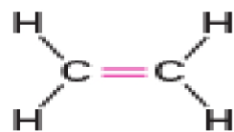
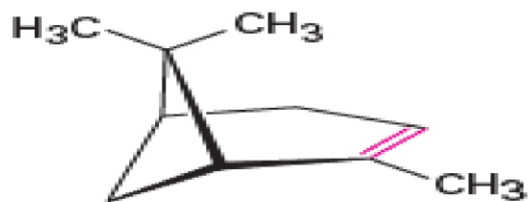


## Alkenes: Structure and Reactivity

An **alkene**, sometimes called an **olefin**, is a hydrocarbon that contains a carbon–carbon double bond. Alkenes occur abundantly in nature. Ethylene, for instance, is a plant hormone that induces ripening in fruit, and  $\alpha$ -pinene is the major component of turpentine. Life itself would be impossible without such alkenes as  $\beta$ -carotene, a compound that contains 11 double bonds. An orange pigment responsible for the color of carrots,  $\beta$ -carotene is an important dietary source of vitamin A and is thought to offer some protection against certain types of cancer.



**Ethylene**



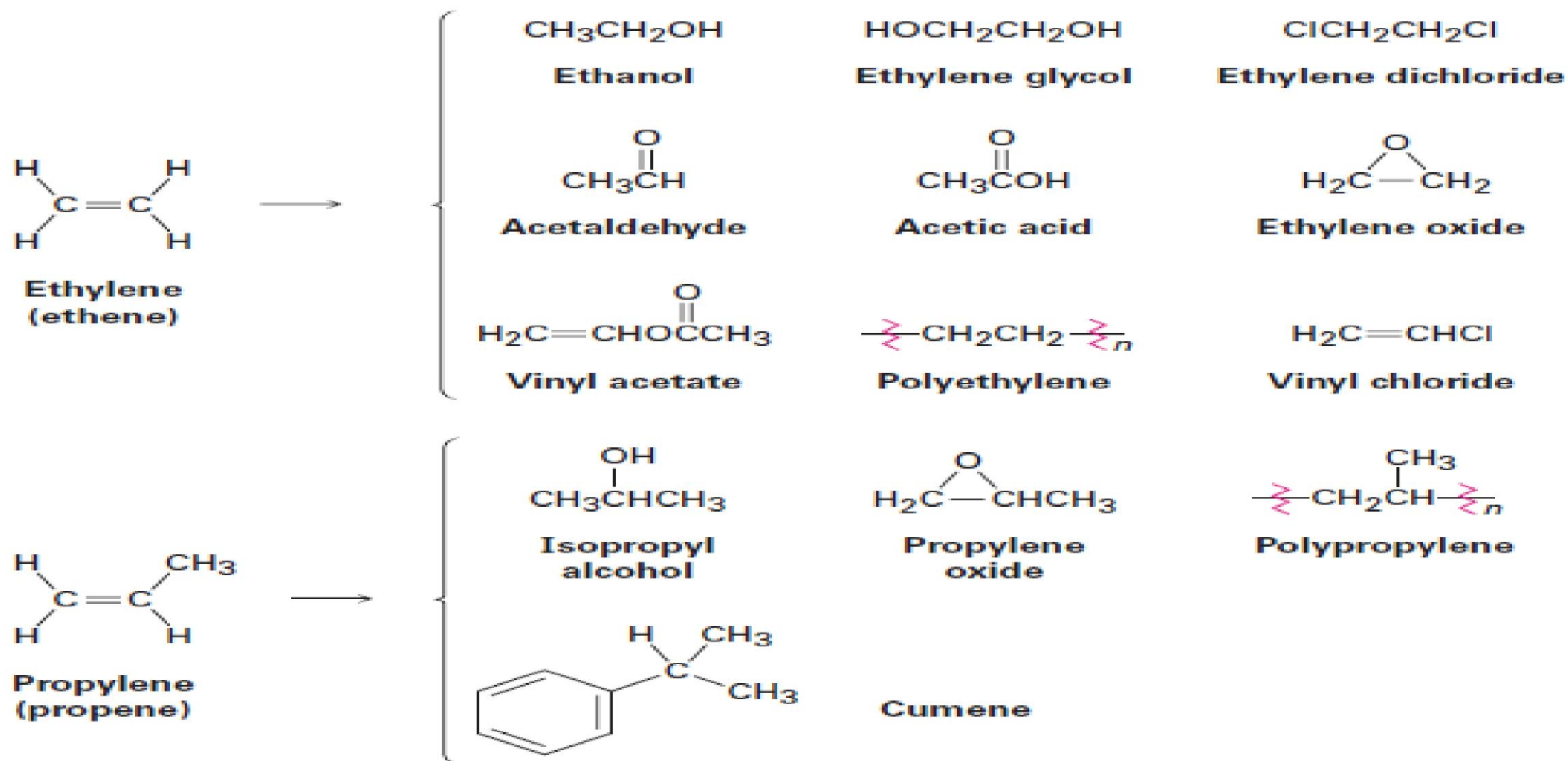
**$\alpha$ -Pinene**



**$\beta$ -Carotene**  
(orange pigment and vitamin A precursor)

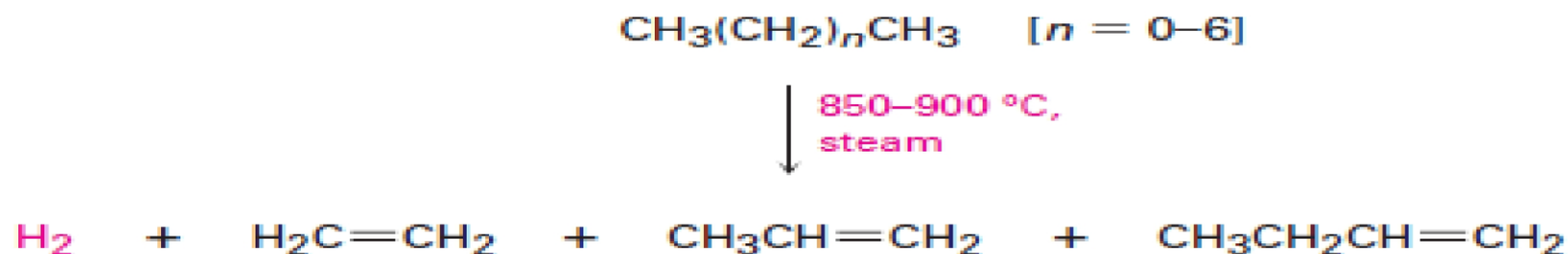
## Industrial Preparation and Use of Alkenes

Ethylene and propylene, the simplest alkenes, are the two most important organic chemicals produced industrially. Approximately 127 million metric tons of ethylene and 54 million metric tons of propylene are produced worldwide each year for use in the synthesis of polyethylene, polypropylene, ethylene glycol, acetic acid, acetaldehyde, and a host of other substances (**Figure 7-1**).

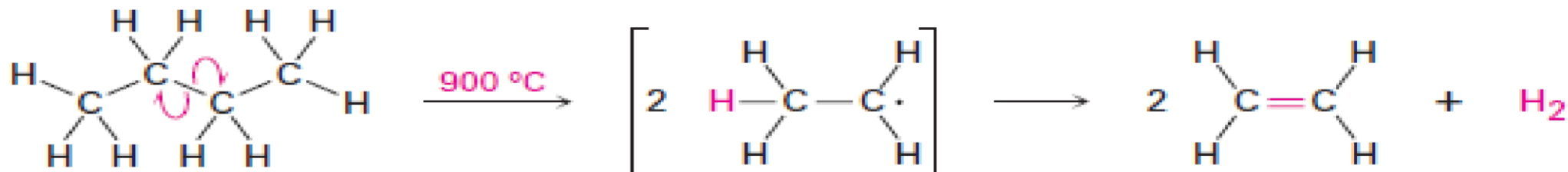


**Figure 7-1** Compounds derived industrially from ethylene and propylene.

Ethylene, propylene, and butene are synthesized industrially by steam cracking of light (C<sub>2</sub>–C<sub>8</sub>) alkanes.



Steam cracking takes place without a catalyst at temperatures up to 900 °C. The process is complex, although it undoubtedly involves radical reactions. The high-temperature reaction conditions cause spontaneous homolytic breaking of C-C and C-H bonds, with resultant formation of smaller fragments. We might imagine, for instance, that a molecule of butane splits into two ethyl radicals, each of which then loses a hydrogen atom to generate two molecules of ethylene.

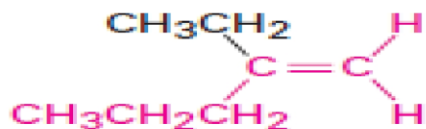


## Naming Alkenes

Alkenes are named using a series of rules similar to those for alkanes, with the suffix *-ene* used instead of *-ane* to identify the functional group. There are three steps to this process.

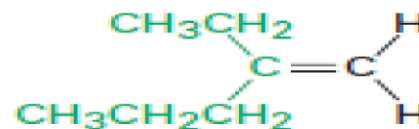
### Step 1

**Name the parent hydrocarbon.** Find the longest carbon chain containing the double bond, and name the compound accordingly, using the suffix *-ene*:



Named as a *pentene*

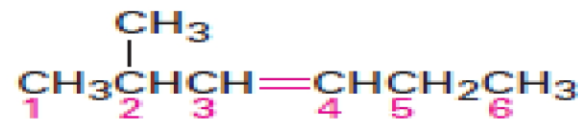
NOT



as a hexene, since the double bond is not contained in the six-carbon chain

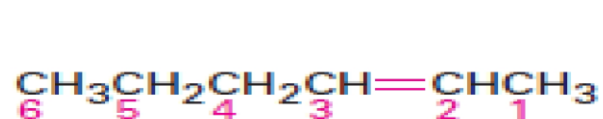
### Step 2

**Number the carbon atoms in the chain.** Begin at the end nearer the double bond or, if the double bond is equidistant from the two ends, begin at the end nearer the first branch point. This rule ensures that the double-bond carbons receive the lowest possible numbers.

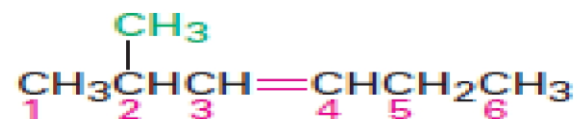


### Step 3

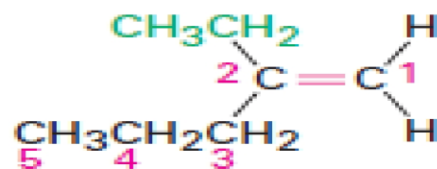
**Write the full name.** Number the substituents according to their positions in the chain, and list them alphabetically. Indicate the position of the double bond by giving the number of the first alkene carbon and placing that number directly before the parent name. If more than one double bond is present, indicate the position of each and use one of the suffixes *-diene*, *-triene*, and so on.



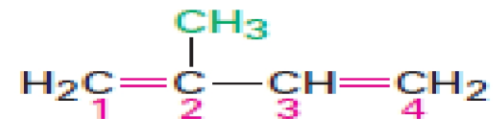
2-Hexene



2-Methyl-3-hexene



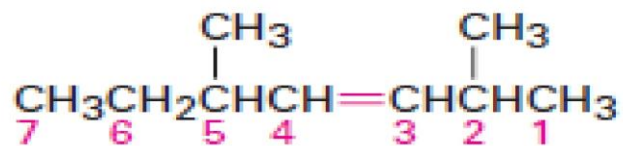
2-Ethyl-1-pentene



2-Methyl-1,3-butadiene

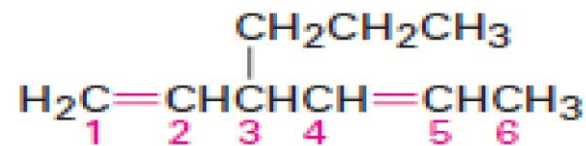
We should also note that IUPAC changed their naming recommendations to place the locant indicating the position of the double bond immediately before the *-ene* suffix rather than before the parent name: but-2-ene rather than 2-butene, for instance. This change has not been widely accepted by the chemical community in the United States, however, so we'll stay with the older but more commonly used names. Be aware, though, that you may occasionally encounter the newer system.





Newer naming system: 2,5-Dimethylhept-3-ene

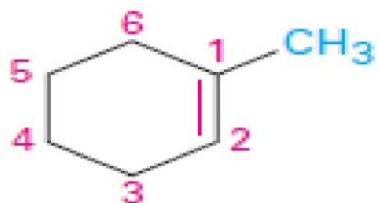
(Older naming system: 2,5-Dimethyl-3-heptene)



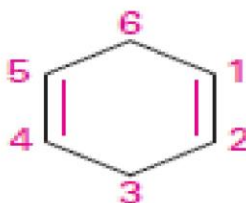
3-Propylhexa-1,4-diene

3-Propyl-1,4-hexadiene)

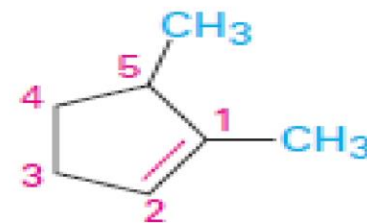
Cycloalkenes are named similarly, but because there is no chain end to begin from, we number the cycloalkene so that the double bond is between C1 and C2 and the first substituent has as low a number as possible. It's not necessary to indicate the position of the double bond in the name because it's always between C1 and C2. As with open-chain alkenes, the newer but not yet widely accepted naming rules place the locant immediately before the suffix in a cyclic alkene.



1-Methylcyclohexene



1,4-Cyclohexadiene  
(New: Cyclohexa-1,4-diene)



1,5-Dimethylcyclopentene

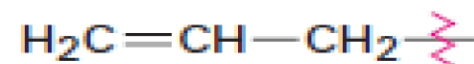
For historical reasons, there are a few alkenes whose names are firmly entrenched in common usage but don't conform to the rules. For example, the alkene derived from ethane should be called *ethene*, but the name *ethylene* has been used for so long that it is accepted by IUPAC. **Table 7-1** lists several other common names that are often used and are recognized by IUPAC. Note also that a  $=\text{CH}_2$  substituent is called a **methylene group**, a  $\text{H}_2\text{C}=\text{CH}-$  substituent is called a **vinyl group**, and a  $\text{H}_2\text{C}=\text{CHCH}_2-$  substituent is called an **allyl group**.



A methylene group



A vinyl group



An allyl group

**TABLE 7-1** Common Names of Some Alkenes

Compound	Systematic name	Common name
$\text{H}_2\text{C}=\text{CH}_2$	Ethene	Ethylene
$\text{CH}_3\text{CH}=\text{CH}_2$	Propene	Propylene
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array}$	2-Methylpropene	Isobutylene
$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	2-Methyl-1,3-butadiene	Isoprene



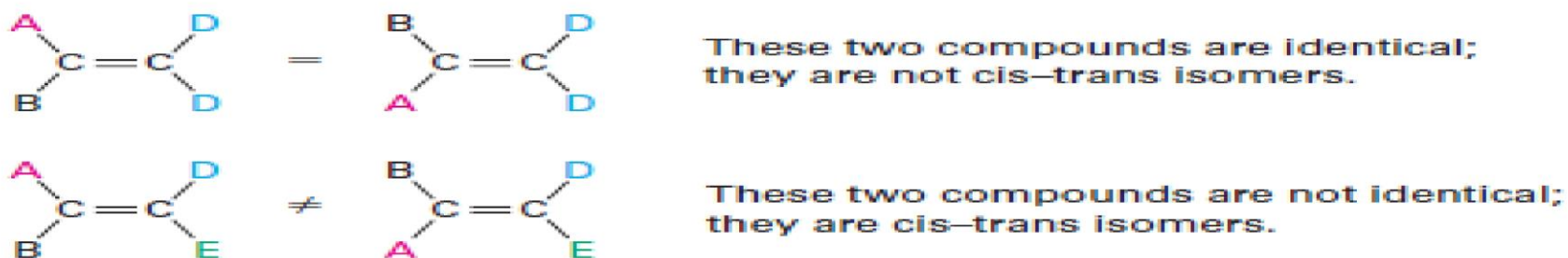
## Cis–Trans Isomerism in Alkenes

The two 2-butenes called *cis–trans stereoisomers*. The compound with substituents on the same side of the double bond is called *cis*-2-butene, and the isomer with substituents on opposite sides is *trans*-2-butene (**Figure 7-3**).



**Figure 7-3** Cis and trans isomers of 2-butene. The *cis* isomer has the two methyl groups on the same side of the double bond, and the *trans* isomer has methyl groups on opposite sides.

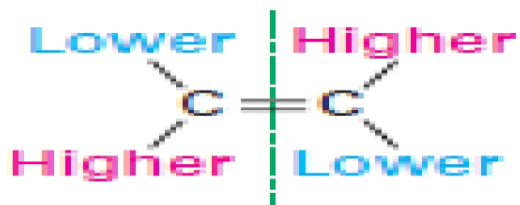
Cis–trans isomerism is not limited to disubstituted alkenes. It can occur whenever both double-bond carbons are attached to two different groups. If one of the double-bond carbons is attached to two identical groups, however, cis–trans isomerism is not possible (**Figure 7-4**).



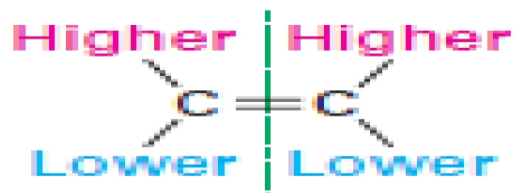
**Figure 7-4** The requirement for cis–trans isomerism in alkenes. Compounds that have one of their carbons bonded to two identical groups can't exist as cis–trans isomers. Only when both carbons are bonded to two different groups is cis–trans isomerism possible.

## Alkene Stereochemistry and the *E,Z* Designation

The cis–trans naming system used in the previous section works only with disubstituted alkenes—compounds that have two substituents other than hydrogen on the double bond. With trisubstituted and tetrasubstituted double bonds, a more general method is needed for describing double-bond geometry. (*Trisubstituted* means three substituents other than hydrogen on the double bond; *tetrasubstituted* means four substituents other than hydrogen.) The method used for describing alkene stereochemistry is called the ***E,Z* system** and employs the same Cahn–Ingold–Prelog sequence rules for specifying the configuration of a chirality center. Let’s briefly review the sequence rules and then see how they’re used to specify double bond geometry. For a more thorough review.



*E* double bond  
(Higher-ranked groups  
are on opposite sides.)



*Z* double bond  
(Higher-ranked groups  
are on the same side.)

## **Rule 1**

Considering each of the double-bond carbons separately, look at the two substituents attached and rank them according to the atomic number of the first atom in each. An atom with higher atomic number ranks higher than an atom with lower atomic number.

## **Rule 2**

If a decision can't be reached by ranking the first atoms in the two substituents, look at the second, third, or fourth atoms away from the double-bond until the first difference is found.