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

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**

\[
\begin{align*}
\text{CH}_3\text{-CH=CH-CH}_2\text{-CH}_3 & \quad \text{2-pentene} \\
1 & 2 & 3 & 4 & 5
\end{align*}
\]

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

\[
\begin{align*}
\begin{array}{c}
\text{6} & 4 & 3 & 2 & 1 \\
\text{7} & 5 & 2 & 1 & \text{3-propyl-1-heptene}
\end{array}
\quad \begin{array}{c}
\text{8} & 7 & \text{Br} \\
\text{6} & 5 & \text{4} & 3 & \text{2} & \text{1} \\
\text{1} & \text{2} & \text{3} & \text{4} & \text{5} & \text{6} & \text{7} & \text{8} & \text{7-bromo-5-ethyl-3-methyl-(3E)-octene}
\end{array}
\end{align*}
\]

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

\[
\begin{align*}
\text{cyclohexene} & \\
\begin{array}{c}
\text{1} & \text{2} & \text{3} & \text{4} & \text{5} & \text{6} \\
\text{Cl} & \text{Br} & \text{4-bromo-5-chlorocyclohexene}
\end{array}
\end{align*}
\]

• 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)

\[
\begin{align*}
\text{(2E, 4E)-hexadiene}
\end{align*}
\]

• Use diene, triene for 2, 3 double bonds, etc.
• Note the name is hexadiene, not hexdiene (do not omit the "A" before diene etc.).
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?

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

- 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 binds 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 us less electron repulsion, lower energy electrons.

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### 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**

![Reaction diagram]

- **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:

- **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....

[Diagram showing carbocation rearrangements]

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 (H$_2$O).

- 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 H$_2$O does NOT give an alcohol (in any reasonable timeframe).

However:

\[
\text{alkene} \xrightarrow{\text{H$_2$O}} \text{alcohol}
\]
• 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, $\text{H}_3\text{O}^+$

$$
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \leftrightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+
$$

- **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 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 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**

$$
\begin{align*}
\text{H}_2\text{SO}_4 \text{(cat.) } / \text{heat} & \quad \rightarrow \\
\text{H}_2\text{O} & \quad \rightarrow \\
\text{alcohol} & \quad \text{Markovnikov product}
\end{align*}
$$

• **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?**

$$
\begin{align*}
\text{H}_2\text{O} \text{(cat.) } / \text{heat} & \quad \rightarrow \\
\text{H}_2\text{SO}_4 & \quad \rightarrow \\
\text{trans-} & \quad \text{cis-}
\end{align*}
$$

• 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.