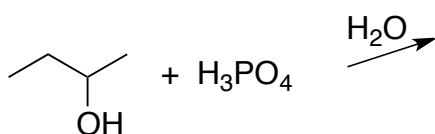
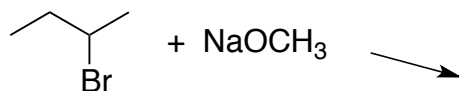


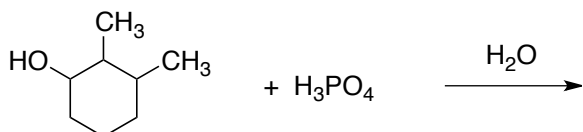
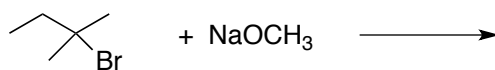
## CHAPTER 8. ALKENES: REACTIONS AND SYNTHESIS

### $\beta$ -Elimination to form Alkenes

These two elimination-reactions create the same major product - what is it?



Predict the major organic products (via  $\beta$ -elimination) of the following reactions:



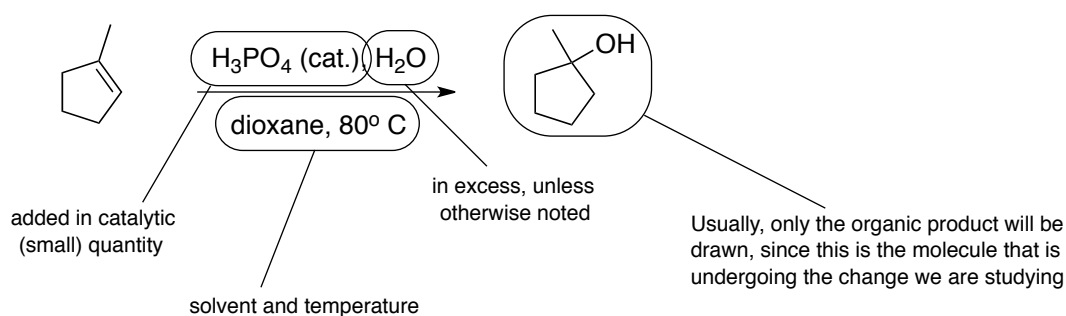
**Electrophilic Addition Reactions.** These additions are *regioselective* because they generally observe Markovnikov's rule - that says, in an electrophilic addition reaction, the hydrogen becomes attached to the carbon with fewer alkyl substituents, and the X group (in this case, a halide) becomes attached to the carbon with the more alkyl substituents:



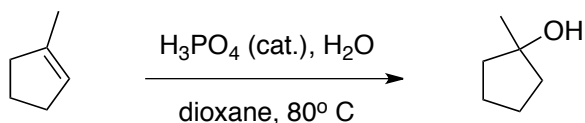
## Acid-Catalyzed Hydration

- remember, acid + water makes hydronium
- like addition of H-X, proceeds through carbocation and is therefore regioselective
- carbocation rearrangement is possible

It is important to filter through the information surrounding the reaction arrow to find the important chemical reagents. In the following, dioxane is the solvent (unreactive) and the temperature indication is simply letting you know that energy is being put into the reaction. Phosphoric acid and water are the important reagents. It is also generally understood that if you are not told how much reagent is present, you should assume an excess is available. In this case, phosphoric acid is added in only small quantities (catalyst), but there is plenty of water around.

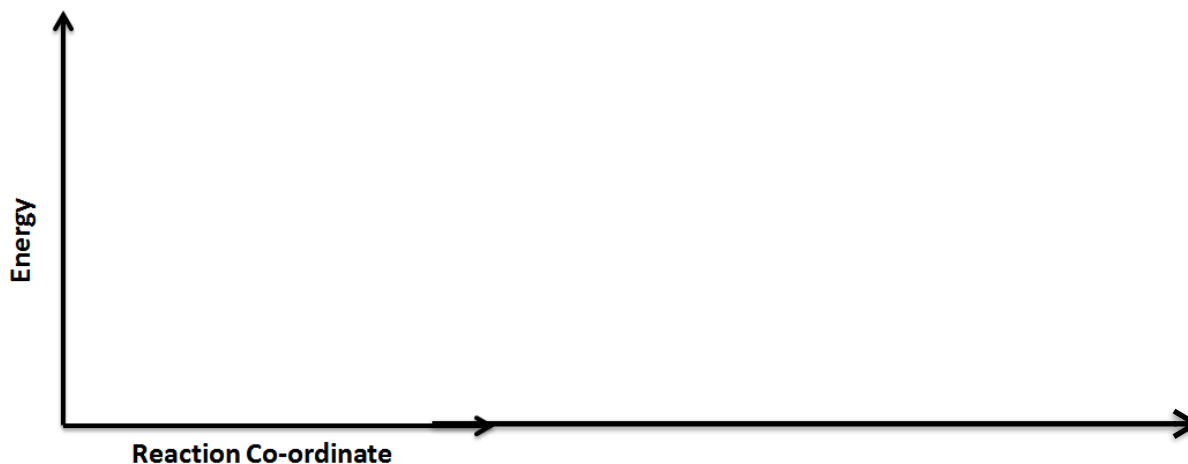


The first step is slow (rate determining). Draw the structure of hydronium in the space below the reaction arrow, then use two arrows to show reaction of the alkene with it. This gives you the FIRST chemical intermediate - a carbocation.

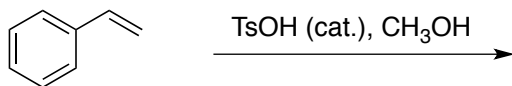


Once the carbocation is formed, use the water you just generated as a nucleophile to create a bond to the carbocation, then use water again (remember, there's lots of water around) to deprotonate/make neutral the oxygen of your newly formed alcohol.

Complete the energy diagram for the reaction on the prior page that includes starting material, product and two intermediates. Your diagram should show three steps.



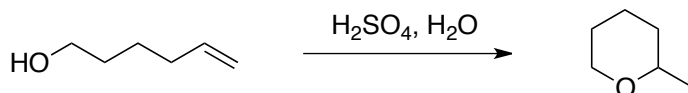
Because of resonance delocalization, the pi-electrons in the benzene ring are mostly - so use the other alkene in this reaction. Draw a mechanism that results in the formation of an ether. TsOH is an acid - don't worry that you've never seen it before.

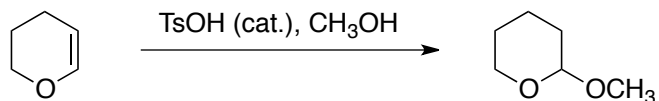


*Don't forget to think about stereochemistry!*

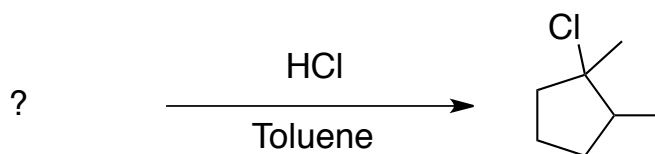
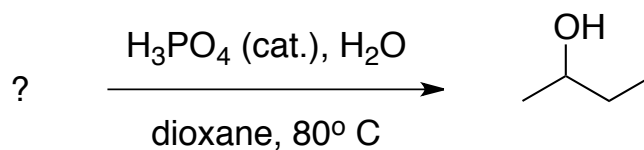
Since we used an alcohol instead of water - we made an ether instead of an alcohol...

Here are two related problems. Provide mechanisms for the following:





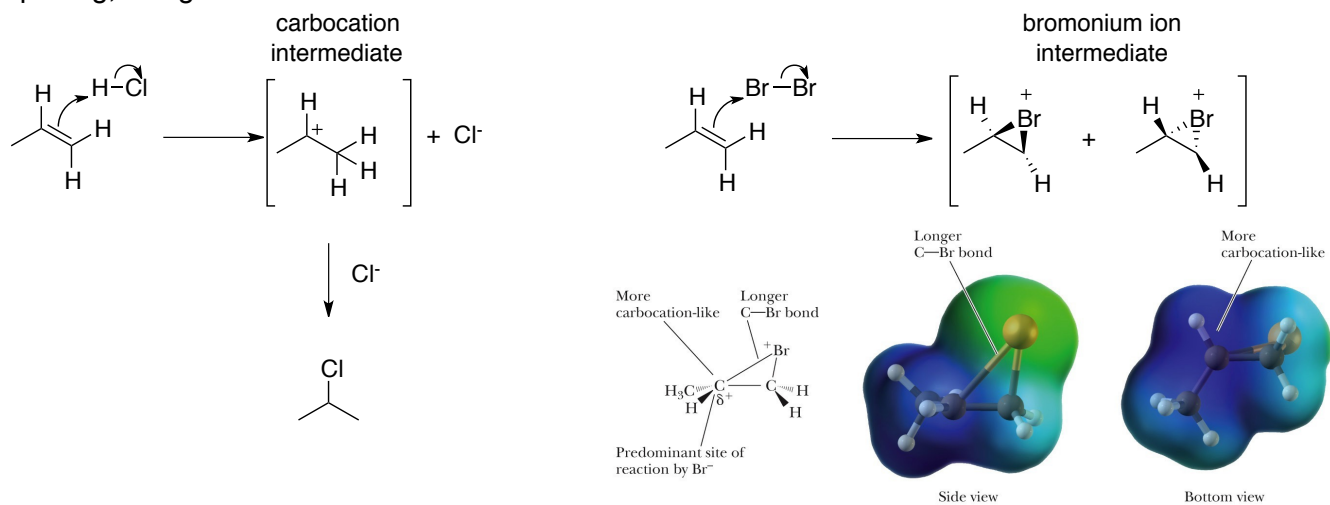
Here's some practice with *RETROSYNTHESIS*. Identify what starting materials would form the molecules shown as their only major organic products. For the first reaction, more than one answer is right, however only one starting material will result in making the second molecule.



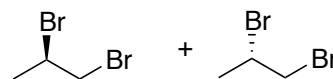
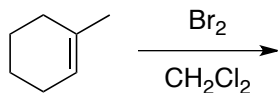
Addition of Halogens (Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>) - F<sub>2</sub> addition is explosive and not very useful!

- concerted formation of three-membered ring intermediate
- addition occurs through anti stereoselectivity - results in *trans* dihalide
- nucleophilic attack occurs at most highly substituted carbon

Why does the addition of Br<sub>2</sub> give an intermediate three-membered ring while addition of HCl does not? Notice the asymmetry in the three-membered ring and the predominant partial positive charge. Given this information, draw two arrows that show the mechanism of the ring opening, using Br<sup>-</sup>.



Draw a stepwise arrow-pushing mechanism that shows the formation of two enantiomers, each having two bromines attached that are TRANS to each other. Think about why must the relationship be trans...



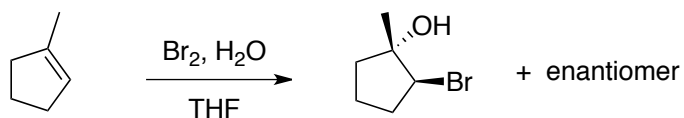
### Formation of Halohydrin

- concerted formation of three-membered ring intermediate
- addition of water occurs through anti stereoselectivity - results in *trans* halohydrin
- nucleophilic attack occurs at most highly substituted carbon

This is very similar to what you've just done.

1. Alkene reacts to form three-membered ring intermediate
2. Ring opening by water is regioselective and stereoselective.

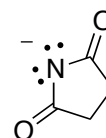
Give the mechanism a try:



$\text{Br}_2$  is highly reactive and can sometimes present complications. N-bromosuccinimide (NBS) is a more common choice of reagent when a halohydrin is made from an alkene.

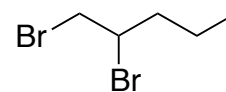
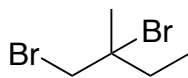
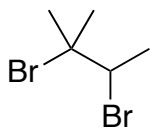


In the process of forming the three-membered intermediate, NBS becomes:

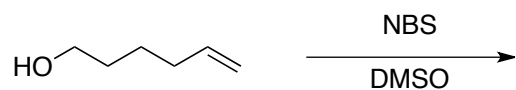


Given this information, draw a mechanism for the formation of the products.

Draw the structure of the alkenes that reacted with  $\text{Br}_2$  to give the each of these products.



Propose a mechanism and product for the following reaction (Hint: The product is a six-membered ring).





Here's something related - a little more challenging. It is important to know that acid-base reactivity is very fast, and is almost always the first thing to happen (given the option). The I in NIS is IODINE.

