



# CHEMISTRY 2500

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Topic #8: Pi Bonds as Nucleophiles  
(*aka* Addition Reactions of Alkenes and Alkynes)

Spring 2020

Dr. Susan Findlay



# Alkenes as Nucleophiles

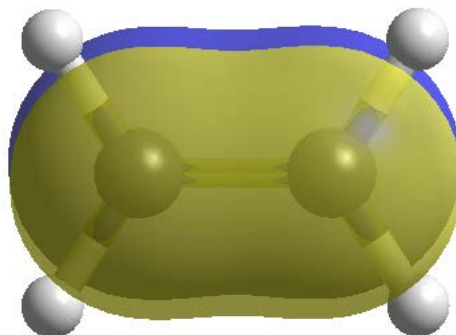
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- Electron rich pi bonds are good electron donors (nucleophiles).
- In organic chemistry, the two main functional groups containing electron rich pi bonds are alkenes and alkynes:
- Both functional groups contain one or more carbon-carbon pi bond (as part of a carbon-carbon multiple bond).

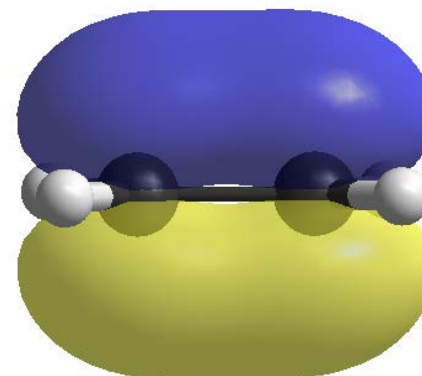
# Alkenes as Nucleophiles

- Recall from CHEM 2000 that when a molecule donates electrons, it reacts with its **HOMO** (**H**ighest **O**ccupied **M**olecular **O**rbital).
- The HOMO for a simple alkene ( $\text{H}_2\text{C}=\text{CH}_2$ ) looks like this:

top view:



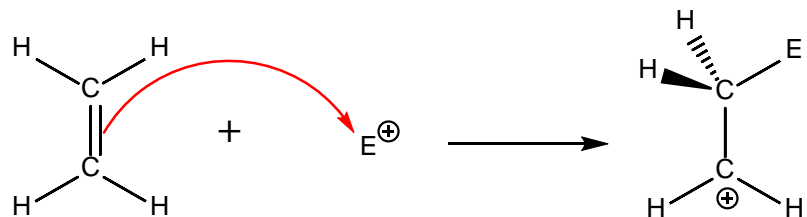
side view:



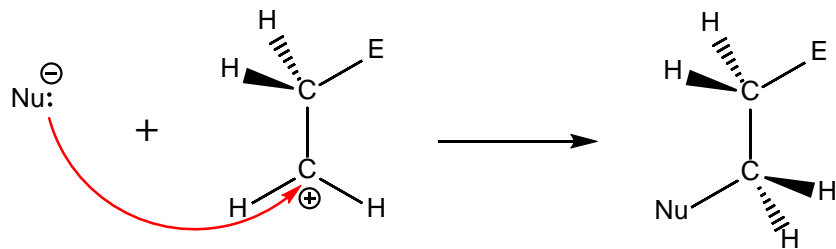
- Is this orbital bonding or antibonding?
- Is this orbital sigma symmetric or pi symmetric?
- Is this orbital polarized toward either carbon atom?
- What does this HOMO tell us about what happens when this compound donates electrons?

# Alkenes as Nucleophiles

- So, looking at the HOMO has shown us that when an alkene donates a pair of electrons, one of the carbon atoms forms a new bond to the electrophile and the pi bond is broken!
- This process can be shown using curved arrows:

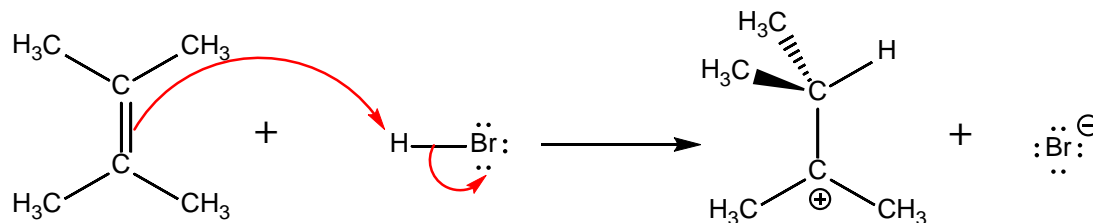


- This creates a **carbocation intermediate** – which will then be attacked by a nucleophile:

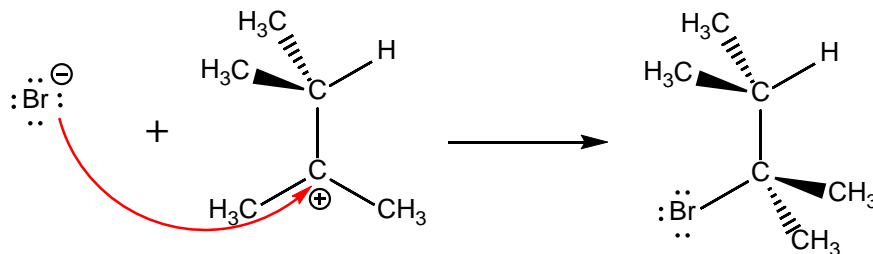


# Addition of HX to Alkenes

- The reactions on the previous page showed generic electrophile and nucleophile adding to an alkene. The simplest concrete example is the addition of hydrogen halides (HCl, HBr or HI):
- In the first step, the alkene is protonated by the strong acid:

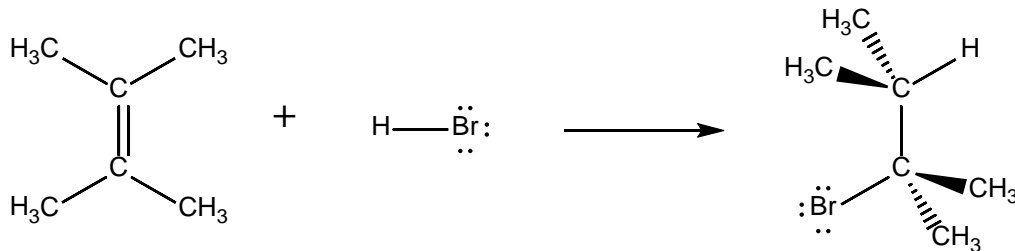


- The resulting carbocation is then attacked by the halide:



# Addition of HX to Alkenes

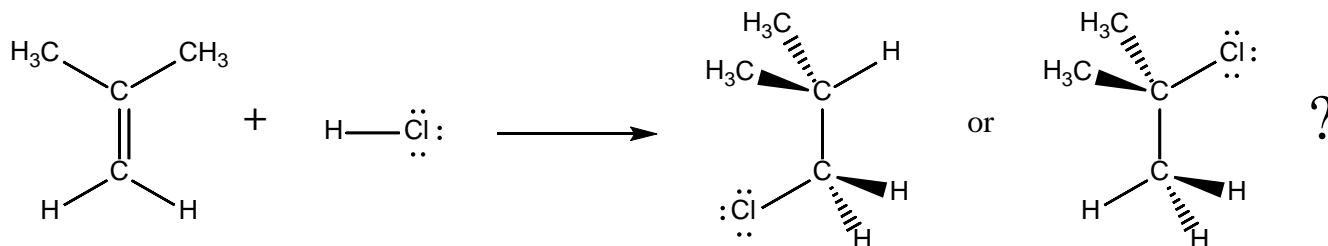
- Looking at the overall reaction, we can see that both components of HBr have been “added” to the alkene, hence the name “addition reaction”:



- When the alkene attacks HBr, why does it react with H instead of Br?

# Addition of HX to Alkenes

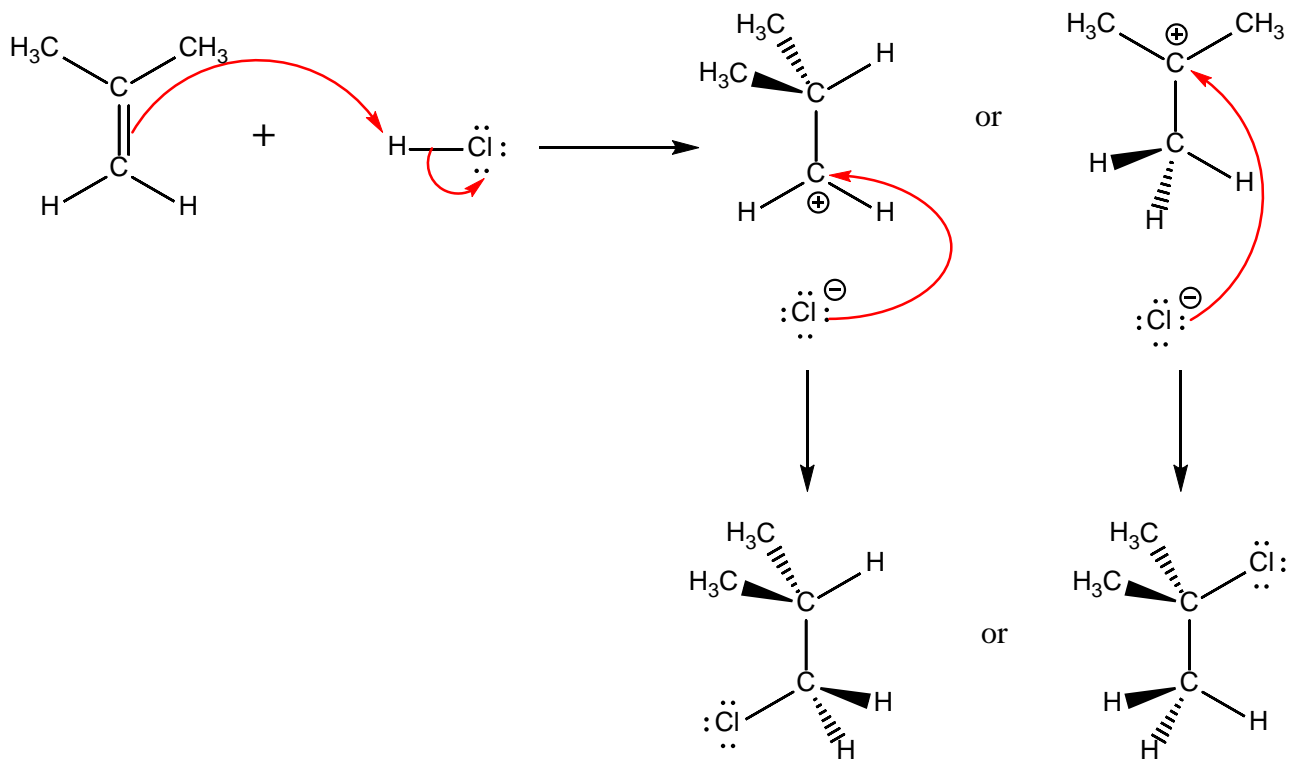
- What if the alkene isn't symmetrical? Which carbon does the hydrogen atom attach to? And which carbon gets the halogen?



- There are two approaches to answering this question, depending on the temperature at which the reaction is run.
  - The **thermodynamic product** is the lower energy product. If the reaction mixture is allowed to reach equilibrium, the thermodynamic product will dominate.
  - The **kinetic product** is the product whose rate determining step has the lowest activation energy. In other words, the product of the reaction path with the easiest "most difficult step".
- For this reaction, the same product is both thermodynamic product and kinetic product. That's pretty common.

# Addition of HX to Alkenes

- Consider the mechanisms for both reaction paths:



- Which step seems harder? Making two ions from two neutral molecules? Or making one neutral molecule from two ions?



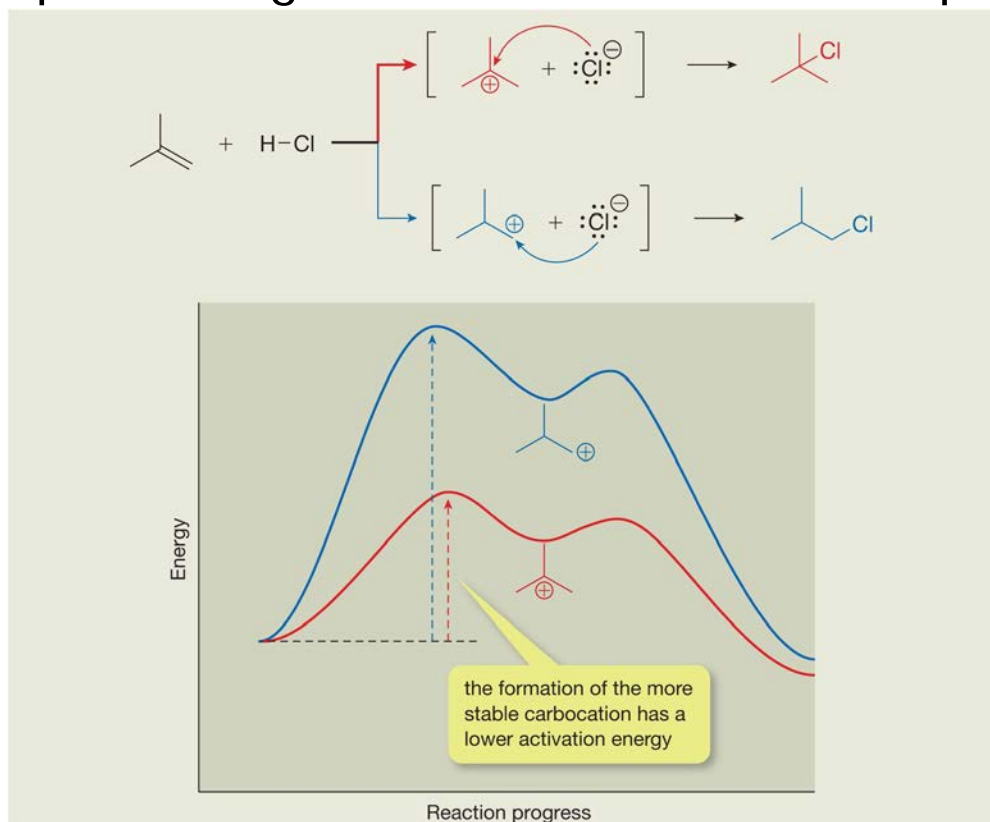
# Addition of HX to Alkenes

Label activation energies for **both** steps of each reaction pathway to clearly show which step is rate-limiting.

- A reaction profile diagram confirms our initial suspicion:

Label the intermediates and transition states on the reaction profile diagram.

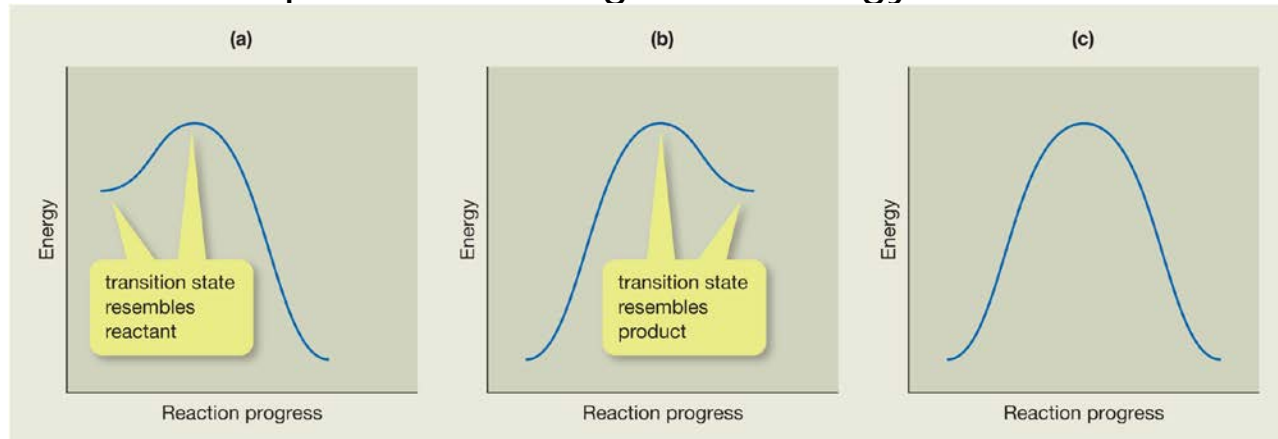
What's the difference between a transition state and an intermediate?



- Regardless of which product is formed, the first step has a higher activation energy than the second step. Carbocation formation is the rate-determining step!

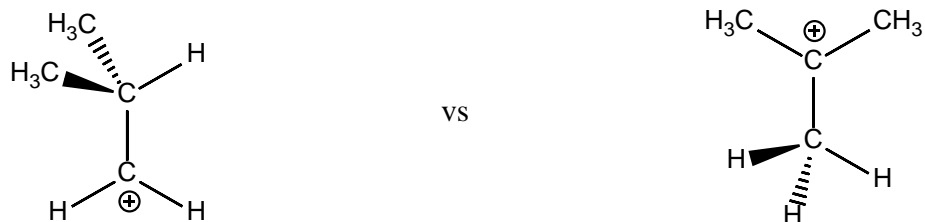
# Addition of HX to Alkenes

- Why is the activation energy for one path so much larger than for the other path? To answer that, we use the **Hammond postulate** which states that a transition state more closely resembles the reactant/product (of that step) which is closest in energy to it. In practice, given the shape of any reaction profile, that means the transition state more closely resembles the higher energy species:
  - An “early transition state” (looks more like reactants than products) occurs if the reactants are higher in energy than the products.
  - A “late transition state” (looks more like products than reactants) occurs if the products are higher in energy than the reactants:



# Addition of HX to Alkenes (C<sup>+</sup> Stability)

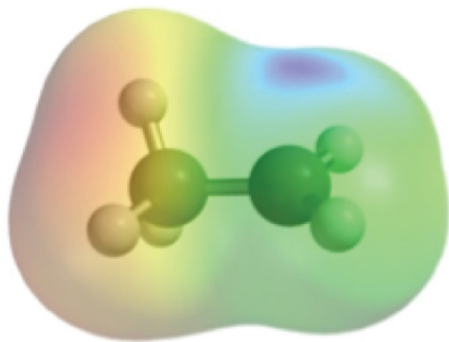
- If the transition states of these reactions closely resemble the carbocation intermediate, we can use the energies of the carbocation intermediates to predict which one is more easily formed:



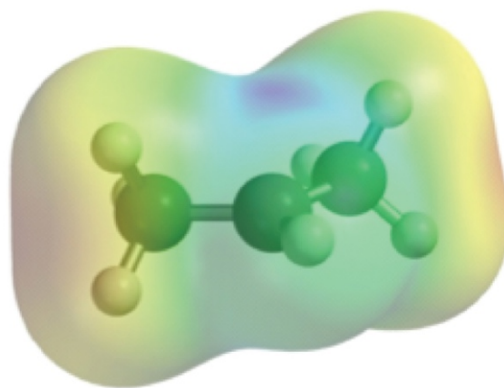
- So, which is the more stable carbocation? Which has the lower activation energy of formation?
- As a general rule of thumb, increasing the number of carbon atoms that are attached to the carbon with the positive charge increases the stability of a carbocation.

# Addition of HX to Alkenes ( $C^+$ Stability)

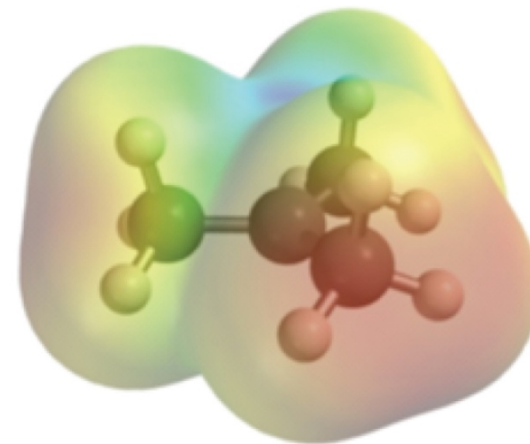
- There are two primary explanations for this phenomenon.
  - The **inductive effect** suggests that a carbocation surrounded by electron rich groups (like alkyl groups) will be more stable than one which is not. This is because some electron density can be donated through the sigma bonds.



primary carbocation  
 $(CH_3C^+(H)_2)$



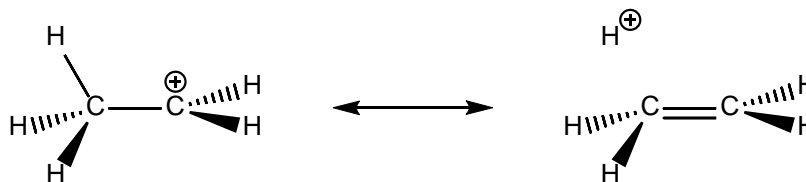
secondary carbocation  
 $(CH_3C^+(H)CH_3)$



tertiary carbocation  
 $(CH_3C^+(CH_3)_2)$

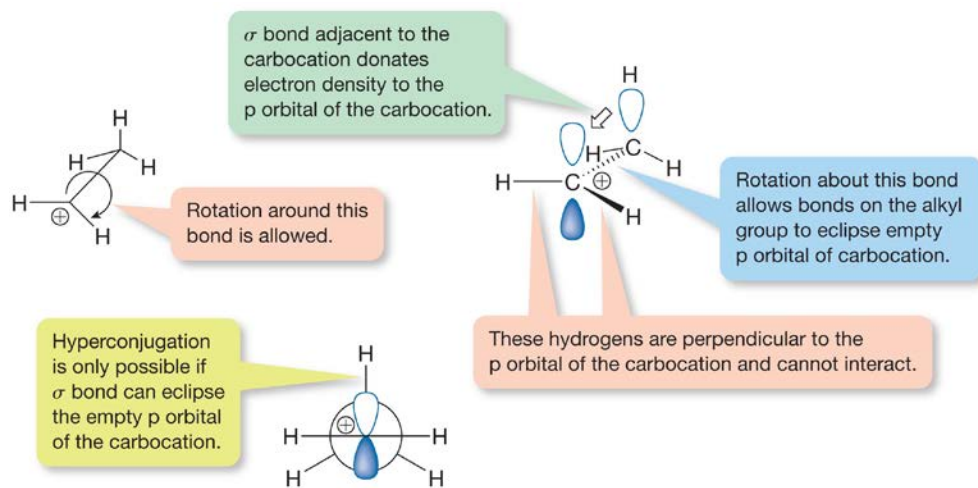
# Addition of HX to Alkenes ( $C^+$ Stability)

- This effect is enhanced by **hyperconjugation**, a phenomenon in which electron-rich sigma bonding MOs align with the empty p orbital of a carbocation, somewhat delocalizing the positive charge:



"no-bond" resonance structure

(These should not be drawn routinely.  
Only under special circumstances like this!)





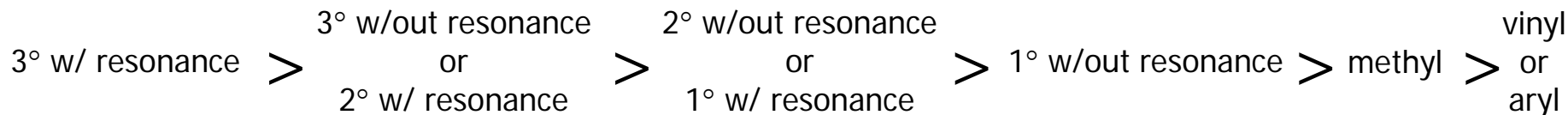
## Addition of HX to Alkenes ( $C^+$ Stability)

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- In the acid-base topic, we saw that charge delocalization (via resonance) is also an important way to stabilize an ion. While it doesn't apply to the example we're currently looking at, it explains why allylic and benzylic cations are more easily formed than would be predicted from whether they are  $1^\circ$ ,  $2^\circ$  or  $3^\circ$ :
  
- Note that vinyl and aryl carbocations cannot be resonance stabilized because the positive charge is perpendicular to the pi system. As such, it is NOT part of the pi system and the charge cannot be delocalized:
  
- Resonance only helps stabilize an ion if it moves the charge... 14

# Addition of HX to Alkenes (C<sup>+</sup> Stability)

- Just as vinyl and aryl carbocations are NOT stabilized by resonance, they are also NOT stabilized by hyperconjugation. The empty p orbital of the carbocation is simply not aligned with any electron rich C-H sigma bonds. Putting a positive charge on a carbon atom with a double bond is usually a bad idea!
- The overall order of carbocation stability is therefore:



*The number of atoms over which a charge can be delocalized matters! Benzylic carbocations (four atoms sharing + charge) are more stable than allylic carbocations (two atoms sharing + charge). Add enough delocalization and even a primary carbocation can become more stable than you'd have thought.*<sup>15</sup>



## Addition of HX to Alkenes (C<sup>+</sup> Stability)

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- All of this combines to justify an observation made long before the mechanism of addition reactions was understood. **Markovnikov's Rule** was originally stated as:
  - Markovnikov's Rule works most of the time; however, if you plan to use it, you must always watch out for resonance-stabilized carbocations! The "real" rule is that

**THE MOST STABLE CARBOCATION INTERMEDIATE  
WILL FORM MOST QUICKLY, LEADING TO THE MAJOR  
ADDITION PRODUCT!**

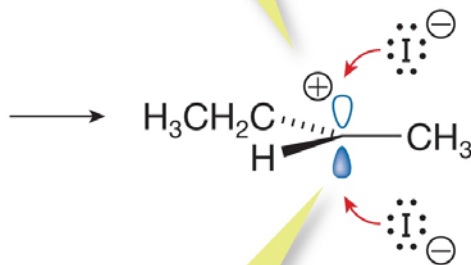
It just works out that making a more substituted carbocation happens to put the new H where there were already more H...



# Addition of HX to Alkenes

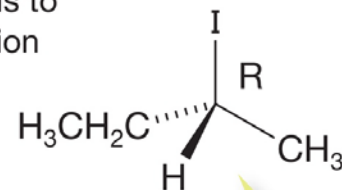
- It is also important to remember that carbocations are flat. As such, the nucleophile can approach the carbocation from above or below, and the reaction will give a mixture of stereoisomers (where applicable):

The carbocation is  $sp^2$  hybridized and flat. It has an empty p orbital that occupies both faces.



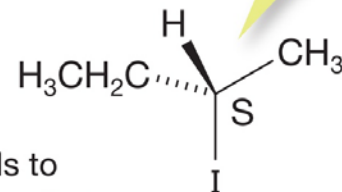
nucleophile adds to empty p orbital

nucleophile adds to top of carbocation



pair of enantiomers

nucleophile adds to bottom of carbocation





## Addition of HX to Alkenes

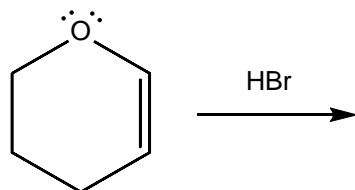
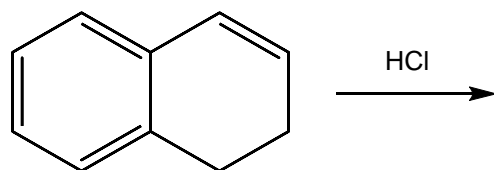
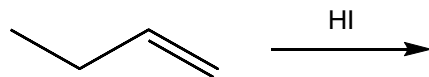
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- Additions of HX to alkenes are NOT **stereoselective**. They do NOT favour one stereoisomer over another:
  
- Additions of HX to alkenes ARE **regioselective**. They DO favour one structural isomer (constitutional isomer) over the other:

*At some point, you may also encounter the term "stereospecific".  
A "stereospecific" reaction is more than "just" stereoselective.  
Its mechanism outright prevents formation of one or more stereoisomers,  
forcing production of a single (specific) stereoisomer.*

# Addition of HX to Alkenes

- Predict the major product(s) for each of the following addition reactions:





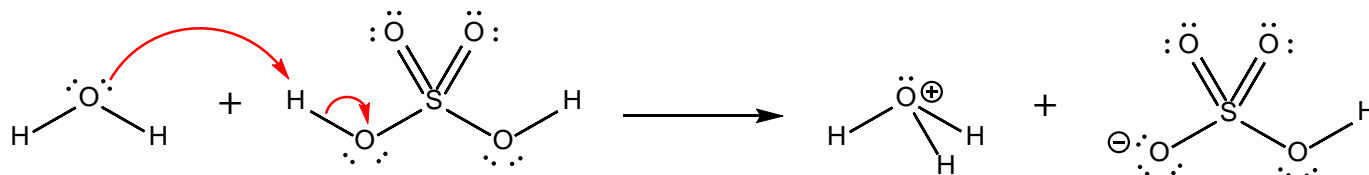
## Addition of HX to Alkenes (H<sub>2</sub>O and ROH)

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- So far, we have only used HCl, HBr and HI as options for HX. They are all strong acids and therefore able to protonate the alkene, forming the required carbocation intermediate. HF, on the other hand, is a weak acid ( $pK_a = 4$ ) so it does not readily protonate alkenes.
- It is possible to add water (H-OH) to an alkene; however, water is an even weaker acid than HF. The  $pK_a$  of water is 14!
- So, if we want to add water to an alkene, we need to add an acid to the mixture! We usually choose sulfuric acid ( $H_2SO_4$ ) or phosphoric acid ( $H_3PO_4$ ) instead of HCl, HBr or HI. They're all strong enough acids, so why avoid HCl, HBr and HI?

# Addition of HX to Alkenes (H<sub>2</sub>O and ROH)

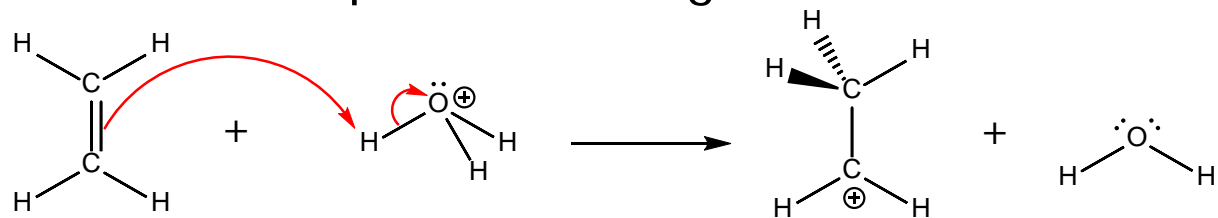
- The mechanism for the addition of water to an alkene is therefore almost identical to the mechanism for the addition of HCl, HBr or HI to an alkene. The only difference is that we must add one “tidy up” deprotonation step at the end!
- Recall that, since sulfuric acid is a strong acid, it fully dissociates in water to give hydronium ions:



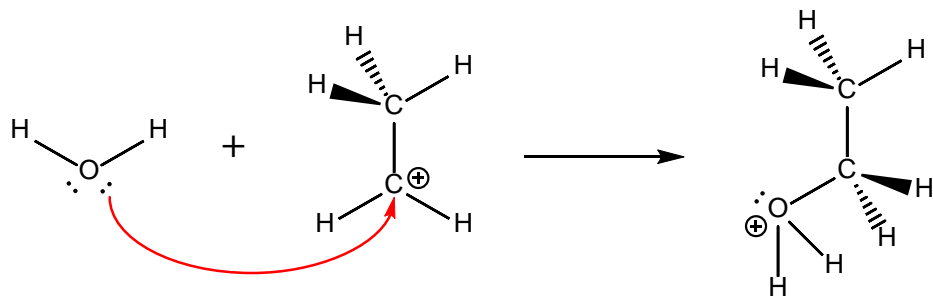
- We will therefore use hydronium ions as our acid in this mechanism since they are the strongest available acid.
- What is the strongest base available in any significant concentration?

# Addition of HX to Alkenes (H<sub>2</sub>O and ROH)

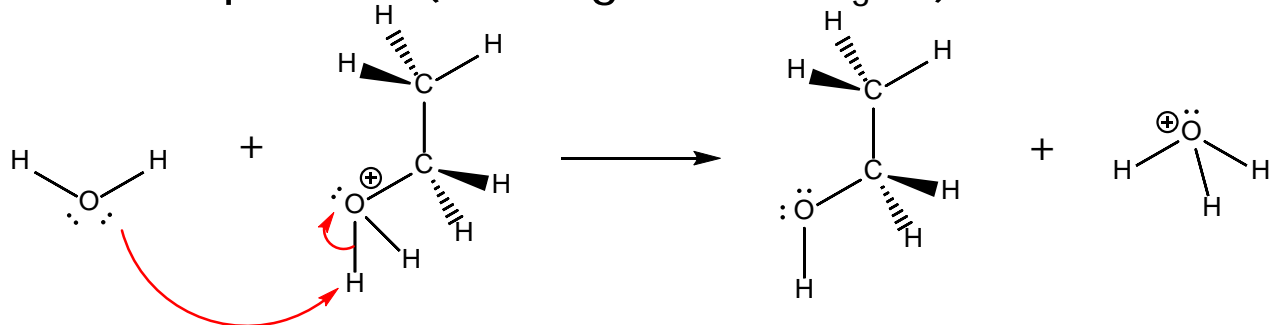
- First, the alkene is protonated to give a carbocation:



- Then the nucleophile (water) attacks the carbocation:



- Finally, the strongest available base deprotonates the oxygen to give a neutral product (and regenerate H<sub>3</sub>O<sup>+</sup>):





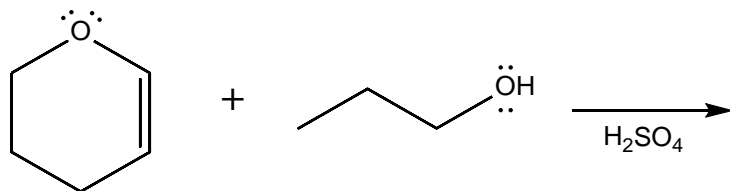
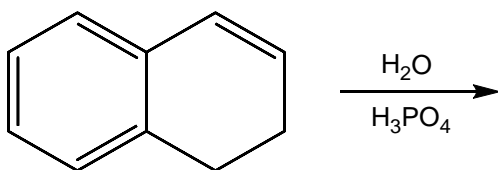
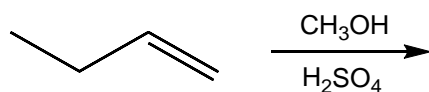
## Addition of HX to Alkenes ( $\text{H}_2\text{O}$ and ROH)

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- The reaction on the previous page can also be performed using any alcohol instead of the water. Draw a reasonable mechanism for the acid-catalyzed addition of ethanol to propene.

# Addition of HX to Alkenes (H<sub>2</sub>O and ROH)

- Predict the major product(s) for each of the following addition reactions:







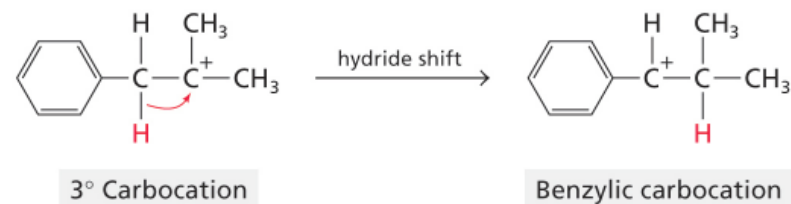
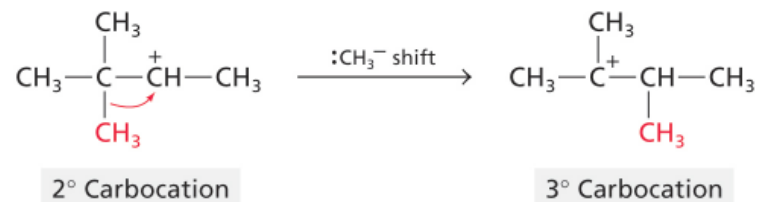
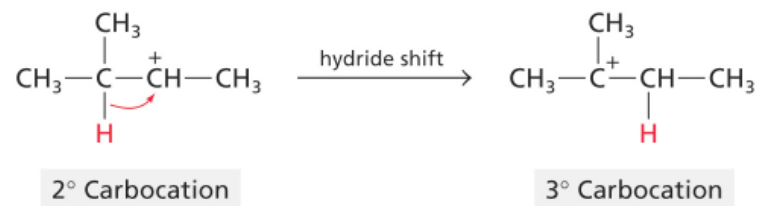
# Addition of HX... (C<sup>+</sup> Rearrangements)

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- Occasionally, reactions involving carbocation intermediates don't give you the product you were initially expecting. This is because most carbocations are inherently unstable species. As such, if a rearrangement of the atoms near the positive charge gives a slightly less unstable carbocation, that will often happen.
- Because these rearrangements involve only the carbocation, they are much faster than reaction with a nucleophile. Reaction between a carbocation and a nucleophile requires the two species to collide with the correct relative orientation, after all!
- The simplest carbocation rearrangements are referred to as **hydride shifts**. Recall that hydride is the name for  $H^-$  – a hydrogen atom with two electrons. So, a hydride shift refers to the movement of a hydrogen atom with two electrons. This is very different from a deprotonation (in which a hydrogen atom is removed and the electrons in the bond to it left behind).

# Addition of HX... (C<sup>+</sup> Rearrangements)

- As shown in the diagram at the right, carbocation rearrangements can involve shifting either a hydride ion or a methyl anion.
- Pay close attention to the way the curly arrows are drawn. They are pointing right at the carbon atom to which the H (or CH<sub>3</sub>) is moving!



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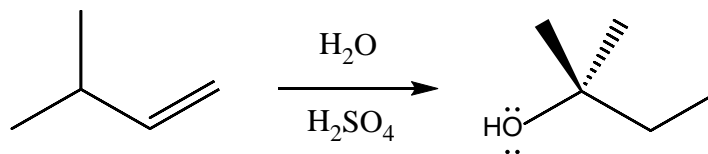
# Addition of HX... ( $C^+$ Rearrangements)

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- Important points to consider for carbocation rearrangements:
  - Carbocation rearrangements are only observed if the resulting carbocation is more stable than the initial carbocation:
  
  
  
  
  
  
  
  
  
  
  - If the initial carbocation is too unstable to form, it doesn't matter how much better the carbocation rearrangement would make it, it won't form in the first place!

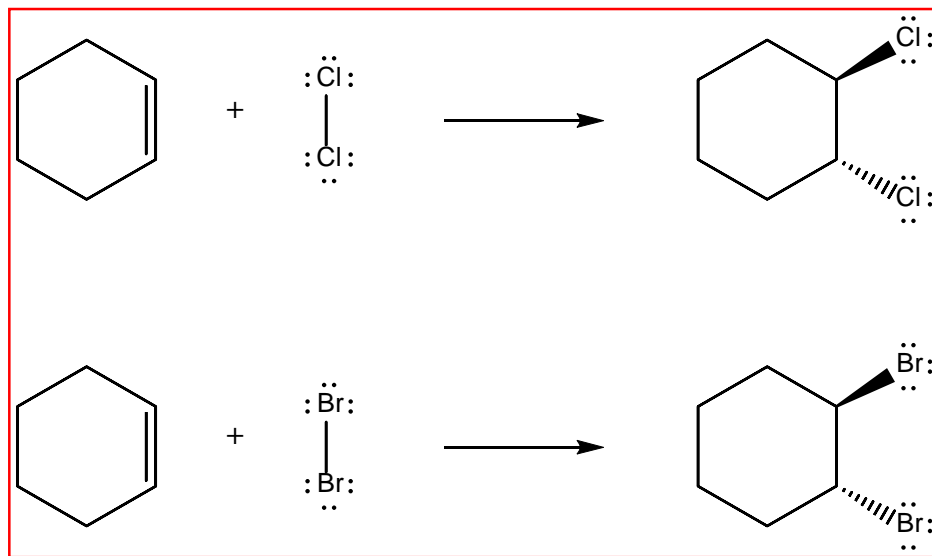
# Addition of HX... (C<sup>+</sup> Rearrangements)

- Draw a mechanism for the following reaction involving a carbocation rearrangement:



# Addition of $X_2$ to Alkenes

- Not all electrophilic addition reactions involve an acid (or water/acid combination). It's also possible to add halogens (usually  $Cl_2$ ,  $Br_2$  or  $I_2$ ) across a nonpolar pi bond:



This is the basis for the most common test for presence of alkenes/alkynes – add  $Br_2$  (a dark brown liquid) and see if its colour disappears.



## Addition of $X_2$ to Alkenes

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- The mechanism for addition of  $X_2$  to alkenes is essentially the same as the mechanism for addition of HX to alkenes.
  - First the nucleophilic pi bond attacks the electrophilic species, generating a cation.
  - Then a nucleophile attacks the cation to give the addition product.

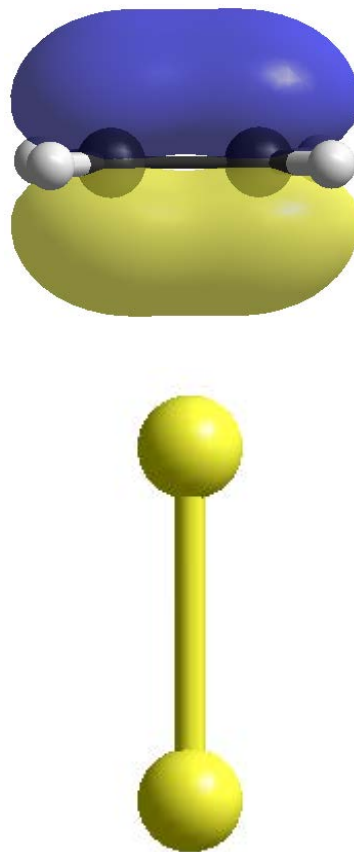
**WAIT A MINUTE!!!**

**HOW IS  $X_2$  AN ELECTROPHILIC SPECIES???**  
**IT DOESN'T HAVE A POSITIVE END!!!**

*OR DOES IT... ?*

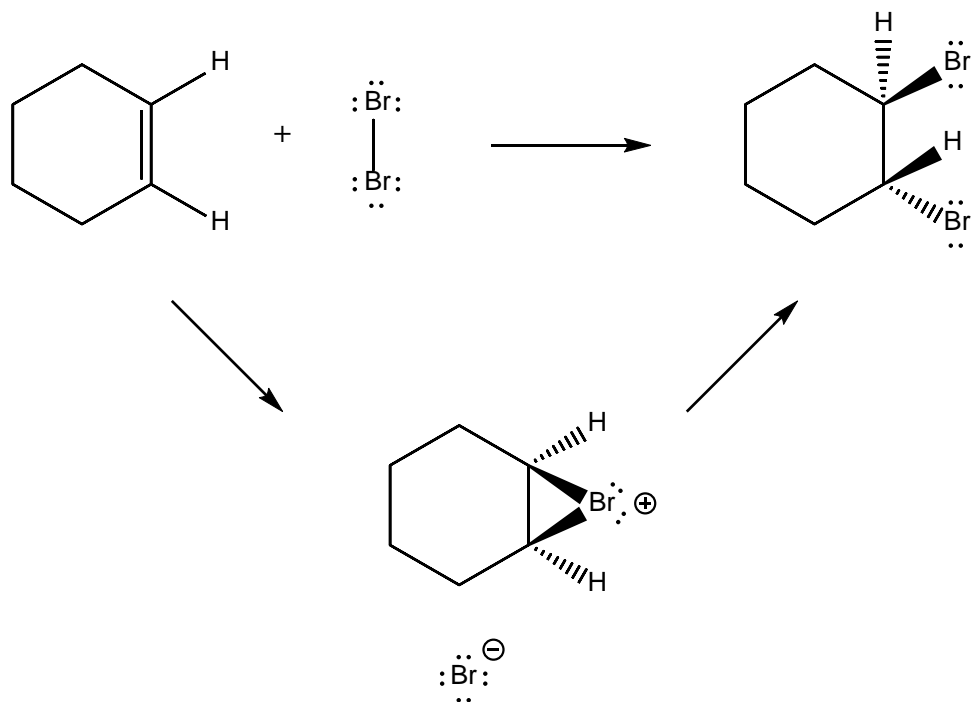
# Addition of $X_2$ to Alkenes

- How is it possible for  $Br_2$  to have a partially positive electrophilic end? What happens to its valence electrons as it approaches the alkene in the proper orientation for reaction?



# Addition of X<sub>2</sub> to Alkenes

- Unlike addition of HX, addition of Cl<sub>2</sub> or Br<sub>2</sub> is **stereospecific**. The two halogen atoms **always add *anti*-** to each other. This is because of the reaction mechanism:

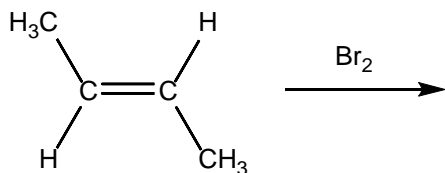
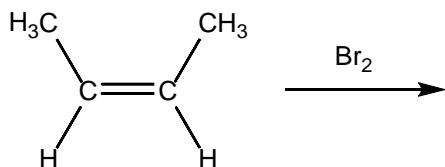


- The **bromonium ion** intermediate forces the bromide ion to attack in an S<sub>N</sub>2-like fashion from the opposite side of the Br<sup>+</sup>. 32



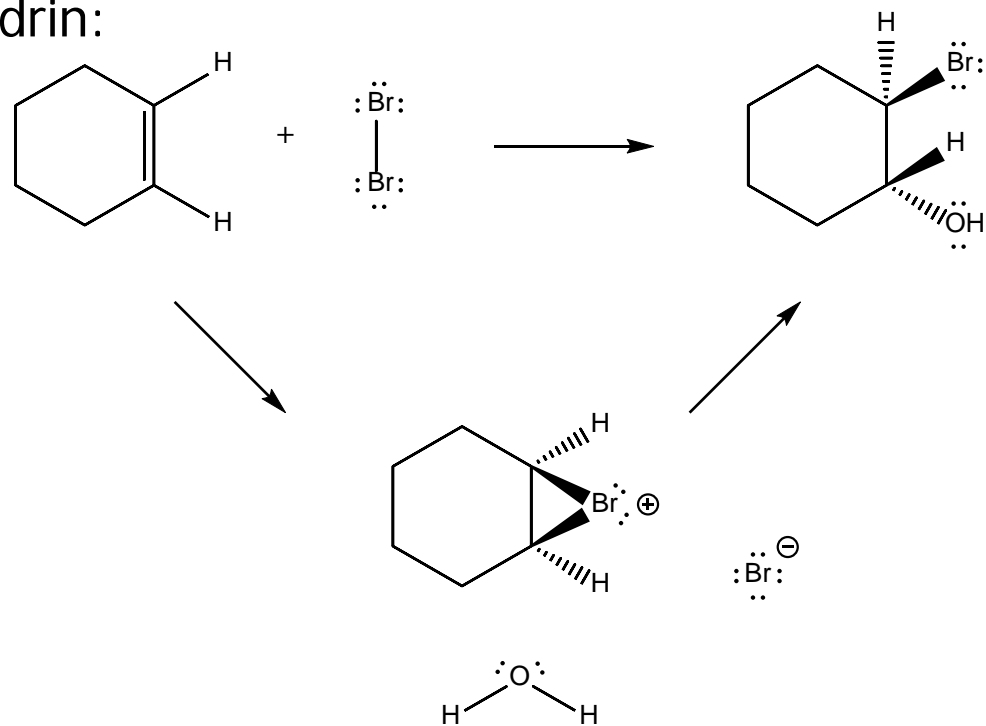
# Addition of X<sub>2</sub> to Alkenes

- Even in acyclic systems, the stereospecificity of these additions often comes into play. Consider the bromination products from *cis*- and *trans*-2-butene:



# Addition of XOH to Alkenes

- When an electrophilic addition is performed in a nucleophilic solvent (usually water), the solvent molecules will greatly outnumber the halide ions. Thus, in water, we get formation of a halohydrin:



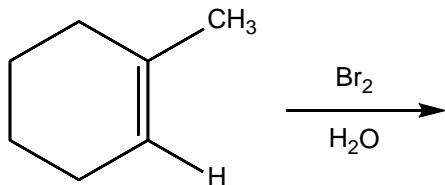
- Traces of the dibromocyclohexane will also form. Why?

# Addition of XOH to Alkenes

- The bromonium ion can be viewed as resonance-stabilized:

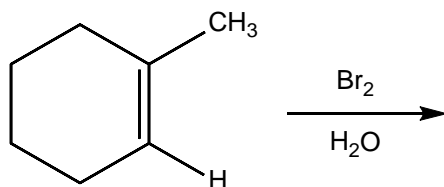
*Both C-Br bonds are strong enough that rotation is NOT possible!  
The true picture is the weighted AVERAGE of these pictures.  
We don't actually get "alternating" resonance structures!*

- If we generate a bromonium ion from an unsymmetrical alkene, which of the two carbocation resonance structures is better? *(contributing more to the average picture)*



# Addition of XOH to Alkenes

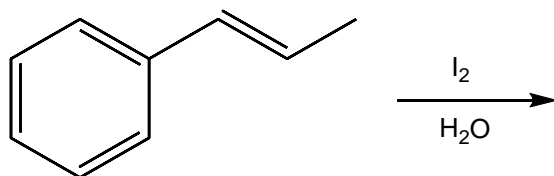
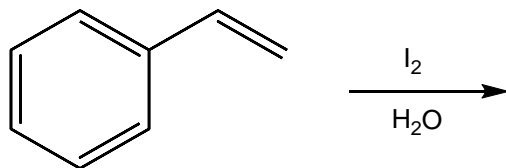
- So, the bromonium ion generated from an unsymmetric alkene will have the bromine atom pulled more tightly toward the carbon atom that makes a less stable carbocation. As such, the nucleophile will attack at the carbon atom that makes a more stable carbocation. **Markovnikov** strikes again!



- Thus, formation of a halohydrin by reacting an alkene with a halogen in water is **stereospecific** and **regioselective**.

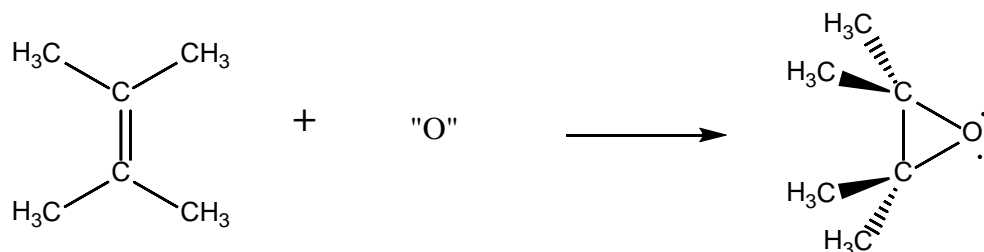
# Addition of XOH to Alkenes

- What are the major product(s) of each of the following reactions?



# Addition of O to Alkenes

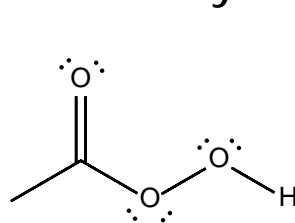
- In one particularly interesting type of addition reaction, a single oxygen atom is added across an alkene, forming one bond to each carbon atom. The resulting functional group is called an **epoxide**:



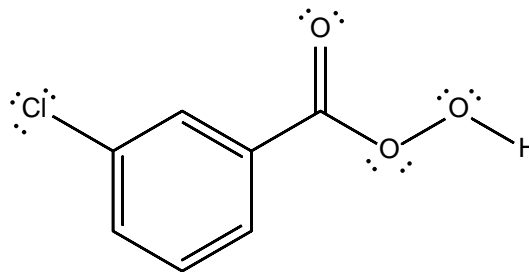
- Of course, oxygen atoms don't tend to exist as free species, so we need to have a molecule that serves as a source of the required oxygen atom...

# Addition of O to Alkenes

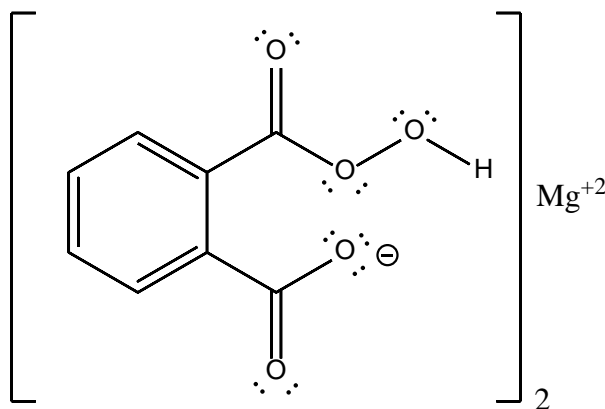
- The source of the oxygen atom that adds across an alkene to make an epoxide is usually a peracid – a carboxylic acid that has “one too many” oxygen atoms



peracetic acid



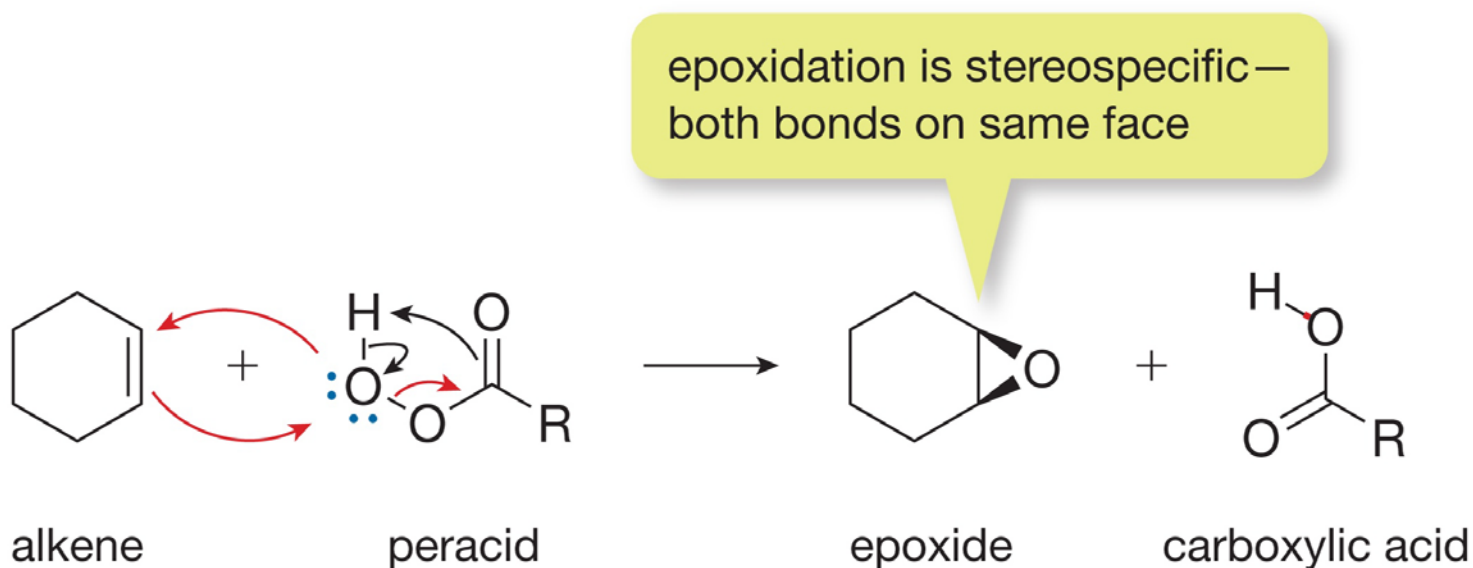
meta-chloroperoxybenzoic acid  
(mCPBA)



monomagnesium peroxyperphthalate  
(MMPP)

# Addition of O to Alkenes

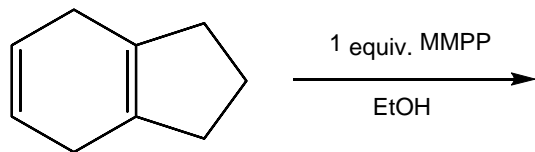
- The exact mechanism for an epoxidation reaction is not known; however, it is known that the alkene serves as nucleophile and the peracid as electrophile.
- The following diagram from your textbook shows a rough outline of how the mechanism may proceed (though likely not all in one step, as implied by the diagram):





# Addition of O to Alkenes

- Since the alkene acts as the nucleophile, if there are two alkenes in the same molecule, we can predict that the more nucleophilic one (the more electron-rich one) will react first. The more electron-rich double bond is usually the one with more carbon groups attached.
- What is the organic product of the reaction below?





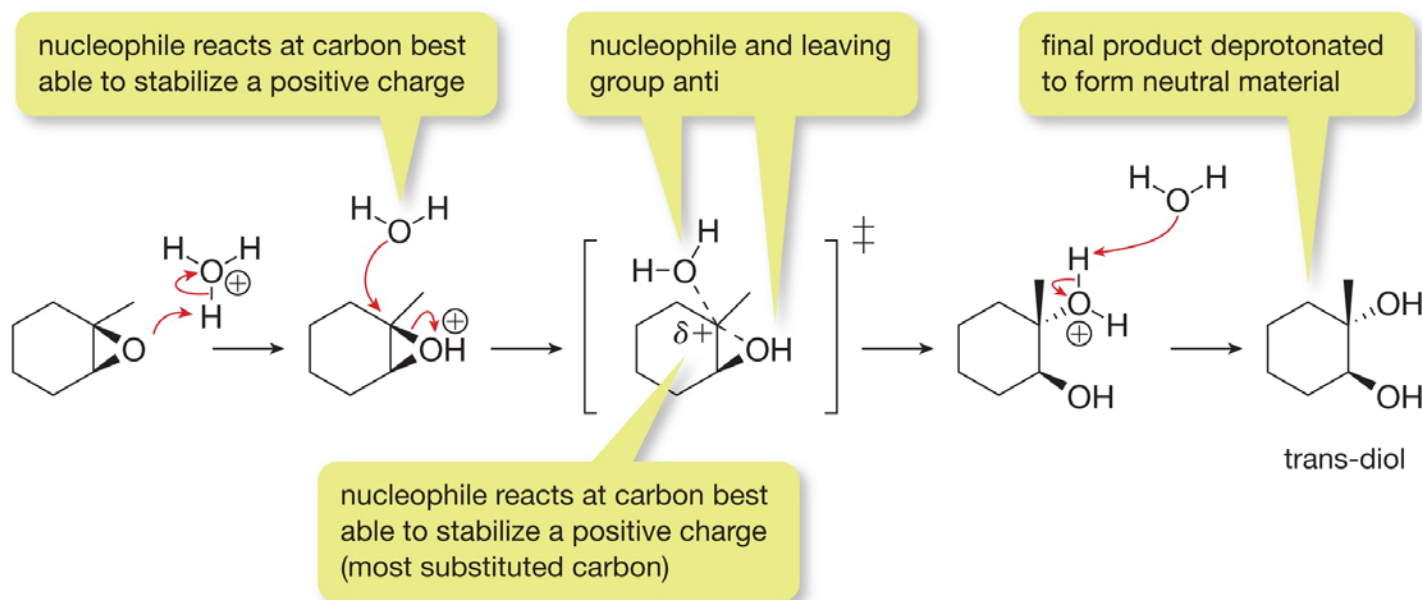
## Addition of O to Alkenes

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- It was noted on page 40 that epoxidation is ALWAYS a **syn addition** (both new bonds formed on the same side of the former alkene). Why do you think this must be?
- Even with syn addition, the resulting epoxide is still quite strained. Why?
- This strain makes it a good electrophile. That's because attacking the epoxide with a nucleophile allows one of the bonds to break and relieve the strain:

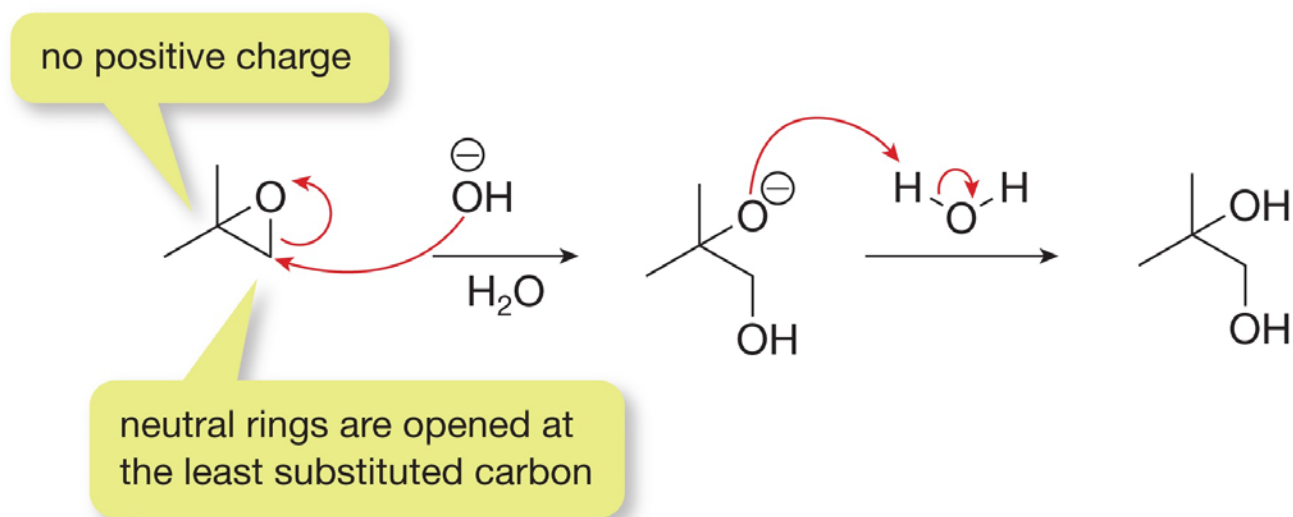
# Addition of O to Alkenes

- If the epoxide is not symmetrical, we need to consider which side will be attacked by the nucleophile. The answer to that question depends on whether the reaction is done under acidic or basic conditions...
  - In acidic conditions, the epoxide gets protonated to give a cation which behaves very much like a bromonium or chloronium ion. The nucleophile attacks at the more positive carbon atom (the more substituted one):



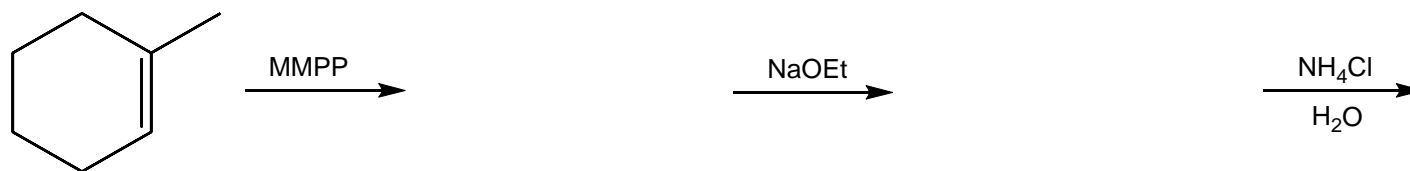
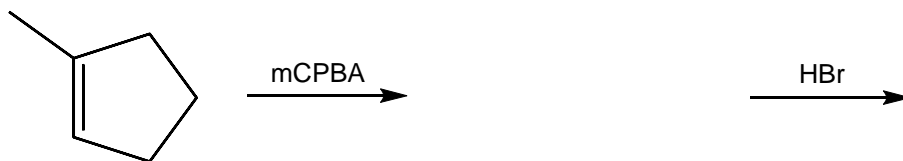
# Addition of O to Alkenes

- In basic conditions, stronger nucleophiles are available that can attack the neutral epoxide. They will attack at the side with the least steric bulk (the less substituted carbon atom):



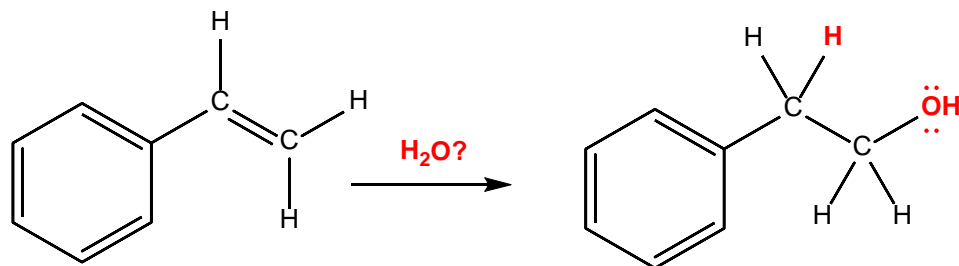
# Addition of O to Alkenes

- Predict the major product(s) for each of the reaction sequences:



# Hydroboration-Oxidation of Alkenes

- All electrophilic addition reactions follow Markovnikov's Rule, but sometimes, we really want to add the small molecule the other way around! How can we accomplish this? In other words, what can we do if we want to do the reaction below?

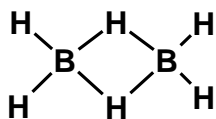


"anti-Markovnikov product"

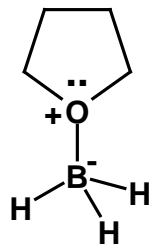
- Problem: We can't add the water directly. We need to add something else that will put the hydrogen where we want it THEN convert the other group into an alcohol. That means we need to add a small molecule in which hydrogen is the MORE electronegative atom. The other part of the small molecule must be something we can convert into -OH after the addition is done.

# Hydroboration-Oxidation of Alkenes

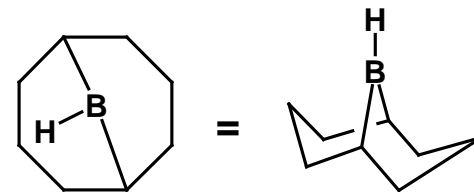
- Solution: a borane ( $\text{H-BR}_2$ )
  - Hydrogen is more electronegative than boron.
  - The  $\text{BR}_2$  part of a borane is bigger than H, so sterics will also help to put H on the more substituted carbon atom.
  - Boranes can be oxidized up to boronate esters (inserting an oxygen between the carbon and the boron) – which can be broken open, leaving behind an alcohol where  $\text{BR}_2$  was.
- Two of the most common borane reagents are  $\text{BH}_3$  (which MUST be in an ether solvent like THF) and 9-BBN:



Borane with no solvent is  $\text{B}_2\text{H}_6$



Borane in THF

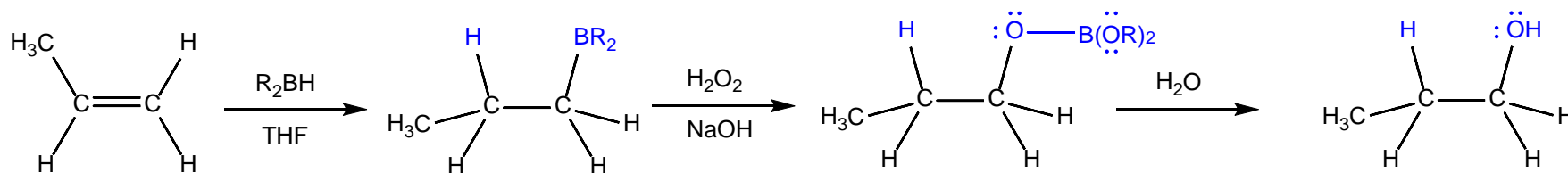


9-BBN  
(9-borabicyclo[3.3.1]nonane)

If regioselectivity is a concern, choose \_\_\_\_\_.

# Hydroboration-Oxidation of Alkenes

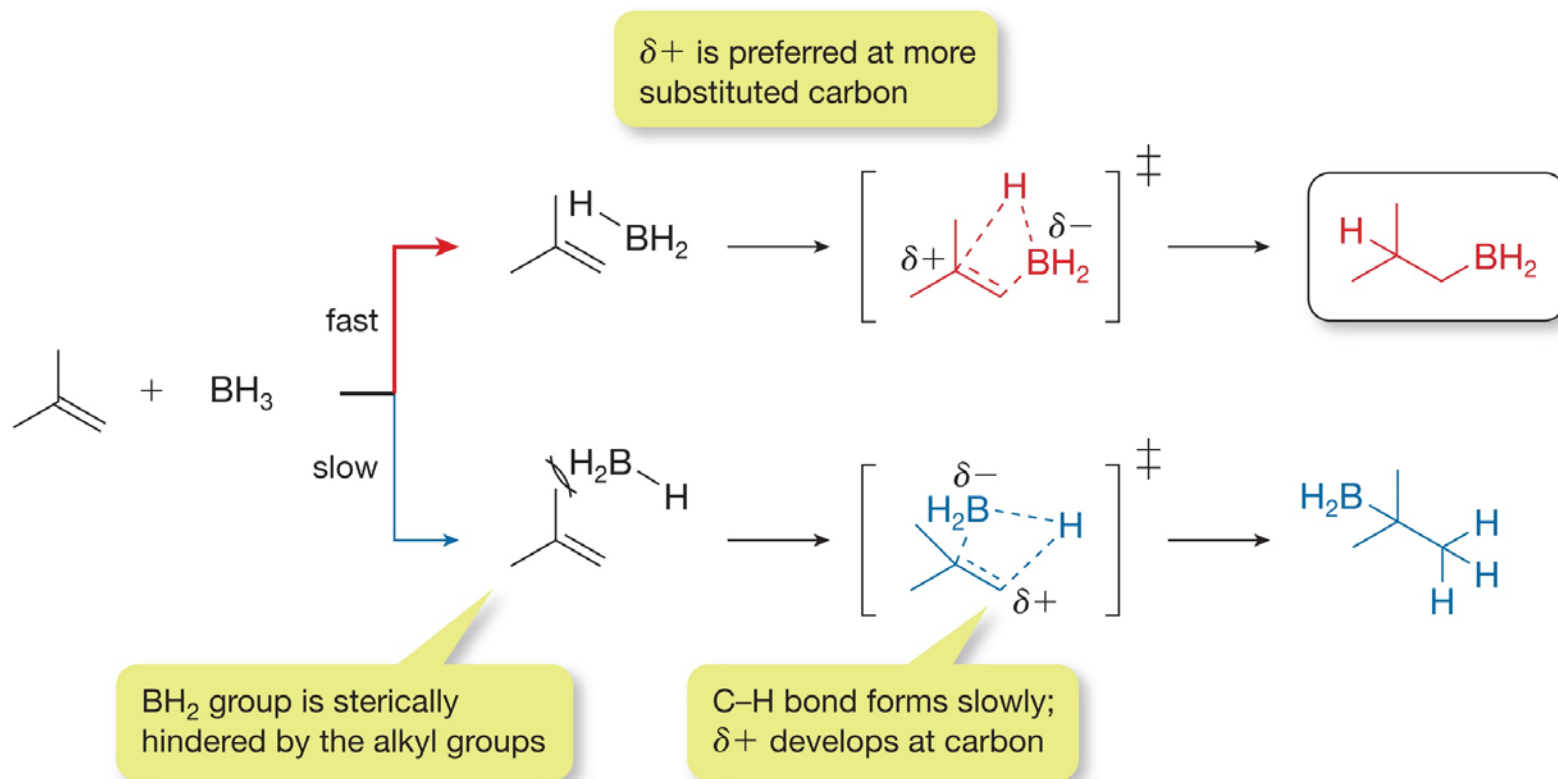
- How does this give us the “anti-Markovnikov” alcohol?





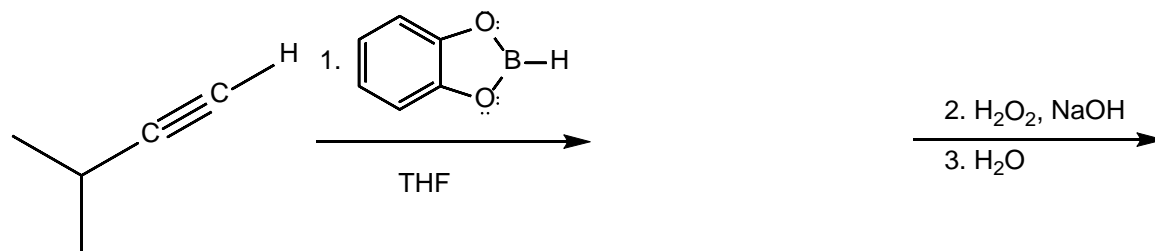
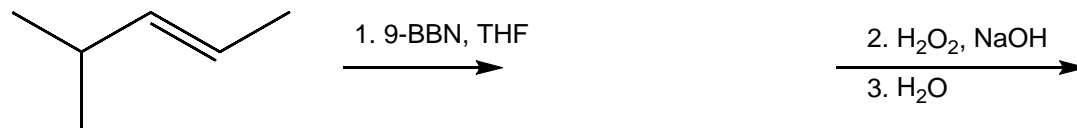
# Hydroboration-Oxidation of Alkenes

- Note that, because both parts of the borane add simultaneously from the same molecule, this is always a *syn*-addition. That makes hydroborations **regioselective** and **stereospecific**.



# Hydroboration-Oxidation of Alkenes

- What are the major products for each of the following reactions?





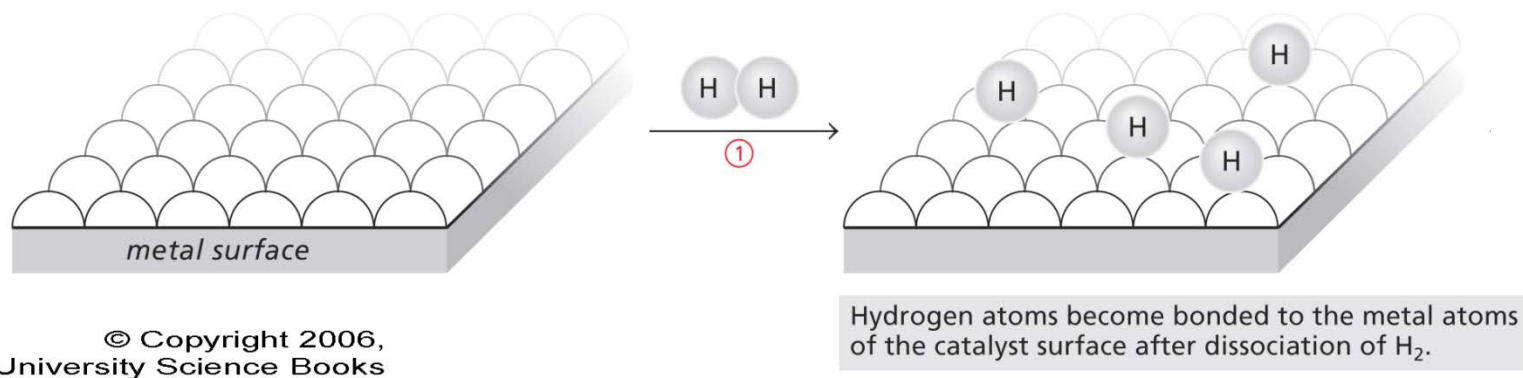
# Hydrogenation of Alkenes

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- We've already seen one reaction which can be considered to be a reduction reaction – the nucleophilic addition of hydrogen to a carbonyl (using  $\text{NaBH}_4$  or  $\text{LiAlH}_4$  as the source of "H<sup>-</sup>):
  
- This was a **chemoselective** reaction – in other words, the reducing agent only reacted with one functional group (the carbonyl) and left others alone (alkenes and alkynes).
- If we want to reduce an alkene or alkyne, we need to use a different kind of hydrogen source – one which can add hydrogen across any  $\pi$  bond. We want our hydrogen source to be, quite literally, hydrogen ( $\text{H}_2$ ).
- Problem: The H-H bond is \*very\* strong. Why is that?

# Hydrogenation of Alkenes

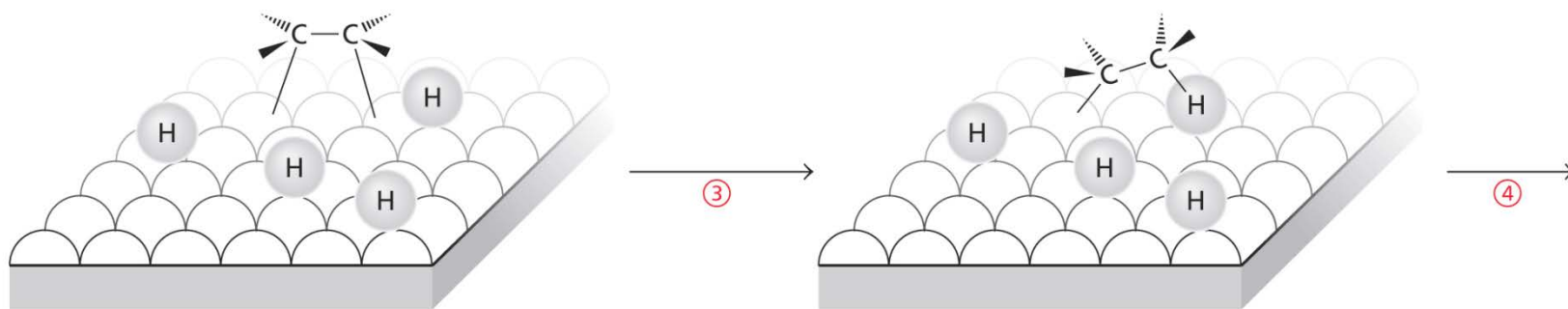
- Solution: Use a catalyst to help break the H-H bond. A transition metal such as Pd or Pt will do this nicely; however, these metals are expensive and the catalysis only occurs at the surface. So, we coat the metal on something cheap like charcoal to maximize catalytic surface area.



- Thus, the standard choice for a hydrogenation catalyst is 5-10% Pd/C (since Pt is more expensive than Pd and they work equally well for most alkenes and alkynes), and  $H_{2(g)}$  is bubbled through a solution of reactant. The catalyst does not dissolve, so stirring is essential to keep it suspended so that alkene (or alkyne) and catalyst come into contact.

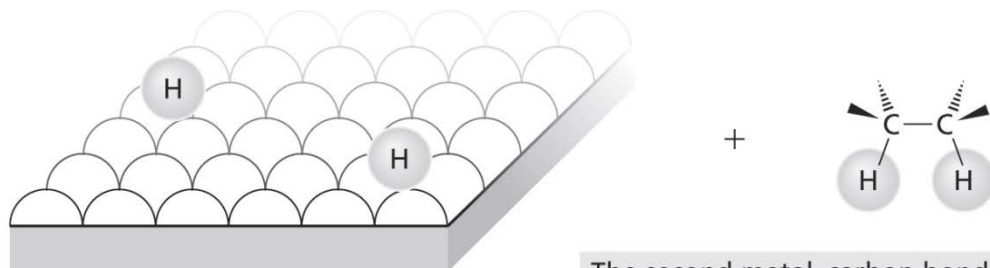
# Hydrogenation of Alkenes

- The addition of  $H_2$  across a  $\pi$  bond using a transition metal catalyst like this is another stereospecific reaction. The addition is **always *syn*** (always gives the ***cis*** product):



Weak metal-carbon bonds are formed from the reaction between the alkene carbon atoms and the metal surface.

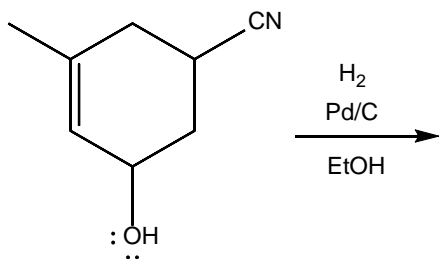
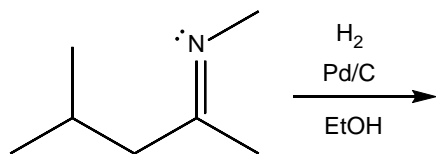
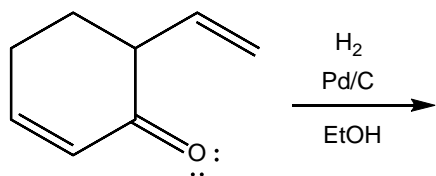
A metal-carbon bond is broken as a carbon-hydrogen bond is formed.



The second metal-carbon bond is broken as another carbon-hydrogen bond is formed; the reduced product dissociates from the surface.

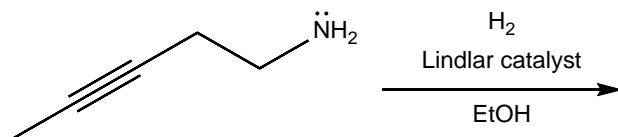
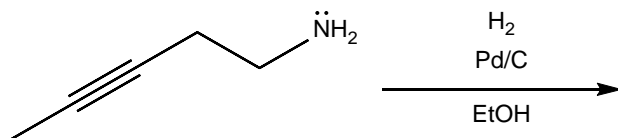
# Hydrogenation of Alkenes

- Any  $\pi$  bond can be hydrogenated, but C=O groups are harder to hydrogenate than C=C, C=N, C $\equiv$ C or C $\equiv$ N groups. Hydrogenation of a carbonyl therefore tends to require a more powerful catalyst, heat, and/or a higher pressure of H<sub>2(g)</sub>. Thus, it is not difficult to hydrogenate an alkene or alkyne in the presence of a carbonyl.
- Draw the major organic product of each hydrogenation reaction:



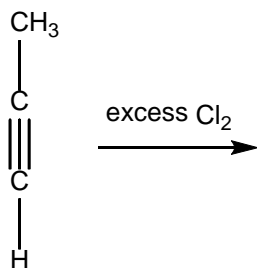
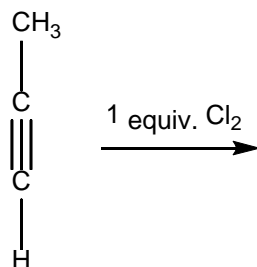
# Hydrogenation of Alkynes

- It is possible to stop hydrogenation of an alkyne at the alkene, but only if a **poisoned catalyst** is used. One “poisoned” hydrogenation catalyst is called Lindlar’s catalyst, in which the Pd is coated on  $\text{CaCO}_3$  instead of charcoal then treated with quinoline and lead(II) acetate to reduce its activity. You can check if your hydrogenation catalyst has been poisoned by checking whether the metal is coated on a salt or on charcoal.
- Hydrogenation of an alkyne with a poisoned catalyst always gives the ***cis*-alkene**:



## Other Addition Reactions of Alkynes

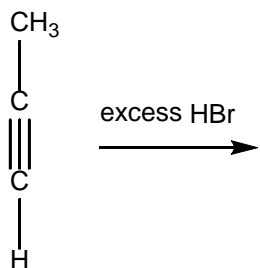
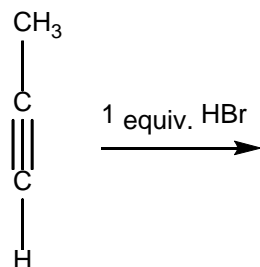
- Alkenes are not the only compounds with nucleophilic  $\pi$  bonds. Alkynes are just as nucleophilic as alkenes; after all, they contain two perpendicular nonpolar pi bonds...
- When a halogen is added to an alkyne, two molecules of  $X_2$  can be added per triple bond:





# Other Addition Reactions of Alkynes

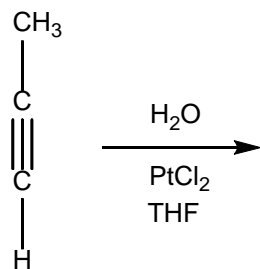
- When a hydrogen halide is added to an alkyne, two molecules of HX can be added per triple bond:



- Markovnikov's Rule applies to both additions.

## Other Addition Reactions of Alkynes

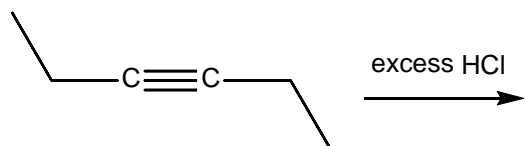
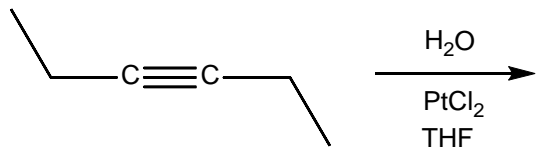
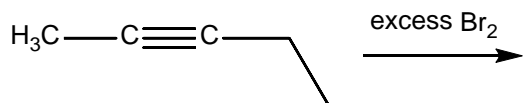
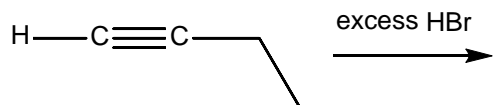
- When a water is to be added to an alkyne, a transition metal catalyst is necessary:



- Addition of one water molecule gives an enol. It **tautomerizes** to the corresponding ketone (a “keto-enol tautomerism”).

# Other Addition Reactions of Alkynes

- Addition of unsymmetrical molecules ( $\text{H}_2\text{O}$  or  $\text{HX}$ ) to an alkyne is only practical if the alkyne is either terminal or symmetrical. Why?
- What are the major products for each of the following reactions?





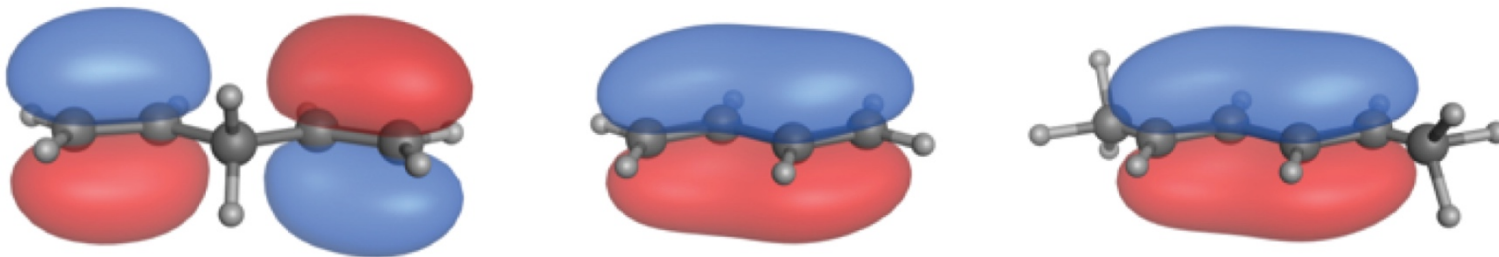
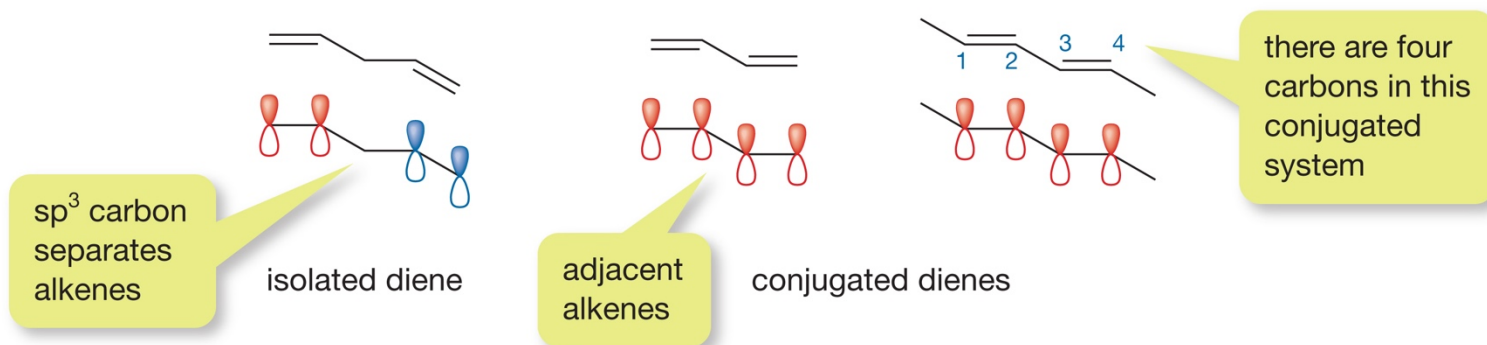
# Addition Reactions of Dienes

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- When a molecule contains multiple  $\pi$ -bonds, their reactivity is dictated in part by their relative locations in the molecule:
  - An **isolated double bond** is separated from all other  $\pi$ -bonds by at least one tetrahedral carbon atom. It is its own  $\pi$ -system and reacts independently of any other  $\pi$ -systems in the molecule.
  - A **conjugated double bond** is part of an extended  $\pi$ -system which reacts as a single entity. This is usually characterized by alternating single and double bonds.
  - A **cumulated double bond** is one of two double bonds involving the same carbon atom. The two  $\pi$ -systems are perpendicular and react completely independently.

# Addition Reactions of Dienes

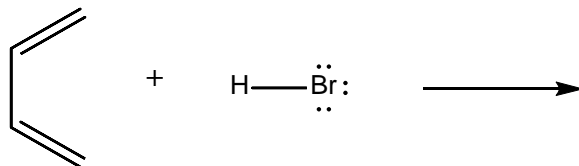
- When we talk about the reactivity of dienes, we are usually talking about conjugated pi systems:



- That's because the whole extended pi system is nucleophilic.

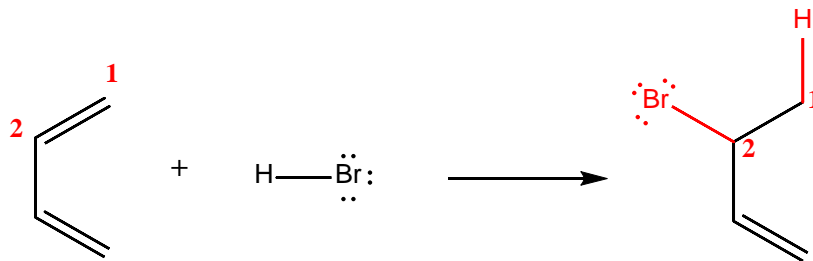
# Addition Reactions of Dienes

- When deciding which carbon atom to attach the electrophilic atom (or acidic hydrogen to), we consider all the same factors as we did with isolated dienes:
  - We want the carbocation to be resonance-stabilized, and
  - We want the carbocation to be as highly substituted as possible.
- If we protonate at either end of a conjugated diene, we will obtain a resonance-stabilized carbocation called an **allylic carbocation**:

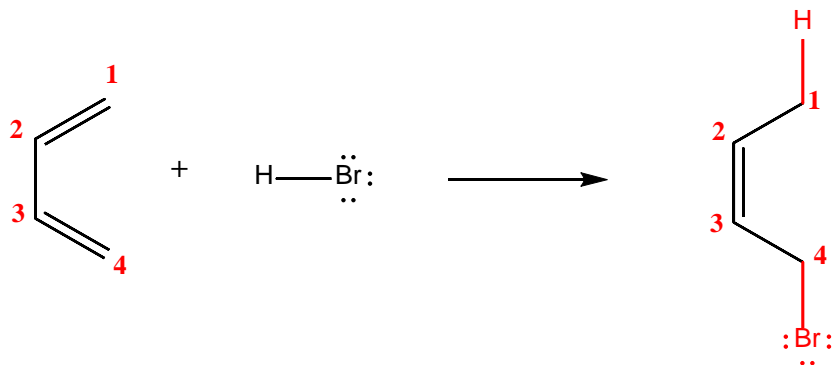


# Addition Reactions of Dienes

- A nucleophile can potentially attack **either** of the two carbon atoms sharing the positive charge.
  - If the nucleophile attacks the carbon atom next to the one where the hydrogen is added, the reaction is called a 1,2-addition:

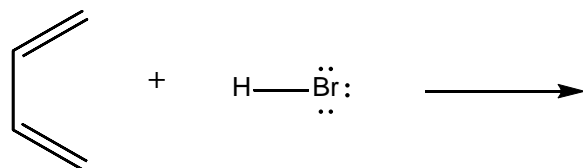


- If the nucleophile attacks the other carbon atom, the reaction is called a 1,4-addition:

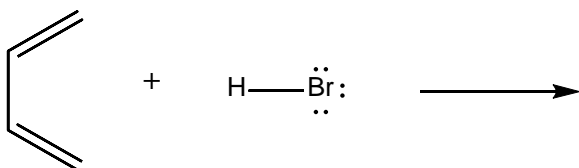


# Addition Reactions of Dienes

- Since the carbocation will more closely resemble the better resonance structure, attack of the nucleophile at that atom is faster. This gives the kinetic product:



- The product with the more substituted double bond is the thermodynamic product:

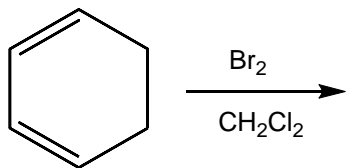
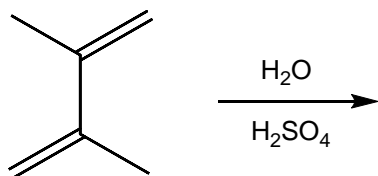






# Addition Reactions of Dienes

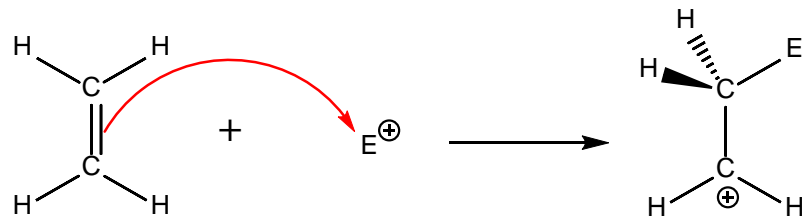
- For each of the following reactions, predict the 1,2-addition product and the 1,4-addition product. Also, indicate which you would expect to be kinetically favoured and which would be thermodynamically favoured.



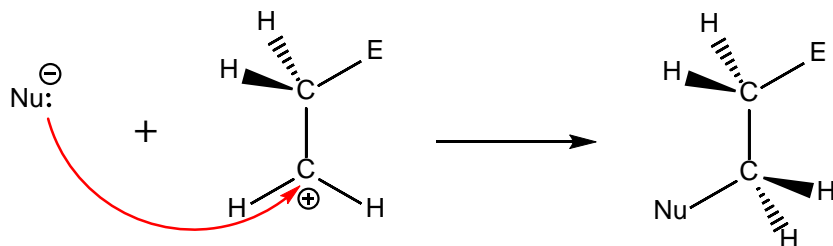
# Summary of Additions to Alkenes

- **Every single reaction** in this chapter can be summarized as follows:

- A nonpolar pi bond (alkene or alkyne) donates electrons to an acid or electrophile, making the best possible carbocation intermediate.

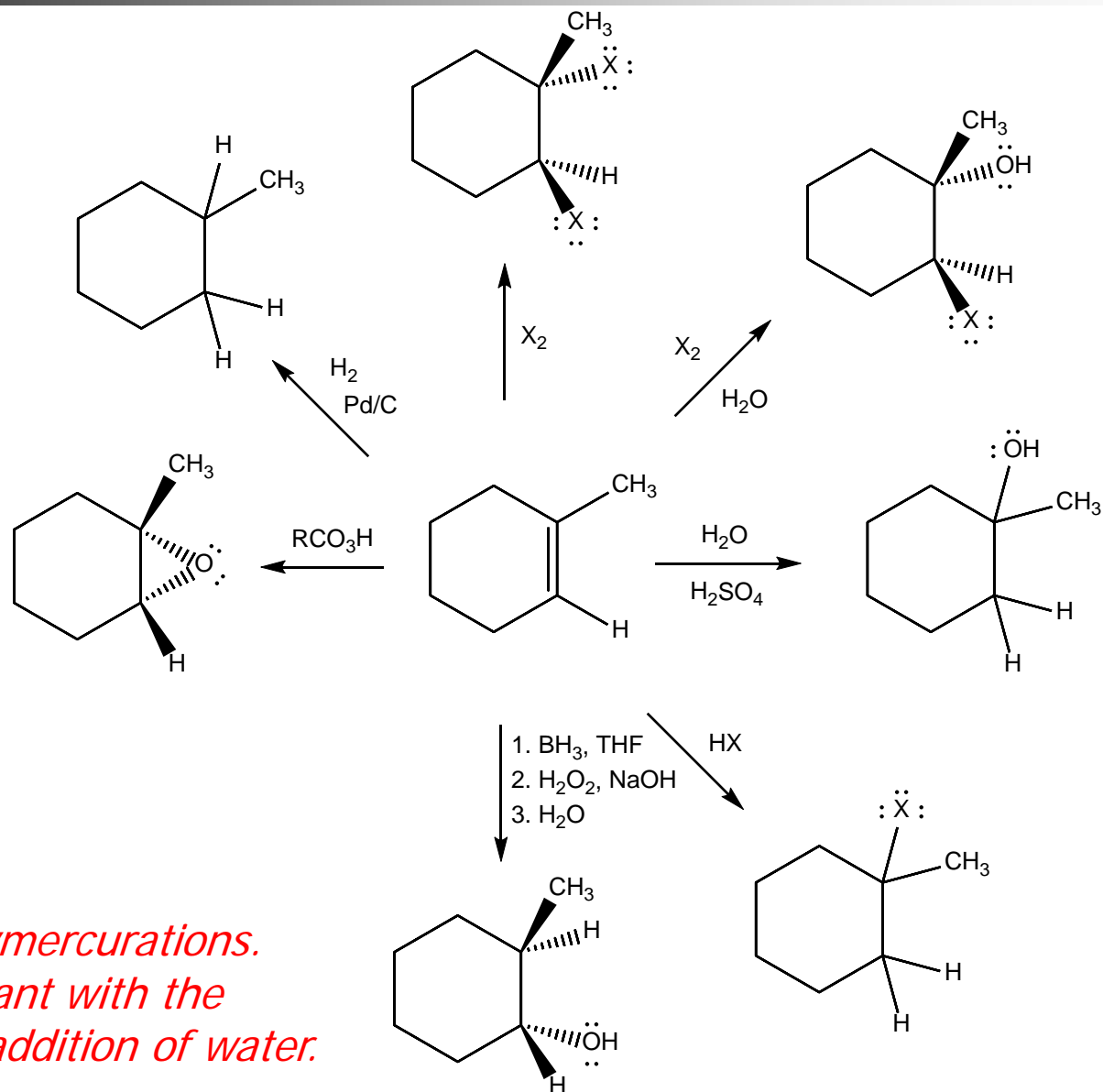


- A nucleophile attacks the carbocation.



- An acid-base "tidy up" step may be needed at the end.

# Summary of Additions to Alkenes



*We skipped oxymercuration. They're redundant with the acid-catalyzed addition of water.*