_c

"pure" chemical shift.
 H_a cis
 H_c geminal



"doublet
of doublets"

Chemistry S-20ab Unsaturation index $U = 1 + C \frac{1}{2} (H + X - N)$ Week 3
Chemistry S-20 3 Name: halogens

Chemistry S-20

3

Name:

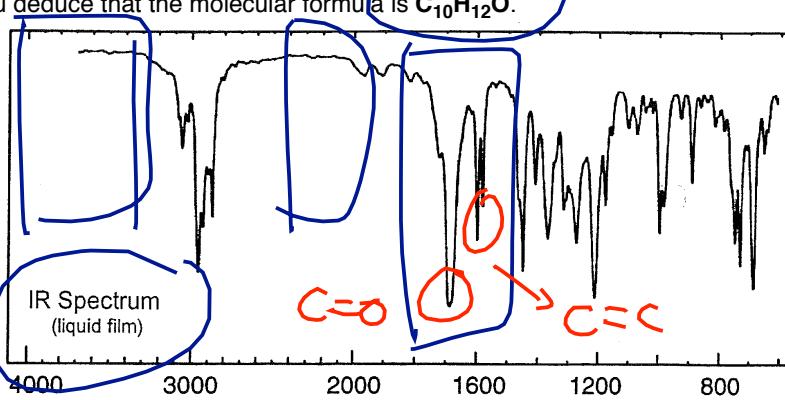
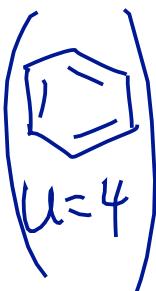
3. You have just synthesized a new compound, and the following spectroscopic data is obtained:

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

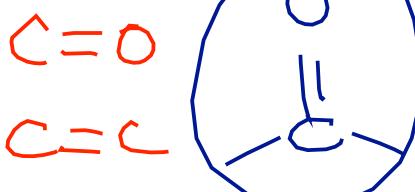
total # of
rings plus π -bonds

$$U = 1 + 10 - \frac{1}{2}(12)$$

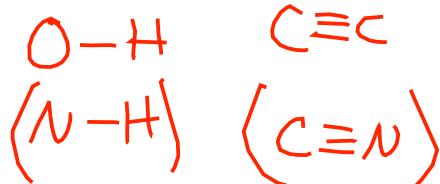
$$T = 5$$



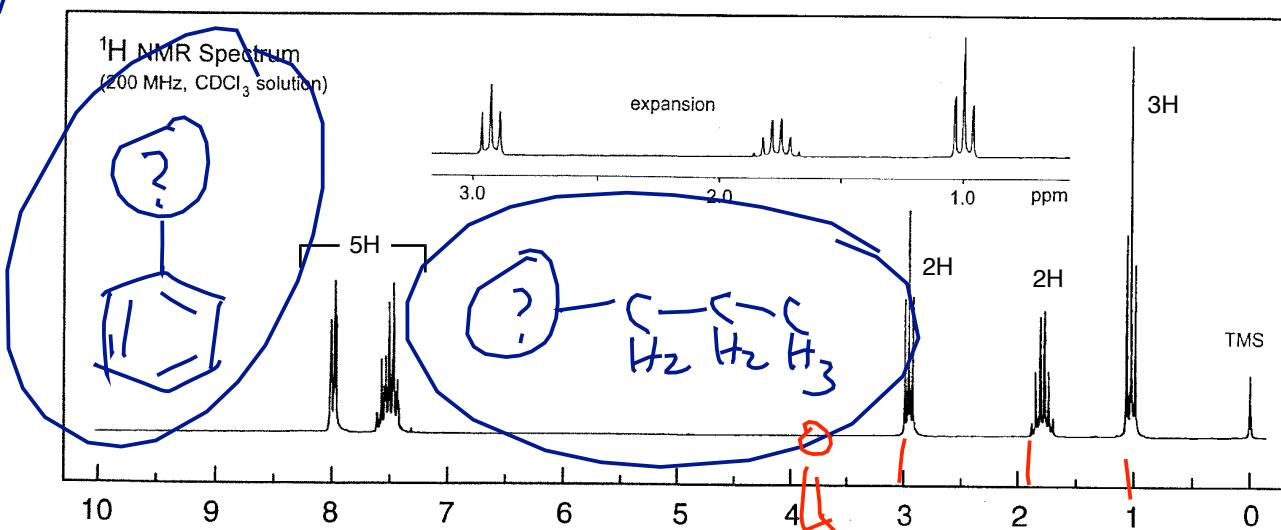
From the infrared spectrum, what functional groups are **definitely** present:



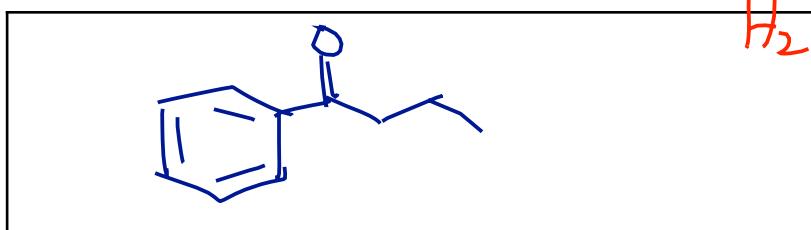
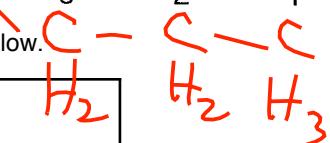
From the infrared spectrum, what functional groups are **definitely absent**:



- The proton NMR spectrum is:



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

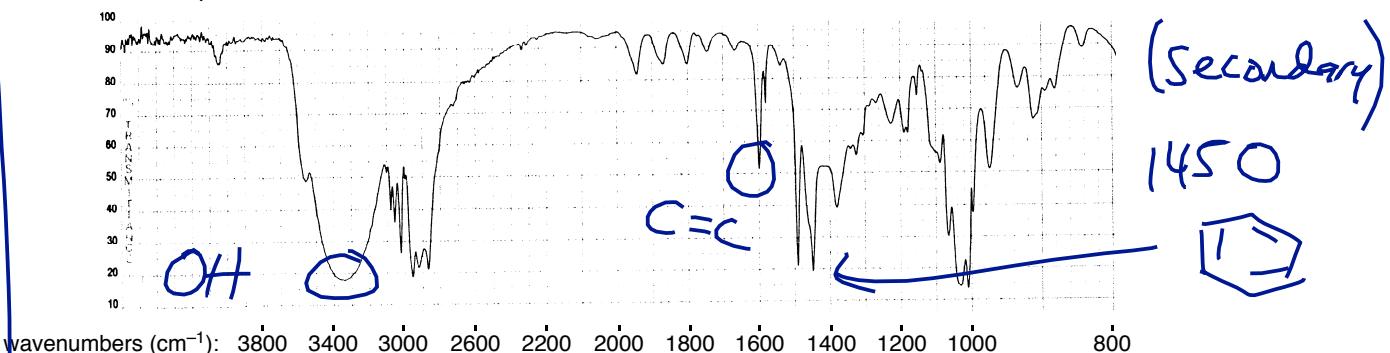


$$U = 1 + 9 - \frac{1}{2}(12) = \boxed{4}$$

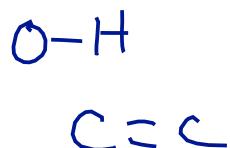
Week 3

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

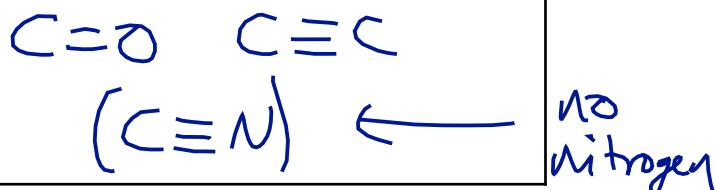
- From the mass spectrum, you deduce that the molecular formula is $C_9H_{12}O$.
- The infrared spectrum is:



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



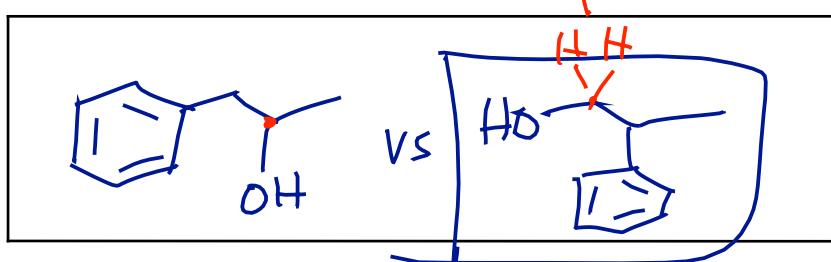
From the infrared spectrum, what functional groups are **definitely absent**:



- The proton NMR spectrum is:



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

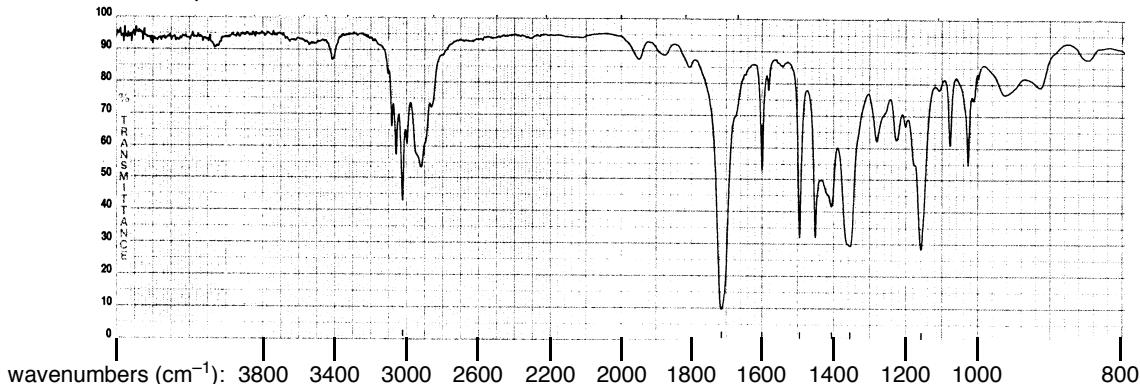


$\text{O}-\text{H}$
(chemical shift varies,
can be broad,
often doesn't split.)

Test Yourself Now!

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

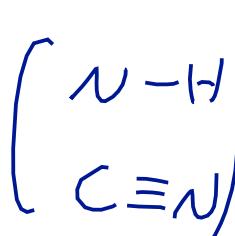
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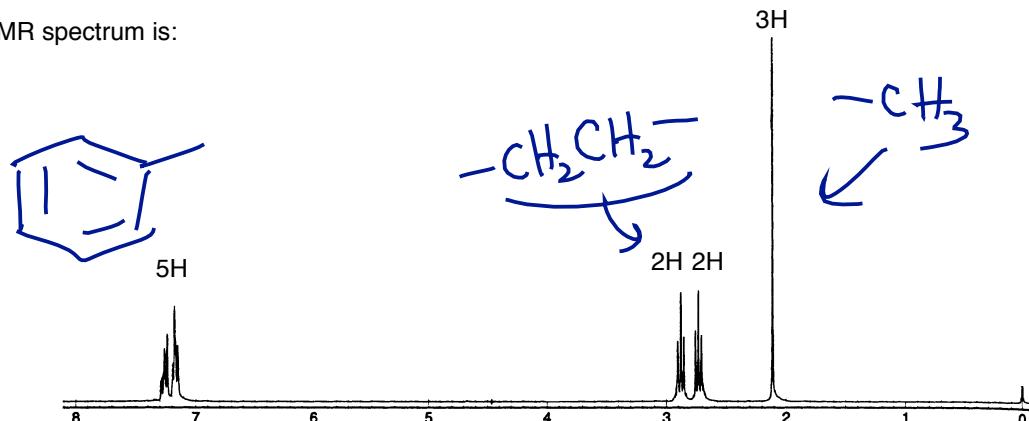
From the infrared spectrum, what functional groups are **definitely present**:



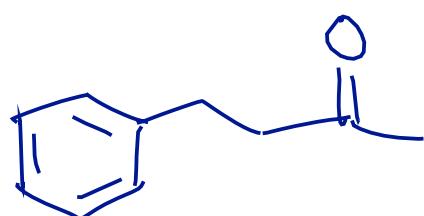
From the infrared spectrum, what functional groups are **definitely absent**:



- The proton NMR spectrum is:



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



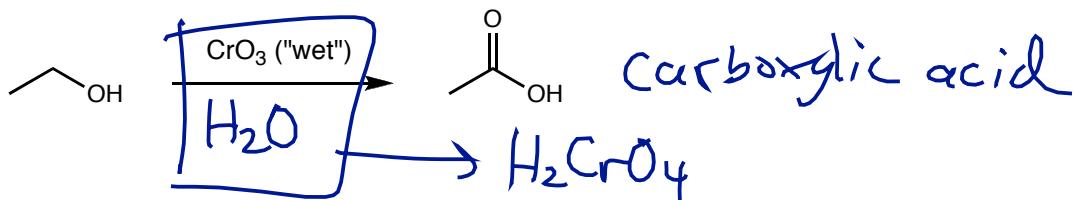
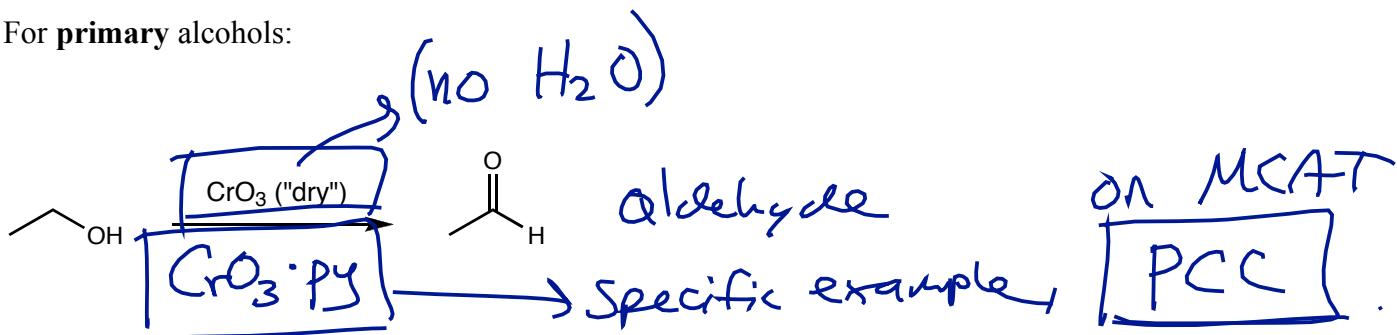
What can you do?

Oxidation of Alcohols

no mech
for now . . .

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

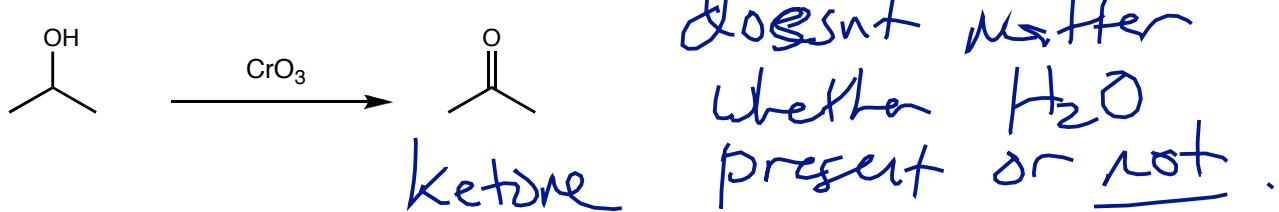
For primary alcohols:



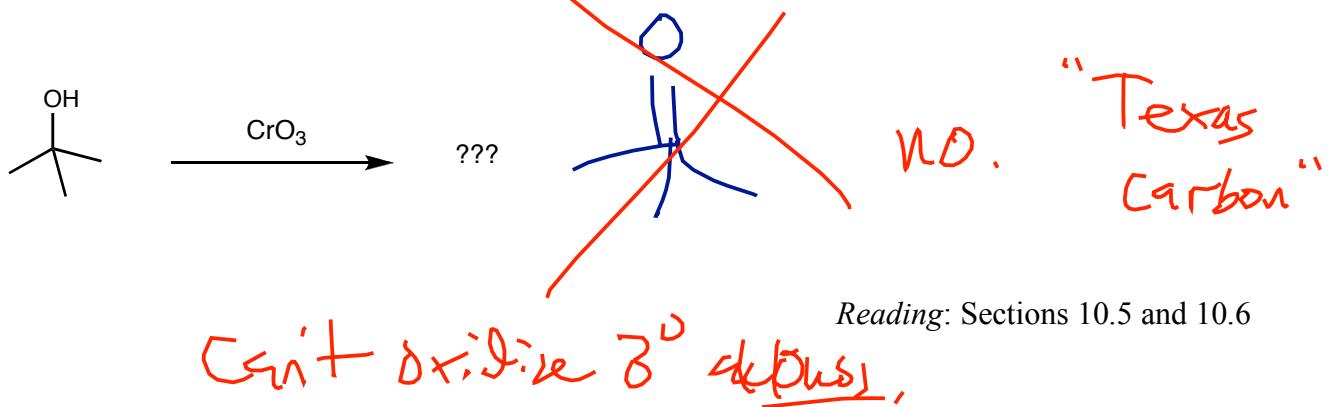
(Where else have you seen an "option" for forming aldehydes versus forming carboxylic acids?)

↳ ozonolysis?

For secondary alcohols:



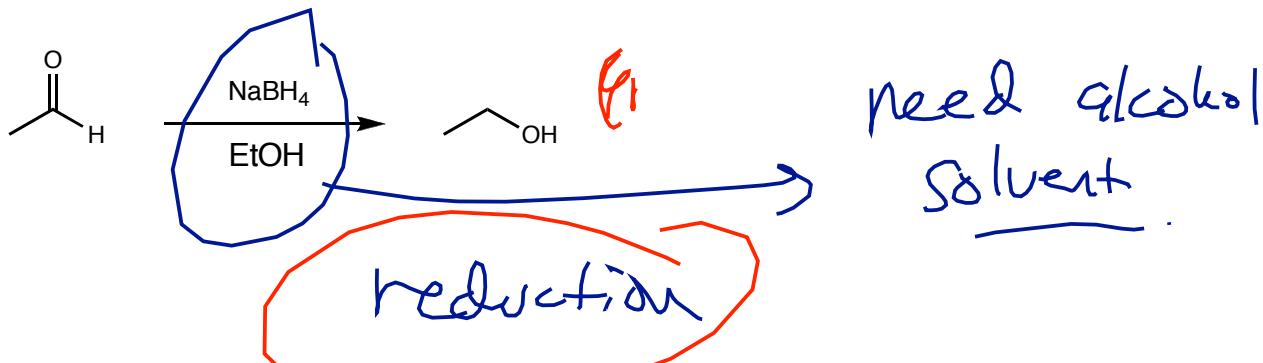
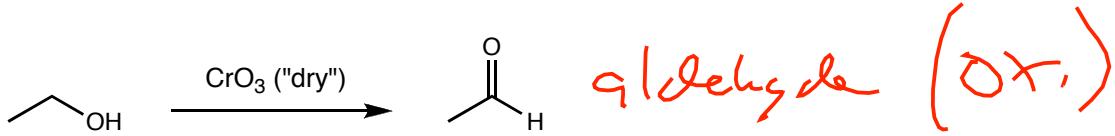
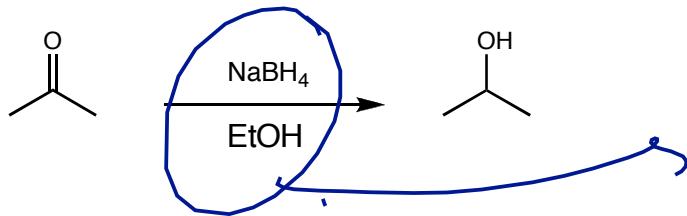
What do you think will happen for tertiary alcohols?



Reading: Sections 10.5 and 10.6

Opposite of oxidation**Reduction of Aldehydes and Ketones**(NO mech
for now)

- 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**:(not carbox.
acids)Interconversion of **secondary** alcohols and **ketones**:

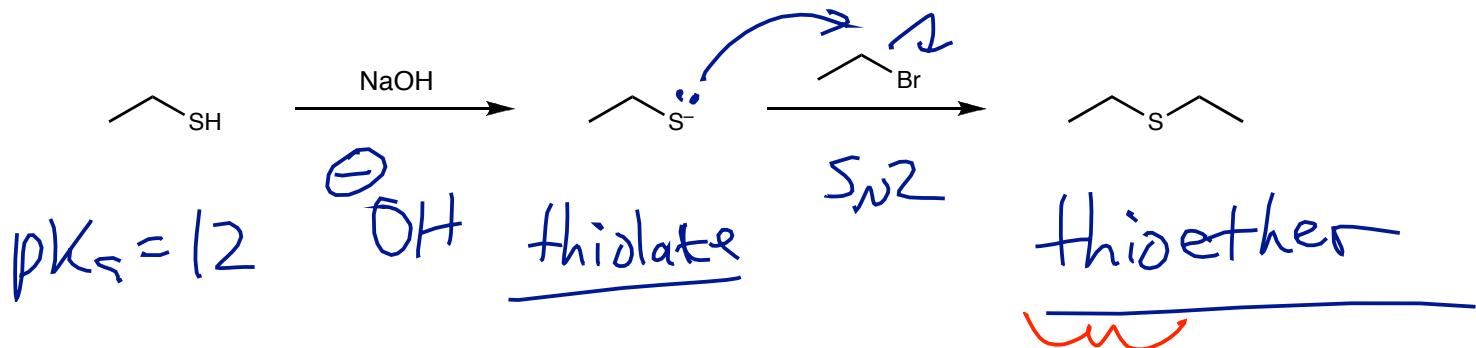
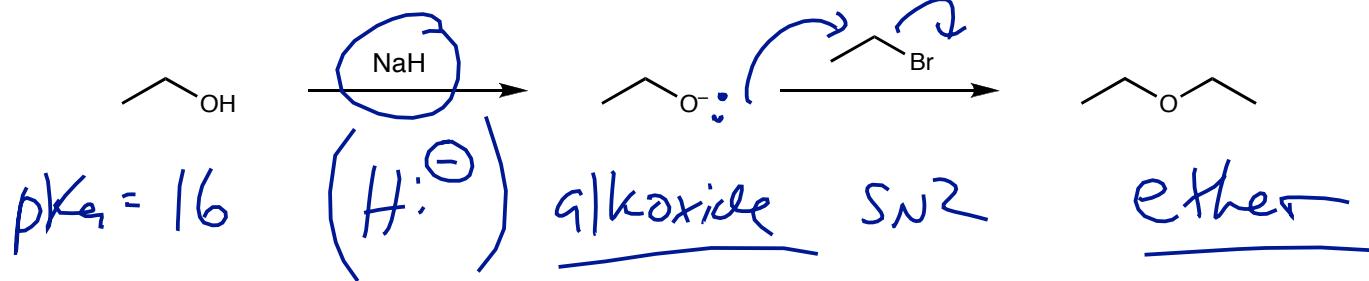
Now you can use aldehyde, ketone

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?



this

"Sulfur in place
of oxygen"

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



S is less e-neg, i. higher HOMO
better donor

Reading: Section 11.1

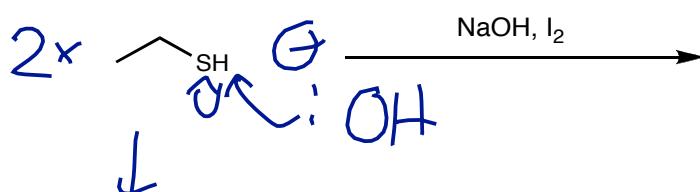
More basic $\text{RO}^{\ominus} > \text{RS}^{\ominus}$ because O-H stronger
than S-H



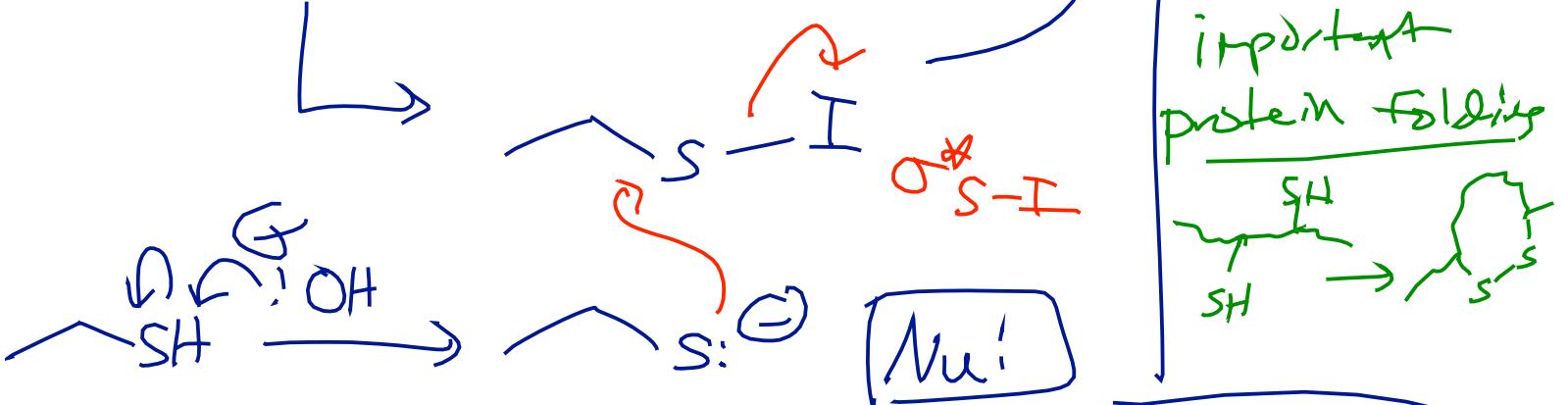
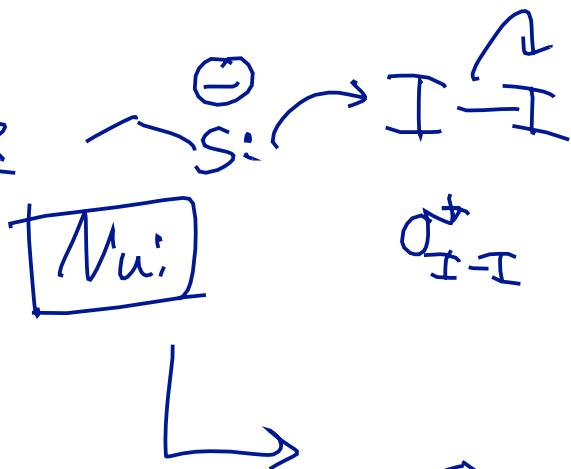
Thiols vs. Alcohols: Differences

- 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:

Mild

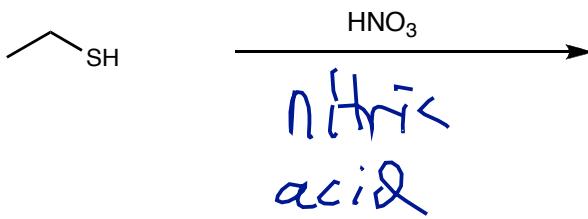


thiolate



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

Strong

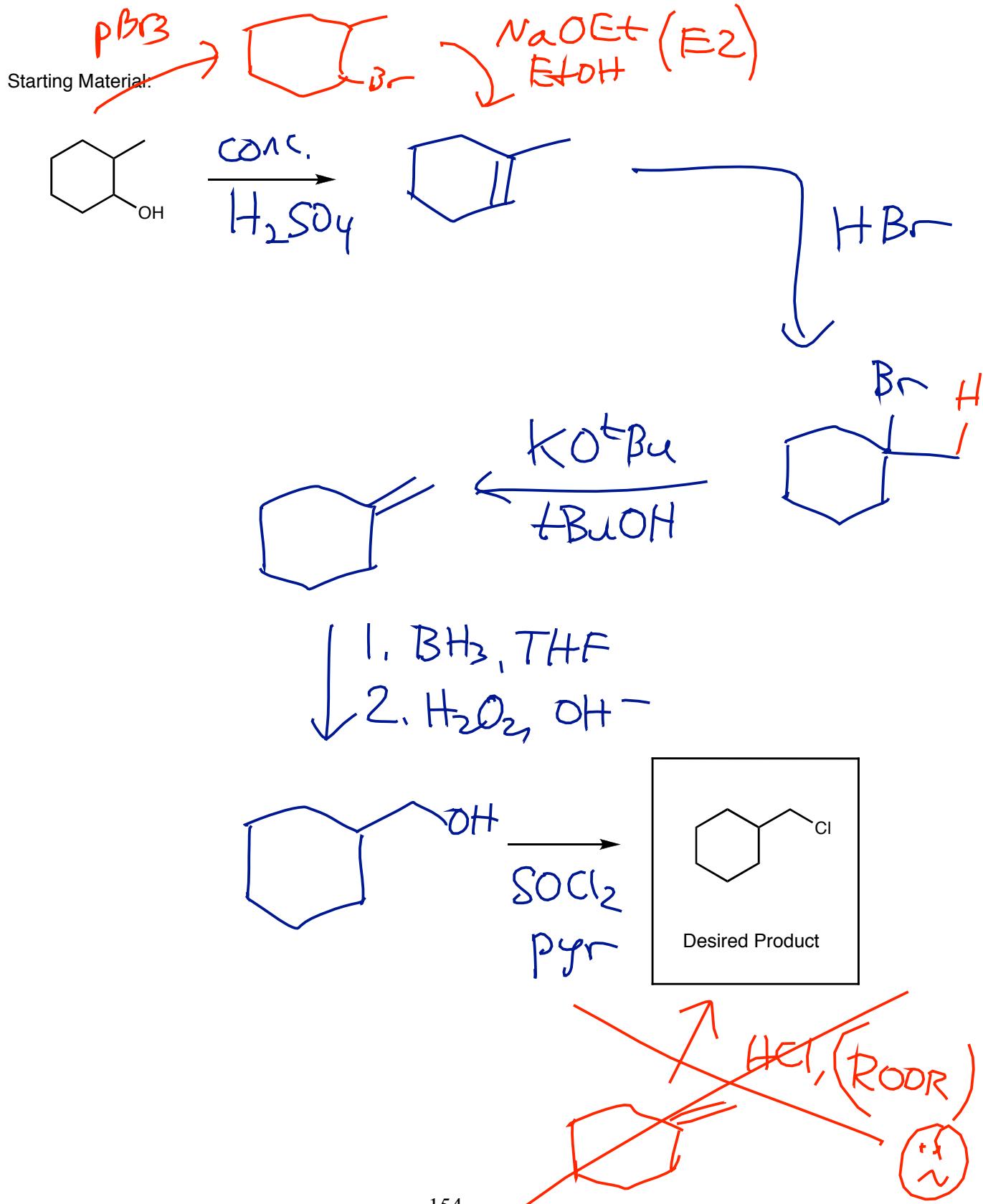


Sulfonic acid

Reading: Section 10.9

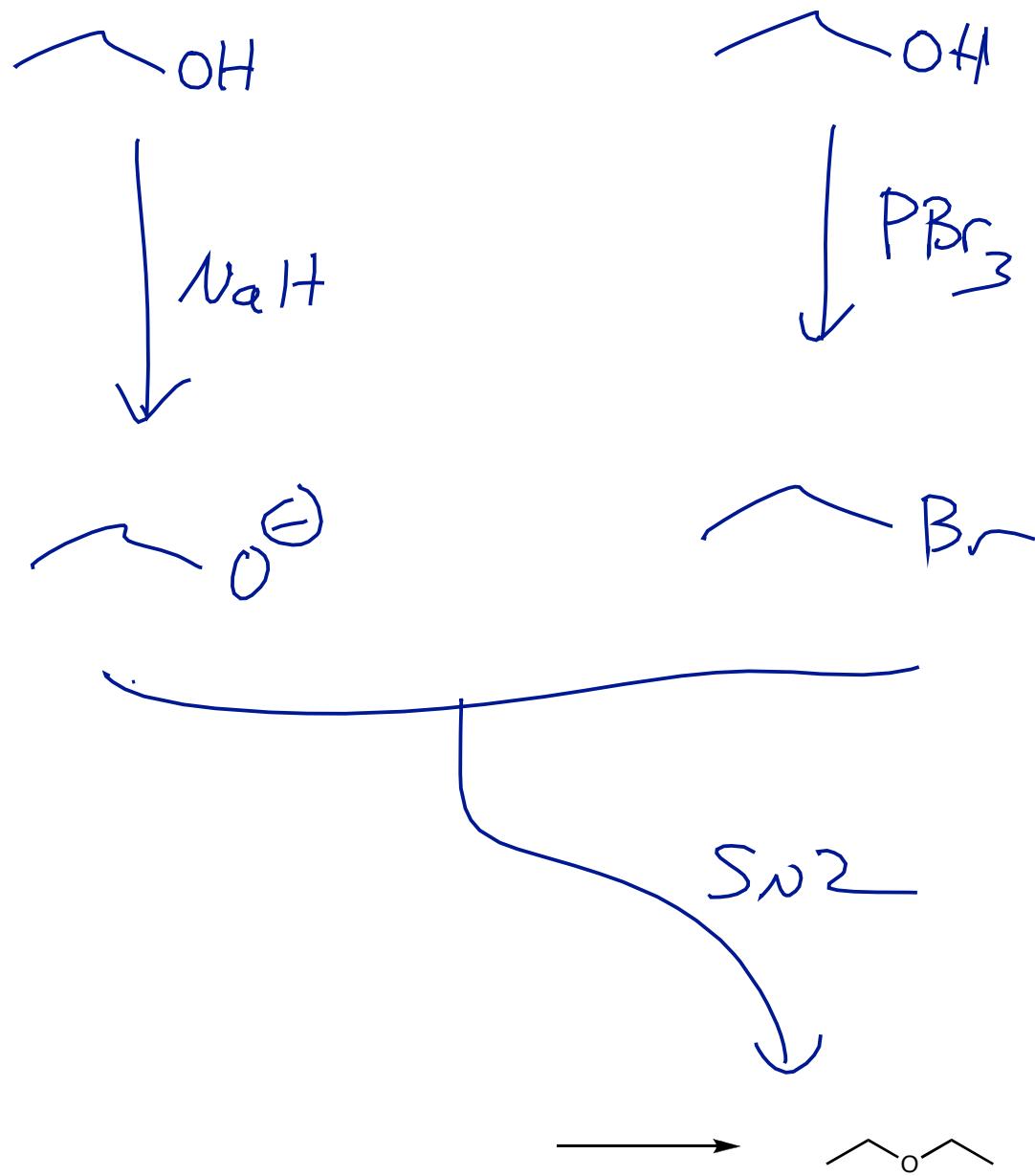
Putting It Together: Synthesis

- 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.



Test Yourself Now!

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

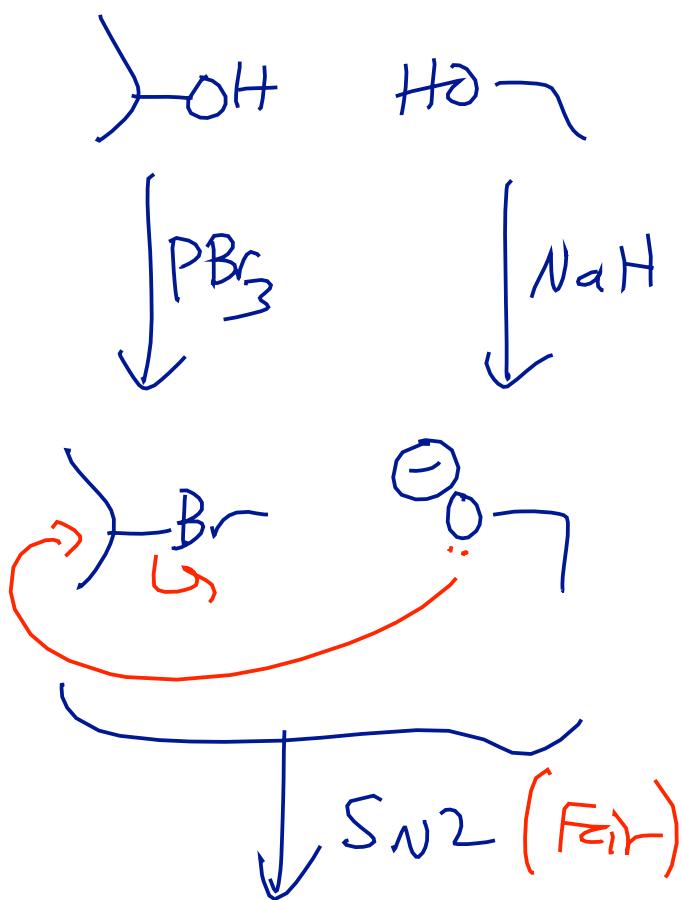


Synthesis of Ethers 1: Williamson Ether Synthesis $\rightarrow (S_N2)$

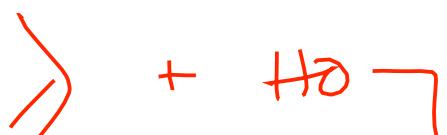
- You already know all of the routes for synthesizing ethers! Let's take a look at the following problem:

Using S_N2

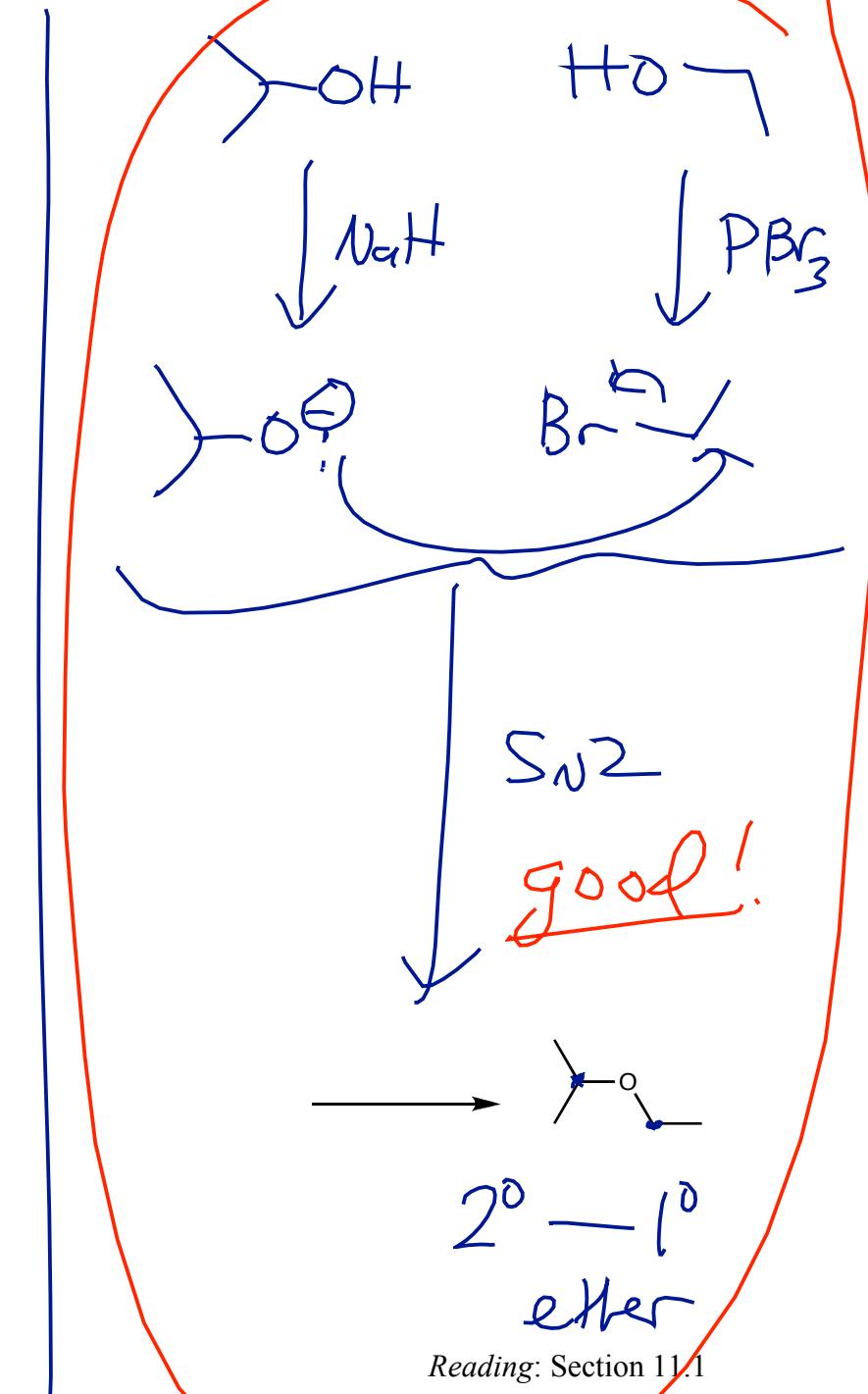
Using **only** alcohols as starting materials, synthesize the following ether:



Predom product
 $E2$



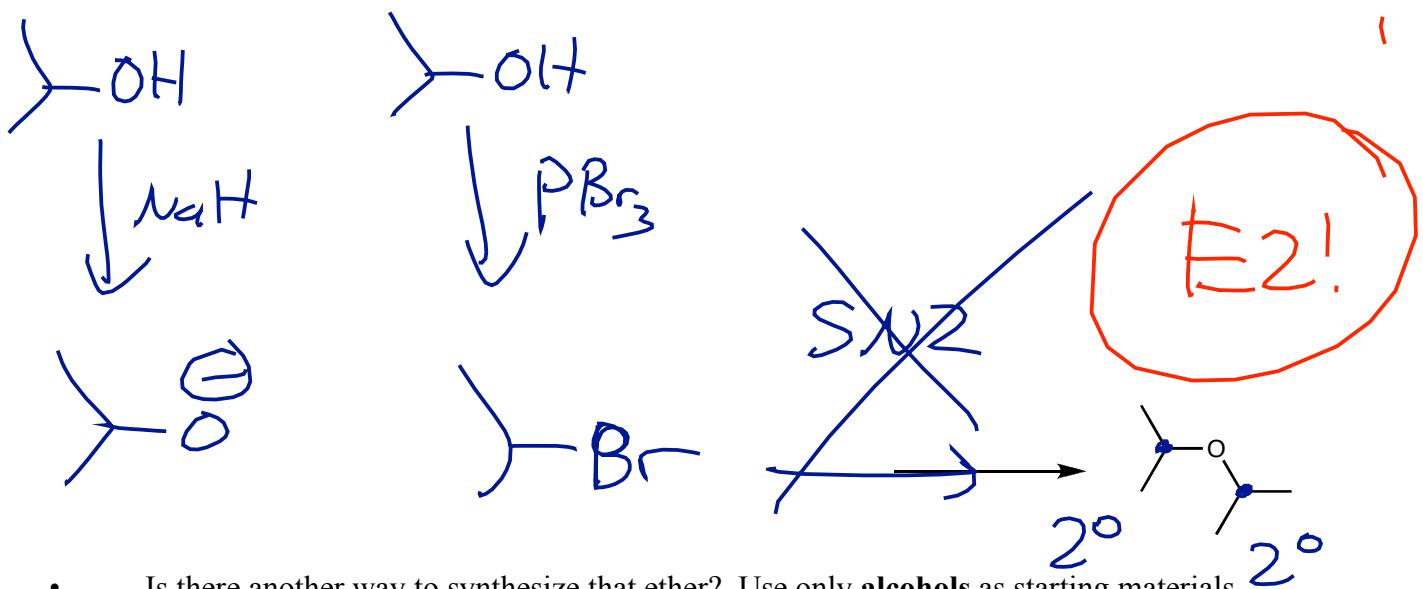
not ideal



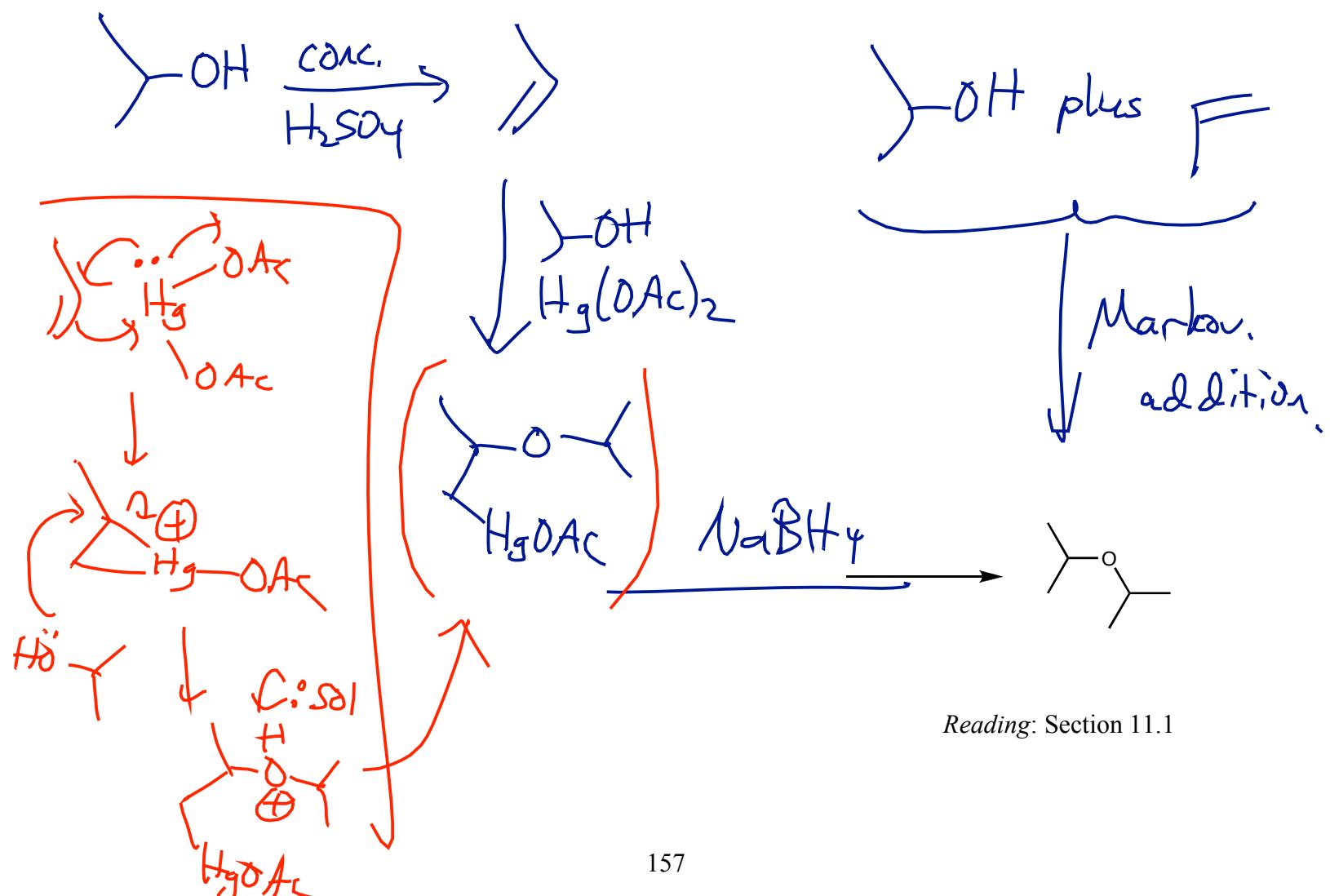
Reading: Section 11.1

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.



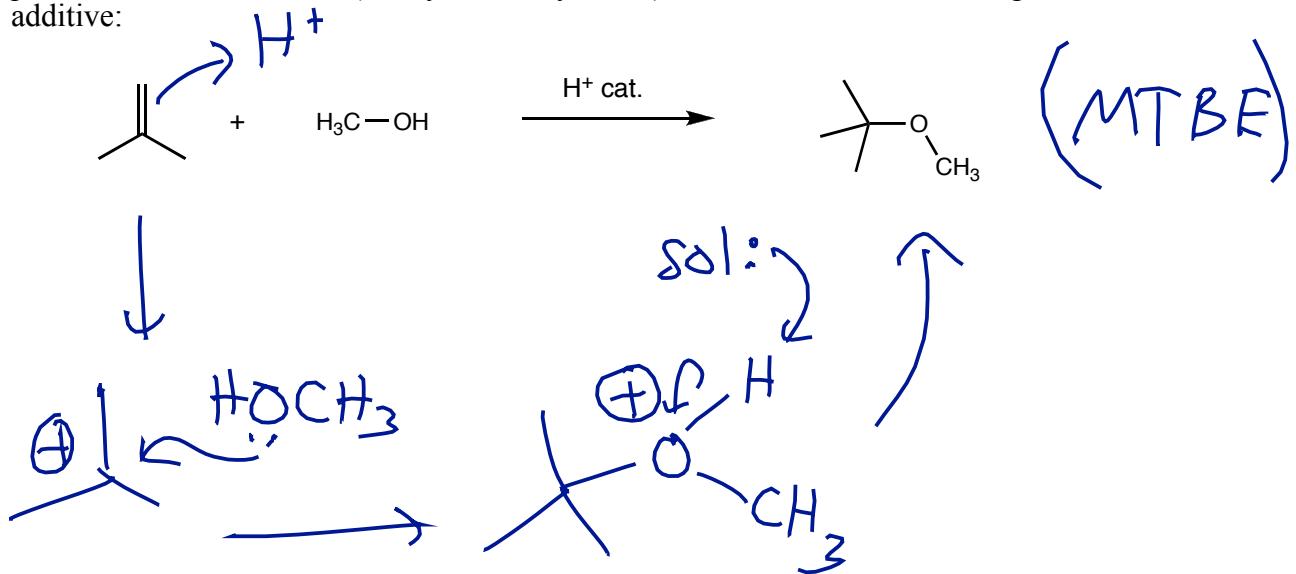
Reading: Section 11.1

3° on one end (or both)

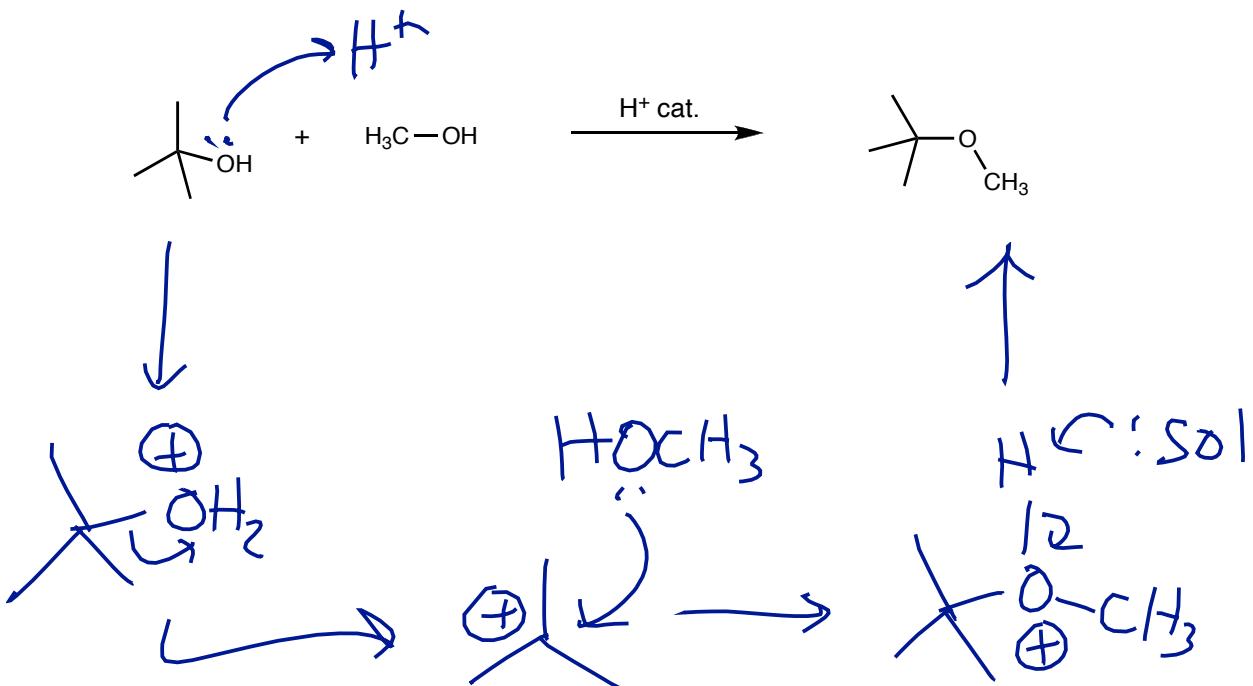
Synthesis of Ethers 3: Routes Involving Carbocations

- 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:

alkene
addition



S_N1



$1^\circ/1^\circ$ or $1^\circ/2^\circ \rightarrow S_N2$

$2^\circ/2^\circ \rightarrow$ alkoxymerc.

$3^\circ \rightarrow$ carbocation

Reading: Section 11.1

What can you do with an ether?

Cleavage of Ethers

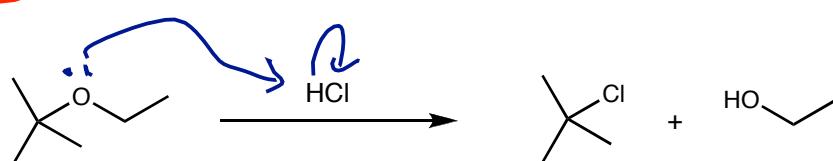
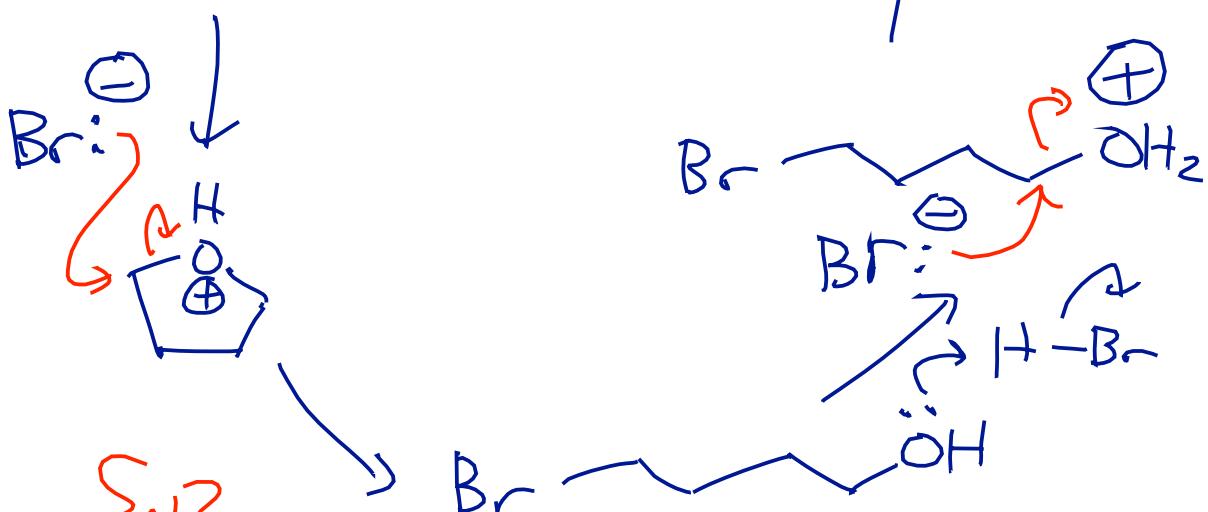
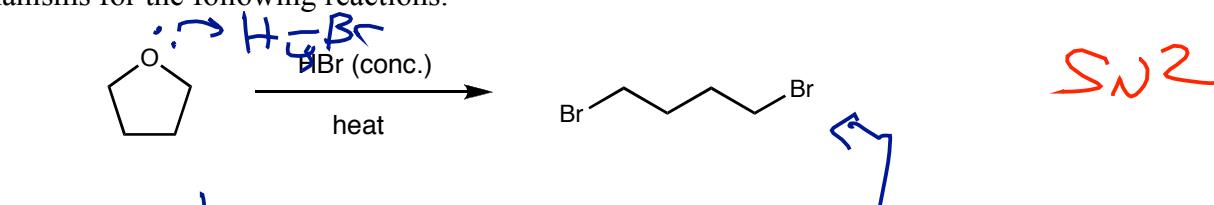
- Ethers are generally inert under most reaction conditions; they are often used as solvents. However, ethers can be cleaved under certain conditions. Draw curved-arrow mechanisms for the following reactions:

1°
ether

HBr
or
HI

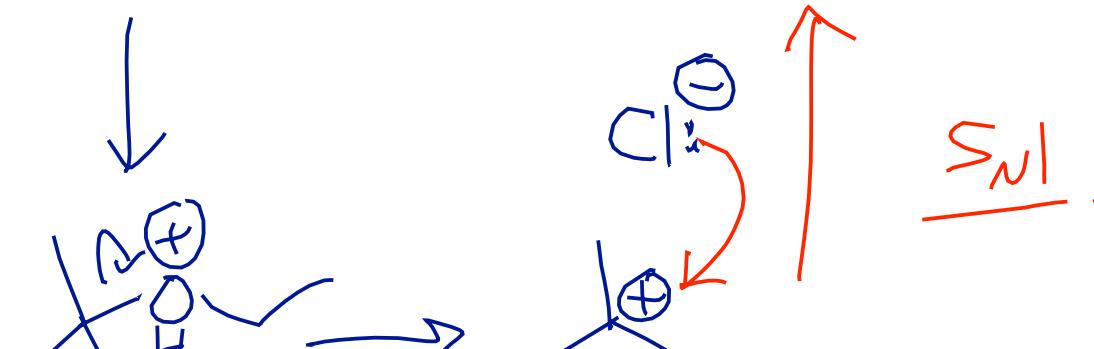
(Not HCl)

Cl^-
not good



3°
ether

$\boxed{\text{SN1}}$



3°

Reading: Section 11.3

Cyclic Ethers and Epoxides

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

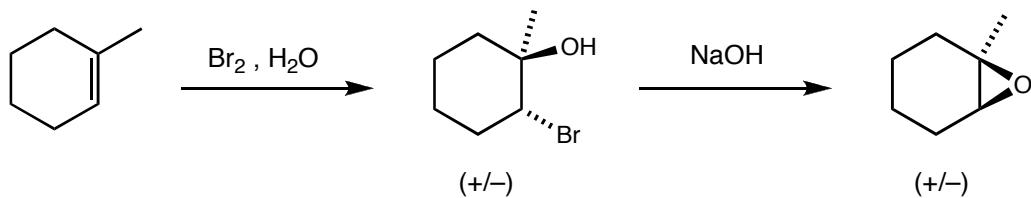


- The three-membered cyclic ether is given the special name **epoxide**. Why might this epoxide exhibit reactivity different from that of the 5-membered ring above?

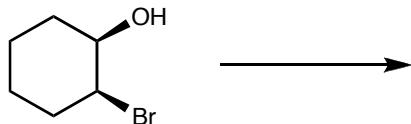
Reading: Section 11.2

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