Alkenes

Electrophilic Addition

1 Alkene Structures

- The \( \pi \)-bond is weaker than the sigma-bond.
- The \( \pi \)-electrons in the \( \pi \)-bond are higher in energy than those in the \( \sigma \)-bond.
- The \( \pi \)-electrons in the \( \pi \)-bond are more chemically reactive than those in the \( \sigma \)-bond.

How do you break a \( \pi \)-bond?

- The alkene uses the electrons in the \( \pi \)-bond when it reacts as a Lewis Base/nucleophile.

• 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 \( \pi \)-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 AOs, the \( \pi \)-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

\[
\text{CH}_3-\text{CH}≡\text{CH}-\text{CH}_2-\text{CH}_3 \quad 2\text{-pentene}
\]

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

\[
\begin{align*}
\text{3-propyl-1-heptene} & \quad \text{build name "in pieces"} \\
\end{align*}
\]

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

\[
\begin{align*}
\text{cyclohexene} & \quad \text{bromine gets 4 alphabetically} \\
\end{align*}
\]

• 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).
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?

\[ \Delta H_{\text{rxn}} = H(\text{alkane}) - (H(\text{alkene}) + H(H_2)) \]

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 Sayetzeff (or Zaitsev) rule**

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Why are more substituted alkene isomers more stable?

**Answer #1:** More substituted alkenes tend to have more bonds to sp2 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**

\[ \text{reactant} \xrightarrow{\text{HBr, CCl}_4} \text{major product} + \text{minor side product} \]

**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 regiospecific.
- The minor product would be a side product of the reaction.
- The mechanism explains the regiospecificity (i.e. why the major product is the major product).

**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:

\[ \text{reactant} \xrightarrow{\text{H-Cl, CCl}_4} \text{major product} + \text{minor side product} \]

**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 Regiospecific, 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 regiospecific (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:

\[
\text{alkene} \quad \text{H}_2\text{O} \quad \text{H}_2\text{SO}_4 \quad \text{heat} \quad \text{alcohol}
\]
• This reaction GOES, the product is **Markovnikov**, i.e. the reaction is again **regiospecific**.
  • The $\text{H}_2\text{SO}_4$ 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, $\text{H}_3\text{O}^+$

\[
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+
\]

- Step 1, $\text{H}_3\text{O}^+$ is a MUCH stronger Lewis (and Bronsted) acid than $\text{H}_2\text{O}$ (it wants electrons more).
- Step 2, $\text{H}_2\text{O}$ is a weak Lewis base, **BUT thecation it reacts with is a STRONG Lewis acid (it is a cation).**
- Step 3, breaks one $\text{O-H}$ bond and makes one (essentially the same) $\text{O-H}$ bond. This is 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**

\[
\text{PhCH} = \text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{PhCH} = \text{CH}_2 - \text{OH}
\]

- **Note:** again, we did **not write** the entire mechanism, we just added the $-\text{H}$ and the $-\text{OH}$ across the C=C bond, with $-\text{OH}$ 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 $-\text{OH}$ to the most substituted carbon

**Is the Reaction Stereospecific?**

\[
\text{H}_2\text{O} \rightarrow \text{trans} + \text{cis}
\]

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

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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.

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

[Diagram: Reaction Mechanism]

**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

![Overall Reaction Diagram]

**Important:** The 1... 2... notation means, FIRST add Hg(OAc)\(_2\)/H\(_2\)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 Hg(OAc)\(_2\) will simply react with the Lewis base NaBH\(_4\) and not with the alkene
- **First** add H\(_2\)O/Hg(OAc)\(_2\), WAIT until that reaction is complete, **SECOND**, add NaBH\(_4\) to remove the HgOAc

**Examples**

- Using Hg(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 H\(_2\)O/Hg(OAc)\(_2\) followed by NaBH\(_4\) and not simply H\(_2\)O with Bronsted acid
- The Bronsted acid catalyzed reaction is usually very slow anyway and is rarely used for this reason

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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 add 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$_2$O is replaced with CH$_3$OH, the alcohol methanol.
- Methanol (CH$_3$OH) 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 -OCH$_3$ adds to the most substituted end of the C=C bond, the major product is the Markovnikov product.
Example Reactions

- **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?

  1. H$_2$O/Hg(OAc)$_2$
  2. NaBH$_4$

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

**New Lewis acid reagent**

\[
\begin{align*}
\text{B} & \quad 1s^2 \quad 2s^2 \quad 2p^1 \\
\text{BH}_3 & \quad \text{borane}
\end{align*}
\]

- 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)

  THF tetrahydrofuran $\xrightarrow{\text{LA}}$ BH$_3$.THF

- BH$_3$.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 BH3.THF, WAIT until that reaction has completed, second, add the -OH/H2O2 (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 BH3 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"
- The 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

1. BH₃·THF
2. −OH/H₂O₂

• 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

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.

Examples

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

\[
\begin{align*}
\text{H}_2\text{C}=\text{CH}_2 \quad + \quad \text{H}^- \quad \rightarrow \quad \text{H}_2\text{C}-\text{CH}_2
\end{align*}
\]

- The reaction is exothermic by \( \approx 30 \text{ kcal/mol} \), but, it is very slow.
- Q. Why is this?
  - A. There is no good (Lewis acid/base) mechanism to do the reaction.

- \( \text{H}_2 \) is a poor Lewis acid, hydride (\( \text{H}^- \)) 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 \( \text{H}_2 \) 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 form 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.

Some heuristics that you should expect to develop for this reactions:
1) This is an addition reaction of -H and -H to a C=C bond
2) The reaction proceeds with syn-addition, cis-stereoisomers will be formed where appropriate
3) The reaction does not proceed via a 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:
  1) You need to be able to give the product of a reaction when the reactant and reagents/conditions are provided
  2) 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:
1) This is an ADDITION reaction, addition of -H and -Br across the C=C bond
2) This is Markovnikov-type addition where appropriate
3) The reaction proceeds via a carbocation intermediate and so we need to look for possible rearrangements
4) This reaction is not stereospecific, although that is not relevant here anyway
• Note that the mechanism wasn't draw 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\(_2\)O) 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\(_2\)O, using a Bronsted acid such as H\(_2\)SO\(_4\)

**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 the 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.

- HCl/CCl₄
- H₂O
- Br₂
- Br₂
- 1. Hg(OAc)₂/H₂O
- 2. NaBH₄
- 1. Hg(OAc)₂/CH₃OH
- 2. NaBH₄
- 1. BH₃-THF
- 2. H₂O₂/NaOH
- H₂
- Pd/C

(±) other possible catalysts: Pt, Raney Ni

specifying the inert solvent is optional
rearrangements are possible, cation intermediate

Y / N

Y / N

Y / N

Y / N

Y / N

Y / N

Y / N

Y / N

Y / N

Y / N

Y / N

Y / N