Chapter 8 - Alkenes and Alkynes II

8.1 - Addition Reactions of Alkenes
- Electrons in the \( \pi \) bond of alkenes react with electrophiles

8.2 - Electrophilic Addition of Hydrogen Halides to Alkenes: Mechanism and Markovnikov’s Rule
- Hydrogen halides can add to the double bond of alkenes
- The order of reactivity of the hydrogen halides in alkene addition is \( \text{HI} > \text{HBr} > \text{HCl} > \text{HF} \)
- Markovnikov's rule states that in the addition of \( HX \) to an alkene, the halide atom adds to the carbon atom of the original double bond with the fewer amount of hydrogen atoms. The hydrogen of \( HX \) will bond to the carbon atom of the greater amount of hydrogen atoms. This is precisely the same thing as stabilizing a carbocation intermediate by having the nucleophile go to the more substituted carbon
- More accurately, the negative portion of an unsymmetrical ionic addition reagent will bond to the carbon of the double bond with the fewer amount of hydrogen atoms while the more positive reagent will restore the stability of the carbocation
- Note that this is \textit{not} in water. Typically, this will happen when the solvent is not listed

8.3 - Stereochemistry of the Ionic Addition to an Alkene
- The enantiomers are produced in equal amounts because the carbocation is trigonal planar

8.4 - Addition of Sulfuric Acid to Alkenes
- Adds a hydroxide group onto the alkene via Markovnikov’s Rule

Allyl and Benzyl Carbocations
- Resonance can stabilize a product

- Revised Carbocation Stability Trend:
Methyl < Primary < Secondary \( \approx \) Primary allylic \( \approx \) Primary benzylic < Tertiary \( \approx \) Secondary allylic \( \approx \) Secondary benzylic < Tertiary allylic \( \approx \) Tertiary benzylic
8.5 - Addition of Water to Alkenes: Acid-Catalyzed Hydration
- Note how this, too, follows Markovnikov’s Rule
- HX in H₂O is the same as H₃O⁺ because HX will be a strong acid (except for HF), and the solvent is in larger quantities. An analogous reaction will occur with CH₃OH that will add OCH₃ because of HX dissociation

- Rearrangements occur in alkene hydration because the first step is the formation of a carboxcation, so this will be rearranged to a more stable position. Example shown below:

8.6 - Alcohols from Alkenes through Oxymercuration-Demercuration: Markovnikov Addition
- The first step, known as oxymercuration, has the water and mercuric acetate adding to the double bond
- The second step, known as demercuration, has sodium borohydride reduce the acetoxymercury group and replace it with hydrogen (note: OAc is acetate)
- Oxymercuration-demercuration follows Markovnikov’s Rule
- Rearrangements rarely occur in oxymercuration-demercuration reactions
- The net result of oxymercuration-demercuration is anti addition of H and OH
8.7 - Alcohols from Alkenes through Hydroboration-Oxidation: Anti-Markovnikov Syn Hydration
- The use of B\textsubscript{2}H\textsubscript{6} or a solution of BH\textsubscript{3}-THF can cause Anti-Markovnikov hydration of a double bond
- The addition of a boron atom and a hydrogen atom to a double bond is called \textit{hydroboration}
- Hydroboration-oxidation takes place with syn stereochemistry
- After hydroboration, the alkylborane intermediate is oxidized and hydrolyzed to an alcohol and boric acid

8.8 - Hydroboration: Synthesis of Alkylboranes, 8.9 - Oxidation and Hydrolysis of Alkylboranes
- In each addition step, the boron atom becomes attached to the least substituted carbon due to electronic and steric factors

8.9 - Oxidation and Hydrolysis of Alkylboranes
- The net result of hydroboration-oxidation is anti-Markovnikov addition of water to an alkene in the form of a hydroxyl group and hydrogen (makes an alcohol)
- Hydroboration-oxidation reactions are syn additions for the H and OH
- The hydroxyl group replaces the boron atom where it stands in the alkylboron compound

8.10 - Summary of Alkene Hydration Methods

8.11 - Protonolysis of Alkylboranes
- Hydrogen replaces the boron where it stands in the alkylborane during protonolysis of an alkylborane
- The overall stereochemistry is syn
- Requires heating an alkylborane with acetic acid

8.12 - Electrophilic Addition of Bromine and Chlorine to Alkenes
- Alkenes react rapidly with bromine or chlorine in nonnucleophilic solvents to form vicinal dihalides (anti addition)
- I personally like to think of this reaction as some bad-ass bromines attacking the life out of the carbon-carbon $\pi$ bond. To get the most out of this attack, the bromine atoms attack from opposite sides
8.13 - Stereospecific Reactions

Addition of Bromine to cis- and trans-2-Butene

cis-2-Butene reacts with bromine to yield the enantiomeric 2,3-dibromobutanes by the following mechanism:

trans-2-Butene reacts with bromine to yield meso-2,3-dibromobutane.

8.14 - Halohydrin Formation

- A halohydrin (halo alcohol) is produced when the halogenation of an alkene is carried out in an aqueous solution as opposed to a nonnucleophilic solvent.
- If the alkene is unsymmetrical, the halogen is added to the carbon atom with the greater number of hydrogen atoms (Anti-Markovnikov)
8.15 - Divalent Carbon Compounds: Carbenes

- Carbenes have carbon atoms that only form two bonds

\[ \text{Alkene} + \text{CH}_2 \rightarrow \text{Carbenoid} \]

8.16 - Oxidation of Alkenes: Syn 1,2-Dihydroxylation

- 1,2-diols (glycols) can be produced using OsO\(_4\) or, less commonly, KMnO\(_4\)
- This is a syn addition

8.17 - Oxidative Cleavage of Alkenes

- O\(_3\) or KMnO\(_4\) can perform oxidative cleavage of alkenes
- Hot, basic KMnO\(_4\) cleaves the double bond of an alkenes. Disubstituted alkene carbons are oxidatively cleaved to ketones while unsubstituted alkene carbons are oxidized to carbon dioxide
- Ozone is the best method to cleave alkenes (ozonolysis)
8.18 - Electrophilic Addition of Bromine and Chlorine to Alkynes
- Alkynes show the same kind of haloaddition as alkenes (anti addition)
- Addition may occur once or twice depending upon the molar equivalents of the halogen

8.19 - Addition of Hydrogen Halides to Alkynes
- Alkynes react with one molar equivalent of HX to form haloalkenes, and with two molar equivalents to form geminal dihalides
- This follows Markovnikov’s Rule

8.20 - Oxidative Cleavage of Alkynes

8.21 - How to Plan a Synthesis
- Practice, practice, practice! Read the textbook for information
### Reaction Summary:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Summary</th>
<th>Conditions</th>
<th>Electrophile</th>
<th>Nucleophile</th>
<th>Key Intermediates or Transition State</th>
<th>Regiochemistry</th>
<th>Stereochemistry</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrohalogenation</td>
<td></td>
<td></td>
<td>H → X</td>
<td></td>
<td></td>
<td>Markovnikov</td>
<td>Not controlled</td>
<td>Nu = X or OH</td>
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<tr>
<td>Hydration (acid cat.)</td>
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<td>Cat. HA, H₂O</td>
<td>H – OH</td>
<td></td>
<td></td>
<td>Markovnikov</td>
<td>Not controlled</td>
<td></td>
</tr>
<tr>
<td>Halogenation</td>
<td></td>
<td></td>
<td>X₂</td>
<td></td>
<td></td>
<td>Not applicable</td>
<td></td>
<td></td>
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<tr>
<td>Haloxydrin Formation</td>
<td></td>
<td></td>
<td>X₂, ROH; R = H or C (nucleophilic solvent)</td>
<td></td>
<td></td>
<td>Markovnikov</td>
<td>Anti</td>
<td>Nu = X or OR</td>
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<tr>
<td>Oxymercuration-Demercuration</td>
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<td></td>
<td>(1) Hg(OAc)₂, HOR; THF (R = H or C) (2) NaBH₄, OH⁻</td>
<td></td>
<td></td>
<td>Markovnikov</td>
<td>Not controlled</td>
<td></td>
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<tr>
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<td></td>
<td>(1) BH₃,THF (2) H₂O₂, HO⁻</td>
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<tr>
<td>1,2-Dihydroxylation</td>
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<td></td>
<td>(1) OsO₄ (2) aq NaHSO₃</td>
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<td></td>
<td>Markovnikov</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The generic alkene chosen has a substitution pattern that allows both regiochemistry and stereochemistry of the products to be discerned.

*The products are formed as a mixture of enantiomers in each case.