1. **The Alkene Functional Group**

Alkenes are also called olefins, or unsaturated hydrocarbons, as compared to alkanes which are referred to as saturated hydrocarbons. In alkenes, there are two or more trivalent carbons with the presence of one or more carbon-carbon double bonds. They have the general formula \( \text{C}_n\text{H}_{2n} \).

![Diagram of bonding in alkenes]

**Bonding in Alkenes**

Hybrid orbitals of \( \text{sp}^2 \) and a \( p \) orbital combine to form a \( \sigma \)-bond and a \( \pi \)-bond, respectively. It should be noted that a double bond is actually comprised of two two-electron bonds (\( \sigma \) and \( \pi \)); this is why double bonds are shorter and stronger than single bonds. The difference between a \( \text{sp}^3 \) hybrid orbital and a \( \text{sp}^2 \) hybrid orbital is the amount of "s" character (25% vs 33%, respectively); since the latter has 33% it makes shorter and stronger sigma bonds to the hydrogens.
b. Cis and Trans Stereoisomerism in Alkenes

The \( \pi \)-bonding in alkenes has substantial consequences when it comes to the conformations of the alkenes. As you will recall from our discussions about rotation around bonds in ethane and butane, it is relatively easy to rotate around a sp\(^3\)-sp\(^3\) sigma bond (i.e. 3-5 Kcal/mole barrier height). Rotation around double bonds requires that the \( \pi \)-bond first be broken (about 50-60 Kcal/mole) before we can then rotate....this requires very high temperatures and is seldom observed.

This lack of free rotation around a \( \pi \)-bond leads to stereochemical consequences, there now exists the possibility of two compounds that have the same carbon connectivity, but different 3-D arrangements of the groups. These are stereoisomers of a specific type called geometric isomers. When we have an alkene which has at least two identical atoms or groups on the two doubly-bonded carbons of the alkene we use the same cis and trans formalism we used to define stereoisomers in cycloalkanes. As shown below, the cis stereoisomers has identical groups on the same side of the alkene, whereas the trans isomer has identical groups on opposite sides of the alkene.

![Stereoisomers of 2-butene](image)

**Stereoisomers of 2-butene**

2. Nomenclature in Alkenes

Nomenclature used for alkenes is much like that used for alkanes...except that the ending changes to **ene**. Thus any compound that ends in ene is an alkene.
### a. Common Names

Some alkenes and alkenyl groups have common names that can be recognized:

- Ethylene
- Propylene
- Isobutylene
- Styrene
- Isoprene

### alkene substituent groups

- Vinyl
- Allyl
- Isoprenyl

### Common Alkenes and Substituent groups

### b. IUPAC Nomenclature

1. Name the longest chain including the double bond.
2. Drop the ane suffix of the base name and add ene.
3. Number from the end nearest the double bond.
4. Complete the name as with alkenes.
5. Specify the cis, trans or E,Z stereoisomer isomer if indicated in structure.
6. If more than one double bond exists in the compound, it is named as a diene, triene,
c. Naming of Stereoisomers, the E/Z Convention

As we have seen, the lack of rotation around the double bond introduces the possibilities of geometric isomerism. Geometric isomers are different compounds with different chemical and physical properties. For example, cis-1,2-dibromoethylene has a boiling point of 110°C whereas the trans isomer has a boiling point of 129°C. Thus, a nomenclature method for differentiating between the different isomers is required. When we have at least two identical atoms (or groups) on the two doubly-bound carbons, as in the compound 2-pentene (draw the structure, the alkyl groups are different...but the H's are identical), we can use the cis/trans formalism. But what about a compound
such as 1-bromo-1-chloro-1-propene? The are now four different substituents on the two carbons of the double bond; a new convention is required.

CAHN, INGOLD, PRELOG SEQUENCE RULES FOR \textit{E,Z} NOMENCLATURE

1. Give the groups on each carbon of a double bond, an order of priority with preference given to the groups with the heavier atom attached to the double bond.
2. If the first atoms of two groups on a carbon are the same, then the group which has the heavier atom attached to the first atom has higher priority.
3. If the second atoms are identical, keep moving out along the group until a difference is found.
4. Multiple bonds count as two, three, etc., bonds to the atom attached.
5. If the groups of highest priority are on the same side of the double bond, name the isomer \textit{Z} (Zusammen).
6. If the groups of highest priority are on the opposite side of the double bond, name the isomer \textit{E} (Entgegen).

\begin{center}
\begin{tikzpicture}

\node at (0,0) [draw] (C1) {$C$};
\node at (1,0) [draw] (C2) {$C$};
\node at (0.5,-0.5) [draw] (H) {$H$};
\node at (0.5,-1) [draw] (H) {$H$};
\node at (1.5,-0.5) [draw] (H) {$H$};
\node at (1.5,-1) [draw] (H) {$H$};
\draw (C1) -- (C2);
\draw (C1) -- (H);
\draw (C2) -- (H);
\node at (0,0) [red] {high priority};
\node at (1,0) [red] {high priority};
\node at (0.5,-0.5) [red] {low priority};
\node at (0.5,-1) [red] {low priority};
\node at (1.5,-0.5) [red] {low priority};
\node at (1.5,-1) [red] {low priority};
\end{tikzpicture}
\end{center}

\textit{Z} (zusammen)....together

\begin{center}
\begin{tikzpicture}

\node at (0,0) [draw] (C1) {$C$};
\node at (1,0) [draw] (C2) {$C$};
\node at (0.5,-0.5) [draw] (H) {$H$};
\node at (0.5,-1) [draw] (H) {$H$};
\node at (1.5,-0.5) [draw] (H) {$H$};
\node at (1.5,-1) [draw] (H) {$H$};
\draw (C1) -- (C2);
\draw (C1) -- (H);
\draw (C2) -- (H);
\node at (0,0) [red] {high priority};
\node at (1,0) [red] {low priority};
\node at (0.5,-0.5) [red] {low priority};
\node at (0.5,-1) [red] {low priority};
\node at (1.5,-0.5) [red] {high priority};
\node at (1.5,-1) [red] {low priority};
\end{tikzpicture}
\end{center}

\textit{E} (entgegen)....across

\textbf{The E/Z Nomenclature of Alkene Stereoisomers}
d. Relative Stabilities of Alkene Geometric Isomers

Trans isomers are more stable than cis isomers because of steric destabilization of the cis isomer. In 2-butene this destabilization favors the trans isomer by 0.69 Kcal/mole, but in 2,2,6,6-tetramethyl-3-hexene (draw the structure of both isomers) the trans isomer is favored by 6.3 Kcal/mole. Additional alkyl substituents on the double bond of the alkene stabilizes the alkene...unless steric effects become too severe.
3. Addition of Hydrogen Halides to Alkenes (Electrophilic Addition Reactions)

Polar molecules add across double bonds in a predictable fashion. The electrons in a \( \pi \)-bond are relatively weakly held by the carbon atoms (\( \pi \)-bond strength \( \approx 50-60 \text{ Kcal/mole} \)). Thus they are available to react with a suitable electron-deficient species; alkenes are weak nucleophiles. When this occurs a new sigma bond is formed, and an electron deficient carbon (a carbocation or carbonium ion) is formed.

When an alkene reacts with an electrophile (in the case of a hydrogen halide HX...a proton), donation of \( \pi \)-electrons from the alkene creates a new C-H bond and an intermediate carbocation (empty p orbital). This then reacts with a nucleophile (in the case of hydrogen halides...a halide anion) to form the observed product.

a. Markovnikov's Rule

Unsymmetrical alkenes often give a highly regioselective reaction (selective addition of an unsymmetrical reagent to an unsymmetrical alkene). The favored product results from the addition of the electrophile (proton, in the case of hydrogen halides) to the carbon which has the least alkyl
substitution or greatest hydrogen substitution. This is often referred to as the Markovnikov Rule after a Russian Chemist who first observed this effect in 1869. The rule is often stated as a slogan:

**Them that has gets.**

Them being carbons bearing the greatest number of hydrogen atoms...and gets being the proton. Markovnikov's Rule is an empirical rule (based on observations of great numbers of examples, but it is based on a simple theoretical explanation. Markovnikov's rule favors the product which passes through the most stable carbocation intermediate.

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**Regiochemistry of addition of HBr to an unsymmetrical alkene**

b. Carbocation Stability

Overlap between the empty p orbital of a carbonium ion center and the \( \text{sp}^3 \) orbital of an adjacent alkyl group creates a stabilizing effect. This overlap results in some electron density being shared with the carbonium ion, somewhat helping the electron deficiency. This phenomenon is called Hyperconjugation and is a very important concept which will reoccur throughout the course. The more nearby alkyl groups the greater the effect. Thus the order of stability of carbocations is: **Tertiary > Secondary > Primary > Methyl**

Thus in the case of addition of HBr to 1-hexene, the major product is 2-bromohexane (as predicted by Markovnikov’s Rule) because addition of the electrophile to the double bond at the number one carbon gives the more stable secondary carbocation at the number 2 carbon.
Relative Stability of Carbocations (Carbonium ions).

Tertiary (3°) > Secondary (2°) > Primary (1°) > Methyl

Hyperconjugation between the empty p orbital and adjacent sigma bonds formed from sp3 orbitals helps to stabilize the carbocation.

Carbocation stability is caused by hyperconjugation

c. Carbonium Ion Rearrangements

In some cases, an initial carbonium ion intermediate will migrate to a different portion of the molecule by shifting a nearby alkyl group or hydride. This is done so as to produce a more stable carbocation. This will give, after trapping by the nucleophile, a rearranged product. The driving force for all these rearrangements is to form a more stable intermediate carbocation! (i.e. primary to secondary, secondary to tertiary, etc.)

**STEP 1:** Electrophillic Addition follows Markovnikov Rule

Intermediate is a secondary cation

**STEP 2:** Rearrangement methyl group shift... forms tertiary carbocation

Rearrangement of Carbonium Ions
4. Hammond Postulate

Certain reactions have their product distributions determined by the rates of a pair of competitive pathways. Since these reactions do not involve product equilibration, it is the relative height of the transition states leading to the two products that determines the ratio of the two products. **Pathways with lower barriers will occur faster, hence more of the reactant will cycle over to this product.** These reactions are said to occur under kinetic control.

The transition state leading to the secondary carbonium ion (TS 1) will have some of the structure of this species. This transition state will be **lower in energy** than the transition state leading to the primary carbonium ion (TS 2), which has some of the structure of the less stable primary carbonium ion. **Thus the rate at which 2-bromopropane will be formed is higher than that for 1-bromopropane; 2-bromopropane will be the predominate product.**