Electrophilic Addition Reactions - Adding XY Across Unsaturated Carbon-Carbon Bonds

This page summarizes the main classes of chemical transformations. Having studied the process of elimination, we are now set to examine the reverse reaction - addition of the elements “XY” across carbon-carbon multiple bonds.

1) Acid-Base - hydrogen swap

\[ \begin{array}{ccc}
\text{acid} & \text{base} & \text{acid} \\
\text{X} & \text{Y} & \text{X} \\
\text{Y} & \text{H} & \text{H} \\
\end{array} \]

2 & 3) Oxidation & Reduction
change in the number of C-H bonds in relation to the number of C-X bonds

4) Substitution - replace C’s substituent (-X) with another (-Y), neither being -H

\[ \begin{array}{ccc}
\text{X} & \text{C} & \text{Y} \\
\text{Y} & \text{C} & \text{X} \\
\end{array} \]

5) Elimination - loss of XY elements with concomitant pi bond formation

6) Addition - gain of XY elements with concomitant loss of pi bond

\[ \begin{array}{ccc}
\text{X} & \text{Y} & \text{Z} \\
\text{Y} & \text{X} & \text{C} \\
\end{array} \]

7) Rearrangement - isomerization process (no atoms lost or gained); results in new bonding connectivity (one of many examples shown as there is no generic representation).

R stands for a generic "residue"
Examples of Addition Reactions to Carbon-Carbon Double Bonds

\[
\begin{array}{c}
\text{CH}_3\text{C}\text{H}_2\text{C} + \text{H–Br}^+ \rightarrow \text{CH}_3\text{C}\text{H}_2\text{C}^+ \\
\text{H}_2\text{C} = \text{CHCH}_3 + \text{H}_2\text{O} \xrightleftharpoons[\text{H}^+]{\text{H}^+} \text{H}_2\text{C} - \text{C} - \text{CH}_3 \\
\text{Br} - \text{Br}^+ \xrightarrow{\text{CH}_2\text{Cl}_2} \text{H} \text{C} - \text{C} - \text{CH}_3 \\
\text{Cl} - \text{Cl}^+ \xrightarrow{\text{H}_2\text{O}} \text{H} \text{C} - \text{C} - \text{CH}_3 + \text{HCl}
\end{array}
\]
Addition Mechanisms Require a New Elementary Step: Association of an Electrophile with a $\pi$-bond $[A_E]$

$E^+$ is the electrophile

This symbol means an electrophile association with a $\pi$-bond

$[A_E]$ involves a $\pi \rightarrow a$ $\sigma$-type interaction

Curved Arrows Imply the Frontier Orbitals

Curved arrows indicate the HOMO-LUMO pair (Frontier Orbitals) involved in an elementary step. For $[A_E]$ the tail of the arrow implies the filled orbital (HOMO) is an electron pair in a pi-bond. The head of the arrow points between one carbon atom of the $\pi$-bond and the $E^+$ suggesting that an atom-centered empty orbital (LUMO, $a$) accepts the electron pair with $\sigma$-type orbital interaction (note: the HOMO for $[A_E]$ will always be $\pi$ but the LUMO will vary according to the specific $E^+$ involved).

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