

## 8.4: HYDRATION OF ALKENES - ADDITION OF H<sub>2</sub>O BY OXYMERCURATION

### OBJECTIVES

After completing this section, you should be able to

- write an equation for the hydration of an alkene with sulfuric acid.
- write an equation for the formation of an alcohol from an alkene by the oxymercuration-demercuration process.
- identify the alkene, the reagents, or both, that should be used to produce a given alcohol by the oxymercuration-demercuration process.
- write the mechanism for the reaction of an alkene with mercury(II) acetate in aqueous tetrahydrofuran (THF).

### KEY TERMS

Make certain that you can define, and use in context, the key terms below.



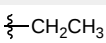
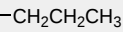


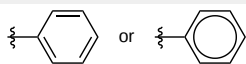
- hydration
- oxymercuration

### STUDY NOTES

*Oxymercuration* is the reaction of an alkene with mercury(II) acetate in aqueous THF, followed by reduction with sodium borohydride. The final product is an alcohol.

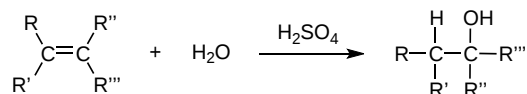
It is important that you recognize the similarity between the mechanisms of bromination and oxymercuration. Recognizing these similarities helps you to reduce the amount of factual material that you need to remember.

Mercuric acetate, or mercury(II) acetate, to give it the preferred IUPAC name, is written as Hg(OAc)<sub>2</sub>; by comparing this formula with the formula Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>, you can equate Ac with -COCH<sub>3</sub>. In fact, Ac is an abbreviation used for the acetyl group with the structure shown below as are other similar abbreviations that you will encounter.

Ac (acetyl)	
Me (methyl)	
Et (ethyl)	
Pr <sup>n</sup> ( <i>n</i> -propyl)	
Pr <sup>i</sup> (isopropyl)	
Bu <sup>t</sup> ( <i>tert</i> -butyl)	
Ph (phenyl)	

### WHAT IS ELECTROPHILIC HYDRATION?

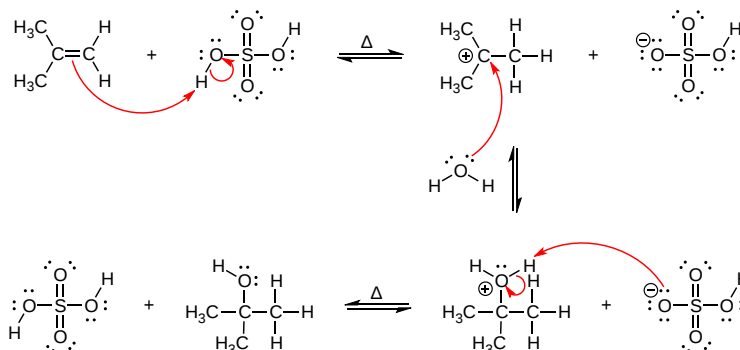
Electrophilic hydration is the act of adding an electrophilic hydrogen from a non-nucleophilic strong acid (a reusable catalyst, examples of which include sulfuric and phosphoric acid) and applying appropriate temperatures to break the alkene's double bond. After a **carbocation** is formed, water bonds with the carbocation to form a 1°, 2°, or 3° alcohol on the alkane. Electrophilic hydration is the reverse dehydration of alcohols and has practical applications in making alcohols for fuels and reagents for other reactions. The basic reaction under certain temperatures (given below) is the following:



An electrophilic hydrogen is essentially a proton: a hydrogen atom stripped of its electron. An electrophilic hydrogen is commonly used to help break double bonds or restore catalysts (see [S<sub>N</sub>2](#) for more details).

### MECHANISM FOR THE FORMATION OF A 3° ALCOHOL (1° AND 2° MECHANISMS ARE SIMILAR)

Hydration is the process where water is added to an alkene to yield an alcohol. Acid-catalyzed hydration is when a strong acid is used as a catalyst to begin the reaction, but let's look at the mechanism below and break down the steps.



Step 1: A hydrogen atom from the acid is attacked by the nucleophilic  $\pi$ -electrons in the double bond. This is similar to the other alkene reactions we have seen so far. In this process, a new C-H bond is formed at the location which creates the more stable carbocation.

Step 2: A nucleophilic water attacks or donates a lone pair to the carbocation intermediate created in the first step. A new C-O bond is formed with the O having a formal charge of +1. The product is a protonated alcohol.

Step 3: To obtain the neutral alcohol product, the final step is to deprotonate the oxygen atom with the +1 formal charge using the conjugate base of the acid catalyst. This final step regenerates the acid catalyst and yields the neutral alcohol product.

Heat is used to catalyze electrophilic hydration; because the reaction is in equilibrium with the dehydration of an alcohol, which requires higher temperatures to form an alkene, lower temperatures are required to form an alcohol. *The exact temperatures used are highly variable and depend on the product being formed.*

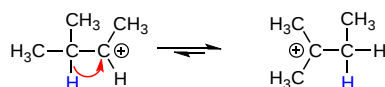
### WHAT IS REGIOCHEMISTRY AND HOW DOES IT APPLY?

Regiochemistry deals with where the substituent bonds on the product is formed. **Zaitsev's** and **Markovnikov's** rules address regiochemistry, but Zaitsev's rule applies when synthesizing an alkene while Markovnikov's rule describes where the substituent bond form in the product of an electrophilic addition. In the case of electrophilic hydration, Markovnikov's rule is the only rule that *directly* applies. See the following for an in-depth explanation of regiochemistry: [Markovnikov explanation: Radical Additions--Anti-Markovnikov Product Formation](#)

In the mechanism for the formation of a 3° alcohol shown above, the H is added to the least-substituted carbon in the nucleophilic double bond (it has less carbons attached to it). This means that the carbocation forms on the 3° carbon, causing it to be more stabilized by *hyperconjugation*—electrons in nearby sigma (single) bonds help fill the empty p-orbital of the carbocation, which lessens the positive charge. More substitution on a carbon means more sigma bonds are available to "help out" (by using overlap) with the positive charge, which creates greater *carbocation stability*. In other words, **carbocations form on the most substituted carbon** in the double bond.

If the carbocation does originally form on the less substituted part of the alkene, carbocation rearrangements occur to form more substituted products:

- **Hydride shifts:** a hydrogen atom bonded to a carbon atom next to the carbocation leaves that carbon to bond with the carbocation (after the hydrogen has taken both electrons from the single bond, it is known as a hydride). This changes the once neighboring carbon to a carbocation, and the former carbocation becomes a neighboring carbon atom.



- **Alkyl shifts:** if no hydrogen atoms are available for a hydride shift, an entire methyl group performs the same shift.

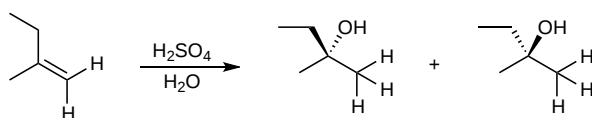


The nucleophile attacks the positive charge formed on the most substituted carbon connected to the double bond, because the nucleophile is seeking that positive charge. In the mechanism for a 3° alcohol shown above, water is the nucleophile. After one H atom is removed from the water molecule, the alcohol is attached to the most substituted carbon. Hence, **electrophilic hydration follows Markovnikov's rule**.

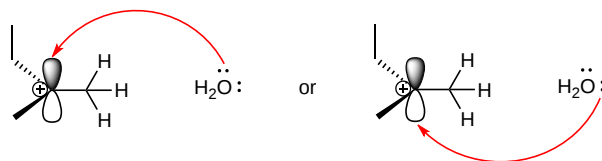
## WHAT IS STEREOCHEMISTRY AND HOW DOES IT APPLY?

**Stereochemistry deals with how the substituent bonds on the product directionally.** Dashes and wedges denote stereochemistry by showing whether the molecule or atom is going into or out of the plane of the board. Whenever the bond is a simple single straight line, the molecule that is bonded is equally likely to be found going into the plane of the board as it is out of the plane of the board. This indicates that **the product is a racemic mixture**.

Electrophilic hydration adopts a stereochemistry wherein the substituent is equally likely to bond pointing into the plane of the board as it is pointing out of the plane of the board. The 3° alcohol product of the following reaction could look like either of the following products:



There is no stereochemical control in acid-catalyzed hydration reactions. This is due to the trigonal planar,  $sp^2$  nature of the carbocation intermediate. Water can act as a nucleophile to form a bond to either face of the carbocation, resulting in a mixture of stereochemical outcomes.



Note: Whenever a straight line is used along with dashes and wedges on the same molecule, it could be denoting that the straight line bond is in the same plane as the board. Practice with a molecular model kit and attempting the practice problems at the end can help eliminate any ambiguity.

### IS THIS A REVERSIBLE SYNTHESIS?

Electrophilic hydration is reversible because an alkene in water is in equilibrium with the alcohol product. To sway the equilibrium one way or another, the temperature or the concentration of the non-nucleophilic strong acid can be changed. For example:

- Less sulfuric or phosphoric acid and an excess of water help synthesize more alcohol product.
- Lower temperatures help synthesize more alcohol product.

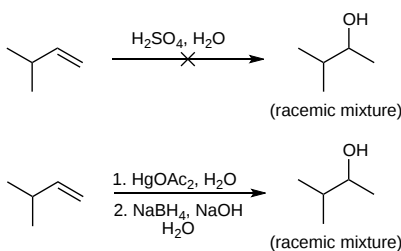
## IS THERE A BETTER WAY TO ADD WATER TO SYNTHESIZE AN ALCOHOL FROM AN ALKENE?

A more efficient pathway does exist: **Oxymercuration - Demercuration**, a special type of electrophilic addition. Oxymercuration does not allow for rearrangements, but it does require the use of mercury, which is highly toxic. Detractions for using electrophilic hydration to make alcohols include:

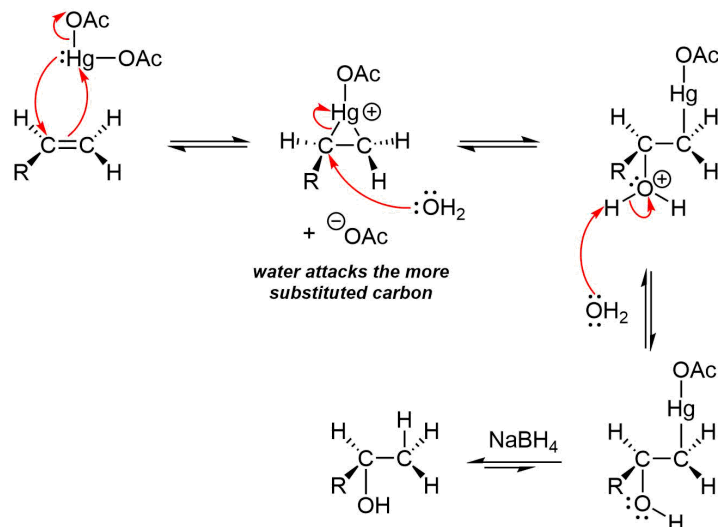
- Allowing for carbocation rearrangements
- Poor yields due to the reactants and products being in equilibrium
- Allowing for product mixtures (such as an (*R*)-enantiomer and an (*S*)-enantiomer)
- Using sulfuric or phosphoric acid

Oxymercuration is a special electrophilic addition. It is anti-stereospecific and regioselective. Regioselectivity is a process in which the substituents choose one direction it prefers to be attached to over all the other possible directions. The good thing about this reaction is that there are no **carbocation rearrangement** due to stabilization of the reactive intermediate. Similar stabilization is also seen in **bromination** addition to alkenes.

One of the major advantages to oxymercuration is that carbocation rearrangements cannot occur under these conditions ( $Hg(OAc)_2$ ,  $H_2O$ ). Carbocation rearrangement is a process in which the carbocation intermediate can undergo a methyl or alkyl shift to form a more stable ion. Due to a possible **carbocation rearrangement**, the reaction below would not generate the product shown in high yields. In contrast, the oxymercuration reaction would proceed to form the desired product.



This reaction involves a mercury acting as a reagent attacking the alkene double bond to form a *Mercurinium Ion Bridge*. A water molecule will then attack the most substituted carbon to open the mercurium ion bridge, followed by proton transfer to solvent water molecule.



The organomercury intermediate is then reduced by sodium borohydride - the mechanism for this final step is beyond the scope of our discussion here. Notice that overall, the oxymercuration - demercuration mechanism follows Markovnikov's regioselectivity with the OH group is attached to the most substituted carbon and the H is attach to the least substituted carbon. The reaction is useful, however, because strong acids are not required, and carbocation rearrangements are avoided because no discreet carbocation intermediate forms.

It is important to note that for the mechanism shown above, the enantiomer of the product shown is also formed. This is the result of formation of the mercurium ion below the alkene in the first step.

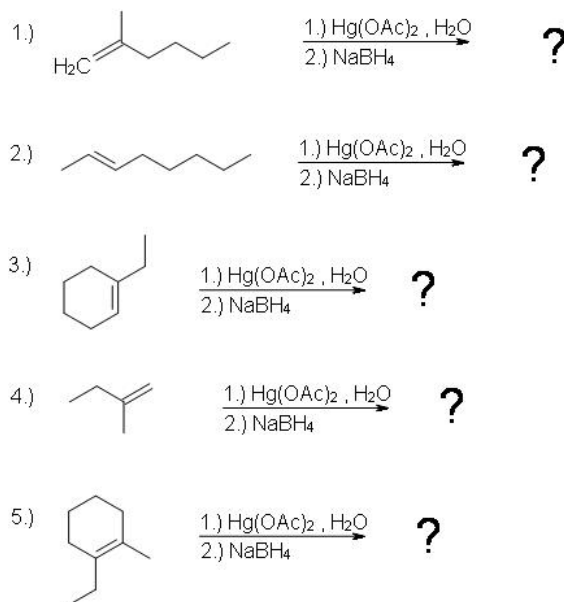
## REFERENCES

1. Vollhardt, K. Peter C. Organic chemistry structure and function. New York: W.H. Freeman, 2007.
2. Smith, Michael B., and Jerry March. March's Advanced Organic Chemistry Reactions, Mechanisms, and Structure (March's Advanced Organic Chemistry). New York: Wiley-Interscience, 2007 2007.
3. Roderic P. Quirk , Robert E. Lea, Reductive demercuration of hex-5-enyl-1-mercuric bromide by metal hydrides. Rearrangement, isotope effects, and mechanism, *J. Am. Chem. Soc.*, 1976, 98 (19), pp 5973–5978.

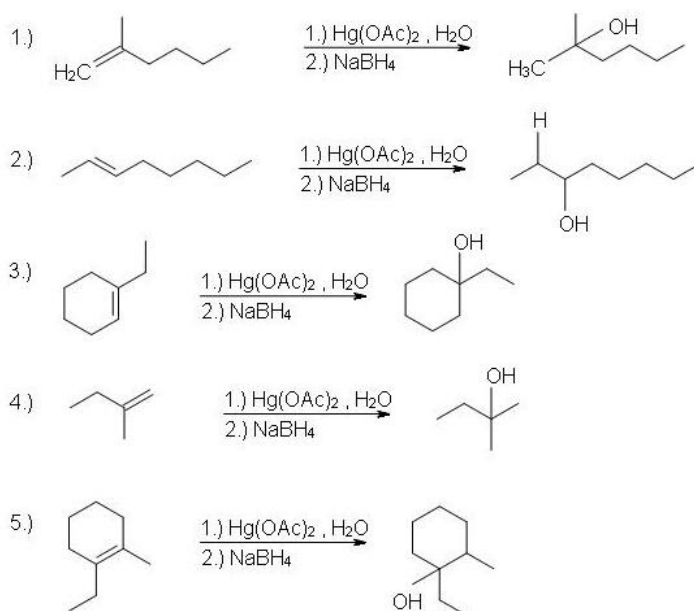
## SOME PRACTICE PROBLEMS

### ? PRACTICE PROBLEMS

What are the end products of these reactants?



### Answer

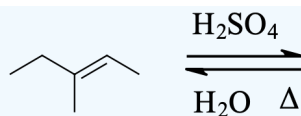


The end product to these practice problems are pretty much very similar. First, you locate where the double bond is on the reactant side. Then, you look at what substituents are attached to each side of the double bond and add the OH group to the more substituent side and the hydrogen on the less substituent side.

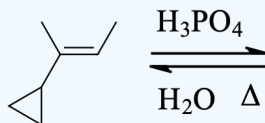
### ? MORE PROBLEMS

Predict the product of each reaction.

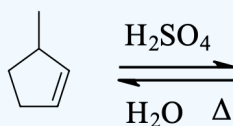
1)



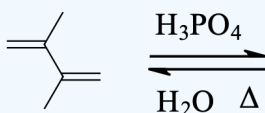
2) How does the cyclopropane group affect the reaction?



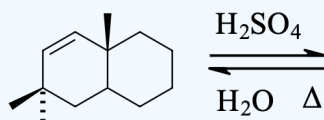
3) (Hint: What is different about this problem?)



4) (Hint: Consider stereochemistry.)

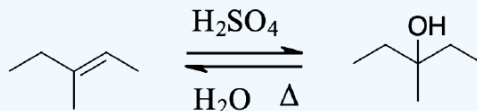


5) Indicate any shifts as well as the major product:

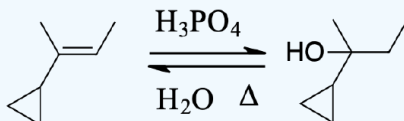


#### Answer

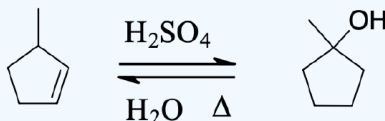
1) This is a simple electrophilic hydration.



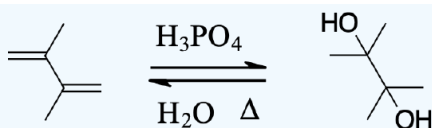
2) The answer is additional side products, but **the major product formed is still the same** (the product shown). Depending on the temperatures used, the cyclopropane may open up into a straight chain, which makes it unlikely that the major product will form (after the reaction, it is unlikely that the 3° carbon will remain as such).



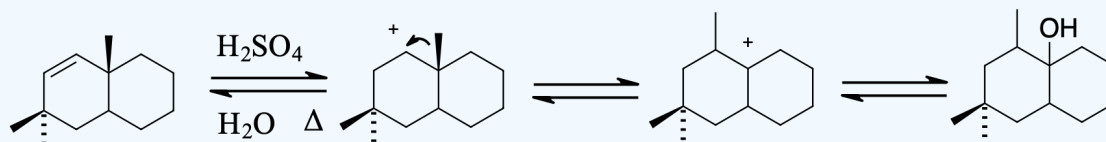
3) A hydride shift actually occurs from the 3 carbon of the 3-methylcyclopentene to where the carbocation had formed.



4) **This reaction will have poor yields due to a very unstable intermediate.** For a brief moment, carbocations can form on the two center carbons, which are more stable than the outer two carbons. The carbocations have an  $\text{sp}^2$  hybridization, and when the water is added on, the carbons change their hybridization to  $\text{sp}^3$ . This makes the methyl and alcohol groups equally likely to be found going into or out of the plane of the paper- the product is racemic.



5) In the first picture shown below, an alkyl shift occurs but a hydride shift (which occurs faster) is possible. Why doesn't a hydride shift occur? The answer is because **the alkyl shift leads to a more stable product**. There is a noticeable amount of side product that forms where the two methyl groups are, but the major product shown below is still the most significant due to the hyperconjugation that occurs by being in between the two cyclohexanes.



This page titled [8.4: Hydration of Alkenes - Addition of H<sub>2</sub>O by Oxymercuration](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Steven Farmer & Dietmar Kennepohl](#).

- [8.4: Hydration of Alkenes - Addition of H<sub>2</sub>O by Oxymercuration](#) by Aliza Bother Duke University, Dietmar Kennepohl, Krista Cunningham, Lauren Reutenauer, Layne Morsch, Steven Farmer is licensed [CC BY-SA 4.0](#).