Alkenes are very useful in syntheses - they allow us to convert into many of the other types of functional groups.

Addition and elimination are two complimentary processes. Alkenes undergo addition reactions. Alkenes can be synthesized by elimination reactions.

Just as a preview to Ch 11, alkyl halides can undergo elimination through use of a strong base like KOH. We will study this mechanism in detail in Ch 11.
7.2 Addition of halogens to alkenes

We've studied electrophilic addition of HX (a strong binary halogen acid) to an alkene to make an alkyl halide.

Addition of an elemental dihalogen to an alkene will give an alkyl dihalide.

The stereochemistry of this addition is **trans** when on a ring - the nucleophilic halide adds to the opposite side of the electrophilic halide.

The stereochemistry is caused by the formation of a 3-membered **bromonium** or **chloronium** ion (the -onium ending means it's positively-charged).

More generally, it's called an **anti addition** when they're added to any double bond.
7.3 Halohydrin formation

A halohydrin is formed when, instead of the $X^-$ ion acting as the nucleophile in the 2nd mechanistic step, an excess of another nucleophile like $H_2O$ adds to the halonium ion.

**Regiochemistry** of halohydrin formation follows Markovnikov's rule:
- $X$ to less substituted C (because it's the electrophile)
- $OH$ to the more substituted C (because $H_2O$ is the nucleophile)

**Stereochemistry** is **anti** just like halogenation because of the halonium intermediate.

![Mechanism of halohydrin formation](image)
7.4 Hydration of alkenes: oxymercuration

H₂O can be added across a double bond with Markovnikov orientation if there’s an acid catalyst.

The H of hydronium is the electrophile, H₂O is the nucleophile. 

7.5 Hydration of alkenes: hydroboration

If non-Markovnikov addition of H₂O across a double bond is desired, hydroboration-oxidation is used.

This time, the B acts as the electrophile and H acts as a nucleophile. (H is more electronegative than B). When the BH₂ group in the intermediate is replaced by OH through oxidation, the non-Markovnikov product is formed.

Stereochemistry comes from the fact that the H and the BH₂ are added at the same time and to the same face via a cyclic intermediate:
Cyclopropanes can be formed by addition of a carbene (a reactive 6-electron carbon with 2 bonds and 1 lone pair) to a double bond.

Chloroform, CHCl₃, will form dichlorocarbene, :CCl₂, when reacted with strong base like KOH. The carbene acts as both a nucleophile and electrophile adding into the double bond.

Stereochemical configuration (cis/trans) of the double bond is retained in the dichlorocyclopropane product.
Addition of a \( \text{CH}_2 \) carbene to a double bond makes a regular cyclopropane with no halogens. \( \text{CH}_2 \) is too unstable to exist, but a \textit{carbenoid} exists which provides the same reactivity.

\[
\text{Diiodomethane} + \text{Zn(Cu)} \rightarrow \text{I} \text{CH}_2 - \text{ZnI} \quad \text{(Iodomethyl)zinc iodide (a carbenoid)}
\]

\[
\begin{align*}
\text{Cyclohexene} & \quad + \quad \text{CH}_2\text{I}_2 \quad \text{(Ether)} \quad \rightarrow \\
\text{Bicyclo[4.1.0]heptane} & \quad \text{(92\%)}
\end{align*}
\]

Reduction in organic chemistry occurs by forming a C-H bond or breaking a C-O, C-N, or C-X bond.

\textbf{Oxidation} is the opposite of reduction.

\textbf{Catalytic hydrogenation} occurs when H\(_2\) is added across the same face of the double bond using catalytic Pt or Pd on carbon.

Stereochemistry is called \textbf{syn} because the hydrogens are added in the same direction. This will make cis-substituted cycloalkanes.

\[\text{CH}_3 \quad \text{CH}_3\]

\[\text{CH}_3 \quad \text{CH}_3\]

\[\text{CH}_3 \quad \text{CH}_3\]

\[\text{CH}_3 \quad \text{CH}_3\]

\[\text{CH}_3 \quad \text{CH}_3\]
7.8 Oxidation of alkenes: epoxidation and dihydroxilation

An epoxide (3-membered oxygen-containing ring) can be formed by oxidizing an alkene with a peroxyacid like MCPBA (general formula RCO\textsubscript{3}H).

\[
\text{\text{Cyclo}\text{heptane}} + \text{\text{mCPBA}} \rightarrow \text{\text{1,2-Epoxy-cycloheptane}}
\]

The O is delivered to one side of the double bond, giving the epoxide specific stereochemistry.

A \textit{trans-1,2-diol} can be formed by reacting an epoxide with H\textsubscript{2}O and acid catalyst.

The O is protonated first, making the carbons more electrophilic. H\textsubscript{2}O will attack a carbon from the opposite face of the epoxide, making it an \textit{anti addition} overall.

If the original double bond was cyclic and disubstituted, a \textit{trans-} cycloalkanediol will be formed.

Syn dihydroxylation

If we want two -OH groups to be added across the double bond but with \textit{cis} stereochemistry, they have to be added at the same time.

Osmium tetroxide will add two oxygens to the same face. It is cleaved with sodium bisulfite.

This is called a \textit{syn addition} (addition to the same face) and cyclic products can have \textit{cis} stereochemistry if the alkene was disubstituted.

\[
\begin{align*}
\text{1.2-Dimethylcyclopentene} & \rightarrow \text{cis-1,2-Dimethyl-1,2-cyclopentanediol (87\%)} \\
\text{1.2-Diphenoxy-} & \text{hexane} \rightarrow \text{anti addition, Markovnikov addition}
\end{align*}
\]

\textbf{Anti dihydroxylation:}

1) mCPBA (RCO\textsubscript{3}H) - epoxidation
2) \text{H}_3\text{O}^+ - epoxide opening forming \textit{trans-1,2-diol}

\textbf{Syn dihydroxylation:}

1) OsO\textsubscript{4} - delivers both oxygens on same face
2) \text{NaHSO}_3 - cleaves cyclic osmium intermediate leaving a \textit{cis}-1,2-diol
Ozone, \( \text{O}_3 \), can cleave double bonds. After adding across the double bond, Zn is used to reduce the unstable product to two carbonyl compounds. The process is called **ozonolysis**.

To predict the products of ozonolysis, simply cleave the double bond, and double bond each of the carbons to an O, forming a carbonyl.

The substitution of the double bond determines whether a ketone or aldehyde will form.

Oxidative cleavage

Potassium permanganate, \( \text{KMnO}_4 \), will also cleave alkenes. The difference is that instead of aldehydes from carbons with one H attached, they will be oxidized to contain the maximum number of oxygens (carboxylic acids or \( \text{CO}_2 \)).
7.10 Polymers

Alkenes can be polymerized using a radical mechanism.

**Initiation:** a molecule splits into two radicals

\[
\text{BzO} \cdot \xrightarrow{\text{Heat}} \text{BzO} - \text{CH}_2\text{CH}_2\cdot
\]

**Propagation:** a radical adds to an alkene to make a new radical

\[
\text{BzO} \cdot + \text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{BzO} - \text{CH}_2\text{CH}_2\cdot
\]

This occurs over and over to make long polymer chains.

**Termination:** two radicals combine to make a neutral molecule.

\[
2 \text{RCH}_2\text{CH}_2\cdot \rightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{R}
\]