

CHAPTER 8. ALKENES: REACTIONS AND SYNTHESIS

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. They are not, however stereoselective because the nucleophile reacts with the electrophilic carbon from both sides of the empty p-orbital.



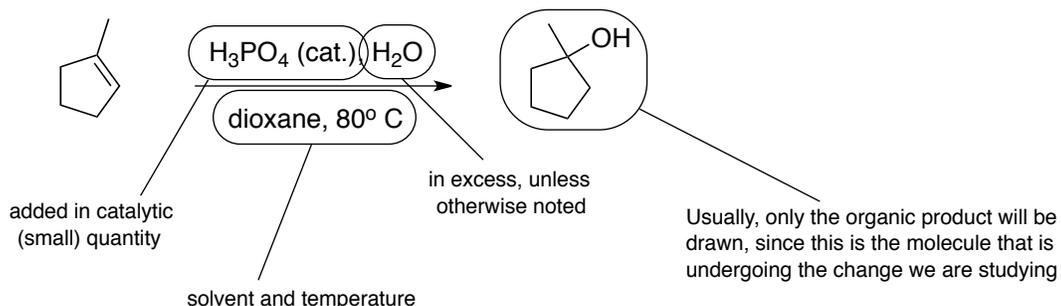
Now you predict the products (below):



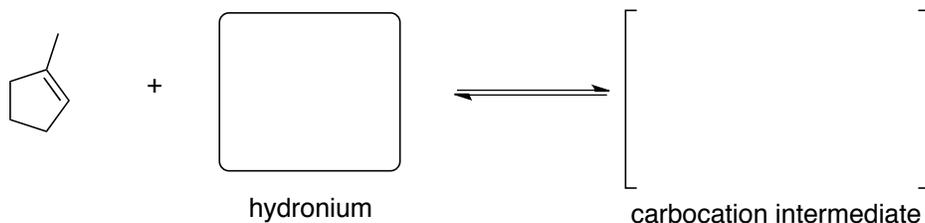
Acid-Catalyzed Hydration

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

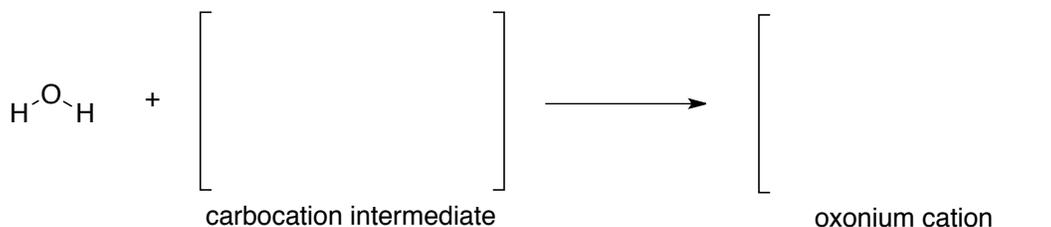
It is important to filter through the information surrounding the reaction arrow to find the important chemical reagents. In the following, dioxane is the solvent (unreactive) and the temperature indication is simply letting you know that energy is being put into the reaction. Phosphoric acid and water 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.



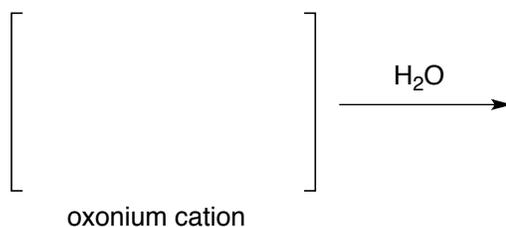
The first step is slow (rate determining). Draw the structure of hydronium in the space below, then use two arrows to show reaction of the alkene with it. This gives you the FIRST chemical intermediate - a carbocation.



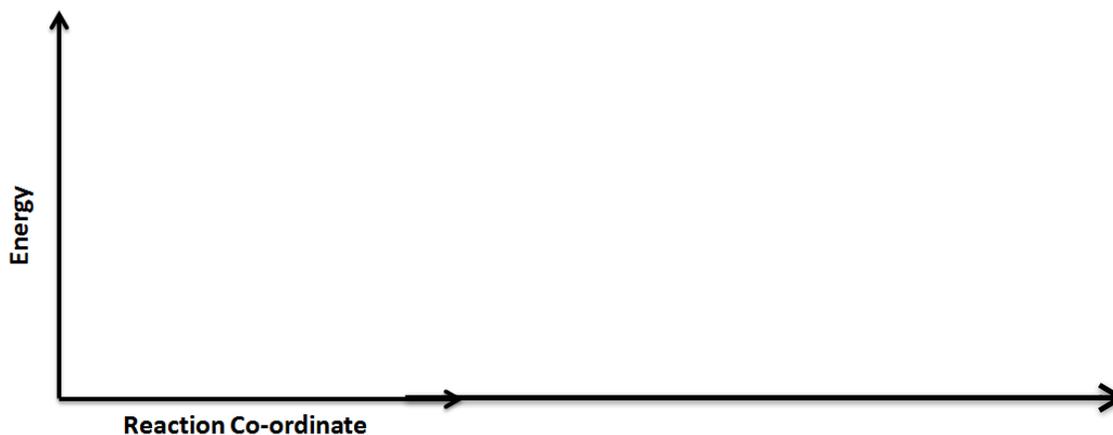
Once the carbocation is formed, use the water you just generated in the prior reaction as a nucleophile to create a bond to the carbocation - this makes an oxonium cation intermediate.



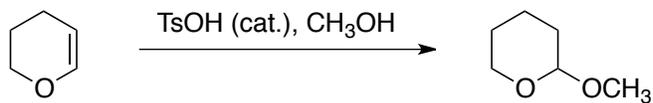
Finally, use water again (remember, there's lots of water around) to deprotonate/make neutral the oxygen of your newly formed alcohol.



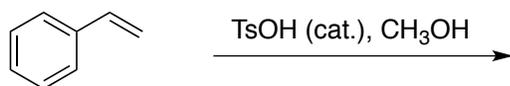
Complete the energy diagram for this reaction that includes starting material, product and two intermediates. Your diagram should show three steps.



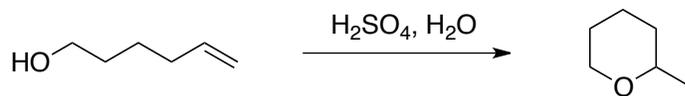
Here's are variations of the reaction using alcohol as nucleophile rather than water. Draw a mechanism and predict the product(s). TsOH is an acid - don't worry that you've never seen it before.



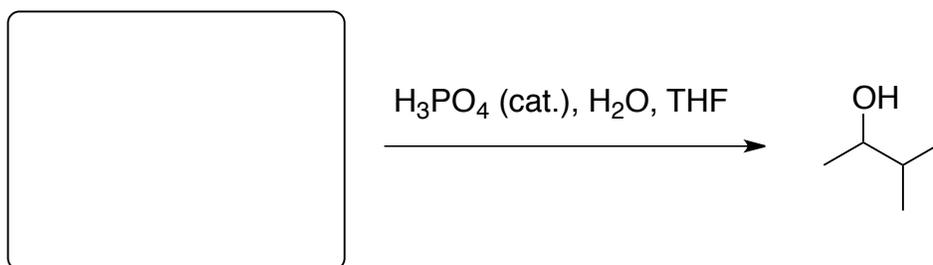
For this one, because of resonance delocalization, the pi-electrons in the benzene ring are mostly - so use the other alkene in this reaction.



Here's a more complex problem. Provide a mechanism for the following:



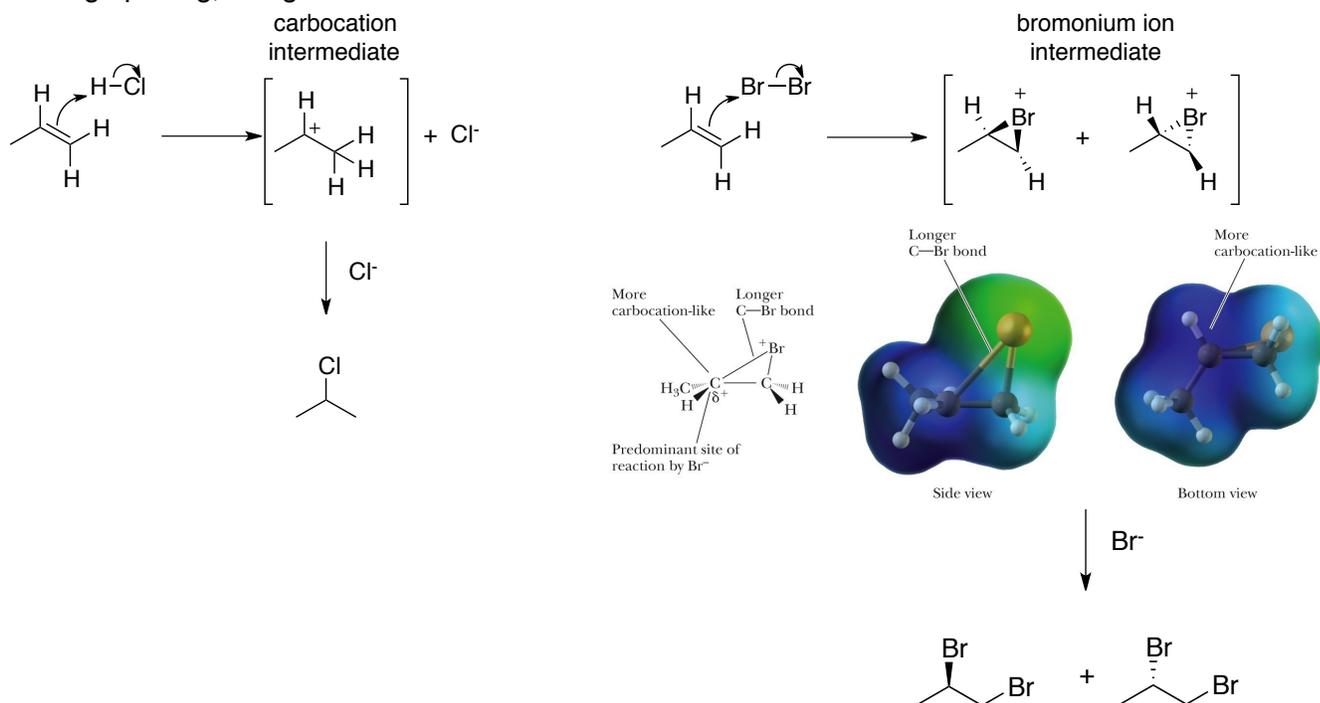
Here's some practice with *RETROSYNTHESIS*. Identify what starting material would make the molecule shown on the right side of the reaction arrow as the only major organic product.



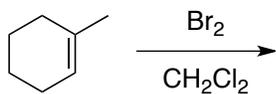
Addition of Halogens (Cl_2 , Br_2 and I_2) - F_2 addition is explosive and not very useful!

- 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_2 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 curved arrows that show the mechanism of the ring opening, using Br^- .



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 the the two bromines must be trans to each other...



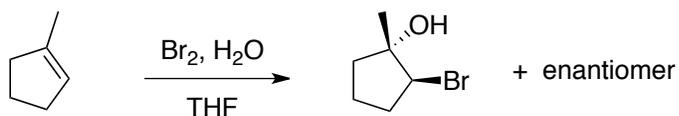
Formation of Halohydrin

- 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.

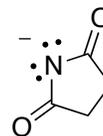
Give the mechanism a try:



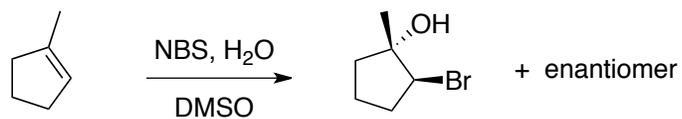
Br_2 is highly reactive and can sometimes present complications. N-bromosuccinimide (NBS) is a more common choice of reagent when a halohydrin is made from an alkene.



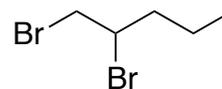
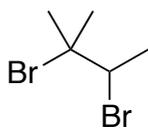
In the process of forming the three-membered intermediate, NBS becomes:



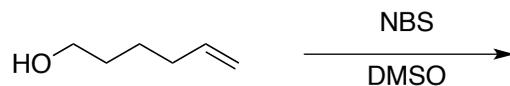
Draw a mechanism for the reaction shown below:



Draw the structure of the alkenes that reacted with Br₂ 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.

