Benzene: Structure and Bonding

“Clearly, the ring had an unwholesome power...”

1.33 Å → 1.47 Å

“expected” structure for 1,3,5-cyclohexatriene

actual structure

1.39 Å

The resonance energy in benzene is **aromatic stabilization**.
Substitution at Aromatic Carbon

We previously studied substitution reactions at \( sp^2 \) carbonyl carbon and learned that the process goes by variations of nucleophilic acyl substitution. Here we examine substitution at \( sp^2 \) aromatic carbon. These substitution reactions often follow the electrophilic aromatic substitution pathway, although 3 other pathways are possible in certain cases.

1) Acid-Base - hydrogen swap

\[
\begin{array}{c}
Y \quad + \quad H \\ \text{base} \\ \hline \\
X \\ \text{acid} \\ \hline \\
H \\ \text{acid} \\ \hline \\
Y \\ \text{base} \\
\end{array}
\]

2 & 3) Oxidation & Reduction

close 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

\[
\begin{array}{c}
Y \\ \text{replaces} \\ X \\
\hline \\
Y \\ \text{replaces} \\ X \\
\hline \\
+ \\
\hline \\
X \\
\end{array}
\]

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

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

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"
Aromatic Substitution: Four Examples

I. Electrophilic Aromatic Substitution

\[
\text{H} + \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{HNO}_2 + \text{H}_2\text{O}
\]

II. Nucleophilic Aromatic Substitution

\[
\text{Cl} + \text{NaOH} \xrightarrow{\text{H}_2\text{O}, 100°C} \text{HNO}_2 + \text{H}_2\text{O}
\]
Aromatic Substitution: Four Examples

III. Substitution via arenediazonium ion

\[ \text{V} \equiv \text{N} \equiv \text{N} : \]

\[ \text{aniline} \quad \xrightarrow{\text{NaNO}_2, \ \text{H}_2\text{SO}_4, \ \text{H}_2\text{O}} \quad \text{arenediazonium} \quad \text{salt} \]

\[ \xrightarrow{\text{H}_2\text{O}, \ \Delta} \quad \text{phenol} \]

IV. Substitution via benzyne intermediate

\[ \begin{align*}
\text{CH}_3 & \\
\text{Cl} & \\
\end{align*} \xrightarrow{\text{Na}} \quad \begin{align*}
\text{CH}_3 & \\
\text{NH}_2 & \\
\end{align*} \quad \begin{align*}
\text{CH}_3 & \\
\text{NH}_2 & \\
\end{align*} + \quad \begin{align*}
\text{CH}_3 & \\
\text{NH}_2 & \\
\end{align*} + \quad \text{NaCl}
\]