CHAPTER II LECTURE NOTES FOR ORGANIC CHEMISTRY

REACTIONS OF ALKENES.

IN A WORD, ADDITION
ELECTROPHILES WILL ADD TO THE DOUBLE BOND TO FORM ADDITION PRODUCTS.
THE FORMATION OF 1 NEW σ BOND IS EXOTHERMIC

IN MANY WAYS ADDITION IS THE REVERSE OF ELIMINATION

ADDITION
\[ \text{C} = \text{C} + \text{X-Y} \rightarrow \text{C} - \text{C} - \text{X} - \text{Y} \]

ELIMINATION
\[ \text{C} - \text{C} - \text{X} - \text{Y} \rightarrow \text{C} = \text{C} + \text{X-Y} \]

ELECTROPHILIC ADDITION TO ALKENES

1) STRONG ELECTROPHILES PULL THE ELECTRONS OUT OF A DOUBLE BOND TO FORM A NEW σ BOND

A CARBONATION RESULTS

![Diagram of carbocation formation]

2) THE CARBONATION THEN DOES WHAT CARBONATIONS DO
REACT WITH A NUCLEOPHILE AS IN A SN1 REACTION

\[ \text{C} - \text{C} - \text{X} - \text{Y} + \text{NuCl}^- \rightarrow \text{C} - \text{C} - \text{X} - \text{Y} \]

Example:
\[ \text{HO}_2^- + \text{C} = \text{C} \rightarrow \text{C} - \text{C} - \text{O}_2\text{H} \]

**TABLE 8-1 Types of Additions to Alkenes**

<table>
<thead>
<tr>
<th>C=C</th>
<th>Type of Addition</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[H₂O] hydration</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[H₂], a reduction</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[HOH], an oxidation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[O₂], an oxidation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[O], an oxidation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>halogenation [X₂], an oxidation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>halohydrin formation [HOX], an oxidation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HX addition [HX]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cyclopropanation [CH₃]</td>
<td></td>
</tr>
</tbody>
</table>

*These are not the reagents used but simply the groups that appear in the product.*
ADDITION OF HYDROGEN HALIDES
HYDROGEN HALIDES ADD TO DOUBLE BONDS REGIOSELECTIVELY
A PROTON ADDS FIRST AND FORMS THE MOST STABLE CATION

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} = \text{CH} - \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} = \text{CH} - \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} = \text{CH} - \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} = \text{CH} - \text{CH}_3 \\
\end{align*}
\]

MARKOVNIKOV'S RULE SAYS THAT THE PROTON WILL ADD TO THE CARBON THAT ALREADY HAS THE MOST HYDROGENS - THIS LEAVES THE CATION ON THE CARBON WITH THE MOST CARBONS WHICH IS THE MOST STABLE CATION

\[\text{HCl and HI react the same way}\]

\[
\begin{align*}
\text{\includegraphics[width=0.2\textwidth]{image.png}} & \quad \text{[MARKOVNIKOV PRODUCT]} \\
\end{align*}
\]

FREE RADICAL ADDITION
WITH FREE RADICAL ADDITION OF HBr, THE ELECTROPHILE IS Br₂⁻ IT ADDS THE SAME WAY, BUT IT ADDS FIRST, A H. SECOND THIS RESULTS IN THE ANTI-MARKOVNIKOV PRODUCT (ONLY HBr DOES THIS)

\[\text{HBr + Peroxides + C=C} \rightarrow \text{C} - \text{C} \quad \text{ANTI-MARKOVNIKOV PRODUCT}\]

PEROXIDES ARE OFTEN USED AS FREE RADICAL INITIATORS

\[\text{H - O - O - H} \quad \text{HEAT} \quad 2 \quad \text{H - O} \quad \text{.}\]

\[\text{H - O} \quad \text{+ HBr} \quad \rightarrow \quad \text{H}_2\text{O} \quad \text{+ Br} \quad \text{.}\]

\[\text{Br} \quad \text{+ \quad CH}_3 \quad \text{C} = \text{CH}_2 \quad \rightarrow \quad \text{CH}_3 \quad \text{C} - \text{C} - \text{CH}_2 \quad \text{+ \quad Br} \quad \text{.}\]

OVERALL

\[\text{HBr + H}_2\text{O} + \text{C=C} \rightarrow \text{C} - \text{C} \quad \text{ANTI-MARKOVNIKOV}\]

ADDITION OF WATER: HYDRATION

\[\text{C=} \quad \text{+ H}_2\text{O} \quad \overset{\text{H}^+}{\rightarrow} \quad \text{C} - \text{O}^-\text{H}\quad \text{MARKOVNIKOV PRODUCT}\]

\[\text{HYDRATION} \quad \rightarrow \quad \text{DEHYDRATION}\]
Hydration and dehydration really are reversible. The mechanism is the reverse of Chapter 7.

1) Protonation

\[
\begin{align*}
\text{H}_2\text{O} & \xrightarrow{+H^+} \text{H}^+ + \text{H}_2\text{O}^+ \\
\text{H}_2\text{O} & \xrightarrow{-C-} \text{H}^+ + \text{H}_2\text{O}^+ \\
\text{H}_2\text{O} & \xrightarrow{-C-} \text{H}^+ + \text{H}_2\text{O}^+ \\
\end{align*}
\]

2) Nearest nucleophile attack

\[
\begin{align*}
\text{H}_2\text{O} & \xrightarrow{+OH^-} \text{OH}^- + \text{H}_2\text{O}^+ \\
\text{H}_2\text{O} & \xrightarrow{-C-} \text{OH}^- + \text{H}_2\text{O}^+ \\
\text{H}_2\text{O} & \xrightarrow{-C-} \text{OH}^- + \text{H}_2\text{O}^+ \\
\end{align*}
\]

3) Loss of a H^+ to water

\[
\begin{align*}
\text{H}_2\text{O} & \xrightarrow{+OH^-} \text{OH}^- + \text{H}_2\text{O}^+ \\
\text{H}_2\text{O} & \xrightarrow{-C-} \text{OH}^- + \text{H}_2\text{O}^+ \\
\text{H}_2\text{O} & \xrightarrow{-C-} \text{OH}^- + \text{H}_2\text{O}^+ \\
\end{align*}
\]

However, many alkenes are insoluble in H_2O, or the equilibrium strongly favors the alcohol. So we use indirect methods.

1) Concentrated H_2SO_4

\[
\begin{align*}
\text{C=C} & \xrightarrow{\text{conc H}_2\text{SO}_4} \text{C}^- + \text{H}_2\text{O}^+ \\
\text{C=C} & \xrightarrow{-C-} \text{C}^- + \text{H}_2\text{O}^+ \\
\text{C=C} & \xrightarrow{-C-} \text{C}^- + \text{H}_2\text{O}^+ \\
\end{align*}
\]

2) Boiling H_2O

\[
\begin{align*}
\text{C=C} & \xrightarrow{\text{boil H}_2\text{O}} \text{C}^- + \text{H}_2\text{O}^+ \\
\text{C=C} & \xrightarrow{-C-} \text{C}^- + \text{H}_2\text{O}^+ \\
\text{C=C} & \xrightarrow{-C-} \text{C}^- + \text{H}_2\text{O}^+ \\
\end{align*}
\]

This step is an Sn1 reaction, HSO_4^- is the leaving group.

Most useful of all (high yield, no carbon rearrangements) is oxymercuration/demercuration.

It's a two-step reaction with some exotic reagents, intermediates that produces a Markovnikov product without rearrangements.

\[
\begin{align*}
\text{C=C} & \xrightarrow{\text{mercuric acetate}} \text{C}^- + \text{H}_2\text{O}^+ \\
\text{C=C} & \xrightarrow{-C-} \text{C}^- + \text{H}_2\text{O}^+ \\
\text{C=C} & \xrightarrow{-C-} \text{C}^- + \text{H}_2\text{O}^+ \\
\end{align*}
\]

NaBH_4 is sodium borohydride, a reducing agent.
**Oxymercuration/Demercuration**

\[
\begin{align*}
\text{Hg(OAc)}_2 + \text{C} = \text{C} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{Hg}^+ \quad (\text{OAc})_2 \\
\end{align*}
\]

**Mercurinium Ion**

\[
\begin{align*}
\text{H}_2\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{Hg(OAc)}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{NaBH}_4 \\
\end{align*}
\]

**Markovnikov**

\[
\begin{align*}
\text{NaBH}_4 \text{ replaces Hg with H} \\
\end{align*}
\]

**This Reaction is Stereospecific**

The cyclic structure of the mercury product forces "anti" addition of OH.

\[
\begin{align*}
\text{H}_2\text{O} \\
\end{align*}
\]

**Alkoxy Mercuration/Demercuration**

Just picture the above reaction in an alcohol solvent R-OH instead of water.

You get the same type of product with a carbon group attached to the oxygen— an ether.

This is addition of an alcohol to the double bond RO-H.

\[
\begin{align*}
\text{CH}_3 \quad \xrightarrow{\text{NaBH}_4} \quad \text{CH}_3\text{CH}_2\text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{Hg(OAc)}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 - \text{C} = \text{C} \quad \text{CH}_3 \\
\end{align*}
\]

As always, it's important to note the danger from mercury toxicity.

In all its forms, metal, alkyl mercury (Hg(CH_3)_2) or mercuric salts like Hg(OAc)_2, mercury is dangerously toxic.

Hg(CH_3)_2 even penetrates latex gloves!
HYDROISORPTION / OXIDATION

MAKE ANTI MARKOVNIKOV ALCOHOLS FROM ALKENES

\[ \text{C} = \text{C} \quad 1) \text{BH}_3 \cdot \text{THF} \quad \rightarrow \quad \text{C} = \text{C} \quad \text{ANTI MARKOVNIKOV} \]

\[ 2) \text{H}_2\text{O}_2, \text{OH}^- \quad \rightarrow \quad \text{C} = \text{C} \quad \text{ANTI MARKOVNIKOV} \]

THIS REACTION INVOLVES A CYCLIC INTERMEDIATE:

\[ \text{CH}_3 \quad \text{C} = \text{C} \quad \text{CH}_3 \quad \rightarrow \quad \left[ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{H} \end{array} \right] \quad \text{THIS S}^+ \text{MOST STABLE} \quad \rightarrow \quad \text{CH}_3 \quad \text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{H} \quad \text{OH} \]

\[ \text{CH}_3 \quad \text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{H}_2\text{O}_2, \text{NaOH} \quad \rightarrow \quad \text{CH}_3 \quad \text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{H} \quad \text{OH} \quad \text{ANTI MARKOVNIKOV} \]

THE STEREO SPECIFICITY OF THE REACTION IS SYN ADDITION

\[ \text{BH}_3 \cdot \text{THF} \quad \rightarrow \quad \left[ \begin{array}{c} \text{S}^+ \end{array} \right] \quad \text{H}_2\text{O}_2, \text{OH}^- \quad \rightarrow \quad \text{RACEMIC, RANDOM TOP OR BOTTOM SYN ADDITION} \]

HYDROGENATION

REDUCTION OF AN ALKENE (ALKENE, C=O) WITH H\(_2\)/Catalyst

HYDROGEN ADOBER ON A METAL SURFACE ADDS TO ONE "FACE" OF THE DOUBLE BOND, USUALLY RANDOM "FACE", BUT OCCASIONALLY ONE FACE IS PREFERRED Fig 5-23 IT IS ALSO POSSIBLE TO USE CHIRAL CATALYSTS FOR ASYMMETRIC INDUCTION P6 219

CARBENES

\(:\text{CH}_2\) IS METHYLENE, THE SIMPLEST CARBENE. IT ADDS TO DOUBLE BONDS TO MAKE CYCLOPROPANES

\[ \text{C} = \text{C} \quad + \quad :\text{CH}_2 \quad \rightarrow \quad \text{C} \quad \text{C} \quad \text{CH}_2 \]
The original carbene reaction uses diazomethane $\text{CH}_2\text{N}_2$.

$$\text{CH}_2\text{N}_2 \xrightarrow{\text{UV}} \xrightarrow{\text{or heat}} \text{CH}_2 + \text{N}_2(\text{g})$$

$$\text{CH}_3-\text{CH} = \text{CH}_2 \xrightarrow{\text{heat}} \text{CH}_3-\overset{\text{C}}{\underset{\text{C}}{\text{C}}} - \overset{\text{H}}{\underset{\text{H}}{\text{H}}} + \text{other products}$$

This, plus the toxic, explosive nature of $\text{CH}_2\text{N}_2$, limits its usefulness.

A better reaction is the Simmons-Smith reaction.

$$\overset{\text{C}}{\underset{\text{C}}{\text{C}}} \xrightarrow{\text{Zn, CICl}} -\overset{\text{C}}{\underset{\text{C}}{\text{C}}} - + 2\text{ZnI}$$

This is the preferred method for making cyclopropanes.

Addition of halogens

Page 355 shows a picture of red/brown bromine (Br$_2$) being "decolorized" by an alkene.

$$\overset{\text{C}}{\underset{\text{C}}{\text{C}}} \xrightarrow{\text{CCl}_4} -\overset{\text{C}}{\underset{\text{C}}{\text{C}}} - + \text{Br}_2$$

The mechanism of this reaction involves a "cyclic bromonium ion" or cyclic "halonium" ion if Cl$_2$ or I$_2$ are used.

$$\overset{\text{C}}{\underset{\text{C}}{\text{C}}} \xrightarrow{\text{Br}_2 + \text{Br}_2} -\overset{\text{C}}{\underset{\text{C}}{\text{C}}} - + \text{Br}_2^-$$

This cyclic ion is opened by bromide.

$$-\overset{\text{C}}{\underset{\text{C}}{\text{C}}} \xrightarrow{\text{Br}_2^-} -\overset{\text{C}}{\underset{\text{C}}{\text{C}}} - \overset{\text{O}_2}{\text{BR}} \overset{\text{Stereo-specific}}{\text{Anti addition}}$$

OR THIS

$$\text{ENANTIOMERI}$$
**HALOHYDRINS**

**HALOGENS PLUS WATER ADD TO ALKENES TO FORM HALOHYDRINS**

\[
\begin{align*}
\text{Br}_2 + \text{H}_2\text{O} & \rightarrow \text{Br}_2^- \text{OH}^- \\
\text{C} = \text{C} & \rightarrow \text{C} - \text{C} \\
\text{H}_2\text{O} & \rightarrow \text{OH}
\end{align*}
\]

A halonium ion is involved, so stereochemistry is **anti** Markovnikov orientation is also observed.

\[
\begin{align*}
\text{CH}_2 = \text{CHCH}_3 + \text{Cl}_2 & \rightarrow \text{Cl} \text{H} \text{C} = \text{C} - \text{CH}_3 \\
\text{H}_2\text{O} & \rightarrow \text{H}^+ \text{Cl}^- \text{H} \\
\text{Anti addition}, & \text{ anti Markovnikov orientation}
\end{align*}
\]

**EP OxidATION**

\[
\begin{align*}
\text{C} = \text{C} & \rightarrow \text{R-C-O- OH} \\
\text{Peroxy acid} & \rightarrow \text{C} = \text{C} - \text{An epoxide}
\end{align*}
\]

**ACID CATALYZED OPENING OF EP Oxides**

\[
\begin{align*}
\text{C} = \text{C} & \rightarrow \text{C} = \text{C} \\
\text{H}_3\text{O}^+ & \rightarrow \text{C} = \text{C} \rightarrow \text{C} - \text{C} + \text{OH}^- \\
\text{OH}^- & \rightarrow \text{C} = \text{C} \\
\text{Enantiomer} & \rightarrow \text{A glycol}
\end{align*}
\]

**WE CAN ALSO MAKE SYN GLYCOLS WITH OsO_4 OSMIUM TETROXIDE OR KMnO_4 (cold/dilute) POTASSIUM PERMANGANATE**

A cyclic intermediate ensures **syn** hydroxylation.

\[
\begin{align*}
\text{C} = \text{C} & \rightarrow \text{KMnO}_4 \rightarrow \text{C} = \text{C} \rightarrow \text{OH}^- \\
\text{OH}^- & \rightarrow \text{C} = \text{C} \rightarrow \text{OH}^- \text{OH}^- \\
\text{C} = \text{C} & \rightarrow \text{C} = \text{C} \rightarrow \text{OH}^- \\
\text{OH}^- & \rightarrow \text{C} = \text{C} \rightarrow \text{OH}^- \\
\text{C} = \text{C} & \rightarrow \text{Cis in rings}
\end{align*}
\]
Oxidative Cleavage  
\[ \text{C} = \text{C} \rightarrow \text{C} = \text{O} + \text{O} = \text{C} \]

OR OZONOLYSIS (MILD)

\[ \text{R}^1 \text{C}=\text{C} - \text{H} \xrightarrow{\text{K MnO}_4} \xrightarrow{\text{conC, heat}} \text{R}^1 \text{C} = \text{O} + \text{O} = \text{C}-\text{H} \]

\[ \text{R}^1 \text{C} = \text{O} + \text{O} = \text{C}-\text{H} \]

Examples

\[ \xrightarrow{\text{O}_3 \text{ Oms}} \text{CH}_3 \text{C} \cdot \text{H} + \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{C} \cdot \text{H} \]

Any \( \text{C} = \text{C} \) is replaced by \( \text{C} = \text{O} \) and \( \text{C} = \text{O} \)

OZONOLYSIS INTERMEDIATE IS CYCLIC, SYN PRODUCTS RESULT

\[ \text{Polymerization} \]

It's arguably the most important reaction of alkenes / epoxides

Polymers are large (MW 10,000 to 7,000,000) molecules made from repeating units (monomers)

Mechanisms are chain reactions, anionic, cationic, free-radical

\[ \text{Methyl cyanoacrylate} \]

"Super Glue" Monomer

\[ \text{Polymer} \]
CATIONIC POLYMERIZATION

ACID-CATALYSED, CATIONIC INTERMEDIATES
ANOTHER EXAMPLE OF ELECTROPHILIC ADDITION
TO AN ALKENE:

**INITIATION**

\[
\text{C} = \text{C}^- + \text{H}^+ \rightarrow \text{H}^- \cdot \text{C}^- \cdot \text{C}^+ \]

**PROPAGATION**

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

\[
\text{CH}_2 = \text{CH}_2 + \text{CH}_2\text{(CH}_2\text{)}_2\text{CH}_3 \rightarrow +\text{CH}_2\text{(CH}_2\text{)}_4\text{CH}_3
\]

THE GROWING CHAIN TERMINATES WHEN A CATION
ELIMINATES A PROTON

\[
\text{CH}_3\text{(CH}_2\text{)}_m\text{CH}_2\text{CH}_3^+ \rightarrow \text{CH}_3\text{(CH}_2\text{)}_m\text{CHCH}_2\text{CH}_3
\]

WORKS BEST WITH 3° CATIONS

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

\[
\text{CH}_3 - \text{C}^- \cdot \text{CH}_3 + \text{CH}_2 = \text{C}^- \cdot \text{CH}_3 \rightarrow \text{CH}_3 - \text{C}^- \cdot \text{CH}_2 - \text{C}^- \cdot \text{CH}_3
\]

THIS POLYMER IS CALLED BUTYL RUBBER
CHAPTER 11

SHOW THE PRODUCTS
OF ADDITION REACTIONS
INC. STEREOCHEM & REGIOCHEM

WORK WITH ALKYNE REACTIONS

MECHANISMS OF ELECTROPHILIC
ADDITION

WATCH FOR REARRANGEMENTS

UNDERSTAND CONJUGATE ADDITION

USE THESE REACTIONS FOR
SYNTHESIS

33-35, 45, 56

32, 33

32, 39, 41, 42

32F, 33C

326

37, 38