**Structure and Synthesis of Alkenes**

Alkenes (olefins) are hydrocarbons which have carbon–carbon double bonds.

\[
\text{CH}_2=\text{CH}_2
\]

A double bond is a \( \sigma \) bond and a \( \pi \) bond.

\[
\begin{align*}
\text{Double bond B.D.E.} & = 146 \text{ kcal/mol} \\
\sigma \text{ bond B.D.E.} & = 83 \text{ kcal/mol}
\end{align*}
\]

Therefore \( \pi \) B.D.E. must = 63 kcal/mol.

**A \( \pi \) bond is weaker than a \( \sigma \) bond.**

\( \pi \) Bonds are *more reactive* than \( \sigma \) bonds, and \( \pi \) bonds are considered to be a functional group.

**Structure of Alkenes**

In ethene (ethylene) each carbon is bonded to 3 other atoms, with zero nonbonding electrons \( \Rightarrow \) \( sp^2 \) hybridization.

![sigma bonding orbitals of ethylene](blob:https://raw.githubusercontent.com/John Doe/Chemistry-Site/master/Ch07AlkenesStruct+synth极少.png)
The C-H bonds are formed by overlap of sp$^2$ orbitals from the Carbon overlapping with 1s orbital from the Hydrogen.

(The C-H bonds in ethane are sp$^3$/1s overlapping orbitals. The ethene C-H bonds contain more s character than the ethane C-H bonds and are therefore shorter and stronger).

sp$^2$ are 1/3 s, whereas sp$^3$ are 1/4 s in character. (s orbitals are closer to the nucleus and lower in energy).

The carbon-carbon bond in ethene is shorter and stronger than in ethane partly because of the sp$^2$-sp$^2$ overlap being stronger than sp$^3$-sp$^3$, but especially because of the extra $\pi$ bond in ethene.
Pi Bond
The unhybridized p orbitals on each carbon align parallel to form a \( \pi \) bond.

The \( \pi \) bond prevents rotation about the C=C bond because it would force the p orbitals into a non overlapping formation (i.e. break the \( \pi \) bond).

The \( \pi \) bond exists with half its electron density above the \( \sigma \) bond, and half below.
Elements of Unsaturation

Alkanes are said to be saturated since they have the maximum number of bonds to hydrogen.

An alkene is unsaturated.

Any $\pi$ system or a ring system reduces the maximum number of hydrogens a molecule can have.

An element of unsaturation relates to 2 missing hydrogens from the saturated formula ($C_nH_{2n+2}$).

Consider alkanes, alkenes, alkynes and cycles:

\[
\begin{align*}
\text{propane, } C_3H_8 & \quad \text{propene, } C_3H_6 \\
\text{saturated} & \quad \text{one element of unsaturation}
\end{align*}
\]

\[
\begin{align*}
\text{cyclopropane, } C_3H_6 & \quad \text{propyne, } C_3H_4 \\
\text{one element of unsaturation} & \quad \text{two elements of unsaturation}
\end{align*}
\]
Heteroatom complications
Heteroatoms are considered anything other than C or H.

Halogens
These simply substitute for hydrogens in the molecular formula.

Therefore just like C₂H₆ is saturated, so is C₂H₄F₂.

Oxygen
CH₃-CH₃ is saturated (C₂H₆)
CH₃-O-CH₃ is also saturated (C₂H₆O)

An oxygen can be added without requiring any additional hydrogens, so ignore the number of oxygens when calculating elements of Unsaturation.

Nitrogen
Nitrogen is trivalent, and when it replaces a C in a chain it requires only one hydrogen (-NH vs. -CH₂), so nitrogens count as half a carbon.

Thus C₄H₉N is equivalent to C₄.₅H₉. (i.e. one element of Unsaturation).]
Nomenclature of Alkenes
Simple alkenes are named like alkanes (root from the longest carbon chain), but the –\textbf{ane} suffix is replaced by -\textbf{ene}.

<table>
<thead>
<tr>
<th>IUPAC names:</th>
<th>CH\textsubscript{2}═CH\textsubscript{2}</th>
<th>CH\textsubscript{2}═CH—CH\textsubscript{3}</th>
<th>cyclohexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common names:</td>
<td>ethene</td>
<td>propene</td>
<td>cyclohexene</td>
</tr>
</tbody>
</table>

When the chain is longer than 3 carbons, number the atoms such that the \textit{double bond} is given the \textbf{lowest} number (i.e. start at the end nearest the double bond).

\begin{enumerate}
\item CH\textsubscript{2}═CH—CH\textsubscript{3} \\
\begin{enumerate}
\item old IUPAC names: but-1-ene \\
\item new IUPAC names: but-1-ene 
\end{enumerate}
\item CH\textsubscript{2}═CH—CH\textsubscript{2}—CH\textsubscript{3} \\
\begin{enumerate}
\item old IUPAC names: 1-pentene \\
\item new IUPAC names: pent-1-ene 
\end{enumerate}
\item CH\textsubscript{3}—CH═CH—CH\textsubscript{3} \\
\begin{enumerate}
\item old IUPAC names: 2-butene \\
\item new IUPAC names: but-2-ene 
\end{enumerate}
\item CH\textsubscript{3}—CH═CH—CH\textsubscript{2}—CH\textsubscript{3} \\
\begin{enumerate}
\item old IUPAC names: 2-pentene \\
\item new IUPAC names: pent-2-ene 
\end{enumerate}
\end{enumerate}
Compounds with 2 double bonds are called *dienes*, 3 double bonds are *triens*, etc.

For branches, each *alkyl* group is given a number, but the **double bond** is still given preference when numbering the chain.
When alkenes are *substituents*, they are termed *alkenyl* groups, and may be named systematically.

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \quad \text{H}_2\text{C}^-\text{C}=\text{CH}_2 \\
\text{methylene} & \quad \text{2-propenyl group} \\
\text{group} & \quad \text{(allyl group)}
\end{align*}
\]

**Geometric isomers**
The *rigidity* of a $\pi$ bond gives rise to geometric isomers.

When similar groups (not H’s) are bound to the *same* side of the double bond the alkene is said to be *cis*.

When similar groups are bound to *opposite* sides of the double bond it is said to be *trans*.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \quad \text{H} \\
\text{H} & \quad \text{CH}_2\text{CH}_3 & \quad \text{H}_3\text{C} & \quad \text{H} \\
\text{trans-pent-2-ene} & \quad \text{cis-pent-2-ene}
\end{align*}
\]

Cycloalkenes must have 8 or more carbons before they are large enough to incorporate a *trans* double bond.

\[
\begin{align*}
\text{cyclohexene} & \quad \text{trans-cyclodecene}
\end{align*}
\]

Therefore cycloalkenes are deemed to be *cis* unless specified otherwise.
E-Z Nomenclature
The assignment of geometrical isomers as either E or Z follows on from the Cahn-Ingold-Prelog convention.

Imagine the double bonds being split into two ends, and assign the priority of the substituents.

If the two highest priority groups are on opposite sides of the double bond (trans), the isomer is assigned E.

If the two highest priority groups are on the same side of the double bond (cis) the isomer is assigned Z.
If there is more than one double bond, then the stereochemistry around each double bond must be specified.

(3Z,5E)-3-bromoocta-3,5-diene
Industrial Uses of Alkenes
Alkenes are useful intermediates in organic synthesis, but their main commercial use is as precursors (monomers) for polymers.

\[
\text{TFE} \quad \xrightarrow{\text{Polymerise}} \quad \text{PTFE}
\]

\[
\text{Styrene} \quad \xrightarrow{\text{Polymerise}} \quad \text{Polystyrene}
\]
Stability of Alkenes
Alkenes are reduced to alkanes by the action of hydrogen gas in the presence of a catalyst.

The exothermicity of this reaction is called the heat of hydrogenation, and these values give information about the stability of the alkene.

We observe that the data confirms the *Saytzeff rule*, that more highly substituted double bonds are more stable.

\[ \text{R}_2\text{C}=\text{CR}_2 > \text{R}_2\text{C}=\text{CRH} > \text{RHC}=\text{CHR} \quad \text{and} \quad \text{R}_2\text{C} = \text{CH}_2 > \text{RCH}=\text{CH}_2 \]

This is because the alkyl groups **stabilize** the double bond.
The stability arises from two factors:
1) the alkyl groups are electron donating (hyperconjugation) and so donate electron density into the $\pi$ bond.
2) A double bond ($sp^2$) carbon separates bulky groups better than an $sp^3$ carbon, thus reducing steric congestion.

Energy differences in Alkenes
Heats of hydrogenation also infer that $trans$ isomers are more stable than $cis$ isomers.

This seems correct since the bulky groups are further separated in space in a trans conformation.
Relative stabilities:

- **ethylene, unsubstituted**: 11 kJ (2.7 kcal)
- **monosubstituted**
  - cis: 18 kJ (4.2 kcal)
  - geminal: 20 kJ (4.8 kcal)
  - trans: 22 kJ (5.2 kcal)
- **disubstituted**
- **trisubstituted**: 25 kJ (5.9 kcal)
- **tetrosubstituted**: 26 kJ (6.2 kcal)
Cycloalkenes
The only difference in reactivity or energetics from acyclic systems occurs when there is significant ring strain in the cycloalkene.

Cyclopentene, -butene and even -propene exist, and these compounds have increasingly more reactive double bonds.

\[
\begin{align*}
\text{cyclobutene} + \text{H}_2 & \xrightarrow{\text{Pt}} \text{cyclobutane} \\
\text{cyclopentene} + \text{H}_2 & \xrightarrow{\text{Pt}} \text{cyclopentane}
\end{align*}
\]

\[\Delta H^\circ = -128 \text{ kJ/mol} \quad (-30.7 \text{ kcal/mol})\]

\[\Delta H^\circ = -111 \text{ kJ/mol} \quad (-26.6 \text{ kcal/mol})\]

Cyclobutene is about 4 kcal/mol more strained than cyclopentene. (Smaller bond angles mean more deviation from 120°).

Bredt’s Rule
We have already seen that cycloalkenes need \(8 \text{ or more C atoms}\) to be large enough to accommodate a \(trans\) double bond.
An extension of this is Bredt’s rule which states:
*A bridged bicyclic compound cannot have a double bond at a bridgehead position unless one of the rings contains at least eight carbon atoms.*

Recall:
*Bicyclic* means two rings.
*Bridgehead carbon* is part of both rings.

![Diagram of bicyclic and bridged bicyclic compounds]

A bridged bicyclic compound has at least one carbon in each of the three links between the bridgehead atoms.

![Diagram showing Bredt’s rule violation and stable trans in a 9 membered ring]
Alkene Synthesis
Typically alkenes are produced by **elimination** reactions.

Recall the E2 elimination of H-X (dehydrohalogenation) can be an excellent synthetic method *if*:
The reactant is a poor $S_N2$ substrate, and a strong base is used.

For example:

$$\text{H}_3\text{C-CH}_3\text{Br} + \text{HO}^- \rightarrow H_2\text{C} = \text{CH}_3 + \text{H}_2\text{O} + \text{Br}^-$$

(*>90%*)

**Use of a bulky base**
A bulky base can further discourage undesired substitution reactions (i.e. a good base, poor nucleophile).

**Common (bulky) bases:**

- tert-butoxide
- diisopropylamine
- triethylamine
- 2,6-dimethylpyridine

E.g.

$$\text{H}_3\text{C-H-H} + (\text{i-Pr})_2\text{NH} \rightarrow \text{H}_2\text{C} = \text{CH}_3$$

(*93%*)
Formation of Other Products
The Saytzeff rule predicts the major alkene product from an elimination to be the more highly substituted alkene.

Sometimes, strong, bulky bases can form products that are not Saytzeff products.

The proton which must be removed to give the more substituted alkene is often the more sterically hindered proton, and the bulky base would rather remove a more accessible proton, which leads to a less stable product.

Such a product is a Hofmann product.

The bulky base (t-butoxide) gives more Hofmann than Saytzeff product.
Dehydrohalogenation by the E1 route
This normally requires a good ionizing solvent, a secondary or tertiary alkyl halide and a weak nucleophile and base.

Typically the E1 elimination is accompanied by $S_N1$ substitution. The mixture of products is undesirable for a synthetic route.

Reduction of Vicinal Dibromides
The action of iodide ion on vicinal dibromides to produce alkenes is an elimination, a reduction and a dehalogenation reaction. (The same reaction can be achieved through the action of zinc metal in acetic acid).

The reaction prefers to go through the anti-coplanar T.S.
Alcohol Dehydration
The dehydration (removal of water) of alcohols is a good synthetic route to alkenes.

Normally strong acids like sulfuric or phosphoric acids are used.

The mechanism of dehydration is similar to the E1 mechanism.

The hydroxyl group is not a good leaving group, but under acidic conditions it will protonate, and the –OH$_2^+$ group is a good leaving group.

The ionization generates a molecule of water and a cation, which then easily deprotonates to give the alkene.

The intermediate cation can undergo rearrangements, and strong acid is often used to promote such reactions.
Other Syntheses of alkenes
These will be covered later in more detail:

**Thermal Cracking**

\[
\text{heat} \quad \text{catalyst} \quad \text{heat} \quad \text{catalyst}
\]

**Dehydrogenation of Alkanes**

\[
-\text{H}_2 \quad \text{catalyst}
\]

**Hydrogenation of Alkynes**

\[
\text{H}_2 \quad \text{catalyst}
\]

**Wittig Reaction**

\[
\text{R}^\prime \text{O} \quad + \quad \text{PPh}_3 \equiv \text{CHR}'' \quad \rightarrow \quad \text{R}^\prime \equiv \text{CHR}'' \quad + \quad \text{Ph}_3 \text{P} = \text{O}
\]