Introduction to Alkenes

- Alkenes or olefins are organic compounds with C=C bonds
- The C=C consists of overlap between two sp² hybrid orbitals (σ bond) and two unhybridized p orbitals (π bond)
- The C=C bond has a dissociation energy of 146 kcal
- This is the result of 83 kcal for the σ bond and 63 kcal for the π bond

Orbital Description of π Bond

Elements of Unsaturation in Hydrocarbons

- The general molecular formula for an alkane is CₙH₂ₙ₊₂
- The general molecular formula for an alkene is CₙH₂ₙ
- A double bond is considered an element or degree of unsaturation
- Other elements of unsaturation include rings and triple bonds
- The number of degrees or elements of unsaturation can be calculated
- Example
  - C₄H₆, if this were completely saturated, it would be C₄H₁₀
  - H₁₀ - H₆ = H₄ or 2 H₂ = 2 degrees or elements of unsaturation present
  - This could be two rings, two C=C, or one triple bond
Elements With a Non-carbon Atom Present
- Heteroatoms are any non-carbon atoms
- For example, halogens, oxygen, and nitrogen count as heteroatoms
- Consider C₈H₉Cl₃
- Halogens count as hydrogens, so formula becomes C₈H₁₂
- If this were completely saturated C₈H₁₈
- H₁₈ – H₁₂ = H₆ or 3 H₂ = 3 degrees of unsaturation
- This could be three C=C, or three rings, etc.

Elements of Unsaturation with Oxygen
- Oxygen usually forms two bonds, and does not change the number of hydrogen or carbon atoms possible
- Therefore, the oxygens can be ignored in the calculation
- C₄H₈O becomes C₄H₈
- If this were completely saturated, it would be C₄H₁₀
- H₁₀ – H₈ = H₂ or 1 degree of unsaturation

Elements of Unsaturation with Nitrogen
- Unlike carbon, nitrogen can only form three bonds
- This means that is one less hydrogen atom present in a molecule with nitrogen present
- When nitrogen is present, subtract one hydrogen atom from the formula
- C₄H₉N becomes C₄H₈
- If completely saturated, C₄H₁₀
- H₁₀ – H₈ = H₂ or 1 degree of unsaturation
IUPAC Nomenclature for Alkenes

- Find the longest continuous chain with C=C
- Number the chain so that the C=C gets the lowest location number
- Take the parent alkane name, drop the –ane and add –ene
- The location number of the C=C must be included in the name
- All alkyl branches are named as before
- All rules which apply to hyphons and dashes still apply

Example

- Consider the molecule shown below

```
CH₃CH=CHCH₂
   CH₃
CH₃
CH₃
1 2 3 4 5 6
```

- Number from the end closest to the C=C

```
CH₃CH=CHCH₂
   CH₃
CH₃
CH₃
1 2 3 4 5 6
```

- 5,5-Dimethyl-2-hexene

Rules for Cyclic Alkenes

- Number C=C so that it falls between C1 and C2
- Number so that the substituents get the lowest location numbers possible

```
3,5-Dimethylcyclohexene
```

```
2-Ethyl-1,3-cyclohexadiene
```
Cis/Trans Isomers

- Alkenes can exist as stereoisomers
- These isomers are also geometric isomers or cis/trans isomers
- They exist because there is no free rotation about the C=C bond

\[
\begin{align*}
\text{CH}_3\text{CH}=&\text{CH}_2 & \text{CH}_3\text{CH}=&\text{CH}_3 \\
\text{A} & \neq \text{B} & \text{A} & \neq \text{D} \\
\text{C} & = \text{D} & \text{B} & = \text{C} \\
\end{align*}
\]

No isomers

<table>
<thead>
<tr>
<th>Trans</th>
<th>Cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{CH}=&amp;\text{CH}_2)</td>
<td>(\text{CH}_3\text{CH}=&amp;\text{CH}_3)</td>
</tr>
</tbody>
</table>

Entgegen and Zusammen

- When the C=C bond is tri and tetra substituted, new rules apply
- We must assign a priority to each group attached to the C=C
- We will use the Cahn-Ingold-Prelog rules
- Divide the C=C in half and assign a priority to each group on each side
- Then compare the high priority groups on each side
- When the high priority groups are on the same side of C=C, this is zusammen
- When the high priority groups are on opposite sides, this is entgegen

<table>
<thead>
<tr>
<th>Zusammen</th>
<th>Entgegen</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{W} \neq \text{Z})</td>
<td>(\text{W} = \text{Z})</td>
</tr>
</tbody>
</table>

Cahn-Ingold-Prelog Rules

- The atoms that are attached directly to the C=C are ranked according to their atomic number
- The higher the atomic number, the higher the priority
- \(\text{I} > \text{S} > \text{O} > \text{N} > ^{13}\text{C} > ^{12}\text{C} > \text{Li} > \text{H}\)

\[
\begin{align*}
\text{Br} & \neq \text{Cl} \\
\text{CH}_3 & = \text{H}_2 \\
\end{align*}
\]
Cahn-Ingold-Prelog Rules

• When there are ties, the next atom along the chain is used to determine priority

\[
\begin{align*}
\text{H} & > \text{Br} > \text{Cl} > \text{CH}_3 > \text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{CH}_3
\end{align*}
\]

Cahn-Ingold-Prelog Rules

• Double and triple bonds are treated as though each were a bond to a separate atom
• Imagine that each π bond is broken and the atoms at both ends are duplicated

\[
\begin{align*}
\text{CO} & \rightarrow \text{O} \quad \text{N} \quad \text{OH} \\
\text{N} & \rightarrow \text{N} \quad \text{C} \\
\text{O} & \rightarrow \text{O} \quad \text{C}
\end{align*}
\]

Problems

• Assign Entgegen or Zusammen to the following molecules

\[
\begin{align*}
\text{Br} & \quad \text{CH}_3 \\
\text{Cl} & \quad \text{H} \\
\text{Br} & \quad \text{CH}_2\text{OH} \\
\text{Cl} & \quad \text{C(CH}_3)_2
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \quad \text{CH}_2\text{OH} \\
\text{Cl} & \quad \text{C(CH}_3)_2 \\
\text{Br} & \quad \text{CH}_2\text{OH} \\
\text{Cl} & \quad \text{CHO}
\end{align*}
\]
Solution

Stability of Alkenes

- Alkene stability is determined by the heat of hydrogenation
- Hydrogen is added across the C=C to give an alkane

\[ \text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3 \]

- The reaction is exothermic
- The more stable the alkene, the less heat released during the reaction

Energy Diagram for Hydrogenation
Degree of Substitution on C=C

- Saytzeff’s Rule states that the more highly substituted double bond is more stable
- Why?
  - As you go from sp³ to sp² to sp hybridization, the carbon becomes more electronegative
  - This change in electronegativity is due to the increase of s character in the orbitals
  - More s character means electrons are held more tightly by the atom
  - More substitution is needed to donate electron density into the bond
  - Alkyl groups donate electron density by inductive effects and hyperconjugation

Sp³-Sp² vs. Sp³-Sp³

- Bonds between sp² and sp³ carbons are stronger than bonds between two sp³ carbons
- Why?
  - The bond length is shorter, and this makes a stronger bond
  - Molecules with stronger bonds are more stable

\[
\begin{align*}
\text{sp}^3-\text{sp}^2 & \quad & \text{sp}^3-\text{sp}^2 \\
\text{sp}^2-\text{sp}^2 & \quad & \text{sp}^3-\text{sp}^3 \\
\text{CH}_3-\text{CH}==\text{CH}-\text{CH}_3 & \quad & \text{CH}_3-\text{CH}_2-\text{CH}==\text{CH}_3 \\
\text{2-Butene} & \quad & \text{1-Butene}
\end{align*}
\]

(more stable)  (less stable)

Reaction of Alkenes

- π bonds are not as strong as σ bonds
- The bond dissociation energy for a π bond is 63 kcal/mol and 83 kcal/mol for a σ bond
- π bonds are areas of loosely held electrons
- This suggests that the π bond will be more reactive
- Because of this, most alkene reactions fall into the category of electrophilic additions
- Electrophilic additions involve the reaction of an electron poor species, electrophile, with an electron rich species
Electrophilic Addition to C=C

• Usually HX is a strong acid such as HBr, HCl, or HI

\[ \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CHCH}_3 \]

Only product

• Why not other products?

\[ \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+ \]

Markovnikov’s Rule

• The H⁺ adds to the carbon in the double bond with the most number of hydrogens attached to it
• Another way of saying this: “The rich get richer!”
• This allows for the formation of the most stable cation
• The product which is formed is the Markovnikov product

\[ \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CHCH}_3 \]

Markovnikov Product
Problems

CH₂⁺ + HI →

C₂H₆⁺ + HCl →

C⁺ + HBr →

Carbocations or Carbonium Ions

• Formed when bond to sp³ hybridized carbon breaks heterolytically
• Positive charge forms, carbon becomes sp² hybridized, unhybridized p orbital is empty
• Stabilized by any donation of electron density from neighboring alkyl groups
• This is known as an inductive effect
• The overlap between an empty p orbital and filled hybrid orbitals is called hyperconjugation

Order of Cation Stability

Less stable → More stable
Rearrangements

- One result of a cation intermediate in a reaction is the possibility of rearrangement
- Not all cations rearrange
- Rearrangement only occurs when a more stable cation intermediate can be achieved
- Two types of rearrangements are common
  - 1,2-Hydride shifts
  - 1,2-Methyl shifts

1,2-Hydride Shift

\[
\begin{align*}
\text{CH}_3\text{CH} &= \text{CH} = \text{CH}_2 + \text{HBr} \\
\text{CH}_3\text{CH} &= \text{CH} = \text{CH}_2 & \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{CH}_3\text{CH} &= \text{CH} = \text{CH}_2 & \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{CH}_3\text{CH} &= \text{CH} = \text{CH}_2 & \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C}
\end{align*}
\]

Minor product | Major product

1,2-Methyl Shift

\[
\begin{align*}
\text{CH}_3\text{CH} &= \text{CH} = \text{CH}_2 + \text{HBr} \\
\text{CH}_3\text{CH} &= \text{CH} = \text{CH}_2 & \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{CH}_3\text{CH} &= \text{CH} = \text{CH}_2 & \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
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\end{align*}
\]

Minor product | Major product
Ring Expansion

- An alkyl shift can occur within a ring
- The ring will expand to create a more stable cation

Problems

Predict the product(s) of reaction between the molecules shown and HCl.

Hammond’s Postulate

- Transition states cannot be observed
- They merely represent energy maxima on a reaction diagram
- How do we take a guess as to the structure of a transition state?
- Hammond’s Postulate states that a transition state resembles the structure of the nearest (energetically) stable species.
- Transition states for endergonic reaction steps resemble products
- Transition states for exergonic reaction steps resemble reactants
Hammond’s Postulate and Alkenes

- How does Hammond’s Postulate relate to addition of electrophiles to alkenes?
- The protonation of an alkene is an endergonic step
- The transition state will resemble the product of this step which the cation intermediate
- The transition state which leads to the formation of a more stable cation will have a lower energy
- A lower energy transition state leads to a faster reaction

Energy Diagrams