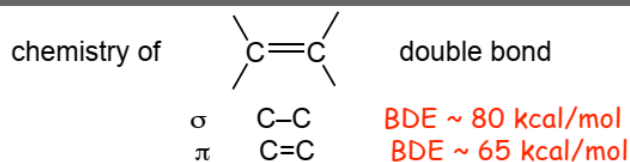


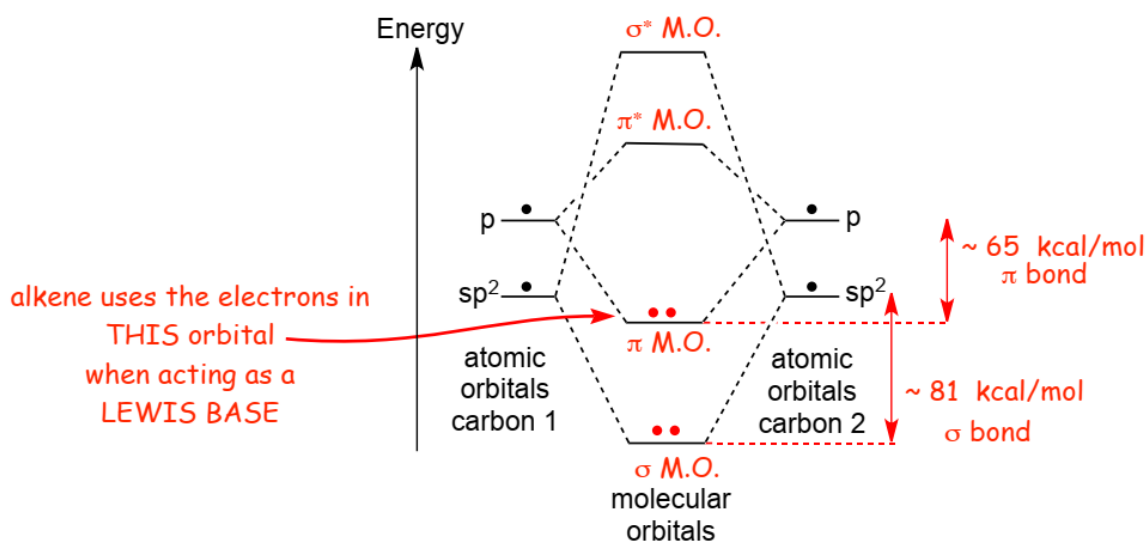
Alkenes

Electrophilic Addition

1 Alkene Structures

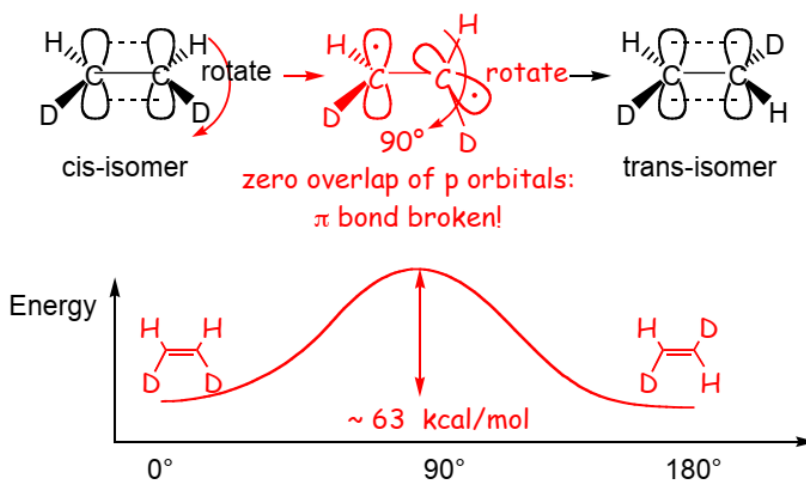


- The π -bond is weaker than the sigma-bond.
- The electrons in the π -bond are higher in energy than those in the σ -bond.
- The electrons in the π -bond are **more chemically** reactive than those in the σ -bond.



- The alkene uses the electrons in the π -bond when it reacts as a **Lewis Base/nucleophile**.

How do you break a π -bond?

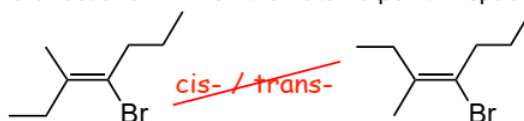


- Rotation around a sigma-bond hardly changes the energy of the electrons in the bond because rotation does not significantly change the overlap of the atomic orbitals that make the bonding M.O.
- Rotation around a π -bond, however, **changes the overlap** of the p AOs that are used to make the bonding M.O., at 90° there is **no overlap** of the p A.O.s, the π -bond is **broken**.

Distinguishing isomers



- By now we are very familiar with cis- and trans-stereoisomers (diastereomers).
- But what about, the following two structures, they can NOT be assigned as cis- or trans-, yet they are definitely stereoisomers (diastereomers), the directions in which their atoms point in space are different.



We Need a different system to distinguish stereoisomers for C=C double bonds: **Use Z/E notation.**

The Cahn-Ingold-Prelog convention "rules"

- 1) Assign priorities to the 2 groups attached to the carbons at each "end" of the C=C bond according to atomic #.
- 2) Compare the 2nd, 3rd etc. atom away from the alkene carbon as necessary, look for first point of difference
- 3) Multiple bonds "add up" (see the example below).
- 4) If the 2 highest priority groups are on the same side, the alkene is Z, otherwise E.

Z = zusammen - together (zame side!)

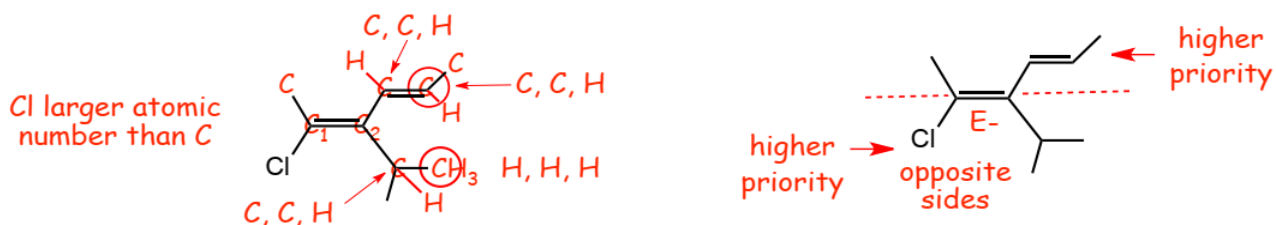
E = entgegen - opposite

Example 1:

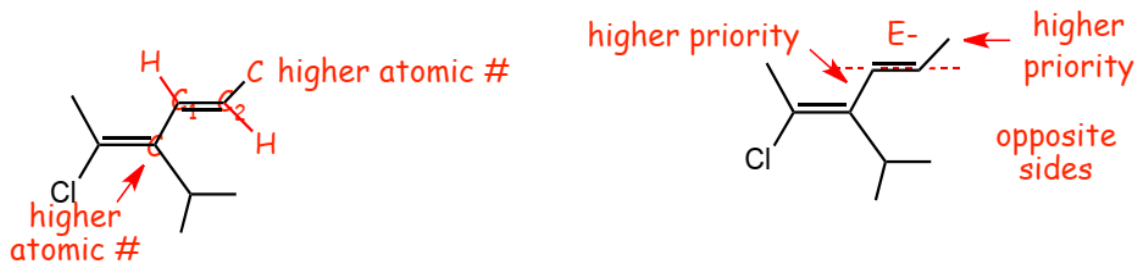


- **First:** compare the 2 groups attached to C1 (at **one "end" of the alkene**) and determine which has **highest priority** at the **FIRST POINT OF DIFFERENCE**, **based on atomic number**, moving "away" from C1 we find a difference when comparing C against H, the lower ethyl group has the higher priority compared to the upper methyl group.
- **Then:** compare the 2 groups attached to C2 (at the **other "end" of the alkene**) and determine which highest priority at the **FIRST POINT OF DIFFERENCE**, **based on atomic number**, moving "away" from C2 we immediately find a difference when comparing C against Br, the lower bromine has higher priority than the upper propyl group.
- **Finally:** divide the alkene **ALONG THE C=C bond axis** and determine whether the highest priority groups are on the **Zame side** (where "sides" are determined by drawing a line through the C=C internuclear axis), in this case the answer is yes, therefore **this is a Z-alkene** (if they were on opposite sides the alkene would be E-).

Example 2:



- **First:** looking at **one "end"**, **C1, Cl has higher priority** than C attached to C1, **based on atomic number**,
- **Then:** at the **other "end"**, **C2, BOTH** first carbons attached to C2 have C, C, H attached to them (count **BOTH** carbons in the C=C bond)
- the **NEXT** carbons away from C2 have C, C, H attached (the upper carbon, go "back one in the C=C bond) and H, H, H attached (either of the -CH₃ groups, it doesn't matter which)
- **Finally:** the highest priority groups are on **OPPOSITE** sides for this double bond, where "sides" are determined by drawing a line through the C=C internuclear axis: **this is an E-alkene**



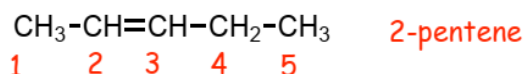
- On **both** C1 and C2 the carbon has higher priority than H based on atomic number.
- The highest priority groups are on **opposite** sides for this double bond, **this is also an E-alkene**.

2 Alkene Nomenclature

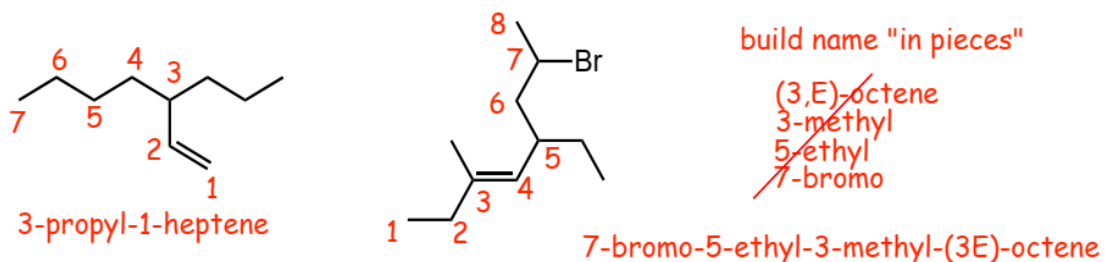
Rules: Same as for alkanes except that **now** we have a functional group, when we have functional groups we must find the longest chain that **contains** the **maximum** number of functional groups (even if there is another chain that is longer), so for alkenes:

- 1) Look for longest chain that **contains** the double bond(s).
- 2) Assign lowest numbers to carbons based on the **alkene and number through the C=C bond(s)**.
- 3) Use the "-ene" suffix instead of "-ane" and identify the position of the C=C bond with a number.

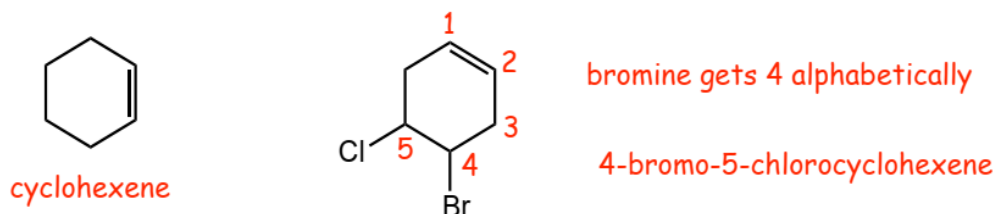
Examples



- Number the chain to give the C=C bond the lowest number.

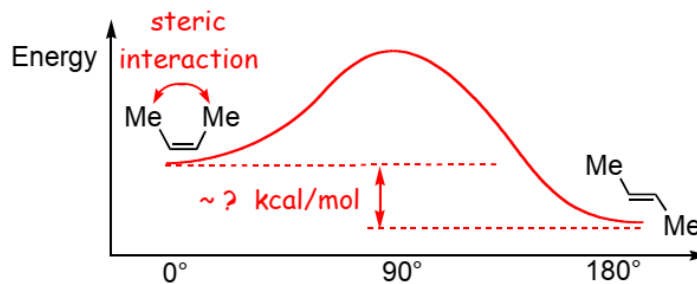


- When the name becomes complex, it is often an idea to write down the fragments and then combine them.

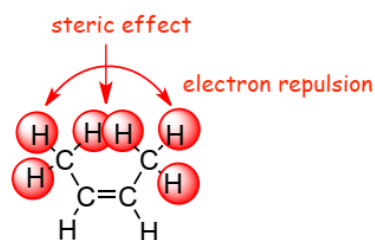


- Cyclohexene isn't really an exception to the rule, because the C=C bond can **ONLY** be number 1, it is normally not included in the name.
- When there are **two** ways of numbering that give the **same** numbers for the substituents, as above, number alphabetically (but do this **only** when all else is equal).

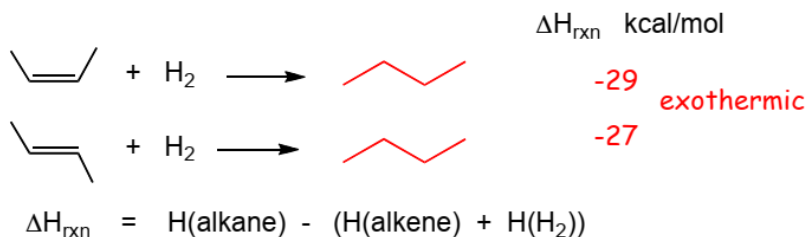
3 Alkene Stabilities



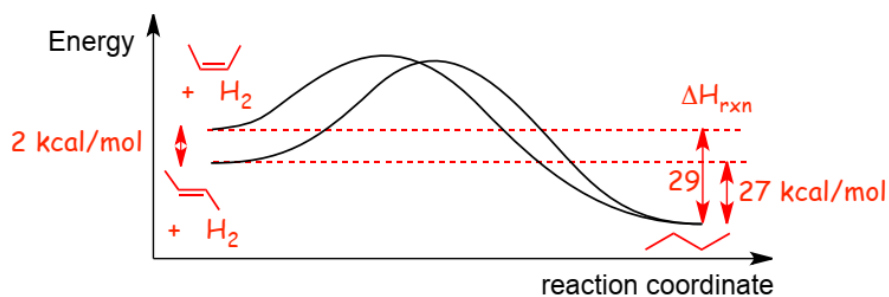
- In general, *trans*-isomers are more stable than *cis*-isomers, due to **electron repulsion** and **steric effects**.



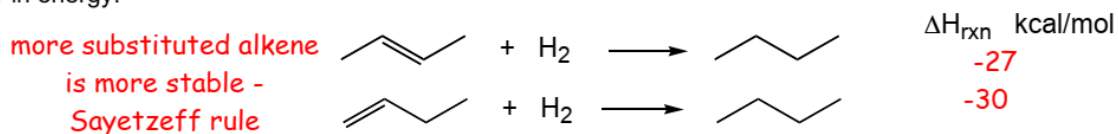
- But how to quantify this difference in energy?



- The *cis*-reaction more exothermic by 2 kcal/mol because *cis*- is less stable by 2 kcal/mol



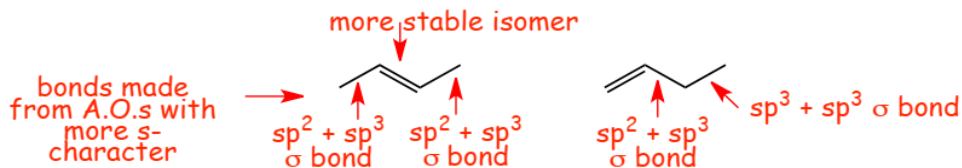
- Note that both reactions are on the same absolute energy scale here, the product is the same, the *cis*- starts higher in energy.



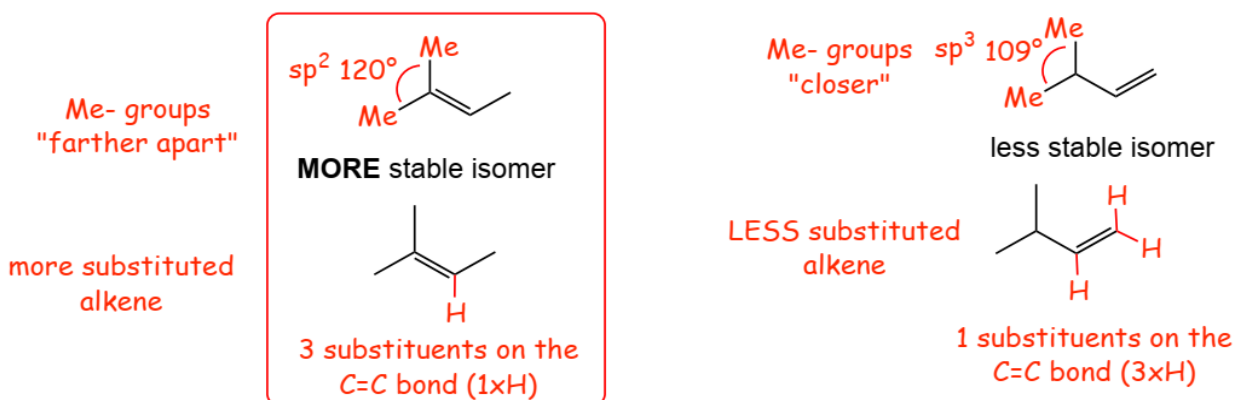
- More substituted alkenes tend to be more stable, they have lower energy electrons (H does not count as a substituent in this context): the Saytzeff (or Zaitsev) rule

Why are more substituted alkene isomers more stable?

Answer #1: More substituted alkenes tend to have more bonds to sp^2 hybridized carbons, these are stronger, the energy of the electrons is lower.



Answer #2: more substituted alkenes tend to have more C-C-C bonds that have 120° angles instead of 109° angles, there is less electron repulsion, lower energy electrons.



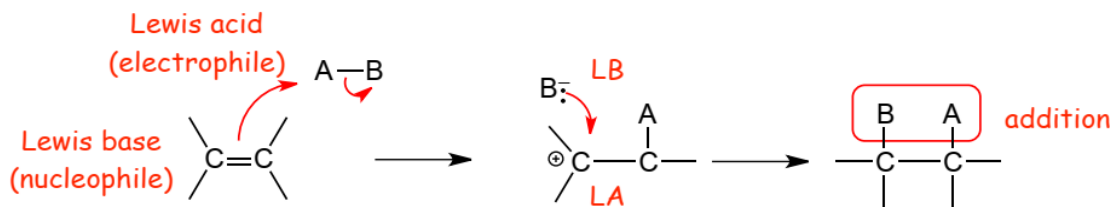
4 Alkene Reactions

• Note that we will be discussing the reactions of ALKENES, remember that another functional group that involves C=C double bonds is the aromatic group.



• Aromatic systems have alternating single and double bonds and will be discussed in detail later.
 • The π -bonds in aromatic systems are considerably less reactive than those in alkenes, aromatic systems **do not undergo the same reactions as alkenes**, aromatic systems **do not do the reactions** described in this section.

• Many reactions of alkenes are **addition** of a **Lewis Acid**/Electrophile: **Electrophilic addition**
Generic 2-step mechanism for electrophilic addition to alkenes

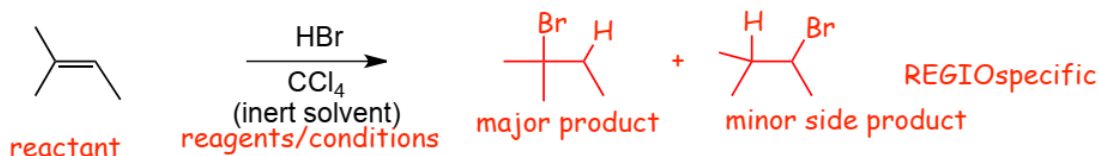


We will define **electrophile** and **nucleophile** more precisely later, for now, we will assume that **Lewis Acid = Electrophile** and **Lewis Base = Nucleophile**.

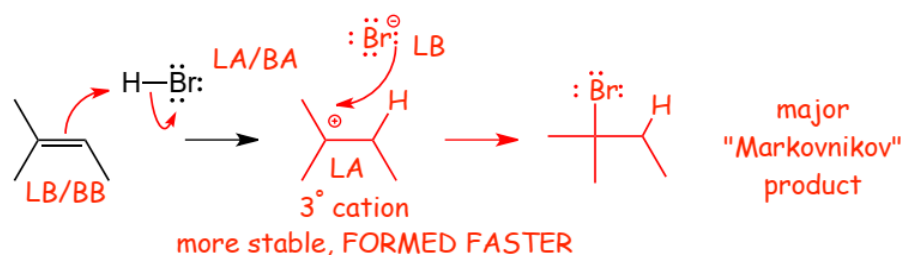
4.1 Addition of HBr, HCl

• This reaction is a functional group transformation, it transforms an alkene into an alkyl bromide.

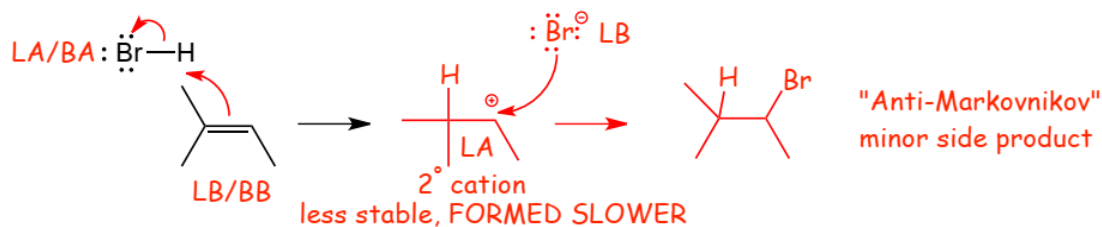
Example



- **Note:** the solvent here is **INERT**, it does not get involved in the reaction, it's only function is to get the reactant alkene and the H-Br into solution so that they can undergo the **collisions required for reaction**
- When two possible **structural isomers** can be formed and one is formed in much higher yield (one the major product), then the reaction is selective, and when a reaction selects for **structural isomers** of the kind shown. here, the reaction is said to be **regioselective or regioselective**
- The **minor** product would be a **side product** of the reaction.
- The **mechanism** explains the **regioselectivity** (i.e. why the major product is the major product).



compared to.....

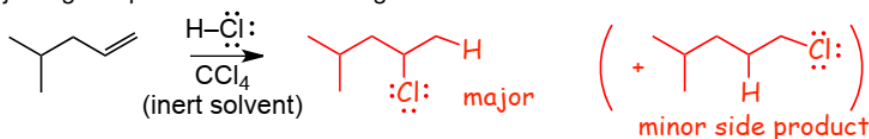


The Markovnikov Rule: Electrophilic addition proceeds via the most stable intermediate because this is formed **fastest** (the reaction is **kinetically controlled**).

- The Markovnikov product is that expected by electrophilic addition via the most stable intermediate.
- The Markovnikov product usually has the more electronegative element (-Br in this case) attached to the carbon that was more substituted in the original alkene.

Example:

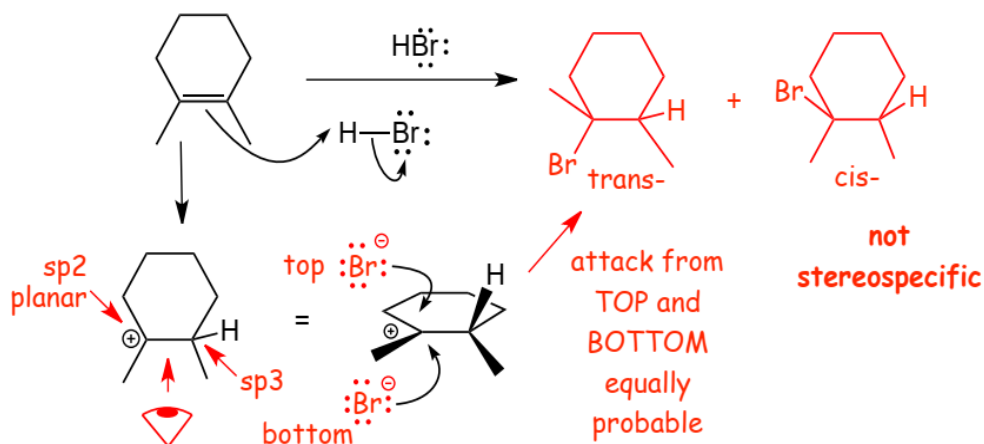
Determine the major organic product of the following reaction:



- **Note:** we did **not write** the entire mechanism, we just added the -H and the -Cl across the C=C bond, with -Cl added to the most substituted carbon of the C=C bond (Markovnikov addition)
- The **algorithmic** solution to this problem would have been to write the entire mechanism, if you have the correct mechanism (algorithm) then you **must** get the correct product
- The quicker heuristic approach to solving the problem simply adds the -Cl to the most substituted carbon and the -H to the least substituted carbon

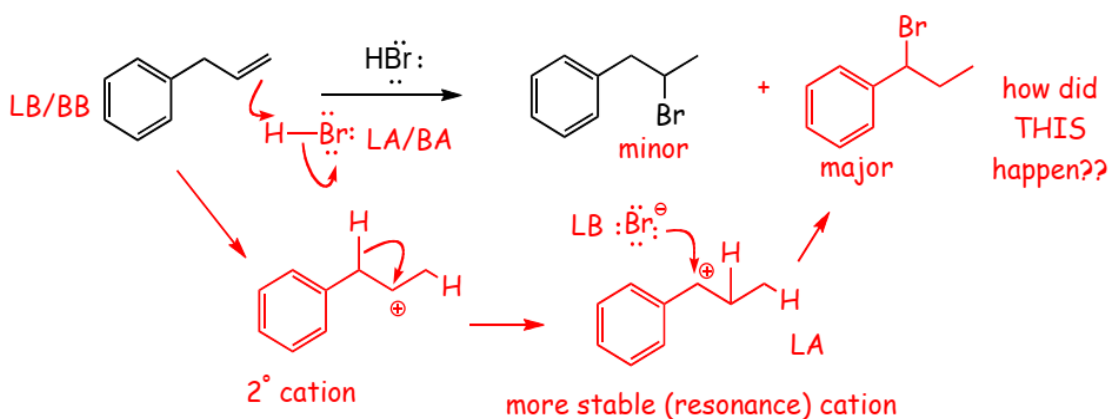
The Reaction is Regioselective, is it also Stereospecific?

In essence, what this question is asking is do the -H and the -Br atoms both add to the same side of the alkene, or do they add to opposite sides, since these two modes of addition would result in stereoisomers?

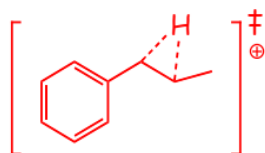


- Attack of the bromide anion on the carbocation intermediate will happen with equal probability at the "top" and the "bottom" of the planar sp² hybridized carbon that carries the positive charge.
- **Thus, the reaction is regioselective** (although that is irrelevant in the example above because both carbons of the alkene are equally substituted), but **not stereospecific**.
- Cis/trans isomers are not always possible for H-Br addition to an alkene, BUT, **IF cis/trans isomers are possible then cis/trans isomers will form**.

4.2 Carbocation Rearrangements

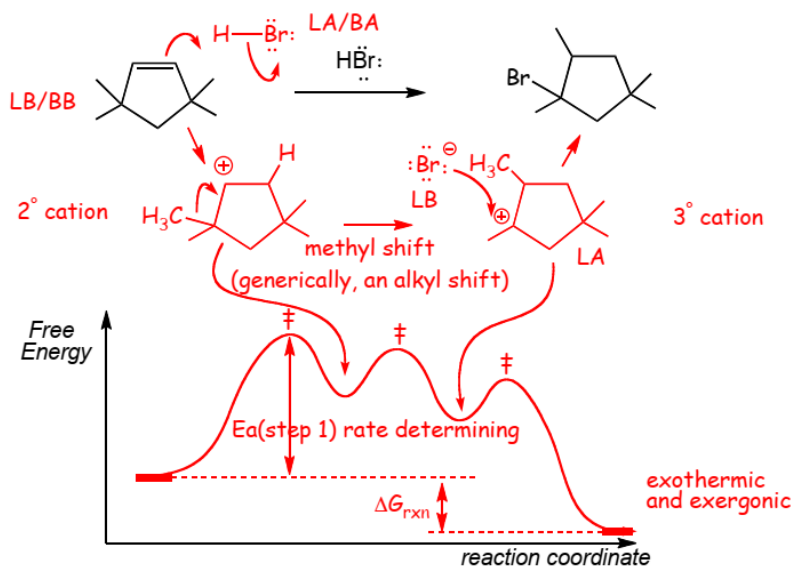


- A "hydride shift" occurred to form a more stable cation intermediate.
- The hydrogen atom moved with BOTH electrons, i.e. equivalent to a hydride anion.
- In our courses, **always** rearrange a carbocation intermediate to a more stable one **if possible!**
- The transition state for the hydride shift....



An Example **mechanism** problem

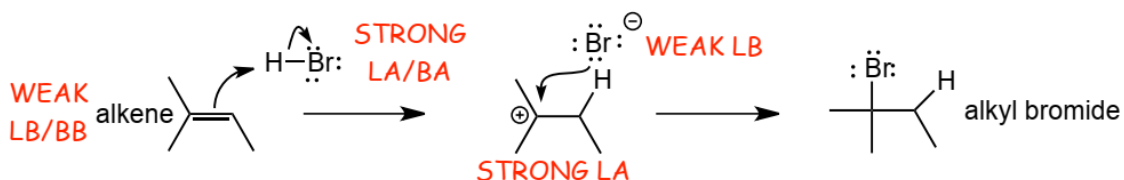
- Here is a typical organic chemistry problem, the product is provided, we need to work out the mechanism, i.e. exactly how the product is formed, based on the Lewis acid/base chemistry and the chemistry of alkenes and carbocations we have learned so far. The product "tells us" what bonds to make and what bonds to break



NOTE: the term Markovnikov loses its meaning when there are cation rearrangements, but the principle behind Markovnikov still holds, the most stable cation intermediate is formed in the first step of the reaction

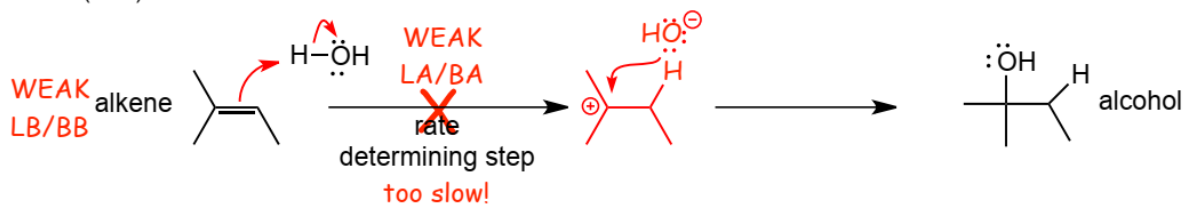
4.3 Addition of Water

- We have now learned how to convert an **ALKENE** functional group into an alkyl bromide by addition of -H and -Br to a C=C bond: a functional group interconversion (FGI)
- Now we will learn how to convert an **alkene** functional group into an **alcohol**, by addition of -H and -OH to a C=C bond: a **new** functional group interconversion (FGI)



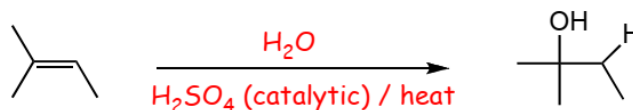
- The mechanism involves TWO Lewis acid/base reactions, in the first step the **alkene is a weak LB/BB** but the acid, **H-Br, is a strong LA/BA**, reactions occurs. In the second step the **bromide anion is a weak LB**, but the **carbocation is a strong LA** (the carbon really wants to make a bond!), the reaction occurs very rapidly.

- In principle, we can convert an alkene into an alcohol by addition of -H and -OH across a C=C bond, i.e. addition of water (H₂O).



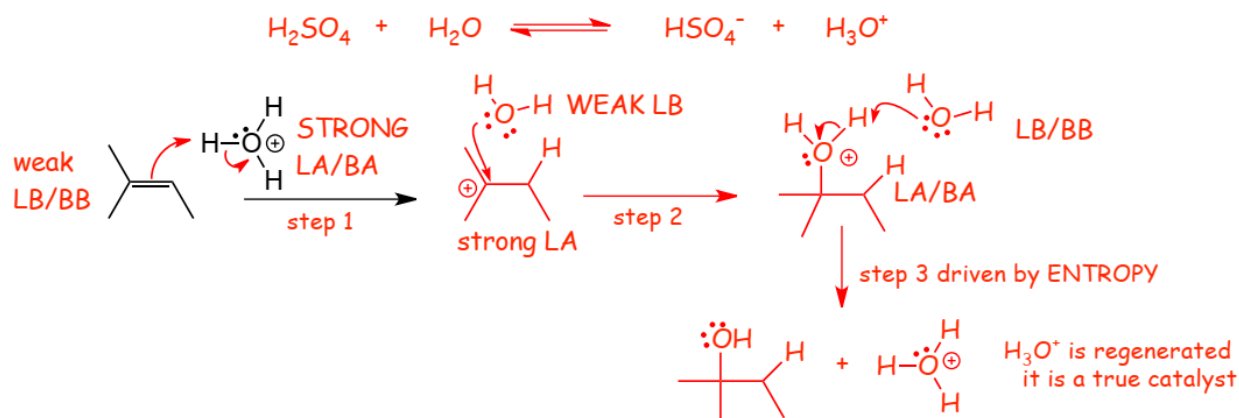
- However, we can't make an alcohol this way, since in the first step the **alkene is a weak LB/BB**, AND, the **water is a weak LA/BA**. The first step is so low that it does not occur on any reasonable timescale. The second step would occur rapidly, but, the **first is the rate determining step and it is too slow**, reaction of an alkene with H₂O does NOT give an alcohol (in any reasonable timeframe).

However:



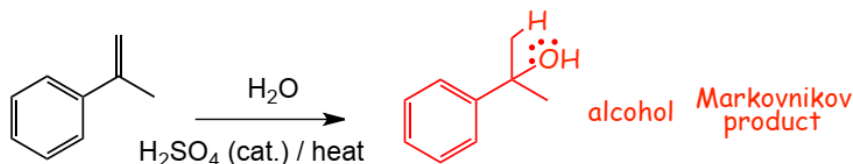
- This reaction GOES, the product is **Markovnikov**, i.e. the reaction is again **regiospecific**.
- The H_2SO_4 is **not consumed** but it makes the reaction go **faster**, it is a **catalyst**.
- the reaction is still a little slow and it usually needs to be heated to go on any reasonable timescale.

The Mechanism: In water, strong inorganic acids such as sulfuric dissociate to form the hydronium ion, H_3O^+

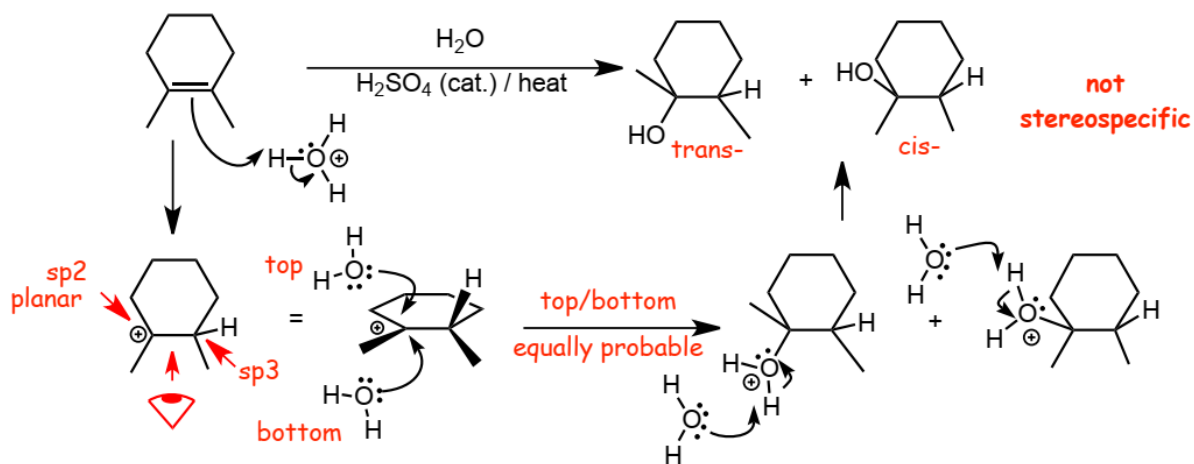


- Step 1, H_3O^+ is a **MUCH stronger Lewis (and Brønsted) acid** than H_2O (it wants electrons more).
- Step 2, H_2O is a weak Lewis base, **BUT the cation it reacts with is a STRONG Lewis acid (it is a cation)**.
- Step 3, breaks one O-H bond and makes one (essentially the same) O-H bond. This reaction is **thermoneutral** (the electron energy doesn't change much), **but it is very favorable due to entropy** there the proton will not stay on the alcohol oxygen if it can be on any of the millions of oxygens in the solvent water.

An Example Reaction

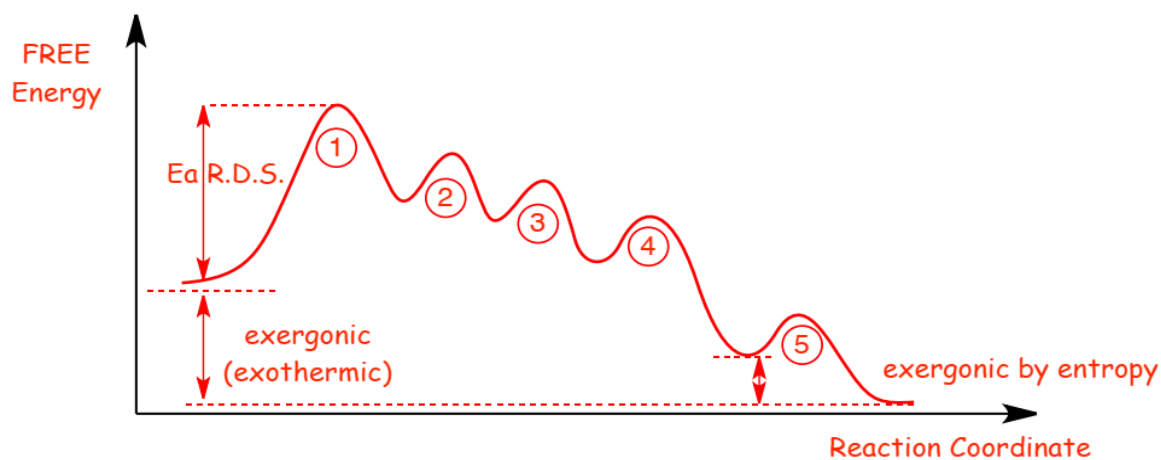
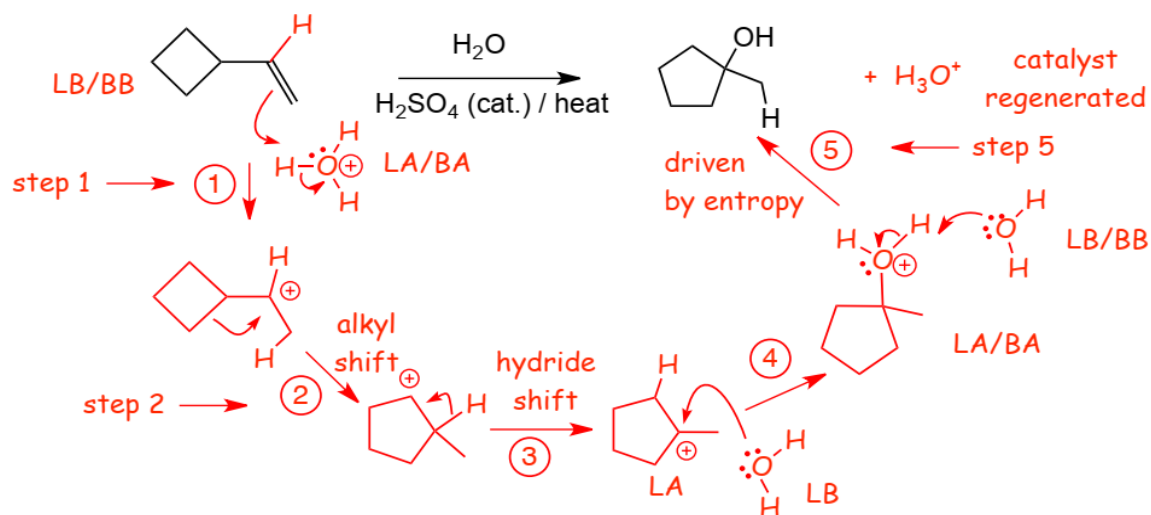


- **Note:** again, we did **not write** the entire mechanism, we just added the -H and the -OH across the C=C bond, with -OH added to the most substituted carbon of the C=C bond (Markovnikov addition)
 - The **algorithmic** solution to this problem would have been to write the entire mechanism, the quicker heuristic approach to solving the problem simply adds the -OH to the most substituted carbon
- Is the Reaction Stereospecific?**



- The reaction is not stereospecific, if cis/trans isomers can be formed they will be (top and bottom attack equally probable).

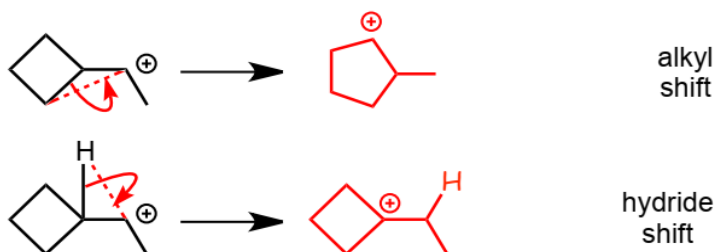
An Example Mechanism Problem



• NOTE: the reaction started "Markovnikov-like" in that the reaction proceeded via the most stable cation intermediate, but because the -H and -Br did not bond to the original two carbon atoms of the C=C bond, **the term Markovnikov loses its conventional meaning in this case**

• ALL reactions involving carbocations potentially involve rearrangements

• **Note** the carbocation rearrangement in this example, it was an alkyl shift that resulted in a ring expansion, as obvious question is why did a hydride shift not occur instead?

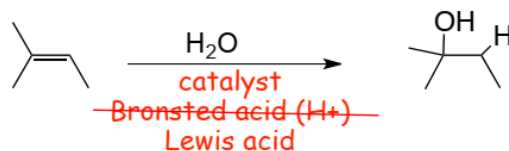


• which one "wins"? Actually, **both will probably occur**, and so if you were asked to give the PRODUCT of the reaction you would not know how to answer because it would not be clear which rearrangement to do.

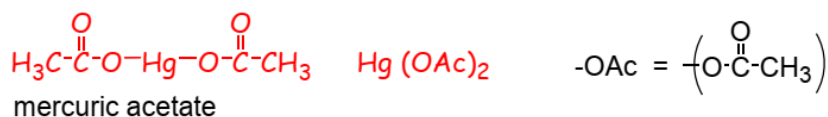
• **However**, this is a **mechanism** problem, i.e. the product is **provided**, and so in this case you know (indirectly) which rearrangement to do, it had to be the ring expansion in order to get to the provided product.

4.4 Oxymercuration: Markovnikov Addition of Water

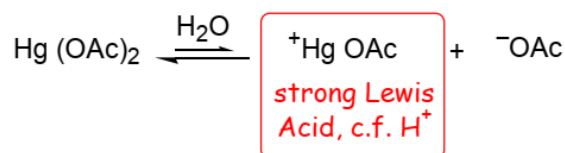
- Oxymercuration is the preferred method for adding water to an alkene in Markovnikov manner.
- We **avoid** using H₂O/H₂SO₄ to do Markovnikov addition of water if possible, since this reaction generates a carbocation intermediate, that even if it doesn't rearrange, can undergo elimination and other unwanted reactions (discussed later in the course). In general, we will always try to avoid reactions that involve carbocation intermediates in useful reactions.



- Using a Bronsted acid catalyst (i.e. a proton) generates a carbocation intermediate, **we can avoid a carbocation by using an appropriate Lewis acid catalyst instead** that will take the place of the proton, H⁺
- It isn't possible work out from first principles what the best Lewis acid should be, this is something that you just have to know

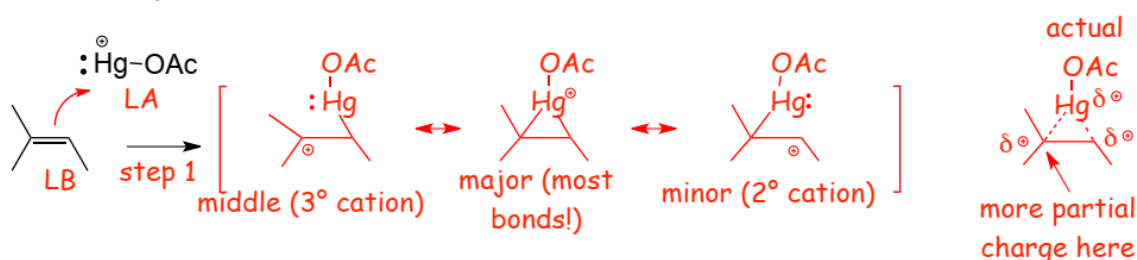


- Mercuric acetate is an electrophile (LA) that can add to an alkene and NOT form a carbocation
- In water, Hg(OAc)₂ is dissociated to a small extent

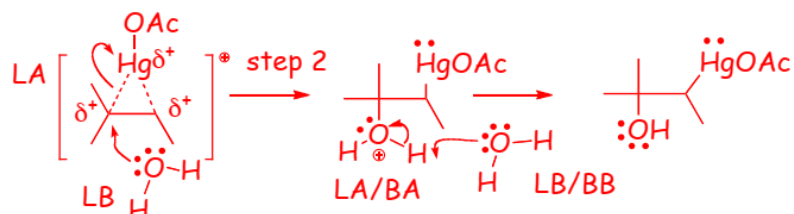


- *HgOAc is a Lewis acid/electrophile, will add to a C=C in just the same way that *H will, the difference is that the new bond will be C-Hg (a metal) instead of C-H
- Compared Bronsted acid catalysis, the mercuric acetate reaction is faster and has higher yields

Mechanism/Example



- Similar to addition of H⁺, except because of the large size and high energy non-bonding electrons on the Hg, the most important resonance contributor in the intermediate mercurinium ion is NOT a carbocation.
- The mercurinium ion then reacts with water JUST like the protonated alkene reacts with water, i.e.



- The reaction is **regiospecific, "Markovnikov"**, the **-OH adds at the most substituted end of the alkene**, since there is more positive charge at that carbon in the mercurinium intermediate. The water adds to carbon because in doing so it makes a stronger bond that it would have done by adding to Hg, this reaction is **FASTER**

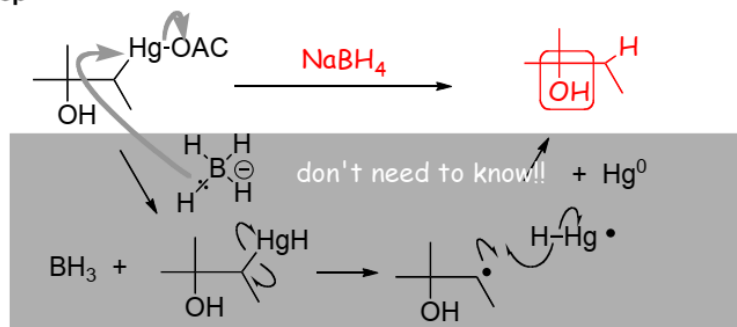
Question: How to get rid of the HgOAc?

Answer: Another New reagent



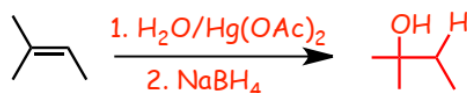
sodium borohydride is usually used as an aqueous solution in the presence of hydroxide anion, but that is a detail you don't need to worry about right now

The final required step



- This mechanism is a bit unusual because it involves a large metal atom, Hg, that doesn't follow exactly the same bonding patterns we usually see for C, H, N, O etc., therefore, knowing this mechanism won't help you learn other mechanisms very much, you would just have to memorize it, therefore it is in a grey "don't need to know" box
- After replacement of the -Hg with -H, the Markovnikov addition of water is now complete!

The overall reaction: The Major organic product is the Markovnikov addition product

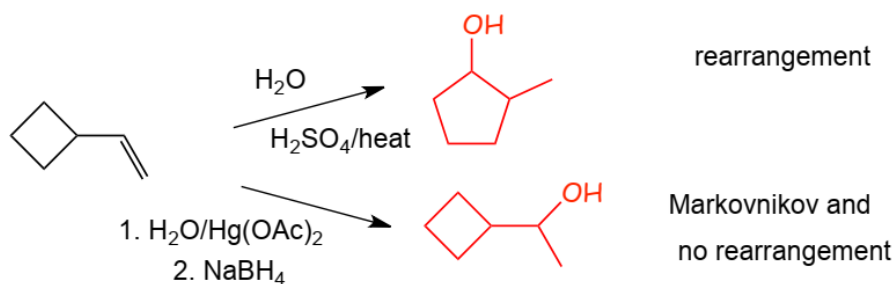


Important: The 1... 2... notation means, **FIRST** add $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$, **NEXT** add the NaBH_4

- It is **important** to include the 1. 2. etc. notation, if you don't, you are implying that all of the reagents are added at the same time, and in this case the Lewis acid $\text{Hg}(\text{OAc})_2$ will simply react with the Lewis base NaBH_4 and not with the alkene

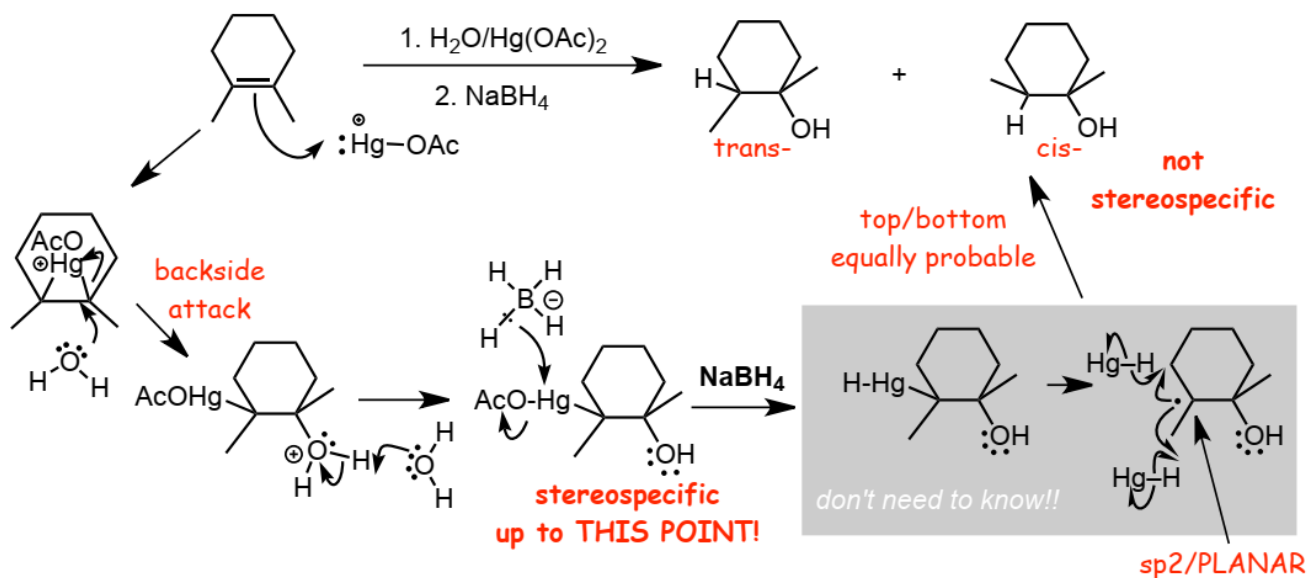
- First** add $\text{H}_2\text{O}/\text{Hg}(\text{OAc})_2$, **WAIT** until that reaction is complete, **SECOND**, add NaBH_4 to remove the HgOAc

Examples



- Using $\text{Hg}(\text{OAc})_2$ there are no carbocation intermediates, no rearrangements
- When asked for the reagents to perform Markovnikov addition to a C=C bond you should always use $\text{H}_2\text{O}/\text{Hg}(\text{OAc})_2$ followed by NaBH_4 and not simply H_2O with Bronsted acid
- The Bronsted acid catalyzed reaction is usually very slow anyway and is rarely used for this reason

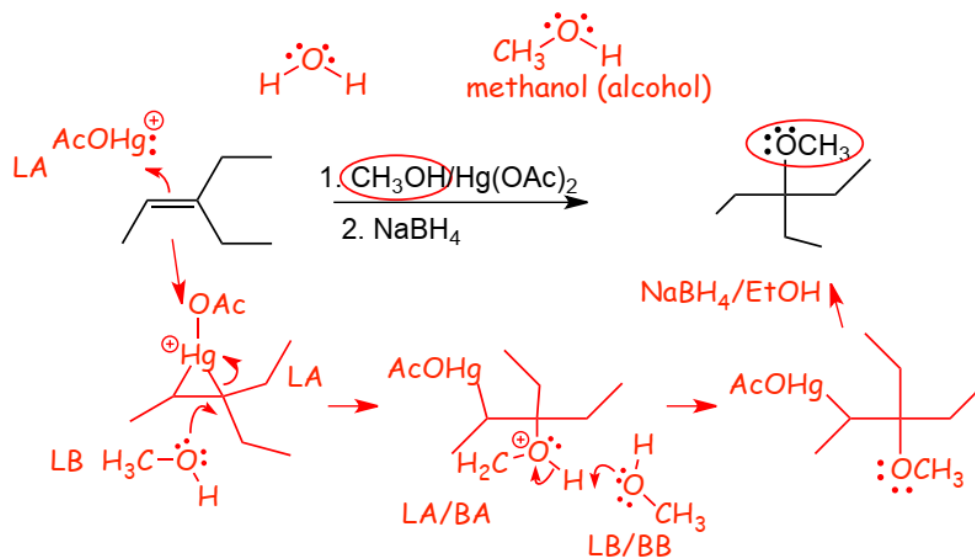
Is the Reaction Stereospecific?



- Because of the requirement for backside attack on the mercurinium ion, this reaction IS STEREOSPECIFIC up until the point where sodium borohydride (NaBH_4) is used to remove the mercury
- In THIS reaction (whose mechanism you do not need to know) there is a radical intermediate, the carbon atom of the radical is PLANAR and sp^2 hybridized and when the hydrogen atom adds it is equally probable that the addition will occur at the "top" and the "bottom" of the radical, and thus the stereoselectivity is LOST!
- IF CIS/TRANS STEREOISOMERS CAN FORM, then cis/trans isomers WILL form

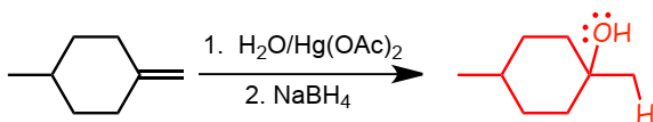
ALCOHOL addition

- NOTE the reagents in this reaction, the H_2O is replaced with CH_3OH , the alcohol methanol
- Methanol (CH_3OH) SHOULD DO, and DOES DO very similar reactions to water, it is also a weak Lewis base

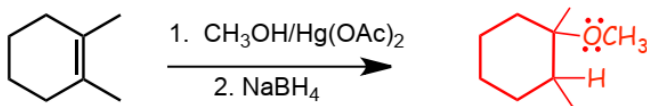


- The overall product of this reaction is an ether, **another** functional group interconversion
- Reaction is again **regiospecific**, the $-\text{OCH}_3$ adds to the most substituted end of the $\text{C}=\text{C}$ bond, the major product is the **Markovnikov** product

Example Reactions



Markovnikov addition of HO-H
no rearrangements
not stereospecific

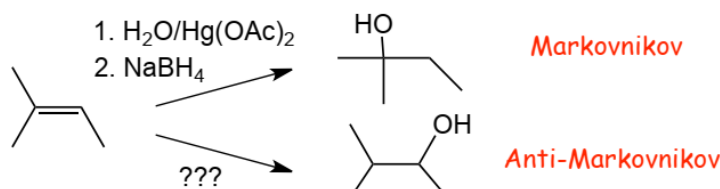


addition of $\text{CH}_3\text{O}-\text{H}$
(Markovnikov has no meaning in this case
because the alkene is symmetrical)
no rearrangements
no stereospecificity

- NOTE the use of heuristics to determine the reaction products

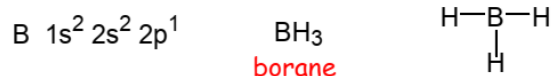
4.5 Hydroboration: Anti-Markovnikov Addition of Water

- OK, so we can do Markovnikov addition to a C=C bond, but what if we really NEED to make the other structural isomer, the ANTI-Markovnikov product?

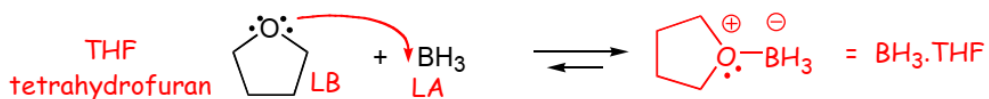


- This will require a different reaction and a DIFFERENT Lewis acid reagent

New Lewis acid reagent

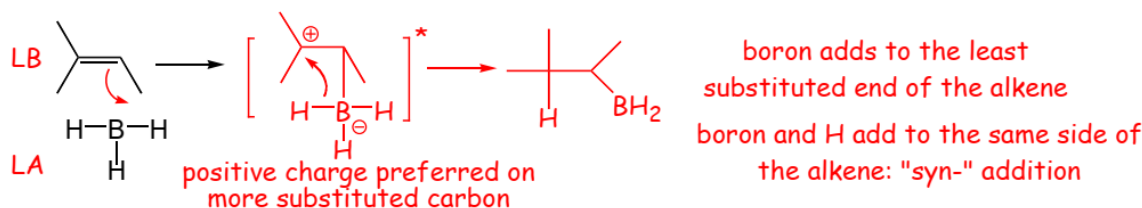


- borane has ONLY 6 valence electrons, is a VERY STRONG Lewis acid (electrophile), too reactive to even exist on its own, it is usually supplied as a complex with tetrahydrofuran (THF)

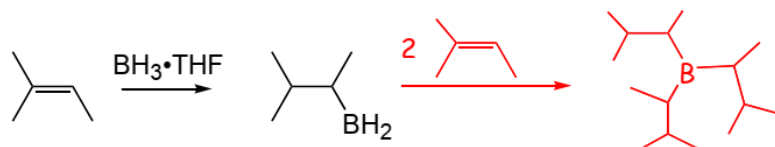


- $\text{BH}_3 \cdot \text{THF}$ complex, useful new reagent, "supplies" the strong electrophile (LA) BH_3

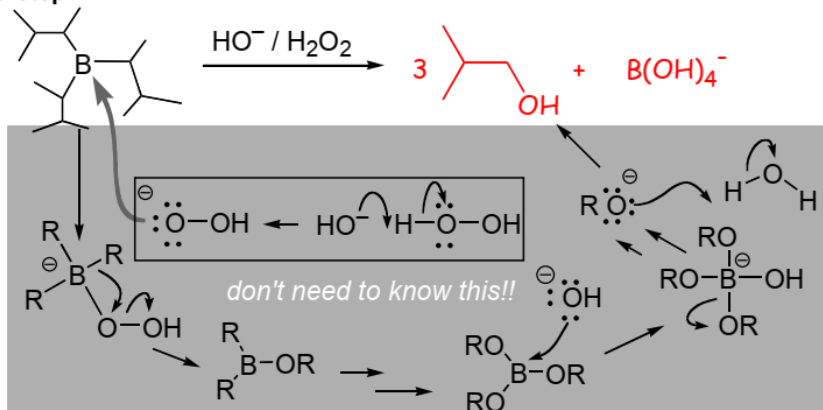
The Mechanism



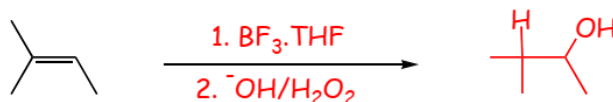
- reaction is **regiospecific**, -OH adds to the LEAST substituted "end" of the C=C bond
- This reaction is **stereospecific**, the H- and the HO- add to the **same side** of the C=C bond, "**syn-**" addition (the opposite of ANTI-Addition)
- the intermediate indicated with the star (*) has an EXTREMELY short lifetime, the hydride shift is very fast. *actually, the best current evidence suggests that the intermediate does not really form, and that the C-B and C-H bonds are formed almost at the same time, with the C-B bond forming somewhat before the C-H bond in an asymmetrical transition state*
- In any case, there is no carbocation intermediate with any substantial lifetime, thus there are no rearrangements

Another detail

- Each borane reacts with three alkenes.
- After one addition, the boron still only has 6 electrons, and so it reacts with additional alkenes.
- After adding to three alkenes it **still** only has 6 electrons, but now it is so sterically crowded that it can't react with another alkene.

The final required step

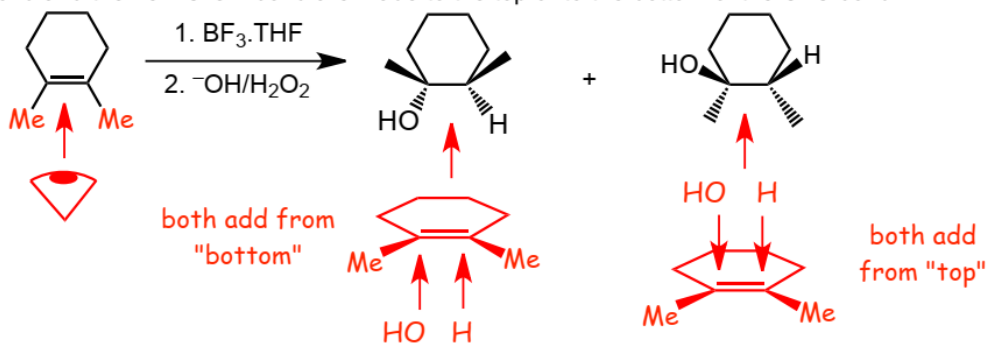
- This is another mechanism that doesn't help you learn other mechanisms particularly well, and so you don't have to know it, at this point you would only be memorizing it anyway, which isn't good.

The overall reaction

- **Again**, note the use of the 1. 2. notation, **FIRST**, react the alkene with the $\text{BH}_3 \cdot \text{THF}$, **WAIT** until that reaction has completed, **second**, add the $\text{OH}^- / \text{H}_2\text{O}_2$ (the OH^- is usually used as sodium hydroxide, NaOH and so it is equally good to specify NaOH too)
- If the 1. 2. notation is missing then it implies that everything is mixed together and the BH_3 will simply react with the OH^- and not the alkene and the reaction will not occur, the 1. 2. notation is **important**

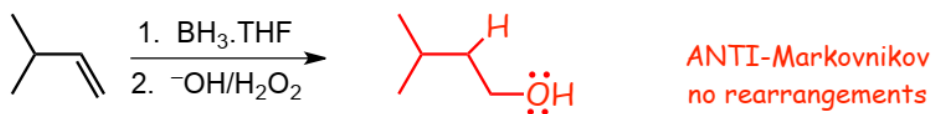
The reaction is Syn-addition, which can have stereochemical consequences

- **Syn-addition** means that both bonds are made to the "side" of the alkene
- Alkene "sides" can be seen by looking at the C-C bond "side on"
- This is particularly easy to see for a cyclic alkene, where it can be seen that **SYN**-addition means either both the new C-H bond and the new C-OH bond are made to the top or to the bottom of the C=C bond

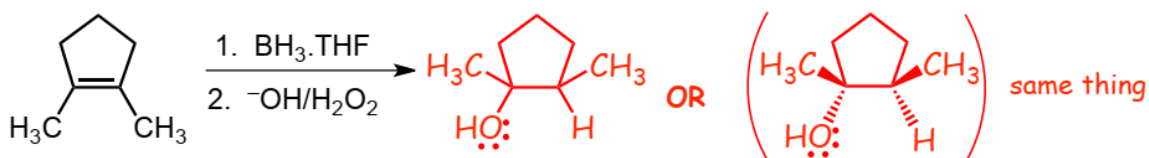


- the result in this case is that the two -Me groups are *cis*- with respect to each other in the product
- And so, if stereoisomers **can form** then the reaction will be **stereospecific**

Examples



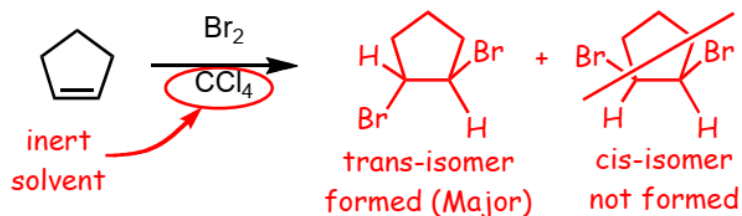
- This reaction is ANTI-MARKOVNIKOV (**regiospecific**), the -OH adds to the least substituted end of the C=C
- There are NO REARRANGEMENTS because there is no cation intermediate
- The **addition is Syn-** but in this case you **can't tell**, there is **no possibility of forming stereoisomers**



- This reaction is ANTI-MARKOVNIKOV (**regiospecific**), the -OH adds to the least substituted end of the C=C
- The **addition is SYN-** AND in this case **you can tell** because only the **cis-stereoisomer is formed** (note the two different and equally correct ways of specifying the stereochemistry in the ring)

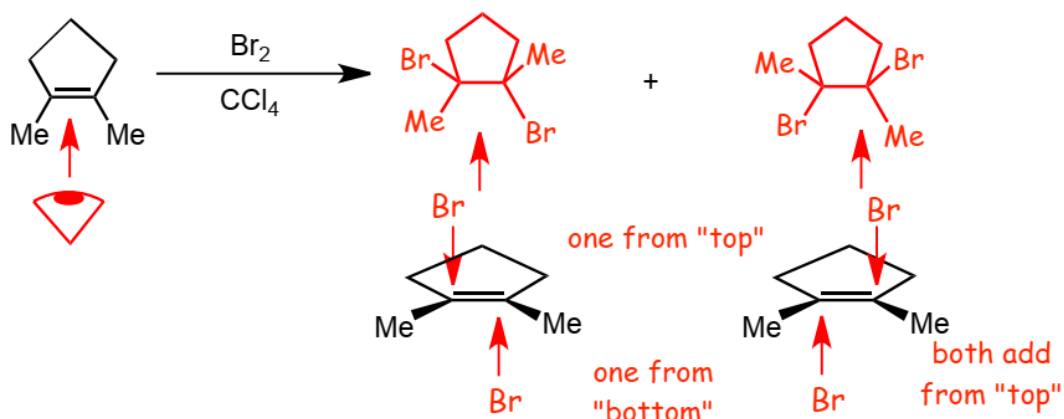
4.6 Addition of Halogens

Example of the Reaction



- the reaction is **stereospecific due to Anti-addition**, the *trans*-product is formed in preference to the *cis*-
- CCl₄ - carbon tetrachloride - inert nonpolar solvent (doesn't get involved in the reaction)

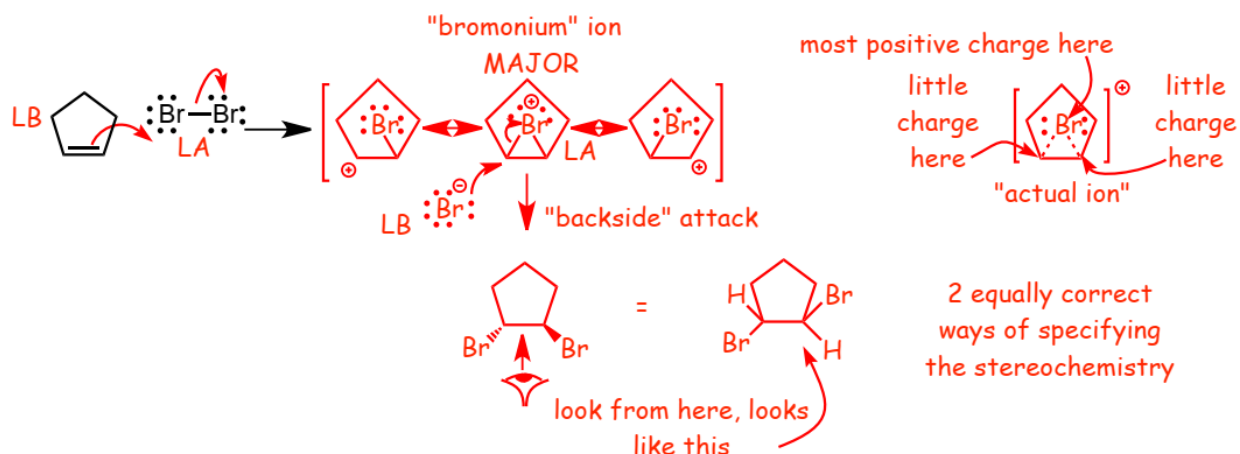
What is Anti-addition? (anti = opposite, as in the Newman projection)



the two trans-dibromocyclopentanes are actually isomers of each other, they represent a form of stereoisomer we have not met yet, and so until we learn about this form of stereoisomerism you could draw either one or the other of these as the product of this reaction

- How does **anti-addition** occur? We need to explain this product distribution - need a **mechanism!**

The Mechanism

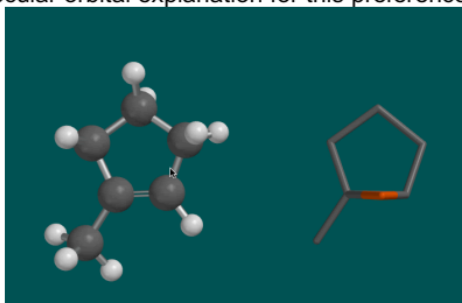


- **Anti-addition**, bromines add to **opposite** sides of the C=C double bond (top and bottom)
- **Note: There are two ways** of specifying the stereochemistry on rings, *trans*- in this case
- **Note:** Because of bromonium ion intermediate (no "free" carbocation) there are no rearrangements - we will use this information later!

A Closer look at "backside" attack: two possible transition states, hard to form partial bonds when both Br are on the same side, when both bromines are on "top", not enough "room" to make partial bonds

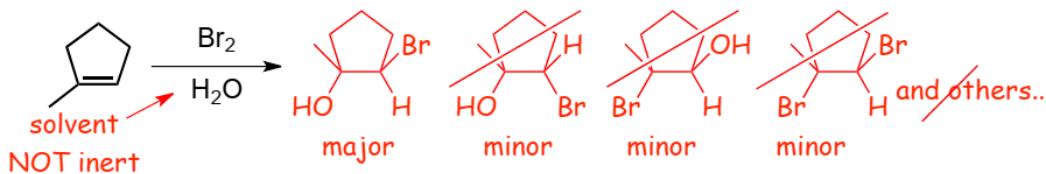


- we will look at a much better molecular orbital explanation for this preference later in the course



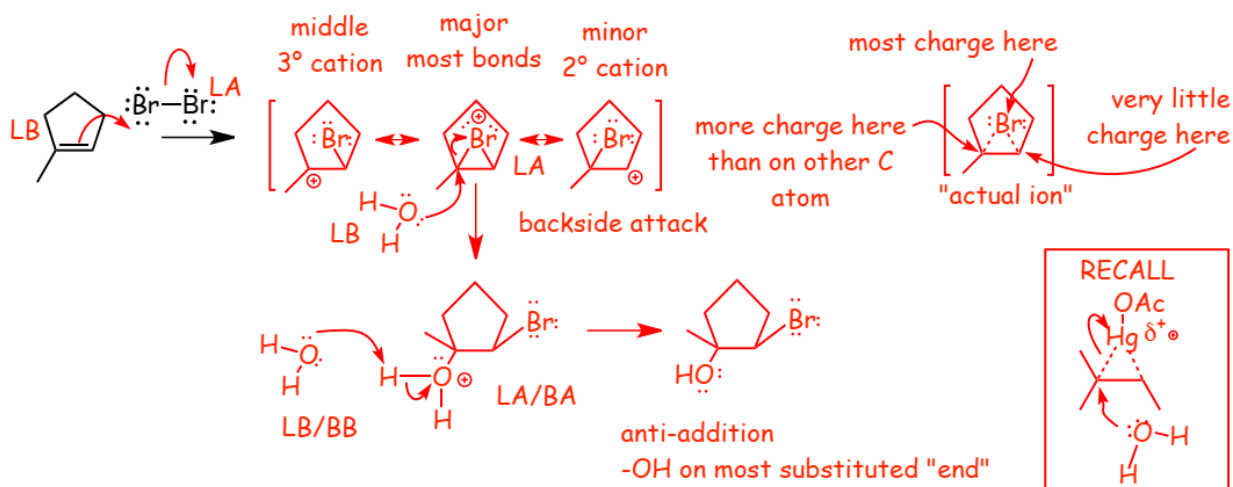
Visualize Backside Attack on a Bromonium Ion

An Example Reaction

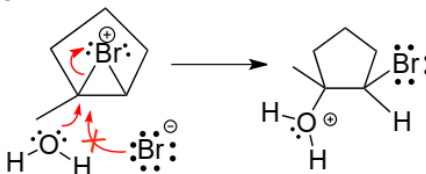


- There are lots of possibilities, mainly one product, to explain need the **mechanism**
- Actually, there is one more major isomer, but we will learn about that one later.....)
- The key point here is that the **solvent water** is a potentially reactive (weak Lewis base) and **does participate**

The Mechanism



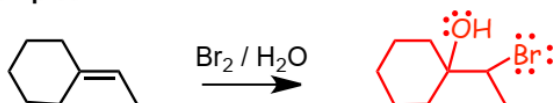
- We already decided that water was too weak an acid to react with the alkene in the first step
- Water also a weak Lewis base, but the carbocation is a strong Lewis acid, thus the 2nd step
- Water attacks the MOST SUBSTITUTED side of the bromonium ion because this carbon carries the largest partial positive charge, this reaction is FASTEST, this reaction is KINETICALLY CONTROLLED
- The last step is driven by entropy again



H₂O "wins" because its concentration is MUCH higher

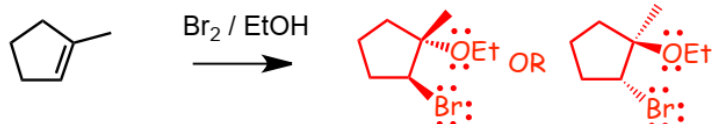
- Br⁻ ion is still present, but the water present at MUCH higher concentration (ca. 55M!!), so it adds in the second step instead of the bromide anion, the steady-state concentrations of intermediates tends to be very low in organic reactions, the bromide concentration is low, the water concentration is high

Examples



ANTI-addition although in this case you can't tell

addition of -Br and -OH
bromonium ion intermediate



ANTI-addition and you CAN tell in this case trans-isomer

either answer is OK for now, we will learn the difference later

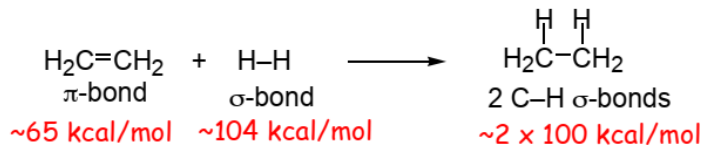
Some **heuristics** that you should expect to develop for these reactions:

- 1) These are ADDITION reactions of -Br and -Br (or a solvent molecule such as -OH, or generically -OR) across the C=C bond
- 2) These reactions are **STEREOSPECIFIC** (anti-addition, which will give trans-products where appropriate)
- 3) These reactions are **REGIOSPECIFIC** (-OH or -OR adds to most substituted end of the C=C bond where appropriate)
- 4) These reactions proceed via a BROMONIUM ION and therefore there will be no rearrangements

4.7 Addition of Hydrogen: Reduction

In organic chemistry:

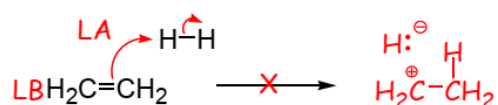
- **REDUCTION** is addition of hydrogen or removal of oxygen atoms
- **OXIDATION** is addition of oxygen or removal of hydrogen atoms



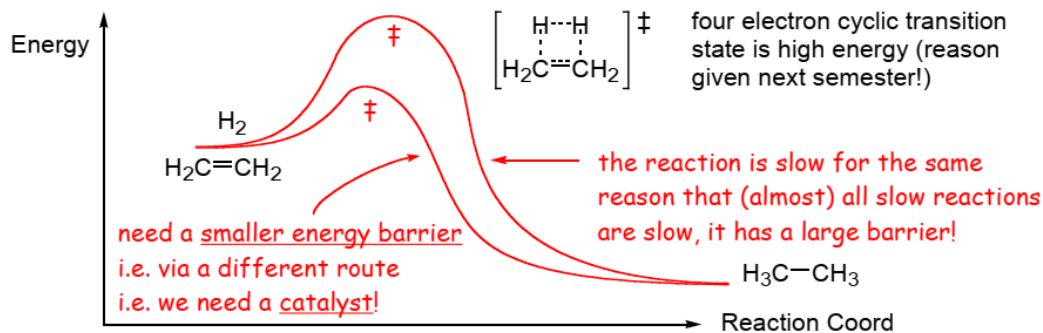
- The reaction is exothermic by ~ 30 kcal/mol, but, it is **very slow**.

Q. Why is this?

A. There is no good (Lewis acid/base) mechanism to do the reaction.



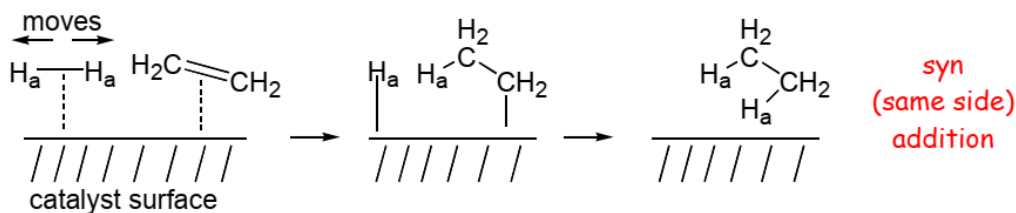
- H_2 is a poor Lewis acid, hydride (H^-) is a very unstable anion (hydrogen is not electronegative), this reaction does not occur!
- An alternate concerted mechanism isn't any better.



Heterogeneous Catalysis: Reaction occurs on the surface of a solid. Almost all of our reactions take place in a solvent, everything is dissolved, everything is in one (liquid) phase, it is HOMOGENEOUS. If we use a metal catalyst, the solid metal is not dissolved, we have more than one phase, the system is HETEROGENEOUS.

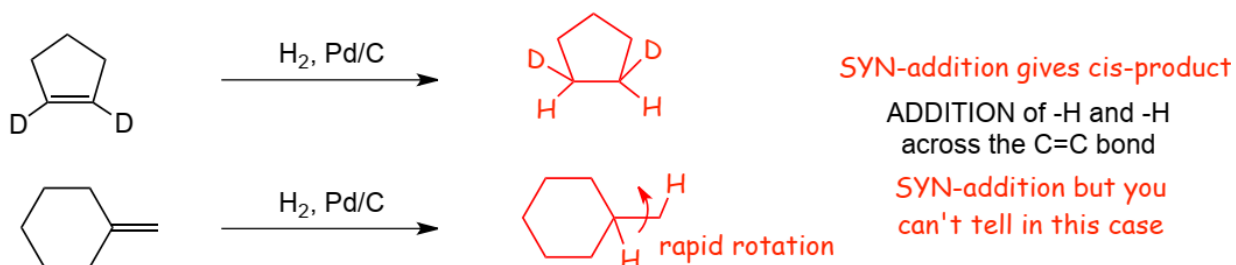
- several catalysts are useful...
 - Pt (platinum metal)
 - Raney Ni (finely divided nickel)
 - Pd/C (palladium on charcoal particles)

The (unusual) Mechanism



- Both H_2 and alkene bind to surface, weakening the H-H and C=C bonds
- This is **not** a Lewis acid/base mechanism, it is difficult to draw and curved arrow-pushing does not work
- The reaction occurs on the **surface** of the solid state catalyst, which is why both H atoms add to the alkene from the **same side**, resulting in **syn**-addition, the reaction is **stereospecific**.

Examples



- The reaction is **stereospecific**, "SYN"-addition, both H-'s add to the SAME SIDE of the C=C bond
- There are a series of mainly oxidation reactions that we need to complete our survey of alkene chemistry.

Some **heuristics** that you should expect to develop for these reactions:

- This is an **addition** reaction of -H and -H to a C=C bond
- The reaction proceeds with **syn-addition**, **cis**-stereoisomers will be formed where appropriate
- The reaction does not proceed via carbocation intermediates, there will be no rearrangements

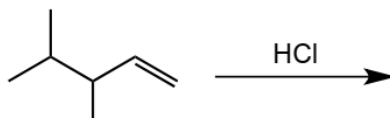
4.8 Learning the Reactions: Algorithmic approach and Heuristic approach

This new material on reactions can be somewhat confusing at first, and it is worth taking some time to talk about how to learn it. You need to be able to do the following:

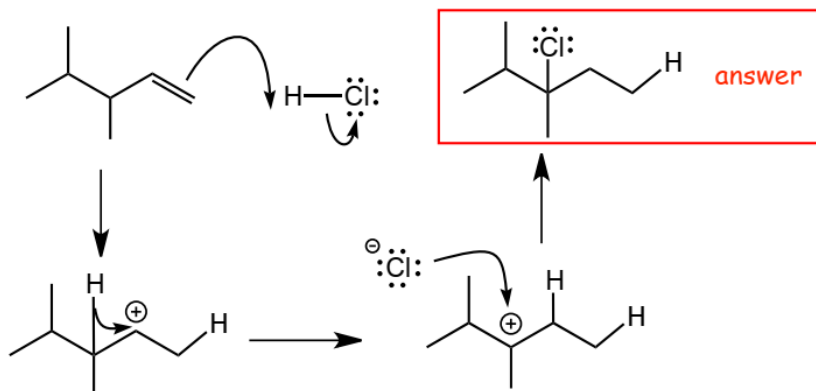
- You need to be able to give the product of a reaction when the reactant and reagents/conditions are provided
- You need to be able to provide the reagents/conditions when given a reactant and a product

You can solve these problems algorithmically or heuristically

Example Problem 1: Provide the product of the following reaction:



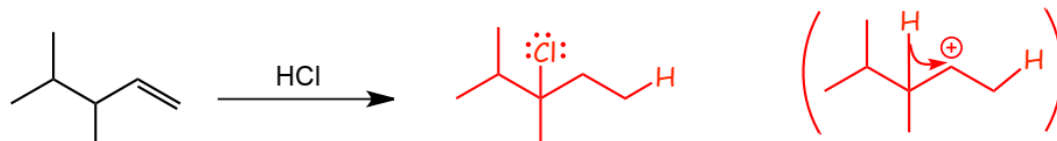
The algorithmic approach to solving this problem involves writing out the entire mechanism. If you don't make any mistakes in the mechanism (the algorithm), then you **MUST** get the correct answer:



However, **most chemists would not solve the problem using the algorithmic approach**, it just takes too long, and after working with the reactions for some time you start to **develop heuristics that allow you to "jump" to the answer without writing out the entire mechanism**, using your pre-existing information. It is important to develop **heuristics** for these reactions so that you can solve problems quickly.

The heuristic approach to solving THIS reaction problem is:

- This is an ADDITION reaction, addition of -H and -Br across the C=C bond
- This is Markovnikov-type addition where appropriate
- The reaction proceeds via a carbocation intermediate and so we need to look for possible rearrangements
- This reaction is not stereospecific, although that is not relevant here anyway

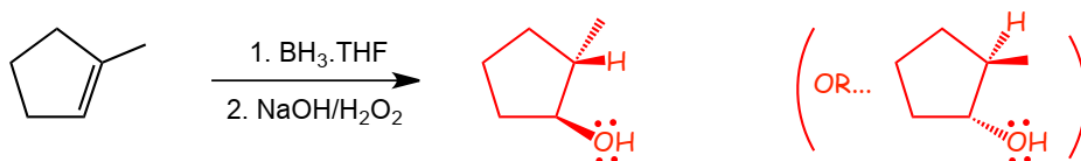


• **Note** that the mechanism wasn't drawn out, just the critical first cation intermediate so that the rearrangement could be identified and not missed

Example Problem 2: Provide the product of the following reaction:

Using the **heuristics approach** instead:

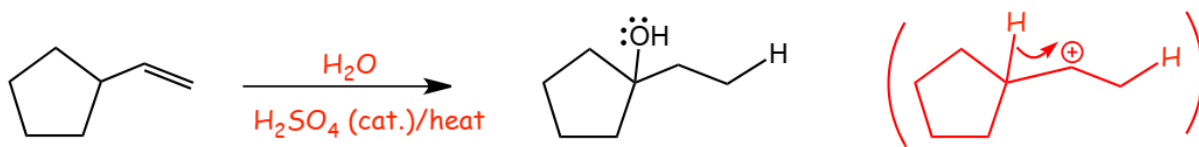
- 1) This is an **addition** reaction, addition of -H and -OH across the C=C bond
- 2) This is **ANTI-Markovnikov** addition and there will be no rearrangements because the reaction does not proceed via a carbocation intermediate
- 3) This reaction **stereospecific**, the -H and -OH need to be on the same side in the product since cis/trans stereoisomers are possible here



Example Problem 3: Provide the **reagents** and **conditions** for the following reaction:

Using the **heuristic approach** instead:

- 1) This is an **addition** reaction of -H and -OH (H_2O) across the C=C bond
- 2) There was a **rearrangement**, therefore the reaction must have proceeded via a carbocation intermediate
- 3) Stereochemistry is irrelevant
- 4) This must be **Bronsted** acid catalyzed addition of H_2O , using a Bronsted acid such as H_2SO_4

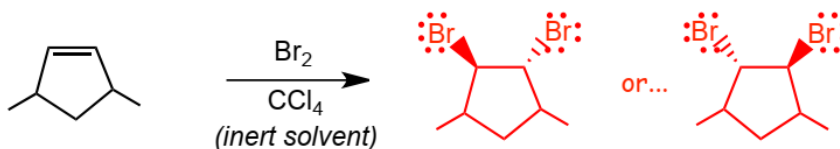


It is **important to develop heuristics** to solve these kinds of reaction problems quickly, but remember, heuristics, by definition, **are not memorized**, they are developed **individually** by working with the material and working the problems.

Example Problem 4: Provide major organic product of the following reaction:

Using the **heuristic approach**:

- 1) This is an **addition** reaction of -Br and -Br (Br_2) across the C=C bond
- 2) The intermediate is the **bromonium ion**, not a carbocation intermediate, therefore no rearrangements
- 3) The solvent does **not** participate in the reaction (it is inert)
- 4) This addition reaction is stereospecific: **anti-**



It is **important to develop heuristics** to solve these kinds of reaction problems quickly, but remember, heuristics, by definition, **are not memorized**, they are developed **individually** by working with the material and working the problems.

5 Reaction Summary

Do not start studying by trying to memorize the reactions here!

Work as many problems as you can, with this list of reactions in front of you if necessary, so that you can get through as many problems as you can without getting stuck on eth reagents/conditions, and so that you can learn and practice solving reaction problems. Use this list AFTER you have worked all of the problems, and just before an exam. By then you will have learned a lot of the reagents/conditions just by using them and you will only have to memorize what you haven't learned yet. Then do the following:

- Cover the entire page of reagents/conditions with a long vertical strip of paper, see if you can write down the reagents/conditions for each reaction, check to see which you get correct, if COMPLETELY correct, circle Y, if incorrect or even slightly incorrect, circle N. In this way, you keep track of what you know and what you don't know.
- Keep coming back to this list and do the same thing only for those reactions you circled N, until all are circled Y.
- Knowing the reagents/conditions on this page is INSUFFICIENT to do well on an exam since you will ALSO need to recognize how to use and solve reaction problems in different contexts, this page ONLY helps you to learn the reagents/conditions that you have **not yet** learned by working problems.

