EAS – Sulfonation

Reaction

\[
\begin{array}{c}
\text{Cyclohexene} \xrightarrow{\text{SO}_3 / \text{H}_2\text{SO}_4 \text{ or fuming } \text{H}_2\text{SO}_4} \text{Cyclohexene-SO}_3\text{H}
\end{array}
\]

Electrophile

Mechanism

The sulfonic acid group is a strong deactivating group.

This reaction is very useful synthetically because the sulfonic acid group is labile, that is, it can be removed from the arene product. Notice the equilibrium arrows. Under mild conditions, that is, either steam distillation or an aqueous solution of the compound and heat the reaction can be reversed.

This later reaction represents a synthetic tool in guiding substituents on the arene final product – a “blocking group.” Phenol produces a trichloro-substituted
phenol in the chlorination EAS reaction. But a good yield of 2,6-dichlorophenol cannot be achieved by this method.

\[
\begin{array}{c}
\text{OH} \\
\text{Cl} \quad \text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\xrightarrow{\text{Cl}_2 / \text{AlCl}_3}
\begin{array}{c}
\text{OH} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
+ \begin{array}{c}
\text{OH} \\
\text{Cl} \\
\end{array}
\approx 85\% \\
\text{only traces}
\end{array}
\]

By placing a blocking group at the para-position and then performing chlorination we are able to achieve our goal.

\[
\begin{array}{c}
\text{OH} \\
\text{Cl} \quad \text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\xrightarrow{\text{SO}_3 / \text{H}_2\text{SO}_4}
\begin{array}{c}
\text{OH} \\
\text{HO}_2\text{S} \\
\text{HO}_2\text{S} \\
\text{HO}_2\text{S} \\
\end{array}
\xrightarrow{\text{Cl}_2 / \text{AlCl}_3}
\begin{array}{c}
\text{OH} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\xrightarrow{\text{H}_2\text{O} / \text{heat}}
\begin{array}{c}
\text{OH} \\
\text{Cl} \\
\end{array}
\]