Chapter 8
Alkenes and Alkynes

from
Organic Chemistry
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Preview

Alkenes are hydrocarbons with C=C bonds and alkynes are hydrocarbons with C≡C bonds. Since C=C bonds have sp² hybridized C, atoms or groups directly attached to a C=C bond lie in a plane and are separated by approximately 120° bond angles. A molecule cannot freely rotate about its C=C bond. As a result, some alkenes have stereoisomers, in addition to structural isomers, with different relative stabilities. Alkenes can also have other functional groups.

Atoms or groups directly bonded to a C≡C bond lie in a straight line since C≡C bonds have sp hybridized C. This makes it difficult to place a C≡C bond in rings of cyclic molecules. The nomenclature of alkynes is analogous to that of alkenes. C=C and C≡C bonds impart characteristic features to NMR and IR spectra of their compounds that aid in their structural identification.

8.1 Alkenes

Alkenes and cycloalkenes are hydrocarbons with one C=C bond. They are also commonly referred to as olefins.

Unbranched Alkenes (8.1A)

Unbranched alkenes are analogous to unbranched alkanes. Since the C=C can be located in different positions in unbranched alkenes with four or more C's, they have structural isomers.

Ethene. The simplest alkene ethene (H₂C=CH₂) is planar with H-C-H and H-C-C bond angles that are close to 120°.

Figure 8.2
These 120° bond angles and the planar geometry are consistent with \( sp^2 \) hybridization for each of ethene's C atoms (Chapter 1). Each C uses its three \( sp^2 \) atomic orbitals to form the two C-H bonds and one of the C-C bonds as we illustrate here.

Figure 8.49
Figure 8.50

In addition to the $\sigma$(sp$^2$-sp$^2$) C-C bond just shown, the other C-C bond in C=C is $\pi$(2p-2p) that results from sideways overlap of the 2p orbitals on each sp$^2$ C.
Propene. We show propene (CH₃CH=CH₂), the next higher mass alkene, in two different views.

Figure 8.5

![Propene structure](image)

The CH₃ group causes bond angles to deviate slightly from the bond angles in ethene because of its larger steric size compared to H. While the C=C bond and its directly attached atoms lie in a plane, CH₃ has a normal tetrahedral geometry.

Figure 8.6

Rotation about C-C single bonds is usually a low energy process (Chapter 2), so propene has different conformations due to rotation about the H₃C-CH bond. The most stable one is (A) where the Cₐ-H bond is staggered between two C-H bonds of CH₃. Conformation (B), where the C=C bond is staggered between C-H bonds of CH₃, has a higher energy than (A) so it is less stable than (A).
1-Butene and 2-Butene. The next higher molecular mass alkenes after ethene and propene are the two different C4 structural isomers 1-butene and 2-butene.

Figure 8.7

\[
\begin{align*}
1\text{-butene} & : \begin{array}{c}
\text{CH}_3\text{-CH}_2\text{-CH=CH}_2
\end{array} \\
2\text{-butene} & : \begin{array}{c}
\text{CH}_3\text{-CH=CH}-\text{CH}_3
\end{array}
\end{align*}
\]

The number prefix in each of these names (1- or 2-) corresponds to the lower C number of the two C's of each C=C bond. Alkenes are numbered so that the C=C bond is in the longest continuous carbon chain and has the lowest possible C number.

Other Alkenes and Cycloalkenes. We name other unbranched alkenes in the same way we just named 1-butene and 2-butene. We always indicate the position of the double bond in acyclic alkenes using a number that precedes the name of the parent alkene, but unbranched cycloalkenes (Figure 8.7a) do not require these number designations since one C of the C=C is always C1.

Figure 8.7a

We give nomenclature of branched and substituted alkenes and cycloalkenes later in this chapter.

Alkene Stereoisomers (8.1B)

Some unbranched alkenes can exist as two different stereoisomers. An example is 2-butene (CH\textsubscript{3}CH=CH\textsubscript{3}).

(E)-2-Butene and (Z)-2-Butene. Atoms directly attached to a C=C bond must lie in a plane, so the terminal CH\textsubscript{3} groups (C1 and C4) of 2-butene can be on the same or opposite sides of the C=C bond (Figure 8.8).

Figure 8.8
These two stereoisomers of 2-butene do not interconvert at normal temperatures so they are different molecules with different properties and names. Interconversion requires C=C rotation that breaks the π(2p-2p) bond and this process requires a large energy input (about 270 kJ/mol).

Figure 8.8a

The two CH₃ groups of (Z)-2-butene are on the same side of the C=C, while its stereoisomer with two CH₃ groups on opposite sides of the C=C is (E)-2-butene (Figure 8.8). E is the first letter of the German word "entgegen" that means "opposite", while Z is the first letter of the German word "zusammen" that means "together".

**Other E and Z Alkenes.** Alkenes have E and Z stereoisomers whenever the two atoms and/or groups on each C of the C=C are different from each other. This is the case for (E) and (Z)-2-butene (Figure 8.9).

Figure 8.9
The two groups on $C_a$ (CH$_3$ and H) are different from each other, and so are the two groups (CH$_3$ and H) on $C_b$. It does not matter that both $C_a$ and $C_b$ have identical pairs of groups (CH$_3$ and H) because we separately consider $C_a$ and $C_b$. We show other examples of alkenes with $E$ and $Z$ stereoisomers in Figure 8.10.

**Figure 8.10**

![Diagram](image)

We will name these alkenes after we learn the $E/Z$ assignment rules in the next section.

**E,Z Assignment Rules.** The rules for assigning the $E$ and $Z$ designations are based on those that we used in Chapter 4 to assign the $R$ and $S$ designations to carbon stereocenters. We give priority numbers 1 and 2 to the two atoms and/or groups bonded to each C of the C=C using the $R,S$ priority assignment rules (Chapter 4). This results in two different general possibilities for all alkenes with $E, Z$ isomers.

**Figure 8.11**

![Diagram](image)

The isomer with the same priority numbers on the same side of the C=C is the $Z$ ("together") isomer, while the isomer with the same priority numbers on opposite sides of the C=C is the $E$
("opposite") isomer. We show once again the examples from Figure 8.10 that have E,Z-isomers and include their priority assignments.

Figure 8.11a

**E and Z Stereoisomers are Diastereomers.** We learned in Chapter 4 that two stereoisomers of a compound may either be enantiomers or diastereomers. Enantiomers are always mirror images (that are non-superimposable), so E and Z stereoisomers are diastereomers because they are not mirror images.

Figure 8.12

E and Z stereoisomers are generally not chiral compounds because each alkene stereoisomer usually has a plane of symmetry defined by the double bond and its attached atoms as we show in Figures 8.13 and 8.14 [next page].
Alkenes that are chiral most often have this property because they additionally have one or more chiral tetrahedral C’s that are chiral.
cis and trans Isomers. Organic chemists generally refer to (E)-2-butene as trans-2-butene, and (Z)-2-butene as cis-2-butene (Figure 8.15).

Before E,Z nomenclature was introduced in 1968, organic chemists exclusively used the terms cis and trans to designate alkene stereoisomers, and these terms remain an integral part of organic chemistry vocabulary. For example, when two groups are on the same side of a C=C we say they are "cis" to each other, while we say that groups on opposite sides of a C=C are "trans". This use of cis and trans is convenient and unambiguous, but this is often not true of their use in specific chemical names. We can unambiguously assign cis and trans to E and Z stereoisomers of 2-butene, but this is not true for many alkenes as we show in Figure 8.16 [next page].

For example we can assign the alkene stereoisomer in Figure 8.16 as Z using the E/Z assignment rules above, but it is not clear whether we should call it cis or trans. As a result, E and Z have replaced cis and trans in systematic nomenclature.

More than One C=C in a Molecule (8.1C)
Hydrocarbons can have more than one C=C bond.

Polyenes. Polyenes have two or more C=C bonds in the same continuous chain (Figure 8.19) [next page].
Figure 8.19

We use prefixes such as di, tri, tetra, penta, hexa, etc. to indicate the number of double bonds in the polyene and we indicate the positions of these C=C bonds with prefix numbers that we choose so that the first C=C bond has the lowest possible C number (Figure 8.20).

Figure 8.20

If this provides two equal choices, the next C=C bonds are numbered until a difference is found.

Similarly, in cyclic polyenes, we choose one C=C as C1-C2 so that subsequent C=C bonds have the lowest C numbers. Where appropriate, we can designate each individual C=C bond of a polyene as E or Z as we previously described for alkenes.

**Allenes.** Compounds where two C=C bonds share a common carbon are called allenes.

Figure 8.20a

We systematically name allenes in the same way as polyenes (Figure 8.19). We discuss them in more detail later in this chapter after we introduce alkynes. Allenes can sometimes isomerize to
alkynes and their chemical properties are more like those of alkynes than those of polyenes in which each C=C is separated by at least one C-C single bond.

**Nomenclature of Substituted Alkenes** (8.1D)

We name substituted alkenes as derivatives of their parent unsubstituted alkenes.

**Alkyl and Halogen Substituted Alkenes.** We designate the position of an alkyl group, or halogen atom on an alkene, with the number of the carbon to which it is bonded based on the numbering of the parent alkene. When we find that either end of the parent alkene can be C1 based on the location of the C=C, we choose C1 so that the first halogen or alkyl substituent has the lowest number (Figure 8.17).

Figure 8.17

**Alkyl and Halogen Substituted Cycloalkenes.** Although we do not use a number to designate the C=C position in an unsubstituted cycloalkene with a number, we need a number to define the position of a halogen atom or alkyl group with respect to the C=C in a substituted cycloalkene. To accomplish this, we assign the C's of C=C as C1 and C2 so that the alkyl group or halogen atom substituent closest to the C=C has the lowest possible number as we show in Figure 8.18.

Figure 8.18
**Alkyl and Halogen Substituted Polyenes.** In order to name substituted polyenes, we select the parent hydrocarbon that has the maximum number of double bonds. As a result, the parent hydrocarbon may have a shorter chain length than the longest chain with a C=C (Figure 8.22).

Figure 8.22
Once we identify the chain with the greatest number of C=C bonds, we number it so that the first C=C bond (or subsequent C=C bonds) has the lowest possible C numbers. When there are two equivalent alternative names for a structure such as those in Figure 8.33, we choose the numbering that gives the lowest number to the first group or atom substituted on the parent chain.

Figure 8.33  [Note: There are no Figures 8.23 through 8.32]

**Alkenes With OH or NH₂ Groups.** Alkenes with OH or NH₂ groups have different types of systematic names than alkyl or halogen substituted alkenes and polyenes. Whenever possible, we name them as **alkenols** (OH group) and **alkenamines** (NH₂ group) using nomenclature analogous to that we described in Chapter 3 for **alcohols** (alkanols) and **amines** (alkanamines).

For **alkenols**, we first identify the chain that contains OH and the most C=C bonds. We number the chain so that the **OH group** has the lowest possible number. When there is more than one way to number a chain that gives the same lowest number to C-OH, we choose the numbering sequence that causes the first (or a subsequent) C=C to have the lowest number (Figure 8.34).

Figure 8.34
We name *alkenamines* in the same way as *alkenols* (Figure 8.35).

Figure 8.35

\[ \text{(2)-2-butene-1-amine} \quad \text{N,N-dimethyl-2-propen-1-amine} \]

\[ \text{CH}_2=\text{CH}-\text{OH} \quad \text{and} \quad \text{CH}_2=\text{CH}-\text{NH}_2 \]. Compounds with OH or NH\(_2\) directly bonded to a C=C bond are unstable and isomerize to their more stable isomers with C=O or C=N groups (Figure 8.35a).

Figure 8.35a

In the resulting equilibria shown above, the *alkenol* and *alkenamine* forms (those with the C=C) are present to only a very small extent. Nonetheless, these minor forms are important in a variety of organic reactions that we describe later. We mentioned the stable compounds with C=O and C=NH groups in Chapter 1 and we describe them later in the text.

**Common Names of Substituted and Unsubstituted Alkenes.** Organic chemists frequently use *common names* for the simple substituted and unsubstituted alkenes such as those we show in Table 8.1.

**Table 8.1. Common Names of Unsubstituted and Substituted Alkenes.**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Common Name</th>
<th>Systematic Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)=CH(_2)</td>
<td>ethylene</td>
<td>ethene</td>
</tr>
<tr>
<td>CH(_3)-CH=CH(_2)</td>
<td>propylene</td>
<td>propene</td>
</tr>
<tr>
<td>(CH(_3))(_2)C=CH(_2)</td>
<td>isobutylene</td>
<td>2-methylpropene</td>
</tr>
<tr>
<td>CH(_2)=C=CH(_2)</td>
<td>allene</td>
<td>propadiene</td>
</tr>
<tr>
<td>CH(_2)=C(CH(_3))CH=CH(_2)</td>
<td>isoprene</td>
<td>2-methyl-1,3-butadiene</td>
</tr>
<tr>
<td>CH(_2)=CH-Cl</td>
<td>vinyl chloride*</td>
<td>chloroethene</td>
</tr>
<tr>
<td>CH(_2)=CH-CH(_2)-Cl</td>
<td>allyl chloride*</td>
<td>3-chloropropene</td>
</tr>
<tr>
<td>CH(_2)=CH-CH(_2)-OH</td>
<td>allyl alcohol</td>
<td>2-propenol</td>
</tr>
<tr>
<td>CH(_2)=CH-CH(_2)-NH(_2)</td>
<td>allyl amine</td>
<td>2-propenamine</td>
</tr>
</tbody>
</table>

* We can replace *chloride* (Cl) by *fluoride* (F), *bromide* (Br), or *iodide* (I).
The terms vinyl and allyl (Table 8.1) are common names for the 1-ethenyl and 2-propenyl groups (Figure 8.36[next page]).

Figure 8.36

They also appear in the common names of other compounds (besides those in Table 8.1) with the general structure CH$_2$=CH-Y and CH$_2$=CH-CH$_2$-Y.

**Alkene Stability** (8.1E)
The relative stability of alkene isomers depends on whether they are E or Z, and the location of the C=C bond in the hydrocarbon chain.

**Relative Stability of Isomeric E and Z Alkenes.** There is an unfavorable steric interaction between two alkyl groups cis to each other on a C=C bond (as in (Z)-2-butene) that causes the molecule to be less stable (have higher energy) than the isomer where those alkyl groups are trans to each other (as in (E)-2-butene).

Figure 8.37

Organic chemists have determined the relative stabilities of isomers such as (E) and (Z)-2-butene by measuring and comparing the heat change in their reactions with molecular hydrogen (H$_2$).

Figure 8.38

\[(Z)-2\text{-butene} + \text{H}_2 \rightarrow \text{butane} + 120 \text{ kJ/mol}\]
\[(E)-2\text{-butene} + \text{H}_2 \rightarrow \text{butane} + 116 \text{ kJ/mol}\]

Since these hydrogenation reactions of (E) and (Z)-2-butene both give butane as the reaction product, the difference between their measured heat changes reflects their comparative thermodynamic stabilities.
These reactions release heat, so both \((Z)\) and \((E)\)-2-butene have higher energies than butane (along with \(H_2\)) so we say that the reactions are *exothermic*. *Hydrogenation* of a mole of \((Z)\)-2-butene produces 4 kJ/mol more heat than hydrogenation of a mole of \((E)\)-2-butene (120 kJ - 116 kJ = 4 kJ), so \((Z)\)-2-butene is 4 kJ/mol *higher in energy* than \((E)\)-2-butene. Alternatively we can say that \((Z)\)-2-butene is 4 kJ/mol *less stable* than its \(E\) isomer. We illustrate these relationships using an energy diagram.

Figure 8.39

\[\text{C=C Substitution and Alkene Stability.}\] The *stability* or *relative energy* of an alkene also depends on the position of the C=C bond in a carbon chain. For example, hydrogenation of 1-butene also gives butane, but releases more heat than hydrogenation of either \((E)\) or \((Z)\)-2-butene.

Figure 8.40

\[
1\text{-butene} + H_2 \rightarrow \text{butane} + 127 \text{ kJ/mol}
\]

This means that 1-butene is less stable (has a higher energy) than either \((Z)\) or \((E)\)-2-butene as we illustrate here.

Figure 8.40a
1-Butene has the general formula \( \text{RCH}=\text{CH}_2 \) while both isomeric (E) and (Z)-2-butene have the general formula \( \text{RCH} = \text{CHR} \). We usually find that an increase in the number of \( \text{R} \) groups on a \( \text{C} = \text{C} \) increases the stability of an alkene (Figure 8.40a and Figure 8.41).

Figure 8.41

\[
\begin{align*}
(\text{CH}_3)_2\text{CHCH}=\text{CH}_2 & \quad + \quad \text{H}_2 \rightarrow (\text{CH}_3)_2\text{CHCH}_2\text{CH}_3 & + & 127 \text{ kJ/mol} \\
\text{CH}_2=\text{C} (\text{CH}_3)\text{CH}_2\text{CH}_3 & \quad + \quad \text{H}_2 \rightarrow (\text{CH}_3)_2\text{CHCH}_2\text{CH}_3 & + & 120 \text{ kJ/mol} \\
(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_3) & \quad + \quad \text{H}_2 \rightarrow (\text{CH}_3)_2\text{C}-\text{CH}_2-\text{CH}_3 & + & 113 \text{ kJ/mol}
\end{align*}
\]

*Hydrogenation* of each of the alkenes in Figure 8.41 gives the same alkane \((\text{CH}_3)_2\text{CHCH}_2\text{CH}_3\), so their heats of hydrogenation reflect the relative stabilities of the three alkenes. The alkene with one \( \text{R} \) group on the \( \text{C} = \text{C} \) is less stable (has a higher heat of hydrogenation) than that with two \( \text{R} \) groups on the \( \text{C} = \text{C} \), while that with three \( \text{R} \) groups on \( \text{C} = \text{C} \) is the most stable (has the smallest heat of hydrogenation).

These and other similar results indicate that the general stability order for isomeric alkenes is:

\[
\text{R}_2\text{C}=\text{CR}_2 > \text{R}_2\text{C}=\text{CHR} > \text{R}_2\text{C}=\text{CH}_2 = \text{trans-RCH}=\text{CHR} > \text{cis-RCH}=\text{CHR} > \text{RCH}=\text{CH}_2 > \text{CH}_2=\text{CH}_2
\]

We explain this order by proposing that electron density from C-H \( \sigma \) bonds in alkyl substituents \( \text{(R)} \) delocalizes into the \( \text{C} = \text{C} \) \( \pi \) bond as we show in Figure 8.59c.
We refer to this \textit{electron density donation} from a $\sigma$ bond to a $\pi$ bond as \textit{hyperconjugation} in the same way we referred to electron density donation from alkyl groups to carbocations as hyperconjugation in Chapter 7.

\textbf{Stability of Cycloalkenes.} Cycloalkenes can have as few as three C atoms, however both cyclopropene (C3) and cyclobutene (C4) are highly strained molecules.

Figure 8.43

These two highly strained cycloalkenes are planar and their internal ring bond angles are much smaller than normal. In contrast, cyclopentene with significantly larger bond angles, and cyclohexene with almost normal bond angles, are both relatively strain-free.

The ring constrains the C=C bond to be exclusively $Z$ (\textit{cis}) for cyclopropene through cycloheptene. However, there are $E$ as well as $Z$ isomers of cyclooctene and higher cycloalkenes.

Figure 8.43a

While the $Z$ isomer (\textit{cis} isomer) of cyclooctene is more stable than its $E$ isomer (\textit{trans} isomer) by about 38 kJ/mol, this energy difference decreases to about 12 kJ/mol for ($E$)- and ($Z$)-cyclononene and continues to decrease with increasing ring size. ($E$)- cycloalkenes (\textit{trans} cycloalkenes)
become more stable than \((Z)\)-cycloalkenes (\textit{cis} cycloalkenes) when there are more than 11 C's in the ring.

8.2 Alkynes

Hydrocarbons with a \(\text{C}≡\text{C}\) bond are systematically named \textit{alkynes} and commonly referred to as \textit{acetylenes}. For reasons that you will see later, we also describe \textit{allenes} (\(\text{R}_2\text{C}≡\text{C}≡\text{CR}_2\)) in this section.

\textbf{Unbranched Alkynes} (8.2A)

Unbranched alkynes have \textit{structural isomers} because the \(\text{C}≡\text{C}\) can be at different locations in the carbon skeleton. However we will see below that they do not have \textit{stereoisomers} associated with the \(\text{C}≡\text{C}\) bond.

\textit{Nomenclature}. We show unbranched alkynes with five or fewer C's in Table 8.2 along with their systematic names and common names where appropriate.

\textbf{Table 8.2. Some Simple Alkynes}

<table>
<thead>
<tr>
<th>Structure</th>
<th>Systematic</th>
<th>Common</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{HC}≡\text{CH})</td>
<td>ethyne</td>
<td>acetylene</td>
</tr>
<tr>
<td>(\text{CH}_3\text{-C}≡\text{CH})</td>
<td>propyne</td>
<td>methylacetylene</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{-C}≡\text{CH})</td>
<td>1-butyne</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{-C}≡\text{CH}_3)</td>
<td>2-butyne</td>
<td>dimethylacetylene</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{CH}_2\text{-C}≡\text{CH})</td>
<td>1-pentyne</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{-C}≡\text{C}≡\text{CH}_3)</td>
<td>2-pentyne</td>
<td></td>
</tr>
</tbody>
</table>

Chemists usually refer to \textit{ethyne} by its common name \textit{acetylene}. We mentioned above that \textit{acetylene} is also used as the common name for the whole class of alkynes.

\textit{Alkyne Structure}. Alkynes (acetylenes) have a \textit{linear geometry} at the \(\text{C}≡\text{C}\) triple bond. In acyclic compounds, the bond angles between the triple bond and bonded atoms or groups are exactly \(180°\) as we show in Figure 8.44.

Figure 8.44
This linear geometry results from the directional character of the sp hybrid atomic orbitals of the C's in a C≡C (Chapter 1). The H-C bonds in ethyne use σ(1s-sp) molecular orbitals, while one of the C-C bonds is σ(sp-sp). The other two bonds in the C≡C group of ethyne (and all other alkynes) are π(2p-2p) bonds resulting from sideways overlap of the two 2p orbitals on each of the sp hybridized C's of the C≡C.

In propyne, the CH₃-C bond is σ(sp³-sp). Tetrahedral carbons in alkynes, such as those in the CH₃ groups in propyne or 2-butyne, and the CH₃ or CH₂ groups in 1-butyne or 2-pentyne, have normal tetrahedral bond angles and C-C rotation as we show using propyne as our example.

\[ \text{Figure 8.44a} \]

With only one group or atom attached to each carbon of the C≡C bond, and 180° C-C≡C bond angles, alkynes have no cis/trans (E/Z) stereoisomers.

\textbf{Polyynes.} More than one C≡C bond can be in the same molecule and the nomenclature rules for these polyynes are analogous to those for polyenes. When a double and triple bond are in the same continuous chain, we name the molecule an \textbf{alkene-ylene} and give double bonds preference over triple bonds in choosing C1.

\[ \text{Figure 8.45} \]

Substitution of alkyl groups, halogen atoms, OH or NH₂ groups on alkynes, polyynes, or ene-ynes gives compounds that are systematically named analogously to OH and NH₂ substituted alkenes.
**Alkyne Stability** (8.2B)
Alkyl groups bonded to the C≡C bond stabilize *alkynes* in the same way that they stabilize *alkenes*. For example, 2-butyne (with the general structure R-C≡C-R) is more stable than its structural isomer 1-butyne (with the general structure R-C≡C-H) as we see by comparing their heats of hydrogenation.

Figure 8.44b

\[
\begin{align*}
\text{1-butyne} & \quad + \quad 2\text{H}_2 & \quad \rightarrow & \quad \text{butane} & \quad + \quad 292 \text{ kJ/mol} \\
\text{2-butyne} & \quad + \quad 2\text{H}_2 & \quad \rightarrow & \quad \text{butane} & \quad + \quad 272 \text{ kJ/mol}
\end{align*}
\]

The favored linear geometry of the C-C≡C-C grouping of alkynes restricts the presence of a C≡C bond in rings to cycloalkynes that are relatively large. *Cyclononyne* (C9) is relatively strain free, while *cyclooctyne* (C8) is strained but has been isolated. In contrast, *cyclohexyne* (C6) and *cycloheptyne* (C7) are very unstable compounds that only exist at very low temperatures for short periods of time.

**C-H and C-C Bond Lengths** (8.2C)
Now that we have described and compared the bonding in *alkanes* (Chapter 2), *alkenes*, *alkynes*, and *allenes*, we compare and contrast their C-H and C-C bond lengths.

**Alkanes, Alkenes, and Alkynes.** We compare calculated bond lengths in *ethene*, and *ethyne*, with those in *ethane* in Table 8.3.

\[
\text{Table 8.3. Approximate C-H and C-C Bond Lengths}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>C Hybridization</th>
<th>C-H (Å)</th>
<th>C-C (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>sp$^3$</td>
<td>1.09</td>
<td>1.53</td>
</tr>
<tr>
<td>ethene</td>
<td>sp$^2$</td>
<td>1.08</td>
<td>1.32</td>
</tr>
<tr>
<td>ethyne</td>
<td>sp</td>
<td>1.06</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Each C-H bond uses a molecular orbital made up of an overlapping $1s$ atomic orbital on H and an $sp^3$, $sp^2$, or $sp$ atomic orbital on C (Chapter 1). The decrease in C-H bond length as C hybridization changes from $sp^3$ to $sp^2$ to $sp$ reflects the decrease in the "length" of the hybrid C atomic orbital used in the C-H bonding MO. This C atomic orbital "length" is determined by the relative amounts of 2s and 2p character in the hybrid AO (Table 8.3a)

\[
\text{Table 8.3a. Relative Amounts of 2s and 2p Character in Hybrid Atomic Orbitals}
\]

<table>
<thead>
<tr>
<th>Atomic Orbital</th>
<th>% -2s Character</th>
<th>% -2p Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp$^3$</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>sp$^2$</td>
<td>33</td>
<td>67</td>
</tr>
<tr>
<td>sp</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>
The amount of 2p character in the hybrid AO determines how "extended" the hybrid AO is from the C nucleus. You can see that %-2p character in these hybrid carbon AO's decreases in the order sp^3 > sp^2 > sp. As a result, the C-H bond lengths resulting from overlap of those AO's with the 1s AO on H decreases in the same order (Table 8.3).

The analogous decrease in C-C bond lengths with a change in C hybridization from sp^3 to sp^2 to sp is more pronounced than the decrease in C-H bond length, and results from two effects. The first is the change in "size" of the C AO's that we have just described to explain C-H bond lengths, while the second is a consequence of π(2p-2p) bonds between the two C's.

Effective sideways overlap of two 2p orbitals to form a π(2p-2p) bond requires that C-C bond lengths be shorter than those associated with just a σ bond considered by itself. For example, the length of the C-C bond (σ(sp^2-sp^2)) for the twisted form of ethene, where the 2p orbitals are perpendicular to each other and cannot overlap (Figure 8.59a), is longer (1.39 Å) than that in planar ethene (1.32 Å) that has both a σ(sp^2-sp^2) bond and a fully developed π(2p-2p) bond.

Figure 8.59a

**Acidity of C≡C-H Hydrogens** (8.2D)
The strong base sodium amide (NaNH₂) removes C≡C-H protons of 1-alkynes, but does not comparably react with C-H's bonded to C=C or to C-C bonds.

\[
\text{R-C≡C-H} + \text{Na}^+ \cdot \text{NH}_2 \rightarrow \text{R-C≡C-}^\cdot \text{Na}^+ + \text{H-NH}_2
\]

This is reflected in the relative pKₐ values of these various types of C-H protons.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>R₃C-H</th>
<th>R₂C=CRH</th>
<th>R-C≡C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKₐ Value</td>
<td>50</td>
<td>44</td>
<td>25</td>
</tr>
</tbody>
</table>
We explain this relatively high C≡C-H acidity by the relatively large amount (50%) of 2s character (Table 8.3a) in a C≡C-H bond that is made up of a C sp hybrid orbital. That relatively large s character makes an sp hybrid C more electronegative than sp² or sp³ C's, and hence more able to stabilize the negative charge resulting from removal of a proton by a base.

Acetylide ions resulting from loss of a C≡C-H proton are nucleophiles and react with a variety of substrates such as those described at the end of Chapter 7 in nucleophilic substitution reactions such as the type shown here.

\[
\text{R-CH}_2\text{-Br} + \text{Na}^+ \cdot \text{C≡C-R'} \rightarrow \text{R-CH}_2\cdot\text{C≡C-R'} + \text{Na}^+ \text{Br}^-
\]

We will see further examples of them serving as nucleophiles in later chapters.

**Allenenes (8.2E)**

We include allenes (R₂C≡C=CR₂) in this alkyne section because the central C of the allene C≡C=C group is sp hybridized like C's in C≡C bonds. Some allenes also isomerize to alkynes.

**Nomenclature.** The systematic name of the simplest allene (C₃) is propadiene, however it is almost always called allene which is its common name. The next higher molecular mass allene is 1,2-butadiene (H₂C≡C=CH-CH₃), followed by 1,2-pentadiene (H₂C≡C=CH-CH₂CH₃) and its structural isomer 2,3-pentadiene (CH₃-CH=C=CH-CH₃).

**A Nomenclature Aside.** Remember that the common name of alkynes is acetylenes and acetylene is also the common name of the simplest alkyne. You can see that the same is true for the class of compounds commonly referred to as allenes.

**Structure and Bonding.** Since the two C=C bonds in allenes share a common C we say that they have cumulated double bonds. The sp hybridization of the central C of C≡C=C is consistent with the 180° C-C-C bond angle of the allene group.
Each C=C has one $\sigma$(sp$^2$-sp) bond and one $\pi$(2p-2p) bond, and all four of the C-H bonds in the specific compound named allene (H$_2$C=C=CH$_2$) are $\sigma$(sp$^2$-1s). The four H atoms of allene lie in two different planes that are perpendicular to each other since each of the two cumulated C=C $\pi$ bonds uses a different 2p orbital on the central sp C atom.

Figure 8.59
**Bond Lengths.** C-H bond lengths in *allene* (H₂C=C=CH₂) are almost the same as those in *ethene* (H₂C=CH₂) since they are σ(1s-sp²) in both compounds.

Figure 8.59b

In contrast, the C-C bond lengths for the compound *allene* have values between those of *ethene* and *ethyne*. Each C-C bond in *allene* uses a σ(sp²-sp) MO that causes the C-C separation to fall between the σ(sp²-sp²) bond in ethene and the σ(sp-sp) bond in ethyne.

### 8.3 Spectrometric Features of C=C and C≡C Bonds

C=C and C≡C bonds impart unique spectrometric characteristics to their molecules. We present the most important of these for NMR and IR spectrometry in this section. You should review the sections on NMR and IR in Chapter 5 before or as you read this section.

**13C NMR Spectrometry** (8.3A)

The ¹³C chemical shift values (δ values) for the C atoms in C=C and C≡C bonds are larger than those for tetrahedral C atoms substituted only with H or alkyl groups. This downfield shift (Chapter 5) is much greater for C=C bonds than for C≡C bonds.

**C≡C Bonds.** The ¹³C chemical shift values (δ values) of C≡C carbons substituted only by H or alkyl groups range from δ110 to δ150. The ¹³C δ value for terminal C≡C carbons (the C of a =CH₂ group) is at the lower end of this range while internal C≡C carbons (those with alkyl substitution) have larger δ values (Figure 8.61).

Figure 8.61
In contrast, a C=C group has only a small effect on $^{13}$C chemical shifts of attached C's as we see by comparing $^{13}$C $\delta$ values for a similar alkane and alkene (Figure 8.62).

Figure 8.62

The C=C carbons show the expected large $\delta$ values, but the corresponding tetrahedral C's have almost identical $\delta$ values in each molecule.

Groups other than alkyl groups substituted on or near a C=C, show a variety of effects on $^{13}$C $\delta$ values of the C=C carbons (Figure 8.63) that depend on whether the C=C is internal or terminal.

Figure 8.63

$C=O$ Bonds. The $\delta$ value for the C in C=O bonds is much greater than $\delta$ values for C's of any C=C. Typically the chemical shift values for C's in C=O are between $\delta 160$ and $\delta 200$ depending on the rest of the chemical structure. We describe compounds containing the C=O group beginning in Chapter 11 and present additional information about their NMR spectrometric characteristics there.

$C=\equiv C$ Bonds. The $^{13}$C $\delta$ values for C≡C carbons are shifted downfield like those of C=C, but the magnitude of the shift is much smaller as we see in a comparison of $^{13}$C shifts for C's in 1-butyne and 1-butene (Figure 8.64) [next page].
Figure 8.64

The chemical shift value of a terminal C in a C≡C is less than that of an internal C as we observed for C=C's.

We can see that the effect of a C≡C on neighboring alkyl groups is greater than that of a C=C by comparing $^{13}$C $\delta$ values for all of the C's in 2-hexyne, (E)-2-hexene, and hexane (Figure 8.65).

Figure 8.65

The $^{13}$C $\delta$ values of C1 and C4 in 2-hexyne are significantly smaller than the $^{13}$C $\delta$ values for the analogous C's in either of the other two compounds.

*Allenes.* The $^{13}$C $\delta$ values for the C's in the C=C=C group of *allenes* are unusual as we illustrate here for 3-methyl-1,2-buta diene.

Figure 8.66

While the central C atom has a very large $^{13}$C $\delta$ value ($\delta207$), the end C's have much smaller values ($\delta73$ and $\delta94$). These comparative $\delta$ values are typical for those of the analogous C's in other allenes.

$^1H$ NMR Spectrometry (8.3B)

The $^1H$ $\delta$ values of H's attached to C=C are much larger than those for H's attached to tetrahedral C with only H or alkyl substitution. However, the $\delta$ values for H-C≡C protons are much smaller and fall within the chemical shift range of H's on alkyl substituted tetrahedral C.

$C≡C-H^1H \delta$ Values. H's attached to C=C have $^1H$ $\delta$ values ranging from approximately $\delta4.7$ to $\delta6$ (Figure 8.67) [next page].
Figure 8.67

Since these $\delta$ values are much longer than those for most other C-H hydrogens, $^1$H NMR is very useful for identifying H-C=C protons in organic molecules. A C=C bond also increases $^1$H chemical shift values of C-H's on directly attached tetrahedral C's by about $\delta 0.7$ as you can see here in the comparison of $^1$H $\delta$ values for pentane and (Z) and (E)-2-pentene.

Figure 8.68

These spectra (Figure 8.68a) clearly show the distinctive location of C=C-$^1$H NMR signals.

Figure 8.68a
**$^1$H Spin-Splitting in Alkenes.** The splitting patterns that arise due to spin splitting between H's attached to the same C=C, and to alkyl groups directly attached to the C=C, are also very useful for spectral identifications. They can help identify whether a substituted C=C is E or Z and confirm the relative relationships of groups substituted on the C=C.

We see in Figure 8.69 that the magnitude of the spin-spin splitting ($J_{ab}$ (Hz)) between two H's attached to the same C=C varies greatly depending on their relative positions.

Figure 8.69

In each case, H$_a$ splits H$_b$ into a doublet and vice-versa, but the magnitude of the splitting ($J_{ab}$) is greatest when the H's are trans, less when they are cis, and very small when they are on the same carbon.

In addition to these splittings, a C=C bond permits **long range splitting** to occur between certain H's even when they are not on the same or adjacent C's as we show in the examples in Figure 8.70.

Figure 8.70

The magnitude of the splitting between two non-equivalent H's on a cycloalkene ring varies greatly with the size of the ring (Figure 8.71).

Figure 8.71
**Alkynes.** A C≡C bond has a much smaller effect on the $^1H$ δ value of an attached H than a C=C bond (Figure 8.72).

Figure 8.72

H's on alkynes exhibit long range splitting similar to that observed for alkenes (Figure 8.73).

Figure 8.73

Origin of the C≡C Effect on $^1H$ δ Values. The small effect of a C≡C on the δ values of a C≡C-H proton is the result of two large effects simultaneously operating in opposite directions. The first effect by itself, seen in the case of the C=CH$_2$ protons, would cause C=CH protons to have much larger δ values (a large downfield shift) compared to those attached to tetrahedral C's. However, the 4π electrons of a C≡C independently interact with the applied magnetic field to setup a magnetic field in the opposite direction to that of the applied magnetic field leading to a predicted upfield shift. The result is that the large downfield shift due to the first effect is canceled out by the correspondingly large upfield shift due to the "ring current" effect (second effect) leads to observed chemical shift values for C≡C-H hydrogens of about δ2. We will discuss this in more detail when we introduce "aromatic" compounds such as benzene (C$_6$H$_6$) in Chapter 12.

**Infrared Spectrometry (8.3C)**

C=C and C≡C bonds give characteristic peaks in infrared (IR) spectra. These IR signals are due to bond stretching and are located between 1640 and 1670 cm$^{-1}$ for C=C bonds, and 2100 and 2260 cm$^{-1}$ for C≡C bonds. The energy required to stretch carbon-carbon bonds has the order C≡C > C=C > C-C. The spectral chart in Figure 8.74 [next page] shows the IR spectral positions of these peaks and their relative energy values as well as those for several other types of chemical bonds.

The relative energies for stretching apart two bonded atoms depends not only on whether they are bonded by a single, double, or triple bond, but also on the specific atoms bonded together.
The energy required to stretch a single bond between a heavy and a light atom such as in a C-H, N-H, or O-H bond is actually greater than the stretching energies of triple bonds (Figure 8.74).

There are relatively few other IR absorptions in either the C=C or C≡C stretching regions, so IR peaks in these regions are very diagnostic for double or triple bonds in the molecule being analyzed. IR peaks in these regions can also be due to C=O, C=N, or C≡N bonds. We discuss the relative positions of the IR signals for different types of double and triple bonds later in the text after we introduce compounds containing C=O, C=N, and C≡N bonds.

**UV-Vis Spectrometry** (8.3D)

C=C and C≡C bonds give absorption signals in UV-Vis spectra only if the compound contains several of these bonds in an arrangement where they alternate with single bonds (are "conjugated"). For this reason we include our discussion of the UV-Vis characteristics of multiple bonds in Chapter 10 where we describe such "conjugated" polyenes and polyynes.

**UV-Vis Spectrometry.** Individual C=C and C≡C bonds do not give UV-Vis spectra (Chapter 5). C=C and C≡C bonds give absorption signals in UV-Vis spectra only if the compound contains several of these bonds in an arrangement where they alternate with single bonds (are "conjugated").

Figure 8.60a Some Conjugated Polyenes and Polyynes that Absorb UV Radiation

- CH₂=CH-CH=CH₂ \( \lambda_{\text{max}} = 217 \text{ nm} \ (\varepsilon = 21,000) \)
- CH₂=CH-CH=CH-CH₂ \( \lambda_{\text{max}} = 253 \text{ nm} \ (\varepsilon = 50,000) \)
- CH₃-C≡C-C≡C=C≡C=CH₃ \( \lambda_{\text{max}} = 207 \text{ nm} \ (\varepsilon = 135,000) \)

For this reason we include our discussion of the UV-Vis characteristics of multiple bonds in Chapter 10 where we describe such "conjugated" polyenes and polyynes. These "conjugated" polyenes (or polyynes) also have special chemical and physical properties that set them apart from alkenes (or polyenes) and alkynes (or polyynes) with isolated (non-conjugated) multiple bonds.
Chapter Review

**Alkenes**

- (1) Alkenes are hydrocarbons with a C=C bond (R₂C=CR₂).
- (2) The C's in the C=C bond are sp² hybridized and the R groups in R₂C=CR₂ lie in a plane with R-C=C bond angles of approximately 120°.
- (3) A high rotational barrier (about 270 kJ/mol) restricts rotation about C=C π(2p-2p) bonds.
- (4) Alkene systematic names use the prefixes eth-, prop-, but-, etc. to indicate the length of the longest carbon chain containing the C=C and the C=C position is assigned the lowest possible carbon number.
- (5) Alkenes with the general structure RₐRₖC=CRₓRᵧ have two stereoisomers labeled E or Z if Rₐ ≠ Rₖ, and Rₓ ≠ Rᵧ.
- (7) In RₐRₖC=CRₓRᵧ, Rₐ and Rₓ are cis to each other if they are on the same side of the C=C, and trans to each other if they are on opposite sides of the C=C.
- (8) Polynes are alkenes with two or more C=C bonds separated by at least one C-C bond.
- (9) Branched alkenes are named as "alkylalkenes", alkenes with halogen atoms (X) are named as "haloalkanes", while those with OH or NH₂ groups are named as alkenols or alkenamines analogously to alkanols and alkanamines.
- (10) cis-alkenes with the general structure RCH=CHR' are generally more thermodynamically stable than their trans isomers.
- (11) Alkene stability increases with increasing alkyl substitution on the C=C.
- (12) Cyclopropene and cyclobutene are very strained due to distortion of the normal R-C=C-R bond angles, while cyclopentene is only slightly strained and cyclohexene is relatively strain free.

**Alkynes**

- (1) Alkynes are hydrocarbons with a C≡C bond (RC≡CR). 
- (2) The C's in the C≡C bond are sp hybridized and the R groups in RC≡CR lie along a straight line with R-C≡C bond angles of 180°.
- (3) Systematic names of unbranched alkynes (RC≡CR') are analogous to those of unbranched alkenes and use the same prefixes eth-, prop-, but-, pent-, followed by the ending -yne.
- (4) Numbers (eg. 1-butyne or 2-butyne) show the position of the C≡C in the unbranched C chain.
- (5) Alkynes do not have E/Z (or cis/trans) stereoisomers.
- (6) Branched alkynes are named as "alkylalkynes", and halogen substituted alkynes are named as "haloalkynes".
- (7) Alkyne stability increases with increasing alkyl substitution on the C≡C.
- (8) Cycloalkynes smaller than C₉ are highly strained compounds due to distortion of the normal 180° R-C≡C-R bond angles.
- (9) Bond lengths between two C's depend on the hybridization of the C leading to a bond length order of C-C > C≡C > C≡C. 
- (10) C-H bond lengths similarly have the order C(sp³)-H > C(sp²)-H > C(sp)-H. 
- (11) C≡C-H protons are much more acidic than other C-H protons. due to the relatively large amount of s character in C-H bonds to sp hybridized C.
- (12) Allenes are 1,2-dienes (R₂C=C=CR₂) whose central C of C=C=C is sp hybridized.
- (13) Allenes readily isomerize to alkynes.
Spectrometric Features of C=C and C≡C Bonds

1. C=C atoms have $^{13}$C chemical shift values from $\delta_{110}$ to $\delta_{150}$ that are affected by attached substituents, but a C=C bond does not significantly affect the $^{13}$C chemical shift of attached C atoms. (2) C≡C atoms have $^{13}$C chemical shifts from $\delta_{65}$ to $\delta_{90}$, and in contrast with alkenes they cause the $^{13}$C $\delta$ value of an attached C to shift to smaller $\delta$ values. (3) $^1$H $\delta$ values for H-C=C are very large ($\delta_{5}$ and $\delta_{6.5}$) and C=C bonds also increase chemical shifts for adjacent C-H atoms. (4) The magnitudes of spin-spin splitting between H's attached to a double bond, and to groups directly attached to the double bond, aid in structure identification. (5) $^1$H chemical shift values of approximately $\delta_{2}$ for H-C≡C are much smaller than those of alkenes. (6) IR stretching frequencies of 1640 to 1670 cm$^{-1}$ for C=C and 2100 to 2260 cm$^{-1}$ for C≡C fall in relatively unique regions of an IR spectrum. (7) Individual C=C or C≡C bonds do not give signals in normal UV-Vis spectra.