**Structure and Synthesis of Alkenes**

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

\[
\text{H} - \text{C}=\text{C} - \text{H}
\]

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

\[
\begin{align*}
\text{Double bond B.D.E.} &= 146 \text{ kcal/mol} \\
\text{\( \sigma \) 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.
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*).
Pi Bond
The unhybridized p orbitals on each carbon align parallel to form a π bond.

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

The π bond exists with half its electron density above the σ 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:

\[
\begin{align*}
\text{propane, } C_3H_8 & \quad \text{saturated} \\
\text{propene, } C_3H_6 & \quad \text{one element of unsaturation} \\
\text{cyclopropane, } C_3H_6 & \quad \text{one element of unsaturation} \\
\text{propyne, } C_3H_4 & \quad \text{two elements of unsaturation}
\end{align*}
\]
Heteroatom complications
Heteroatoms are considered anything other than C or H.

Halogens
These simply substitute for hydrogens in the molecular formula.

Therefore just like $\text{C}_2\text{H}_6$ is saturated, so is $\text{C}_2\text{H}_4\text{F}_2$.

Oxygen
$\text{CH}_3-\text{CH}_3$ is saturated ($\text{C}_2\text{H}_6$)
$\text{CH}_3-\text{O}-\text{CH}_3$ is also saturated ($\text{C}_2\text{H}_6\text{O}$)

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. -CH$_2$-), so nitrogens count as half a carbon.

Thus $\text{C}_4\text{H}_9\text{N}$ is equivalent to $\text{C}_{4.5}\text{H}_9$. (i.e. one element of Unsaturation).]
Nomenclature of Alkenes
Simple alkenes are named like alkanes (root from the longest carbon chain), but the –ane suffix is replaced by -ene.

IUPAC names:
Common names:

\[
\begin{align*}
\text{CH}_2\equiv\text{CH}_2 & \quad \text{ethene} & \quad \text{ethylene} \\
\text{CH}_2\equiv\text{CH}_\text{–CH}_3 & \quad \text{propene} & \quad \text{propylene} \\
\end{align*}
\]

When the chain is longer than 3 carbons, number the atoms such that the double bond is given the lowest number (i.e. start at the end nearest the double bond).
Compounds with 2 double bonds are called dienes, 3 double bonds are trienes, 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.

\[
\begin{align*}
&\text{methylene} \quad \text{2-propenyl group} \\
&\text{group} \quad \text{(allyl group)}
\end{align*}
\]

**Geometric isomers**

The *rigidity* of a π 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*.

*trans*-pent-2-ene  
* cis*-pent-2-ene

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

*trans*-cyclodecene

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.
**Industrial Uses of Alkenes**

Alkenes are useful intermediates in organic synthesis, but their main commercial use is as precursors (monomers) for polymers.

![TFE and PTFE](image1)

![Styrene and Polystyrene](image2)
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.

\[ R_2\text{C}=\text{CR}_2 > R_2\text{C}=\text{CRH} > \text{RHC}=\text{CHR} \text{ and } R_2\text{C}=\text{CH}_2 > \text{RCH}=\text{CH}_2 \]

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
- Monosubstituted
- Disubstituted (cis, geminal, trans)
- Trisubstituted
- Tetrasubstituted

Energy differences:
- 11 kJ (2.7 kcal)
- 18 kJ (4.2 kcal)
- 20 kJ (4.8 kcal)
- 22 kJ (5.2 kcal)
- 25 kJ (5.9 kcal)
- 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.

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

**Bredt’s Rule**
We have already seen that cycloalkenes need 8 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.

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

Bredt's rule violation

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 SN2 substrate, and a strong base is used.

For example:

\[
\text{ CH}_3\text{CH}_3\text{Br} + \text{HO}^- \rightarrow \text{ CH}_3\text{CH}=\text{CH}_3 + \text{H}_2\text{O} + \text{Br}^- \\
(>90\%)
\]

**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.

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{CH}-\text{Br} &\quad \text{(i-Pr)}_2\text{NH} \\
\rightarrow &\quad \text{CH}_2=\text{CH}_2 \\
(93\%)
\end{align*}
\]
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 **Hoffman** product.

The bulky base (t-butoxide) gives more **Hoffman** 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.

\[
\begin{align*}
\text{acid} & \quad \text{H} \quad \text{H} \\
\text{OH} & \quad \text{CH}_2=\text{CH}_2 \\
\text{H}_2\text{O} & \\
\end{align*}
\]

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**

\[ \text{alkane} \xrightarrow{\text{heat}} \text{alkane} + \text{alkene} \]

**Dehydrogenation of Alkanes**

\[ \text{alkane} \xrightarrow{-\text{H}_2} \text{alkene} \]

**Hydrogenation of Alkynes**

\[ \text{alkyne} \xrightarrow{\text{H}_2} \text{alkene} \]

**Wittig Reaction**

\[ R'CO + PPh_3=CHR'' \rightarrow R''=CHR'' + PPh_3=O \]