Chapter 6

1. The Reactions of Alkenes
2. The Stereochemistry of Addition Reactions

Midterm 3, Wednesday March 7

Chapter 5: 5.6 – 5.12 inclusively (5.13, 5.14)
Chapter 6: all sections
Chapter 7: 7.1 – 7.6 (inclusively)
Practice Questions

What is the major product obtained by addition of HBr to the following alkenes

a. 

b. 

c. 
**summary of reactions**

**electrophilic addition; H → element**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Carbocation?</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBr</td>
<td>Yes</td>
</tr>
<tr>
<td>H₂O, H₂SO₄</td>
<td>Yes</td>
</tr>
<tr>
<td>CH₃OH, H₂SO₄</td>
<td>Yes</td>
</tr>
<tr>
<td>1. R₂B-H</td>
<td>No</td>
</tr>
<tr>
<td>2. H₂O₂, HO⁻</td>
<td>No</td>
</tr>
</tbody>
</table>

**hydroboration/oxidation**

**summary of reactions**

**electrophilic addition; element → element**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Intermediate/Transition state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br₂</td>
<td>Nu⁺ (I) halogen addition</td>
</tr>
<tr>
<td>Br₂, H₂O</td>
<td>Nu⁺ (TS) bromohyrin formation</td>
</tr>
<tr>
<td>Peroxyacid</td>
<td>Nu⁺ (TS) epoxidation</td>
</tr>
<tr>
<td>O₃, CH₃SCH₃</td>
<td>O₃⁻ (I) ozonolysis, O₃⁺ (I) ozonide</td>
</tr>
</tbody>
</table>
summary of reactions

Racemic Mixture is Formed from Simple Alkenes

If the reactant does not have an asymmetric center and the reaction forms a product with an asymmetric center, the product will be a racemic mixture.
Racemic Mixture is Formed from Simple Alkenes

If the reactant does not have an asymmetric center and the reaction forms a product with an asymmetric center, the product will be a racemic mixture.

Alkene now has an asymmetric center
Alkene now has an asymmetric center

If the starting compound has an asymmetric center and the reaction forms a product with a new asymmetric center, the product will be a pair of diastereomers.

If the starting compound has an asymmetric center and the reaction forms a product with a new asymmetric center, the product will be a pair of diastereomers.
How many new Asymmetric Centers are formed?

\[
\text{HCl} 
\xrightarrow{\text{syn addition}} \quad \text{new bonds on the same side of the double bond}
\]

\[
\text{HCl} 
\xrightarrow{\text{anti addition}} \quad \text{new bonds on the opposite side of the double bond}
\]
Four Stereoisomers are Obtained if the Reaction Forms a Carbocation Intermediate

The stereoisomers obtained as products depend on the mechanism of the reaction.

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**syn and anti additions: same with acyclic substrates**

\[ \text{syn addition} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad + \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \rightarrow \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{HCl} \]

\[ \text{anti addition} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad + \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \rightarrow \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{HCl} \]

**Same with acyclic substrates**

\[ \text{syn addition} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad + \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \rightarrow \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{HCl} \]

\[ \text{anti addition} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad + \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \rightarrow \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{HCl} \]
Same with acyclic substrates

**syn** addition

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{H} \\
\text{H} \quad \text{Cl}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{H} \\
\text{H} \quad \text{Cl}
\end{array}
\end{align*}
\]

\[\text{HCl} \to \]

**anti** addition

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{H} \\
\text{H} \quad \text{Cl}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{H} \\
\text{H} \quad \text{Cl}
\end{array}
\end{align*}
\]

**syn** addition

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{H} \\
\text{H} \quad \text{Cl}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{H} \\
\text{H} \quad \text{Cl}
\end{array}
\end{align*}
\]

\[\text{HCl} \to \]

**anti** addition

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{H} \\
\text{H} \quad \text{Cl}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \text{H} \\
\text{H} \quad \text{Cl}
\end{array}
\end{align*}
\]

**syn** or **anti** addition?

\[
\begin{align*}
\begin{array}{c}
\text{MCPBA}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{MCPBA}
\end{array}
\end{align*}
\]
epoxidation: *syn* or *anti* addition?

MCPBA

\[
\text{R} \quad (TS)
\]

epoxidation: *syn* or *anti* addition?

MCPBA

\[
\text{R} \quad (TS)
\]
epoxidation: syn or anti addition?

only syn addition

\[ \text{MCPBA} \]

syn or anti addition?

1. BH$_3$ (or 9-BBN)
2. H$_2$O$_2$, HO$^-$
hydroboration/oxidation: *syn* or *anti* addition?

1. BH$_3$ (or 9-BBN)
2. H$_2$O$_2$, HO$^-$

preferred
more stable transition state

only *syn* addition
The Stereochemistry of Hydrogen Addition

addition of H₂ is a syn addition

only syn addition

Syn H₂ Addition Forms Only the Cis Stereoisomers..

The products can also be seen as mirror images.
If the Substituents are the Same, The Cis Stereoisomer gives a *Meso* compound

H$_2$, Pd/C

---

**syn** or **anti** addition?

Br$_2$, CH$_2$Cl$_2$ (solvent)

same for Br$_2$, H$_2$O or Br$_2$, CH$_3$OH

mechanism:
bromonium ion: *anti* addition

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

**mechanism:**

\[
\begin{align*}
\text{Br} & \quad \text{H} \\
\text{Br} & \quad \text{H} \\
\text{Br}^+ & \quad \text{H} \\
\text{Br} & \quad \text{H} \\
\end{align*}
\]

only anti addition

---

bromonium ion: *anti* addition

\[
\begin{align*}
\text{(Z)-2-pentene} & \quad \text{Br}_2, \text{CH}_2\text{Cl}_2 \text{ (solvent)} \\
& \quad \text{Br}_2, \text{CH}_2\text{Cl}_2 \text{ (solvent)} \\
\end{align*}
\]

\[
\begin{align*}
\text{(E)-2-pentene} & \quad \text{Br}_2, \text{CH}_2\text{Cl}_2 \text{ (solvent)} \\
& \quad \text{Br}_2, \text{CH}_2\text{Cl}_2 \text{ (solvent)} \\
\end{align*}
\]
bromonium ion: \textit{anti} addition

\[
\begin{align*}
\text{(Z)-2-pentene} & \xrightarrow{\text{Br}_2, \text{CH}_2\text{Cl}_2 \text{ (solvent)}} \text{same as} \\
\text{(E)-2-pentene} & \xrightarrow{\text{Br}_2, \text{CH}_2\text{Cl}_2 \text{ (solvent)}}
\end{align*}
\]

\textit{Br}_2 \text{ addition is a stereospecific reaction}

\textbf{If the Substituents are the Same, the Cis (or Z) alkene gives is a Meso Compound}

\[
\begin{align*}
\text{(Z)-2-butene} & \xrightarrow{\text{Br}_2, \text{CH}_2\text{Cl}_2 \text{ (solvent)}} \text{enantiomers} \\
\text{(E)-2-butene} & \xrightarrow{\text{Br}_2, \text{CH}_2\text{Cl}_2 \text{ (solvent)}} \text{meso (achiral)}
\end{align*}
\]
Anti Addition to a Cis Isomer Forms
Only the Trans Stereoisomers

Table 6.1 Stereochemistry of Alkene Addition Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type of addition</th>
<th>Stereoisomers formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition reactions that create one asymmetric center in the product</td>
<td>If the reactant does not have an asymmetric center, then a racemic mixture is formed.</td>
<td></td>
</tr>
<tr>
<td>Addition reactions that create two asymmetric centers in the product</td>
<td>If the reactant has an asymmetric center, then unequal amounts of a pair of diastereomers are formed.</td>
<td></td>
</tr>
<tr>
<td>Addition of reagents that form a carbocation intermediate</td>
<td>syn and anti</td>
<td>Four stereoisomers are formed; the cis and trans isomers each form the same products.</td>
</tr>
<tr>
<td>Addition of H₂</td>
<td>syn</td>
<td>cis (\rightarrow) erythro or cis enantiomers*</td>
</tr>
<tr>
<td>Addition of a peroxyacid</td>
<td>syn</td>
<td>trans (\rightarrow) three or trans enantiomers</td>
</tr>
<tr>
<td>Addition of BH₃ or BHR₂</td>
<td>syn</td>
<td></td>
</tr>
<tr>
<td>Addition of Br₂, Br₂ + H₂O, Br₂ + ROH (any reaction that forms a cyclic bromonium or chloronium ion intermediate)</td>
<td>anti</td>
<td>cis (\rightarrow) threo or trans enantiomers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>trans (\rightarrow) erythro or cis enantiomers*</td>
</tr>
</tbody>
</table>

*An acyclic compound forms the erythro enantiomers; a cyclic compound forms the cis enantiomers. If the two asymmetric centers have the same substituents, a meso compound will be formed instead of the pair of erythro or cis enantiomers.
Compounds That Can Be Formed From an Alkene