Electrophilic Aromatic Substitution

- Aromatic ring systems react with electrophiles differently than alkenes.
- We obtain a substitution rather than an addition product.

Mechanism

First, we get a carbocation intermediate. At the carbon that adds the electrophile, rehybridization ($sp^2 \rightarrow sp^3$) takes place. Molecule loses aromatic character.
Mechanism

Carbocation is resonance stabilized.

Mechanism

The electron-rich part of the reagent can act either as nucleophile in an addition reaction or as a base to remove a proton.
Mechanism

The two reactions would result in different products.

The exceptional stabilization for the aromatic compounds leads only to the substitution (addition elimination) product.

Energy Profile
**Electrophilic Aromatic Substitution**

**Halogenation:**
1\textsuperscript{st} step is generating an electrophile:

\[
\text{Br}^\delta- + \text{FeBr}_3 \rightleftharpoons \text{Br}^\delta- + \text{FeBr}_3
\]

\[
\text{FeBr}_3 \text{ is a Lewis acid that coordinates with Br}_2 \text{ and polarizes it, generating an electrophilic Br}^+\]

\[
\text{Br}^\delta- + \text{FeBr}_3 \rightleftharpoons \text{Br}^\delta- + \text{FeBr}_3
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\text{Br}^\delta- + \text{FeBr}_3 \rightleftharpoons \text{Br}^\delta- + \text{FeBr}_3
\]

**Nitration:**
1\textsuperscript{st} step is generating an electrophile, the nitronium ion:

\[
\text{H}^\delta+\text{NO}_2^- + \text{H}^\delta+\text{SO}_3\text{H} \rightleftharpoons \text{HSO}_4^- + \text{H}^\delta+\text{NO}_2^+
\]

\[
\text{NO}_2^+ + \text{H}_2\text{O}
\]
Electrophilic Aromatic Substitution

The highly electrophilic nitronium ion attacks the aromatic ring.

$$\text{NO}_2^+ \rightarrow \text{NO}_2$$

Electrophilic Aromatic Substitution

Sulfonation: generating the electrophile

$$\text{HSO}_3^- + \text{HSO}_3^- \rightarrow \text{SO}_3^- + \text{H}_2\text{O}$$
Electrophilic Aromatic Substitution

Sulfonation: reaction of electrophile with aromatic ring

\[
\begin{align*}
\text{C}_{\text{aromatic}} + \text{S} = \text{O}^{-} & \rightleftharpoons \text{C}_{\text{aromatic-SO}_3^\text{H}} \\
\end{align*}
\]
Electrophilic Aromatic Substitution

Friedel–Crafts Acylation

\[ \text{R–Cl} + \text{AlCl}_3 \xrightarrow{-\text{AlCl}_4} \text{R–C} = \text{O}^{\oplus} \]

\[ \text{R–C} = \text{O}^{\ominus} + \text{C}_6\text{H}_5 \xrightarrow{-\text{H}^+} \text{C}_6\text{H}_5\text{R} \]

Electrophilic Aromatic Substitution

Friedel–Crafts Alkylation

\[ \text{R}’\text{CH}_2\text{Cl} + \text{AlCl}_3 \xrightarrow{-\text{AlCl}_4} \text{R}’\text{CH}_2 \]

\[ \text{R’CH}_2 + \text{C}_6\text{H}_5 \xrightarrow{-\text{H}^+} \text{C}_6\text{H}_5\text{R’CH}_2 \]