Electrophilic Alkene Halogenation and Hydrohalogenation

Adds -Br and -Br (or -Br and -OH) \textit{anti} onto double bond, to yield trans-products.

Reactions are diastereoselective; no \textit{cis}-adducts are observed.

Epoxides

\textbf{Epoxide:} A three-membered ring made of two carbons and one oxygen.

Very reactive towards nucleophiles.

\textit{Example from biology:}

benzo[a]pyrene

\textit{a polyaromatic hydrocarbon (PAH) byproduct of burning tobacco, charring meat}

benzo[a]pyrene oxide

reacts with nucleophiles in DNA to generate DNA “lesions”, which can produce cancer-causing mutations
Synthesis of Epoxides

Via isotope labeling studies, we know which oxygen from peroxycacid adds.

Stereochemistry of alkene starting material is retained in epoxide product.

So, a cis-alkene... gives a cis-epoxide.

Ring-Opening Reactions of Epoxides

In acid, nucleophile adds to site of most stable carbocation.

Example:

In base, nucleophile adds to least hindered carbon.
**Dihydroxylation of Alkenes**

*anti*-Dihydroxylation via epoxides:

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{mCPBA} \xrightarrow{\text{H}_2\text{O}} \text{epoxide} \xrightarrow{\text{spontaneously}} \text{trans-diol} (+ \text{enantiomer})
\]

In non-nucleophilic solvents (e.g., CH\(_2\)Cl\(_2\)), reaction stops at epoxide.

*syn*-Dihydroxylation with permanganate:

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{KMnO}_4 \xrightarrow{\text{H}_2\text{O}/\text{H}_2\text{O}} \text{epoxide} \xrightarrow{\text{OH} \text{ cleavage}} \text{cis-diol}
\]

**Alkene Ozonolysis**

Splits C=C double bonds, converts alkene carbons into carbonyls (C=O).

\[
\begin{align*}
\text{H}_3\text{C} & \xrightarrow{1. \text{O}_3} \text{H}_3\text{C} - \text{C} = \text{O} \\
\text{H}_3\text{C} & \xrightarrow{2. (\text{CH}_3)_2\text{S}} \text{H}_3\text{C} - \text{O} = \text{H}
\end{align*}
\]