Alkenes: Structure & Properties

Alkane (acyclic): $C_nH_{2n+2}$ > saturated.

Alkene (acyclic): $C_nH_{2n}$ > unsaturated.

*eg* ethylene (IUPAC: ethene), $C_2H_4$: $H_2C=CH_2$

The carbon-carbon double bond is the distinguishing feature of alkenes.

It is formed between two sp$^2$ carbons. One bond is $\sigma$, formed by head to head overlap of sp$^2$ orbitals; the second is $\pi$, formed by overlap of parallel 2p orbitals. The $\pi$ bond has two halves, one above and the other below the plane defined by the two carbons and the four other atoms to which they are attached.

The bond angles around the sp$^2$ carbons are $\approx 120^\circ$.

$\sigma$-bond requires *ca.* 360kJ (90 kcal)/mole to break.

$\pi$-bond requires *ca.* 260kJ (65 kcal)/mole to break.

Owing to the shape of the $\pi$-bond and its strength, there is not free rotation around a double bond as there is around most single bonds.
The butenes: $\text{C}_4\text{H}_8$

$\text{CH}_3\text{-CH}_2\text{-CH}=\text{CH}_2$: 1-butene,
$(\text{CH}_3)_2\text{C}=\text{CH}_2$: 2-methylpropene
$\text{CH}_3\text{-CH}=\text{CH-CH}_3$: 2-butene

Appear to be 3 isomers, but look again!

There are two isomeric 2-butenes, for 4 butene isomers in all.

The cis/trans isomers are configurational (not conformational) stereoisomers and are sometimes called geometric isomers.

These isomers have different properties:
cis- $\text{bp} = 4^\circ\text{C}$, $\text{mp} = -139^\circ\text{C}$;
trans- $\text{bp} = 1^\circ\text{C}$, $\text{mp} = -106^\circ\text{C}$.

The potential for geometric isomerism will exist in alkenes unless at least one of the carbons joined by the double bond carries two identical groups.
If one of the carbons is part of a ring to which the double bond is exocyclic, the carbon is considered to carry two identical groups if, starting at the trigonal carbon, traversing the ring in the clockwise direction is the same as traversing it in a counterclockwise direction.

Traversing this ring in clockwise direction from $\equiv C$: $\text{CH(CH}_3\text{)}, \text{CH}_2, \text{CH}_2$; counterclockwise: $\text{CH}_2, \text{CH}_2, \text{CH(CH}_3\text{)}$.

Since we get a different result depending on the direction of our traverse, and since the other doubly bonded carbon has two different groups ($\text{H, CH}_3$) attached, these are geometric isomers.

Traversing this ring in either direction leads to: $\text{CH}_2, \text{CH(CH}_3\text{)}, \text{CH}_2$.

Therefore, there are no geometric isomers here even though there are two different groups on the other $\equiv C$. 
E, Z System for Naming Geometric Isomers ---

1) At each atom joined by the double bond determine which of the groups attached by single bonds has the higher priority (vide infra). If the groups of higher priority are on the same side of the double bond: Z; if on opposite sides: E.

![Diagram showing Z and E configurations]

2) To establish priorities at each doubly bonded atom, consider the atoms directly attached by single bonds to the atom bearing the double bond, and rank them in order of decreasing (highest first) atomic number (atomic mass for isotopes).

Some examples in which the higher priority group is on top, as shown to the right.

![Examples of Z and E configurations]
3) If a decision cannot be made by the above rule, work outward to the first point of difference, then use rule 2 comparing atoms of highest atomic number, then, *if a decision cannot be made*, next lower atomic number, *etc.*

Some examples in which the higher priority group is on top, as shown to the right.

\[
\begin{align*}
\text{CH}_3\text{CH}_2 & \quad \text{HOCH}_2\text{O} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{CH}_3 & \quad \text{H}_3\text{CCH}_2\text{O} \\
(\text{H}_3\text{C})_2\text{CH} & \quad \text{H}_2\text{NCH}_2 \\
\text{C} & \quad \text{C} \\
\text{H}_3\text{CCH}_2 & \quad (\text{H}_3\text{C})_3\text{C}
\end{align*}
\]
4) If a group has multiple bonds, the multiple bonds are converted to single bonds for purposes of E/Z naming; this is done in the following way. A multiple bond from atom A to atom B is considered to be equivalent to the same number of single bonds from atom A to atom B. This results in “dummy” bonds and atoms – shown in red below.

Once the conversion is complete, priority assignment is done in the usual way.
becomes

becomes

becomes
(E)-2-butene is more stable than (Z)-2-butene.

Evidence:

1) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
24\% \text{Z} & \\
\end{align*}
\]

1) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
24\% \text{Z} & \\
\end{align*}
\]

\[\xrightarrow{\text{H}^+}\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
76\% \text{E} & \\
\end{align*}
\]

2) \[
\begin{align*}
(Z)-2\text{-butene} + \text{H}_2 & \rightarrow \text{butane} + 28.6 \text{ kcal/mole} \\
(E)-2\text{-butene} + \text{H}_2 & \rightarrow \text{butane} + 27.6 \text{ kcal/mole} \\
\end{align*}
\]

Why?

Steric repulsion of methyl groups in Z isomer.
$\Delta H$ for hydrogenation of alkenes also indicates the following order of stability of alkenes (compared to the product alkanes).

Most stable, least energy:

\[
\begin{align*}
\text{R} & \quad \text{R} & \quad \text{C=CYC} & \quad \text{small} & \quad \text{R} & \quad \text{R} & \quad \text{H} & \quad \text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} & \quad \text{C=CYC} & \quad \text{small} & \quad \text{R} & \quad \text{R} & \quad \text{H} & \quad \text{R} & \quad \text{R}
\end{align*}
\]

Least stable, most energy:

\[
\begin{align*}
\text{R} & \quad \text{H} & \quad \text{R} & \quad \text{R} & \quad \text{C=CYC} & \quad \text{R} & \quad \text{R} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{R} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]
Why?

Some controversy; two possibilities ---

1) Orbital interaction between $\pi^*$-orbital and $\sigma$-orbital of the first carbon in R (not the $\sigma$-orbital joining R to the trigonal carbon) which lowers the energy of the occupied $\sigma$-orbital and raises the energy of the unoccupied $\pi^*$-orbital.

2) The more highly substituted alkenes have a greater number of $sp^3$ - $sp^2$ C-C bonds: these $\sigma$-bonds are stronger than those between two $sp^3$ carbons.