

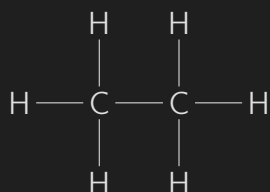
# Organic Chemistry II

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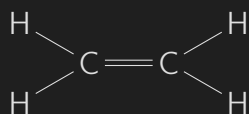
# 14: Alkenes

## Alkenes Basics/Review

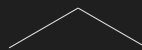
▷ Alkanes vs alkenes:



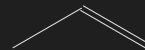
Saturated  
alkanes ethane



Unsaturated  
alkenes ethene



propane



propene

▷ We will fully investigate the nomenclature of alkenes ↗ later.

▷ Some relevant facts to start:

- **Alkene**: a hydrocarbon that contains a carbon-carbon double bond.
  - IUPAC recommends using alkene for only acyclic hydrocarbons with just one double bond; an **olefin** is a hydrocarbon with one or more double bonds.
- Generally prepared through beta elimination, which results in the formation of alkenes from alkanes.

## Types of Alkenes

- Basic types of alkenes:



Terminal Alkene

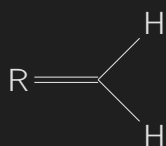


Internal Alkene

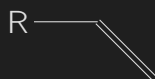


Cycloalkene

- Types of terminal alkenes:



Methylene



Vinyl

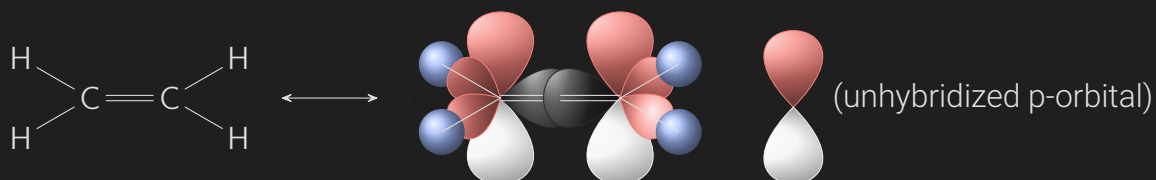


Allyl

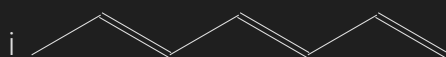
- “R” always tells you it’s a carbon containing functional group, or hydrogen.
- “A” can be used to represent any functional group.

## Relevant Review

- **Electronegativity:** negative charges on atoms with lower hybridization result in greater stability due to proximity (overlap) to positive nucleus. More s character results in greater stability.
  - I.e.,  $sp$  (50% s) >  $sp^2$  (33% s) >  $sp^3$  (25% s)
  - E.g., ethene has two carbons that are both  $sp^2$  due to one unhybridized p-orbital. This gives ethene a trigonal planar geometry.



- **Hydrogen deficiency index (HDI):** the measure of degrees of unsaturation.
  - E.g., two degrees of unsaturation results in a HDI of 2.
  - Degrees of freedom help represent possible structures, indicating possible double bounds, triple bounds, rings, or various combinations of each.
  - Only helpful when molecular formula is known for certainty.
  - Formula:  $HDI = \frac{1}{2}(2C + 2 + N - H - X)$ 
    - X: halogen atoms.
- What is the HDI for the following molecules?



i  $\frac{1}{2}(2(7) + 2 + (0) - (3 + (5(1)) + 2) - 0) = 3$



ii  $\frac{1}{2}(2(6) + 2 + 0 - (6(1)) - 0) = 4$

- **Degree of substitution:** not a substitution reaction, but the **number of groups** connected to the double bond.



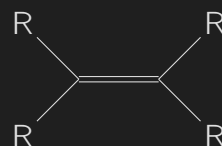
Monosubstituted



Disubstituted



Trisubstituted



Tetrasubstituted

## Common Patterns Between Formal Charge and Lone Pairs

### ◦ Associated Patterns for Oxygen

- A negative ( $\ominus$ ) charge corresponds with 1 bond and 3 lone pairs.
- The absence of charge corresponds with 2 bonds and 2 lone pairs.
- A positive ( $\oplus$ ) charge corresponds with 3 bonds and 1 lone pair.

### ◦ Associated Patterns for Nitrogen

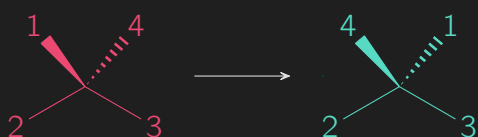
- A negative charge corresponds with 2 bonds and 2 lone pairs.
- The absence of charge corresponds with 3 bonds and 1 lone pair.
- A positive charge corresponds with 4 bonds and 0 lone pairs.

## Chirality

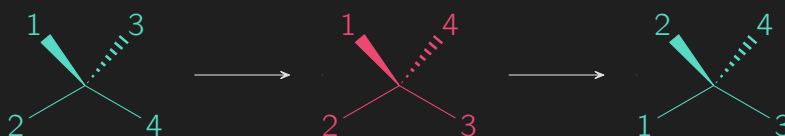
- **Achiral (nonsuperimposable):** when an object's mirrored version is identical to the actual object.
- **Chiral:** objects that are not superimposable.
  - The most common source of molecular chirality is the presence of a carbon bearing four different groups.
- All three-dimensional objects can be classified as either chiral or achiral.
- **Enantiomer:** the nonsuperimposable mirror image of a chiral compound.
  - Can be used in speech the same way the word twin is used
  - The easiest way to draw enantiomers is to simply change wedges and dashes, but there are multiples ways to mirror a molecule, so it can be more complex.
- **Diastereomers:** non-identical stereoisomers (nonsuperimposable) that are not mirror images of one another.
  - Enantiomers have the same physical properties, while diastereomers have different physical properties.
  - Differences between enantiomers and diastereomers are especially relevant when comparing compounds with more than one chiral center.
  - Maximum (could be less) number of stereoisomers:  $2^n$ 
    - $n$ : number of chiral centers
    - $\frac{2^n}{2}$ : max pairs of enantiomers.

## Cahn-Ingold-Prelog System

- **Cahn-Ingold-Prelog system:** a system of nomenclature for identifying each enantiomer individually.
  1. Assign priorities to each of the four groups based on atomic number; the highest atomic number has the highest priority.
  2. Rotate the molecule so that the fourth priority group is on a dash (behind)
  3. Determine the configuration, i.e., sequence of 1–2–3 groups;
    - clockwise (*R*, *rectus*, *right*) or counterclockwise (*S*, *sinister*, *left*).
- If there is a tie between the atoms connected, then continue outward until a difference is found.
  - Do not add the sum of all atomic numbers attached to each atom, just the first in which the atoms differ.
  - Any multiple bonded atom, (2 or 3) is treated as if connected to multiple atoms equal to number of bonds.
- Switching any two groups on a chiral center will invert the configuration, e.g.,



- Switching twice results in a change without changing configuration, e.g.,



- **Configuration in IUPAC nomenclature:**
  - The configuration of the chiral center is indicated at the beginning of the name, italicized, and surrounded by parentheses.
  - When multiple centers are present, then each must be preceded by a locant.

## Rearrangements

- There are several kinds of rearrangements, but only those relating to carbocation rearrangements are focused here.
- **Hyperconjugation:** carbocations that can be stabilized by neighboring groups due to molecular orbitals that slightly overlap with empty *p* orbitals, placing some of its electron density there.

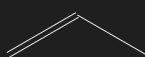
- **Primary (1°), secondary (2°), and tertiary (3°):** refers to the number of groups directly attached to the carbocation.
- Tertiary are the most stable (more slight overlap) and primary are the least (less overlap)
- **Hydride shift:** involves the migration of a  $\text{H}^-$ .
  - Involves the rearrangement of the carbocation to a more stable variant due to change migration of the  $\text{H}^-$ .
- **Methyl shift:** similar to a hydride, except a whole methyl group is migrated instead.
  - The methyl group must be attached to the carbon atom that is adjacent to the carbocation for this to occur.

## Nomenclature of Alkenes

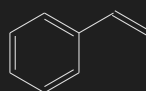
- ▷ Alkenes are named using the same four steps in the previously used nomenclature, though the suffix of “ane” is replaced with “ene.”
- ▷ When choosing the parent chain, choose the parent chain that **includes** the double bond.
- ▷ When numbering the parent chain, the double bond should receive the **lowest** number possible.
  - Define the location  $k$  of the double bond as being the number of its first carbon.
  - The locant ( $k$ ) of the double bond should be placed right before the suffix of “ene,” though, it was previously recommended before the parent (both are acceptable), e.g., 2-pentene = pent-2-ene
- ▷ Name and the side groups (other than hydrogen) according to the appropriate rules.
- ▷ Define the position of each side group as the number of the chain carbon it is attached to.
- ▷ **E-Z notation:** recommended instead of *cis* and *trans* in order to account for cases that has more than two different groups attached to the double bond by first determining the **CIP priority** ↗.
  - **E**, *entgegen*, “opposite”.
  - **Z**, *zusammen*, “together”; “on ze zame zide.”
- ▷ Commonly recognized alternative names:



Ethylene



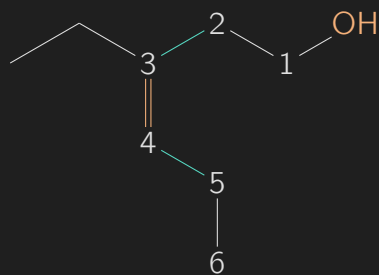
Propylene



Styrene

- ▷ Groups containing C=C have common names as well, which can be found under **types of alkenes** ↗.
- ▷ If there is **more than 1** functional group, then the **alcohol** has the **higher priority** over alkenes.
  - There are more rules depending on functional groups, but for now the distinction between alcohol and alkenes are all that is needed.
  - I.e., find the longest chain and number in a way that the carbon **containing the OH** gets the **lowest** possible number while still including both the OH and alkene.

- An example with alcohol:

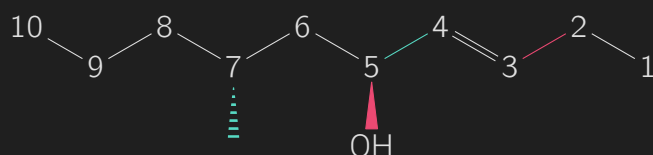


(3Z)-3-propyl-hex-3-en-1-ol

or

(3Z)-3-propyl-3-hexen-1-ol

- An example with OH still being lowest (name still ends with -ol), but alkene happens to be lower:



(3E,5S,7R)-4-methyl-3-en-5-ol

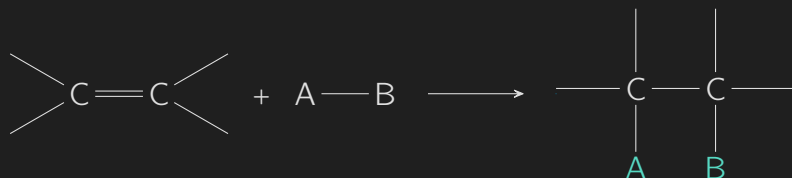
- Note: if planar geometry was not given, R and S could not be determined. Check out the [Cahn-Ingold-Prelog System](#) ↗ for review.



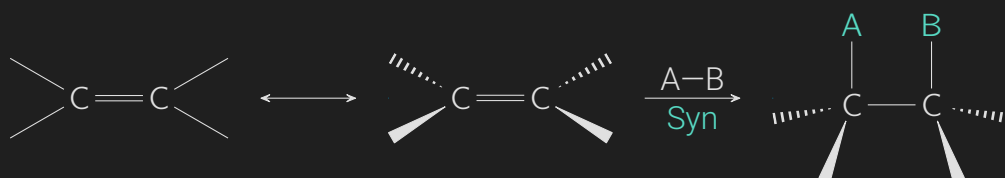
## Addition Reactions of Alkenes

### Syn Addition

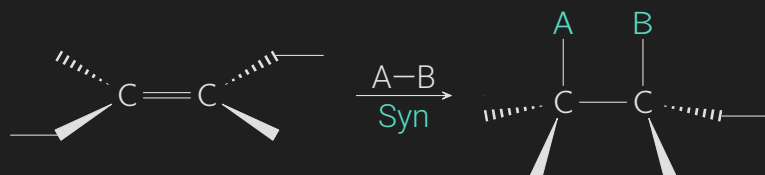
- Syn addition means that both components (A & B) came in from the same side.



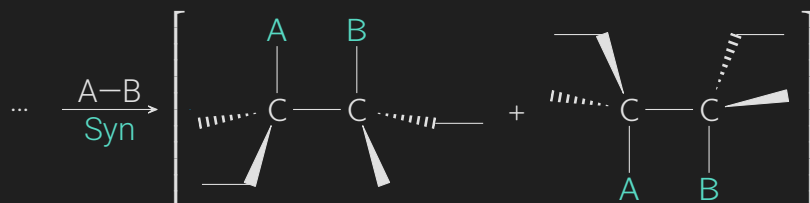
- When there is mixture of products, then the stereochemistry is important—A & B could come from different directions.
- Switching to a 3D perspective, with groups pointing towards and away from the viewer, rather than a flat view:



- The final product above results in no chiral compounds (no carbons contain four different groups). If a product does have chiral compounds, you must show the other possible products.

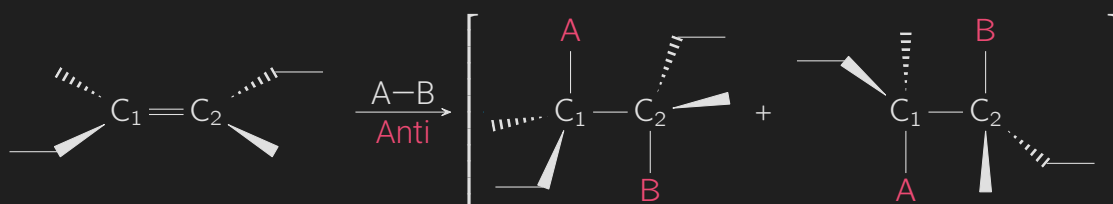


- The product in this case has **chiral centers** ↗, so enantiomers must be considered.



### Anti Addition

- Anti addition means that the added components come in from different sides.



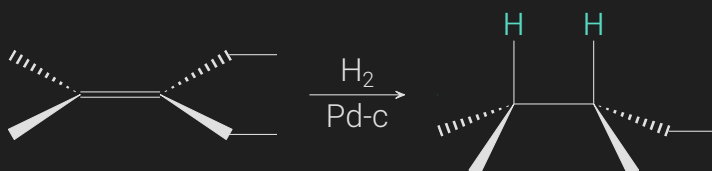
## Hydrogenation

- **Hydrogenation:** a chemical reaction between molecular hydrogen  $H_2$  and another compound or element, usually in the presence of a catalyst such as nickel, palladium (typically  $pd$ , due to cost) or platinum.
  - Commonly employed to **reduce** ( $\pi$  bonds) or **saturate** (add hydrogens) organic compounds.
  - Usually constitutes the addition of pairs of hydrogen atoms to a molecule, often an alkene.
  - Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperatures.
  - Always occurs with **syn addition**, with hydrogen entering from the least hindered side.
- Hydrogenation of 2-methyl-3-ethyl-2-pentene:

- First convert to 3D view:

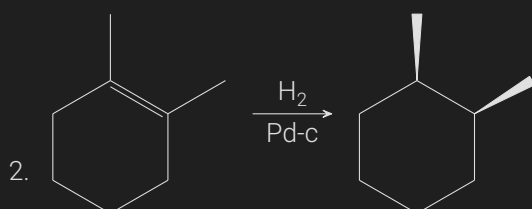
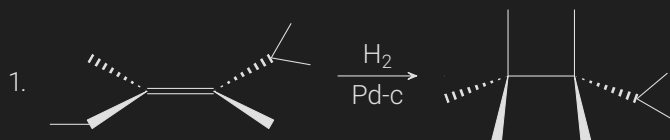


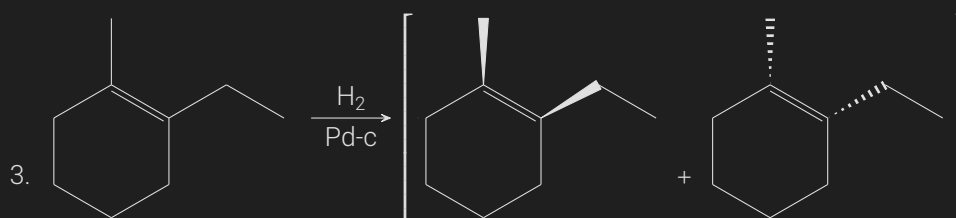
- Then apply  $H_2$  with catalyst to trigger syn addition:



- Product is achiral; no enantiomers. Bottom would attack just flips the orientation; not a different product.

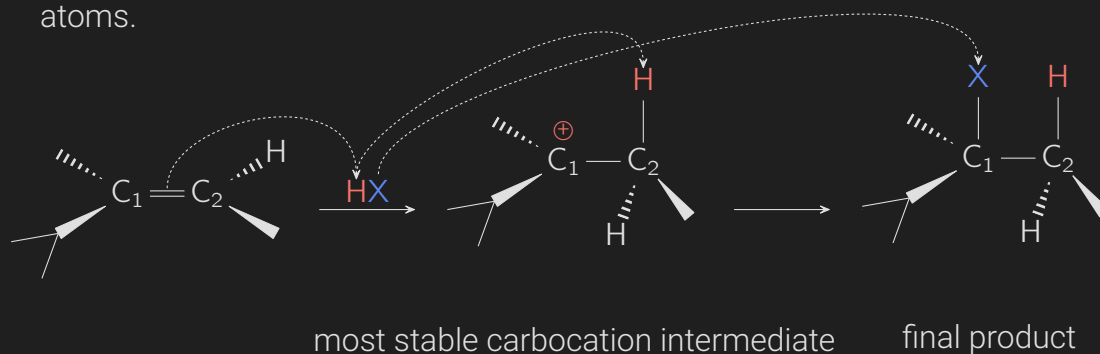
## Hydrogenation Practice Problems



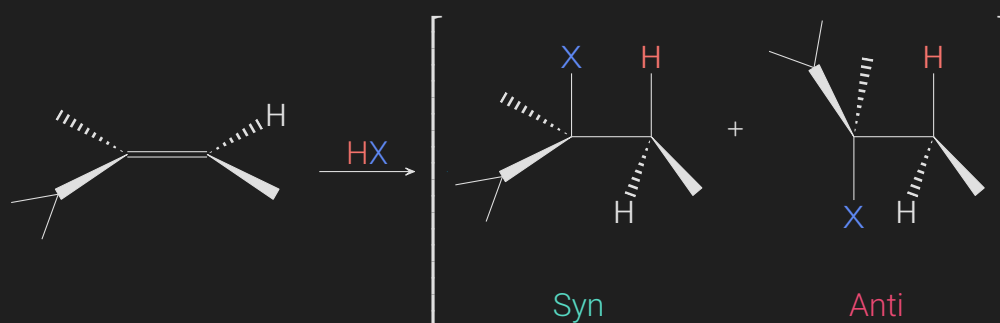


## Hydrohalogenation

- **Hydrohalogenation**: the electrophilic addition ( $\pi \rightarrow 2\sigma$  bonds) of hydrohalic acids (HX, e.g., HCl or HBr) to alkenes to yield the corresponding haloalkanes.
- **Markovnikov's rule**: an addition of a protic acid (HX) or other polar reagent to an asymmetric alkene results in the **electropositive part (usually H)** gets attached to the carbon with **more hydrogen substituents**, and the **electronegative part (usually the halide)** attaches to the carbon with **more alkyl substituents**.
  - Alternatively:  $H^+$  is added to the carbon with the **greatest** number of hydrogen atoms while the  $X^-$  component is added to the carbon with the **fewest** hydrogen atoms.

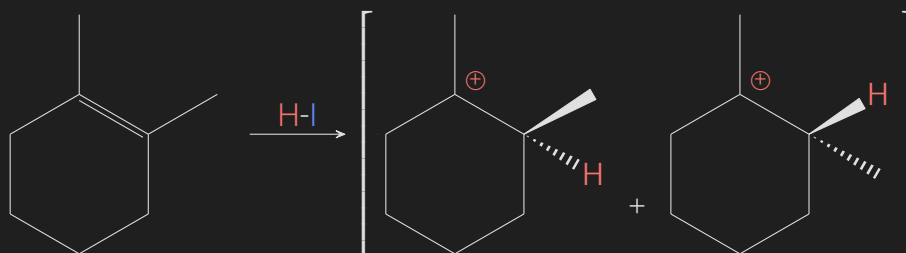


- However, we have a chiral carbon, so we have to take enantiomers into account:

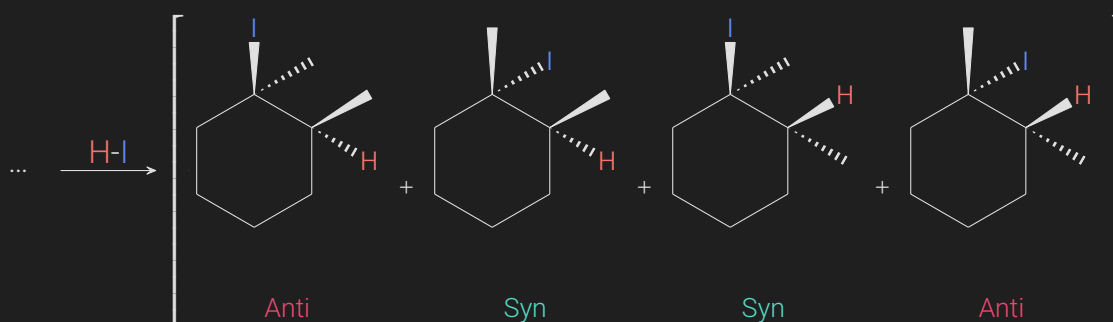


- The previous example is an example of a regioselective reaction, i.e., it's a chemical reaction where one reaction site is preferred over another.
  - Markovnikov additions are common examples of regioselective reactions since there is a specific region in where the hydrogen is supposed to go.

- Another example that contains multiple products:

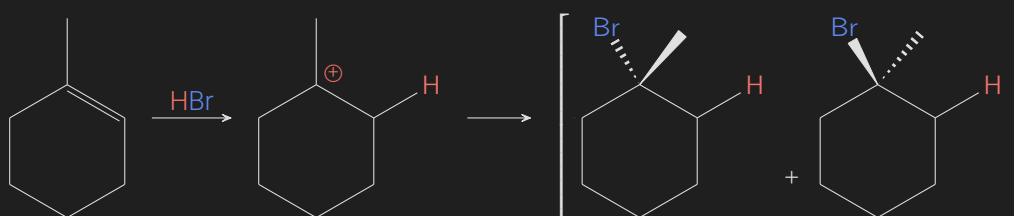


- Again, this first step shows the most stable carbocation intermediate, which helps determine where the  $\text{H}^+$  will attach to. In this case either location works, so four products are formed, each with syn and anti enantiomers.



- The above products are all **stereoisomers** of each other. Note: not all chemical reactions produce all possible stereoisomers.

### Hydrohalogenation Practice Examples

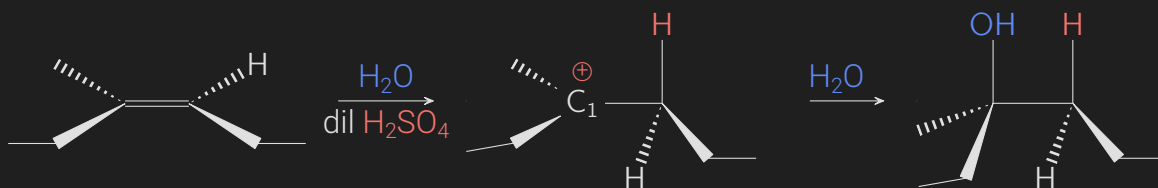


### Addition of Water or Alcohol

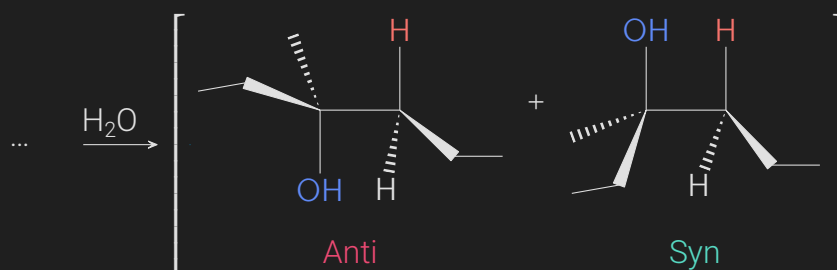
**Addition of Water or Alcohol (ROH):** analogous to that of hydrohalogenation (HX); both of which involve a carbocation intermediate, syn/anti stereochemistry, and Markovnikov regioselectivity.

- Note: the hydronium ion ( $\text{H}_3\text{O}^+$ ) forms via the reaction of  $\text{H}_2\text{SO}_4$  with  $\text{H}_2\text{O}$ , and is the source of the proton that reacts with the starting alkene.
- $\text{H}-\text{OH}$  and  $\text{RO}-\text{H}$  helps to visualize where the proton is coming from. What ever works with water also works with alcohol and vice versa.

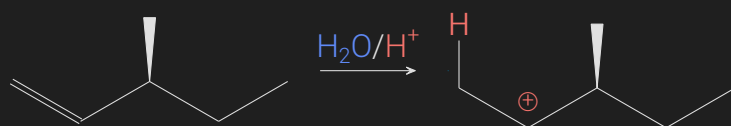
- An example that is very similar to the example from hydrohalogenation ↗:



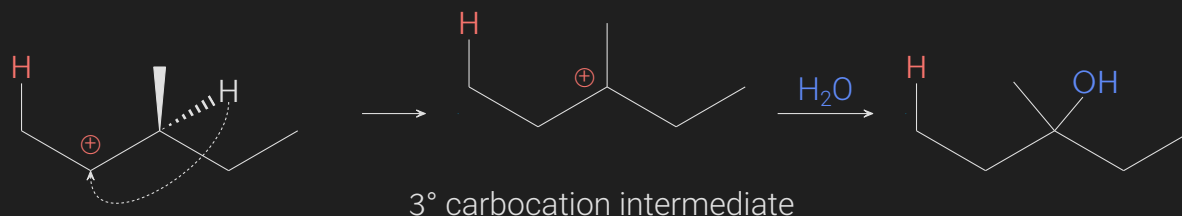
- Note:  $\text{H}_2\text{SO}_4$  is a **strong acid** and can be generalized to  $\text{H}^+$  or  $\text{HA}$ .
- Note: I occasionally use **red** for **cations**, **acids**, and  $E^+$  (electrophile). I also use **blue** for **anions**, **bases**, and  $nu^-$  (nucleophile) to help easily keep track of things. This is an arbitrary color choice, but it holds weight in these notes. However, not all bases/acids are nucleophile/electrophiles, so keep that in mind.
- Again, this reaction is stereoselective, so there is actually more than one product:



- Example 2:

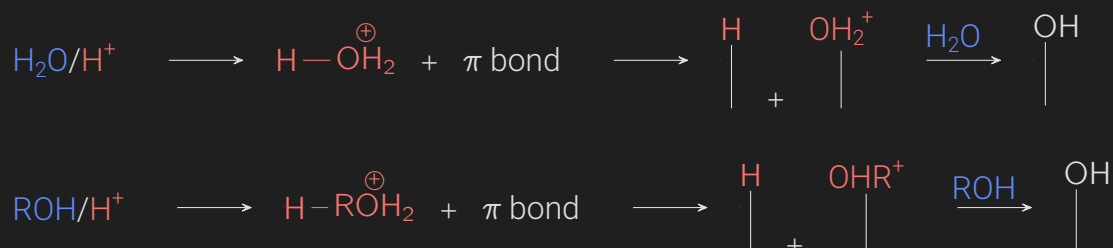


- **Rearrangement** ↗ is always a possibility to be considered when cation are generated. In this case, a  $2^\circ$  carbocation was generated, but we can do better:
- Note: showing H is not necessary, but useful to visualize the hydride shift and avoid the urge to move the methyl. "Why move a sofa when you can move a chair?"



- Note: the carbocation intermediate changes planar geometry due to change in hybridization ( $sp^3 \rightarrow sp^2$ ).
- Top and bottom attacks do not need to be considered in this case, as there are chiral centers; no enantiomers.

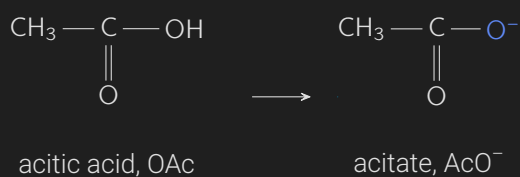
- Reminder,  $\text{H}_2\text{O}$  and alcohols ( $\text{ROH}$ ) behave very similarly; the reduction of the  $\pi$  bond generates  $2\sigma$  bonds, one of which takes a **hydrogen**, and the other (with possible carbocation rearrangement first) which first takes up the **cation** generated in the medium, then interacts with **base**, removing an **H** and leaving **OH**.
  - Note: the OH is not actually negatively charged on the end, I just keep the blue there to help show where it's coming from; it helps determine syn/anti if needed.



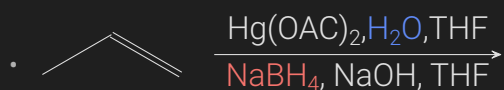
- **Problems of going through carbocation intermediate:**
  - Carbocations are  $sp^2$ , which makes them trigonal planar, so  $\text{nu}^-$  can attack from top or bottom.
  - $\text{C}^+$  can cause rearrangements leading to **multiple products**.

## Oxymercuration-Demercuration

- **Oxymercuration-Demercuration** is another electrophilic addition organic reaction that transforms an alkene into a neutral alcohol.
  - Reacts with mercuric acetate ( $\text{AcO}-\text{Hg}-\text{OAc}$ ) in aqueous solution to yield the addition of an acetoxymcury ( $\text{HgOAc}$ ) group and a hydroxy ( $\text{OH}$ ) group across the double bond.

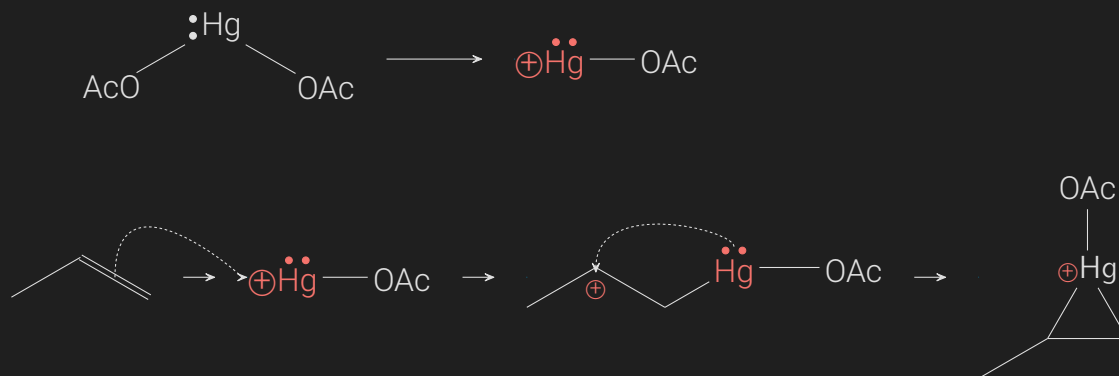


- Carbocations are not formed in this process and thus rearrangements are not observed.
- The reaction follows **Markovnikov's rule** ↗.
- The reaction is stereospecific—it is always an **anti addition**.
- Example using propylene:

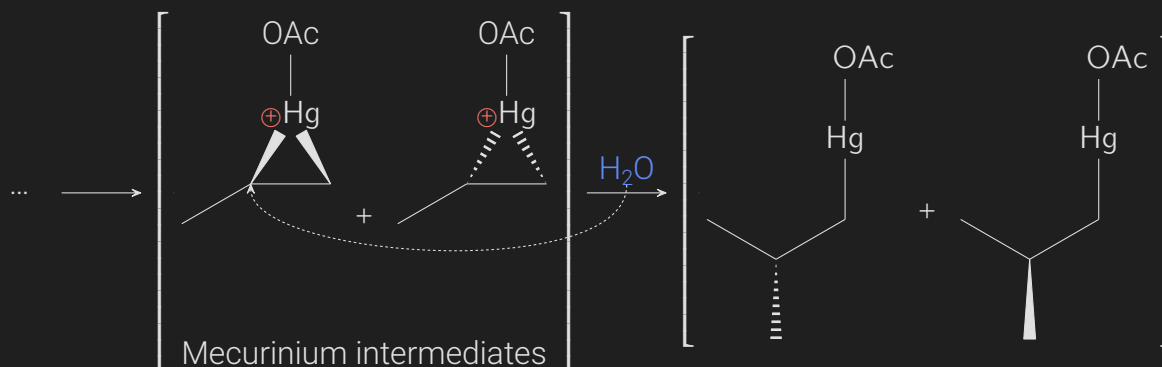


- $\text{H}_2\text{O}$  is  $\text{nu}^-$ ;  $\text{ROH}$  can be used instead.
- THF has no function directly; it is the solvent.

- $\text{NaBH}_4$  is the reducing agent.

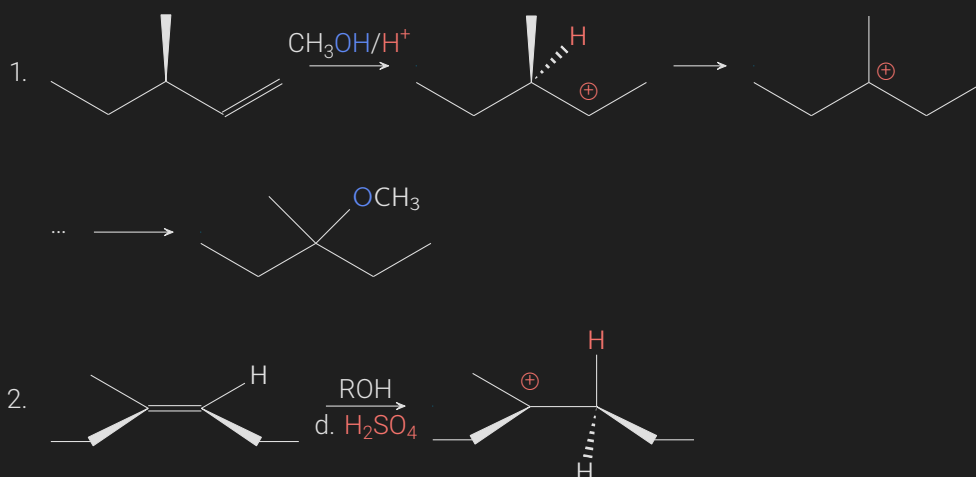


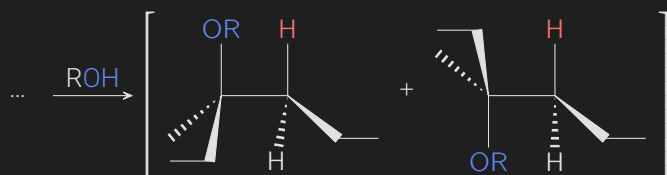
- Note: the above is a concerted (one step) process, but drawn out for illustration.
- Also, we are not done, we have a chiral center that forms, plus it is just an intermediate step, a nucleophilic attack will occur on the strained (highly reactive) epoxide:



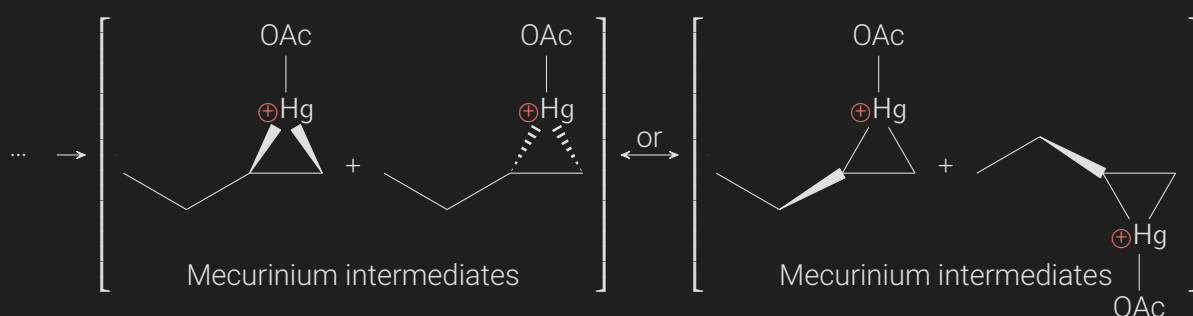
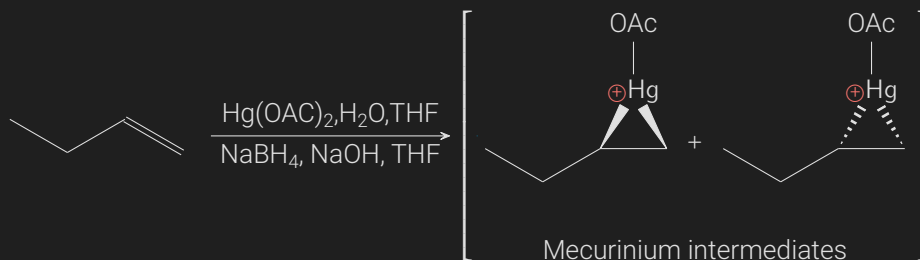
- Notice the nucleophile attacks the carbon with the greater flow of electrons (more substituted), since there was a positive charge on mercury. Epoxides with no charge are attacked on the side with less steric hindrance.
- Also, the nucleophilic attack occurs on the opposite side of the plane since there is less hindrance on that side.

## Related Practice Problems

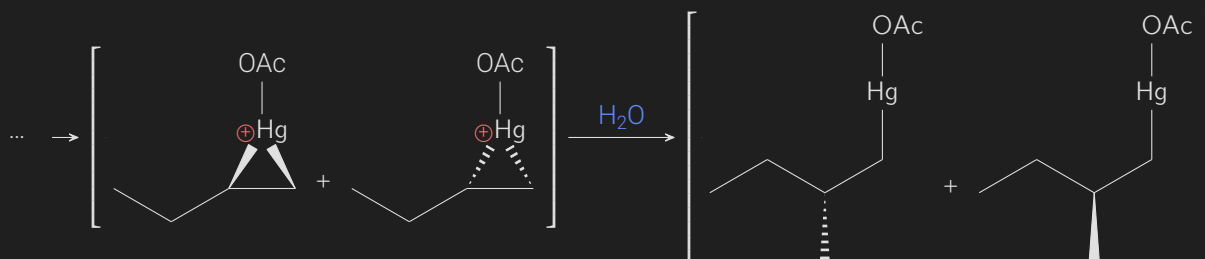




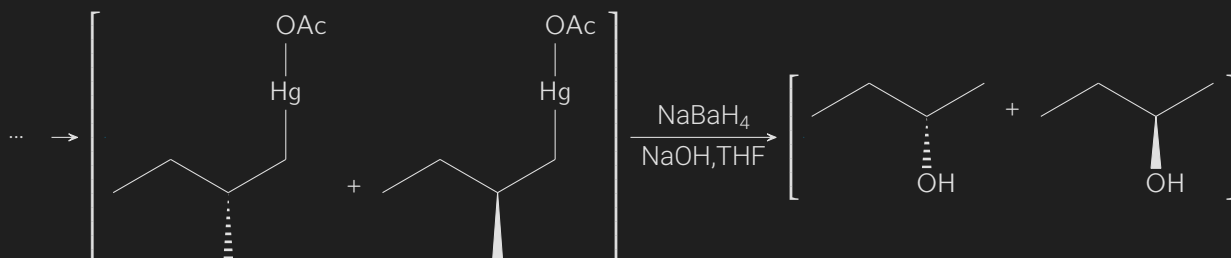
3. + Alternate ways of drawing rings (was done in lecture):



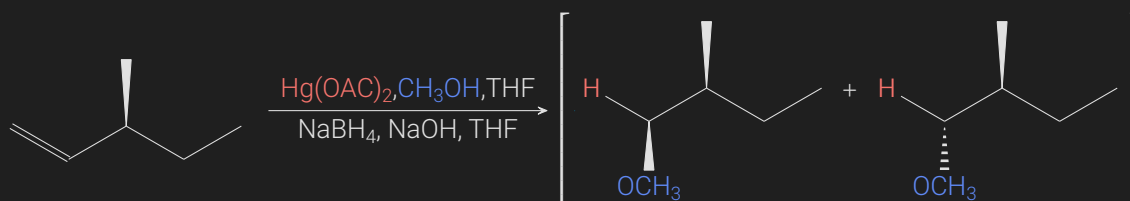
**Oxymercuration:**



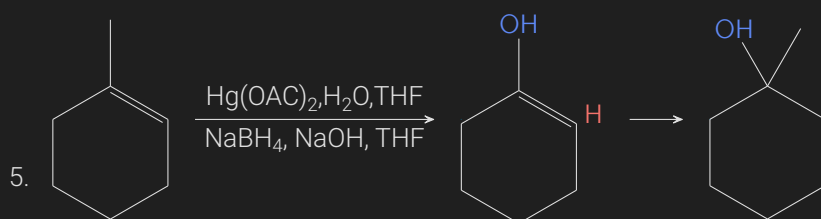
**Demercuration:**



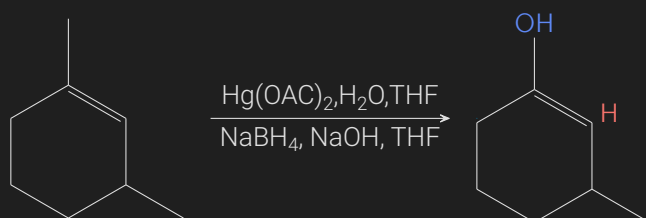
4.



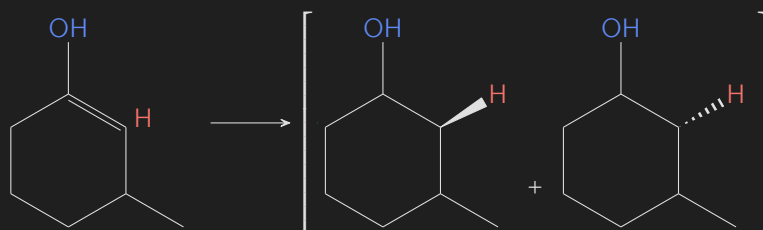




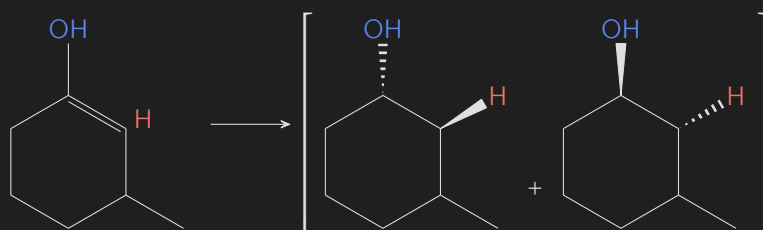
6. (was done in lecture)



- We know these are the locations of the H and OH, so we can start by labeling them.



- The methyl will be the same no matter what, so we can ignore that.
- H has two options, which gives us the above.
- Since oxymercuration-demercuration is always an **anti addition**, then we know OH must be **anti** to the hydrogen in both of the products:



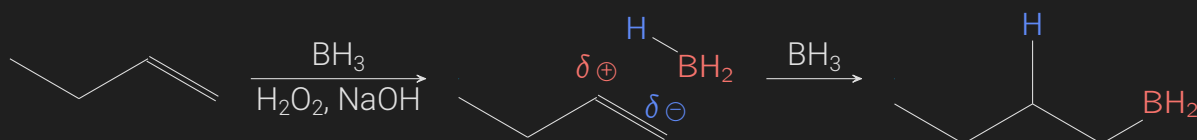
## Hydroboration-Oxidation

- Hydroboration-Oxidation:** a two-step hydration reaction that converts an alkene into an alcohol.
  - Results in the **syn addition** of a hydrogen and a hydroxyl group where the double bond had been.
  - An anti-Markovnikov reaction—the hydroxyl group attaches to the less-substituted carbon.
  - Provides a more stereospecific and complementary regiochemical alternative to other hydration reactions such as acid-catalyzed addition (stereoselective) and oxymercuration-demercuration (stereospecific for anti).

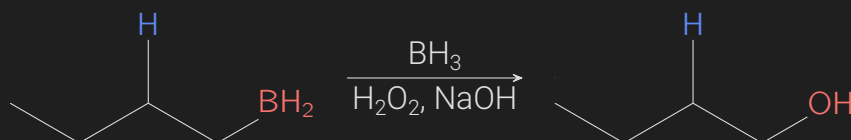
- Usually  $\text{BH}_3$ ,  $\text{B}_2\text{H}_6$ ,  $\text{R}_2\text{BH}$  are used. The presence of Boron is key.
- Like  $\text{H}_2\text{O}$  and  $\text{ROH}$ , it's useful to think of them in the following way:



- Unlike water/alcohol, the hydrogen is now the partial negative component and the boron is the positive.



- There are no chiral centers, but there is still one more step—the oxidation:

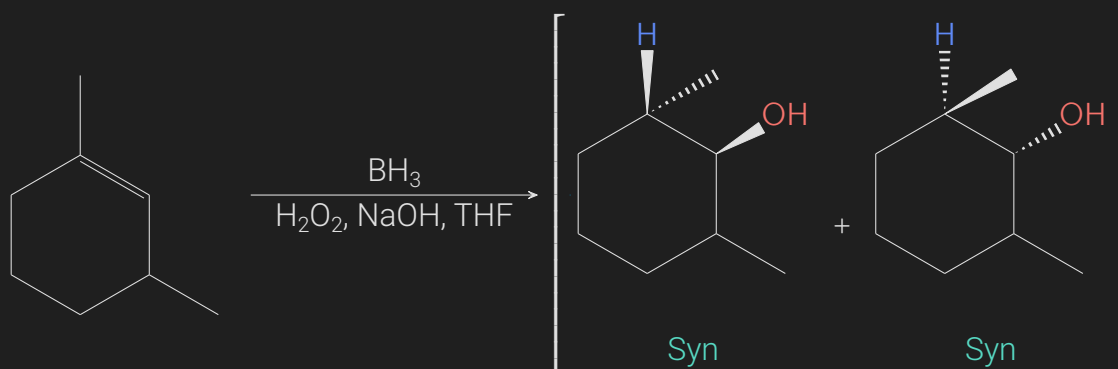


- If we had used  $\text{Hg}(\text{OAc})_2$ , then the above reaction would be different; partial charges

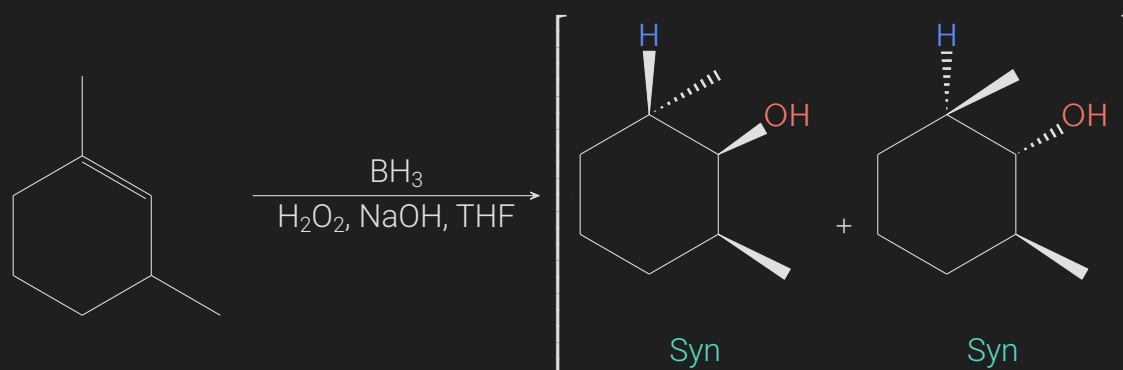
change the possible final products:  $\overset{\delta^-}{\text{H}}-\overset{\delta^+}{\text{B}}\text{H}_2$  vs.  $\overset{\delta^+}{\text{H}}-\overset{\delta^-}{\text{O}}\text{H}_2$ :



- Revisiting a practice example, using different reagents:

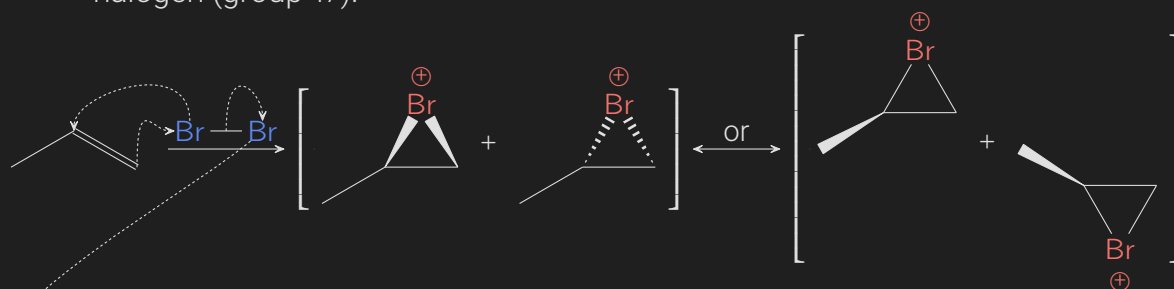


- If the untouched methyl happened to be above or below the plane initially, then you would keep that the same, e.g:

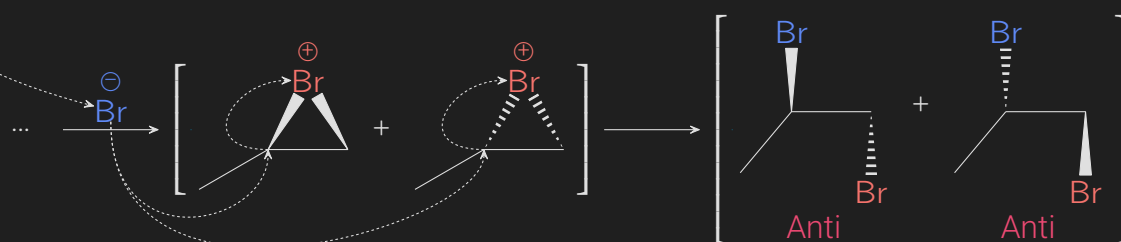


## Halogenation

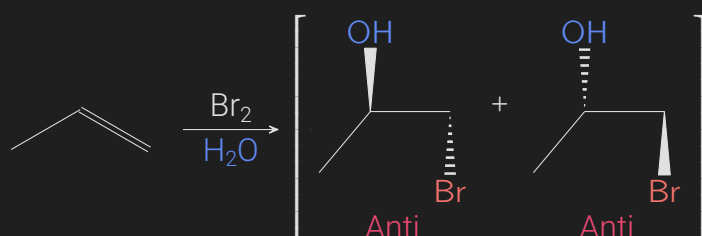
- **Halogenation**: a reaction that involves the addition of one or more halogens to a compound or material.
  - The addition of halogens to alkenes proceeds via intermediate halonium ions.
  - **Halonium ion**: any onium ion containing a halogen atom carrying a positive charge. This cation has the general structure:  $\text{R}-\text{X}^+-\text{R}'$
  - **Onium ion**: a cation formally obtained by the protonation of mononuclear parent hydride of a pnictogen (group 15 of the periodic table), chalcogen (group 16), or halogen (group 17).



- In the above example we see a cyclic bromonium ion intermediate being formed. Next, one bromine is now left to act as the  $\text{nu}^-$ :



- Alternatively, if you did the reaction in  $\text{H}_2\text{O}$ , then water would become the dominant  $\text{nu}^-$ , leaving OH.



## 15: Alkynes

## 16: Oxidation and Reduction

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# 17: Mass Spectrometry and Infrared Spectroscopy

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# 18: Nuclear Magnetic Resonance Spectroscopy

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## 19: Free Radical Reactions

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## 20: Conjugation and Resonance

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## 21: Benzene and Aromaticity

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## 22: Reactions of Aromatic Compounds

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