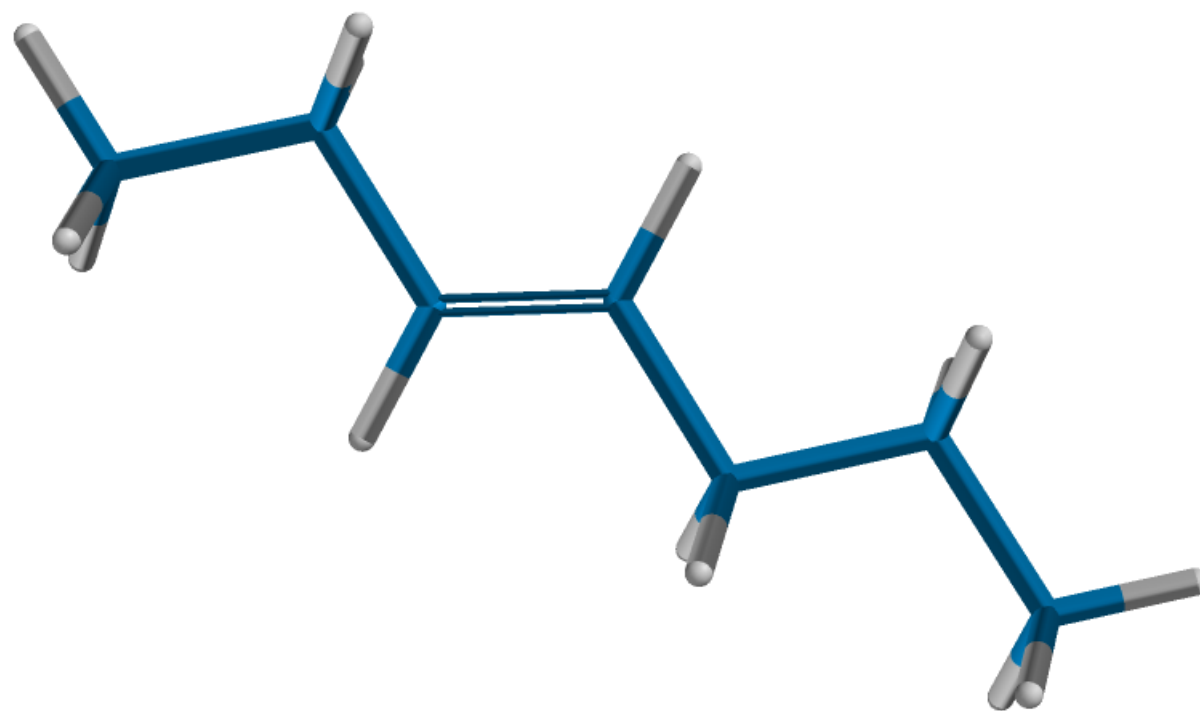


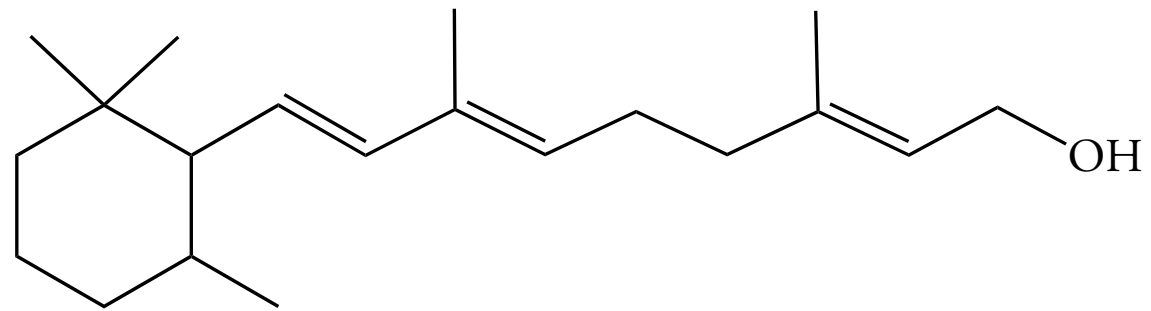
5

# ALKENES

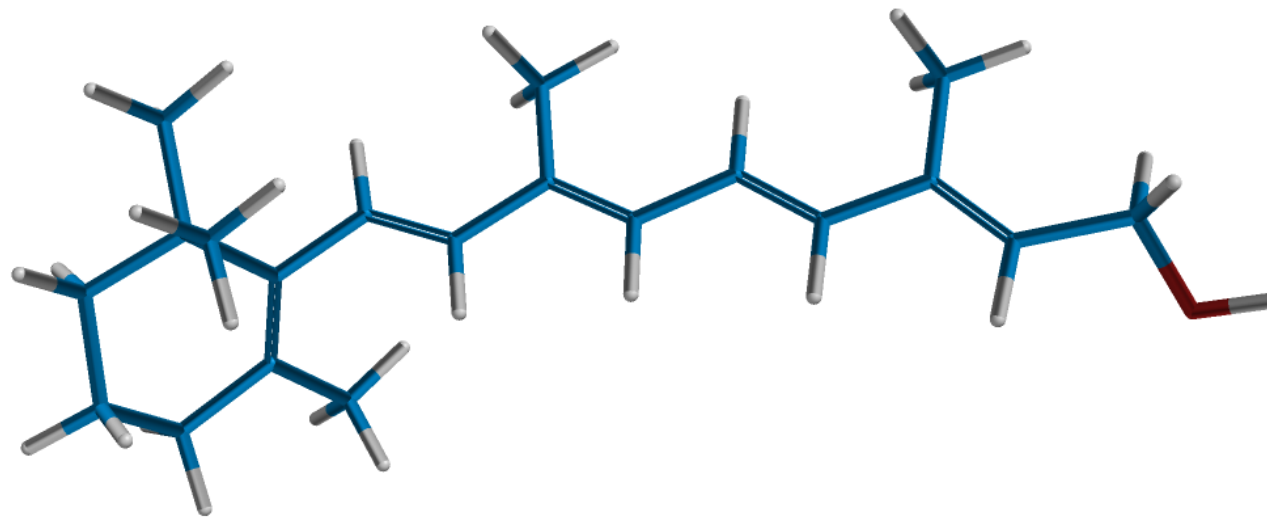
## STRUCTURES AND PROPERTIES



## 5.1 ALKENES

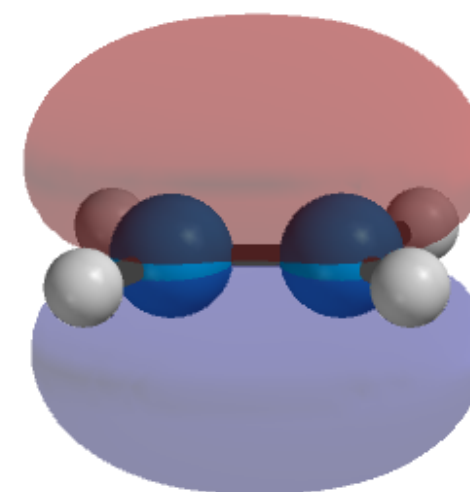
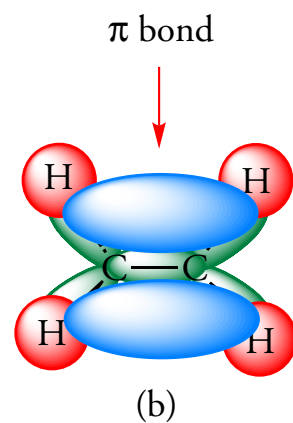
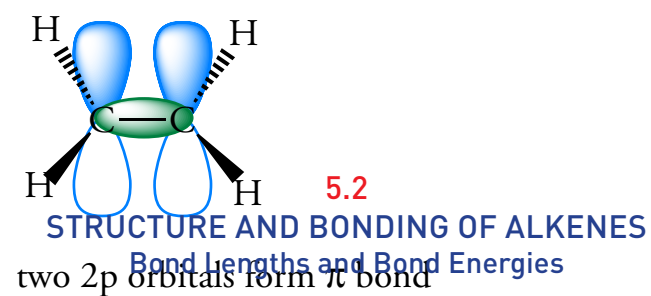
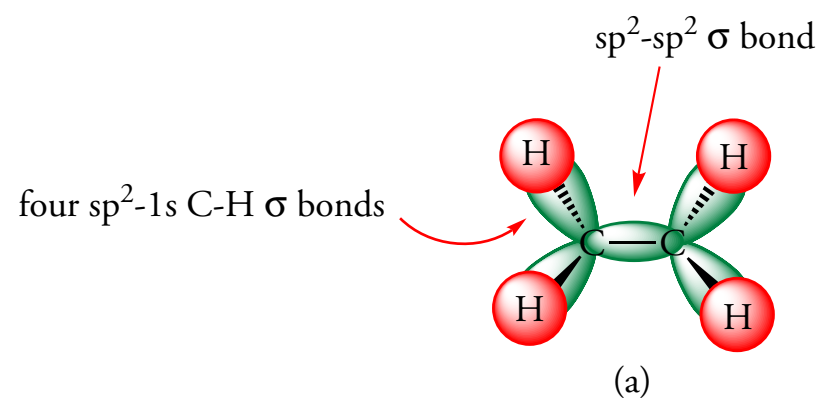
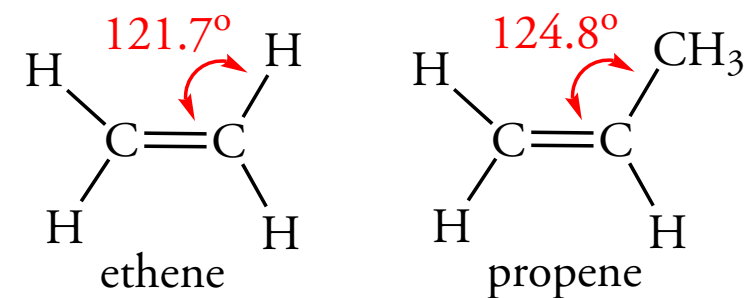


Vitamin A



## Figure 5.1 Structure of Ethene

(a) The  $\pi$  bond is formed by sideways overlap of the parallel 2p orbitals of adjacent carbon atoms. Carbon forms sigma bonds with  $sp^2$  hybrid orbitals. (b) Schematic diagram of bonding in ethene. (c) The highest occupied molecular orbital of ethene is the  $\pi$  bond.



(c) The  $\pi$  bond of ethene

## 5.2 STRUCTURE AND BONDING OF ALKENES

### Bond Lengths and Bond Energies

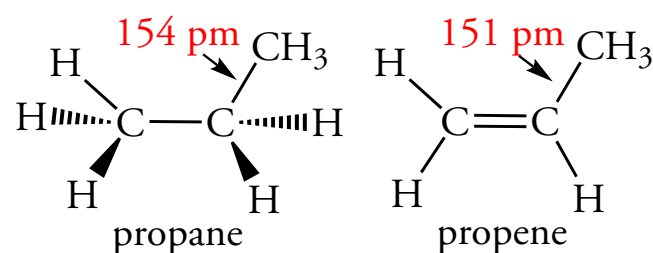


Table 5.1

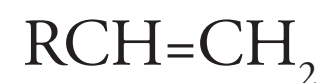
#### Bonds Lengths and Bond Strengths in Alkanes vs Alkenes

<i>Bond</i>	<i>Bond Length</i> ( <i>pm</i> )	<i>DH</i> <sup>o</sup> <i>kJ mole</i> <sup>-1</sup>
CH <sub>3</sub> —CH <sub>3</sub> (sp <sup>3</sup> — sp <sup>3</sup> )	154	347
CH <sub>2</sub> =CH <sub>2</sub> (sp <sup>2</sup> — sp <sup>2</sup> )	133	610
CH <sub>2</sub> =CH—CH <sub>3</sub>	151	121
CH <sub>3</sub> CH <sub>2</sub> —H	109	422
CH <sub>2</sub> =CH—H	107	452

## 5.2 STRUCTURE AND BONDING OF ALKENES

### Classification of Alkenes

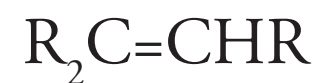
monosubstituted:



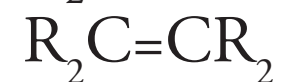
disubstituted:



trisubstituted:

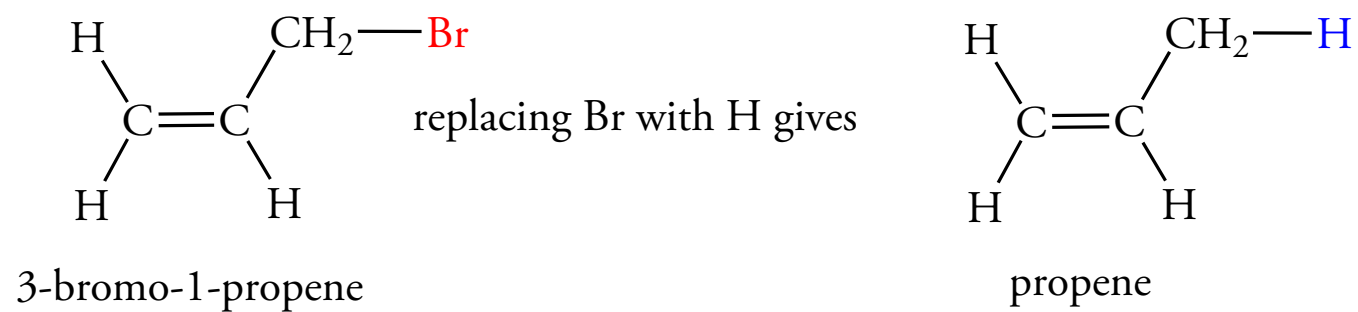


tetrasubstituted:



## 5.3 UNSATURATION NUMBER

$$\text{unsaturation number} = \frac{[2(\text{number of carbon atoms}) + 2] - \text{number of H atoms}}{2}$$

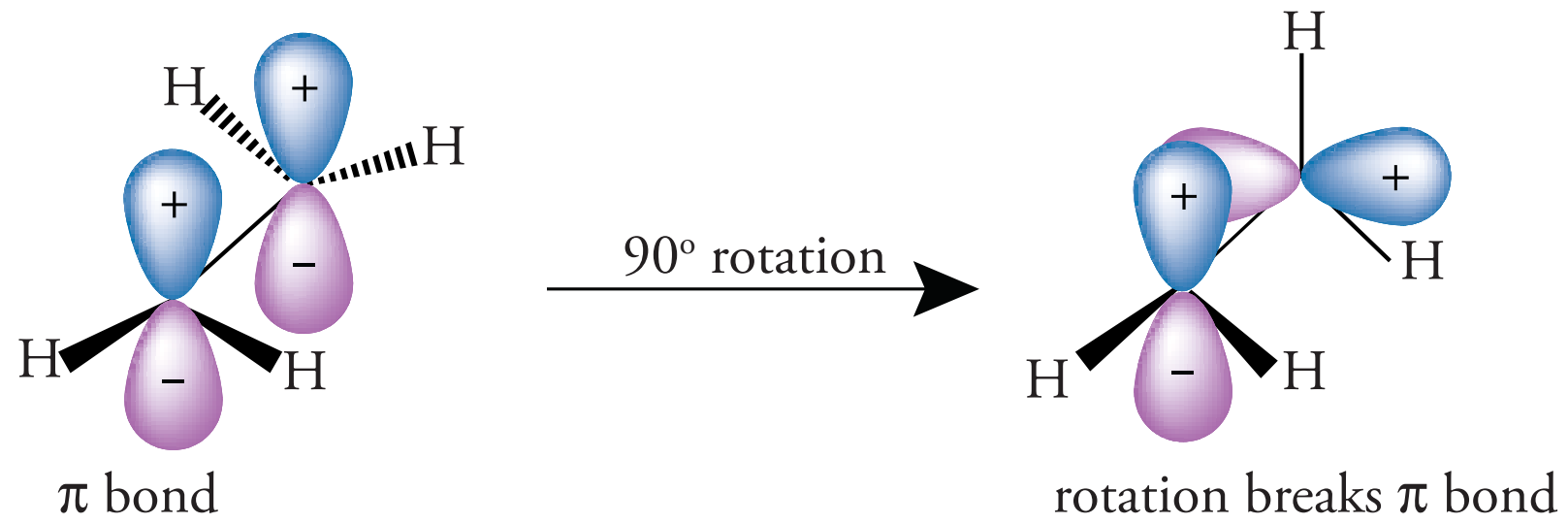


$$\text{unsaturation number} = \frac{[2(3) + 2] - 6}{2} = 1$$

## 5.4 GEOMETRIC ISOMERISM

**Figure 5.2 Rotation About the  $\pi$  Bond**

For rotation to occur about a carbon—carbon double bond, the  $\pi$  bond must break. Loss of overlap between parallel 2p orbitals requires about  $240 \text{ kJ mole}^{-1}$ .

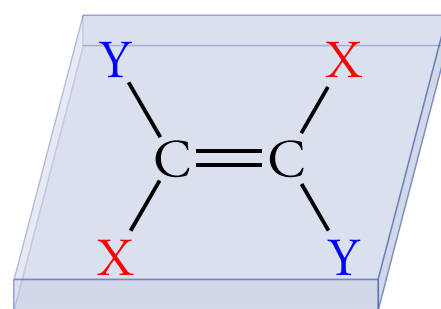


## 5.4 GEOMETRIC ISOMERISM

### Figure 5.3 Geometric Isomers of Alkenes

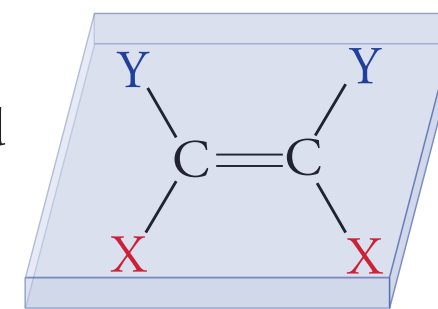
All six atoms lie in the same plane. In the *cis* isomer two "X" and "Y" groups lie on the same side of the double bond. In the *trans* isomer "X" and "Y" groups lie on opposite sides of the double bond. They do not interconvert because rotation around the  $\pi$  bond does not occur.

all atoms coplanar



*trans* geometric isomer

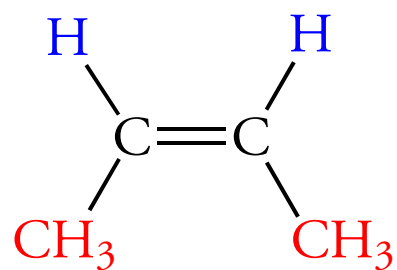
no rotation around  
double bond



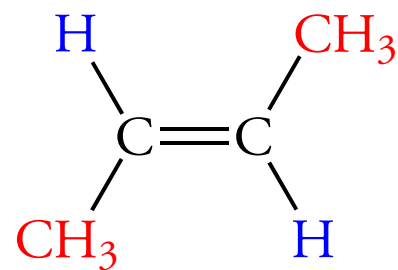
*cis* geometric isomer



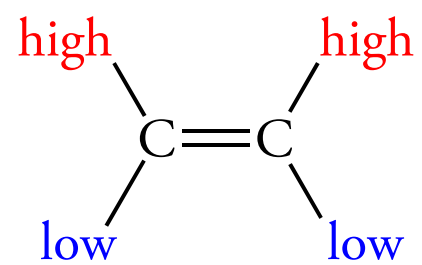
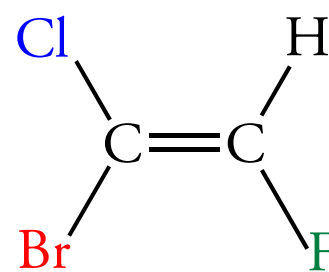
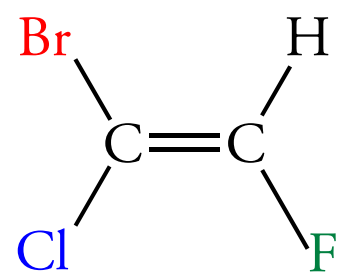
## 5.5 E,Z NOMENCLATURE OF GEOMETRICAL ISOMERS



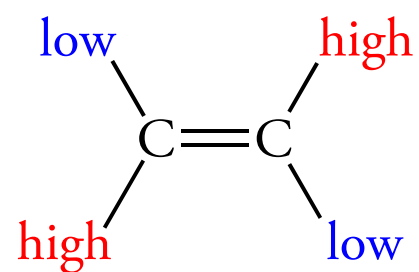
*cis*-2-butene



*trans*-2-butene



*Z* isomer



*E* isomer

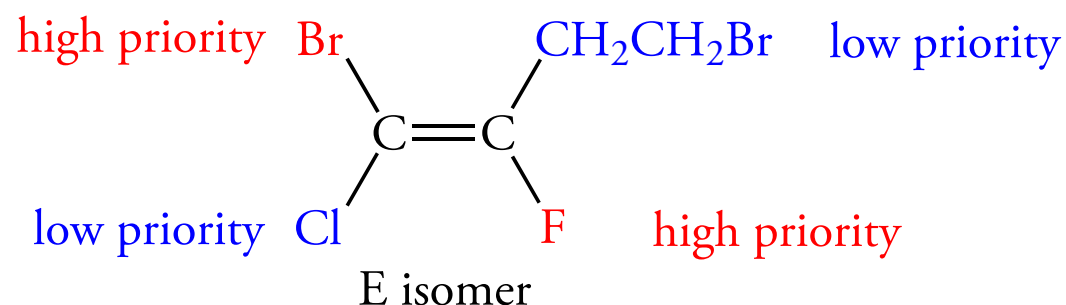
## 5.5 E,Z NOMENCLATURE OF GEOMETRICAL ISOMERS

### Sequence Rules

#### Sequence Rules-1

1. If two atoms with different atomic numbers *are directly bonded* to a double bond, the atom with the higher atomic number receives a higher priority.

The priority order of some common elements is  $\text{Br} > \text{Cl} > \text{F} > \text{O} > \text{N} > \text{C} > {}^2\text{H} > \text{H}$ .



#### Sequence Rule-2

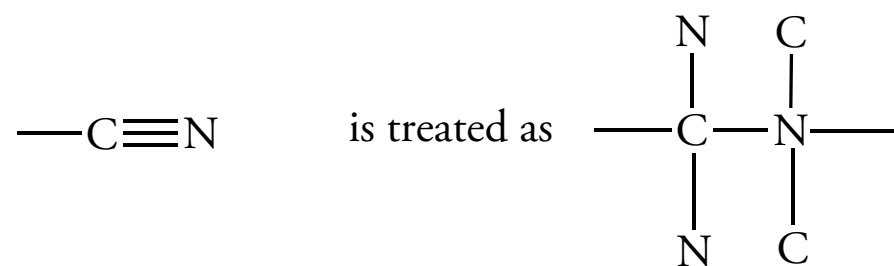
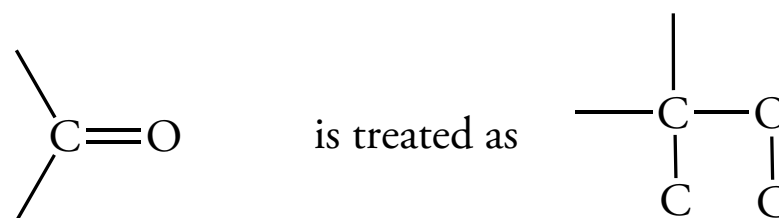
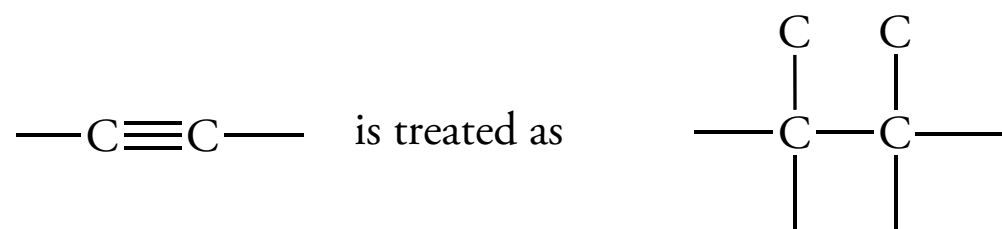
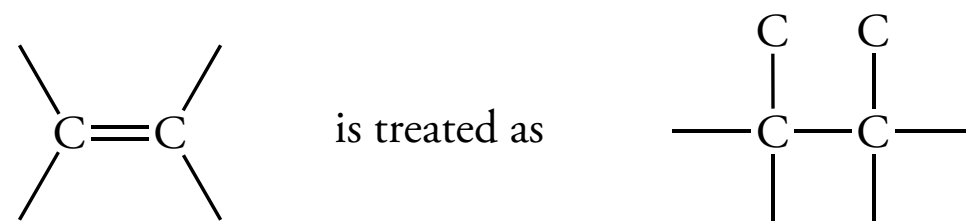
2. If the atoms directly attached to the carbon atom of the double bond have the same atomic number, consider the second, third, and farther atoms until a difference is found. Then apply rule 1.

## 5.5 E,Z NOMENCLATURE OF GEOMETRICAL ISOMERS

### Sequence Rules

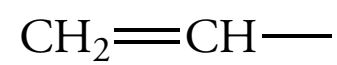
#### Sequence Rule-3

3. A multiple bond is considered equivalent to the same number of single bonds to like atoms. Thus, a double bond is counted as two single bonds for both of the atoms in the double bond. The same principle is used for a triple bond.

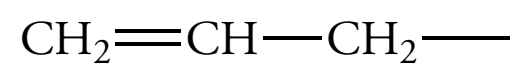


## 5.6 NOMENCLATURE OF ALKENES

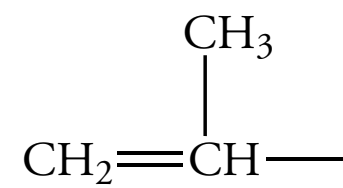
### Common Names of Alkenyl Groups



vinyl



allyl



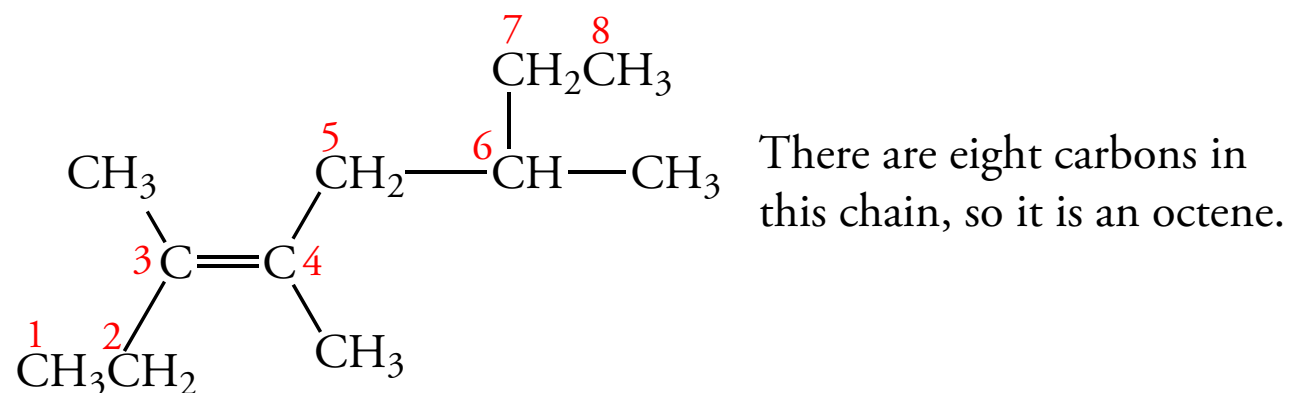
isopropenyl

## 5.6 NOMENCLATURE OF ALKENES

### IUPAC Rules for Naming Alkenes

#### Rule 1

1. The longest continuous chain of carbon atoms that contains the double bond is the parent alkene.



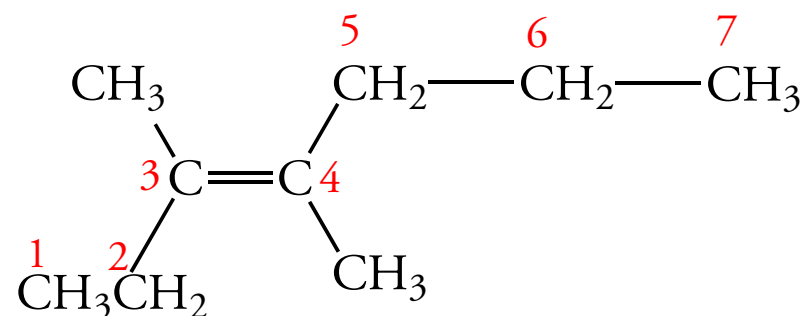
#### Rule 2

2. If the atoms directly attached to the carbon atom of the double bond have the same atomic number, the second, third, and farther atoms are considered until a difference is found. Then apply rule 1.

## 5.6 NOMENCLATURE OF ALKENES

### Rule 3

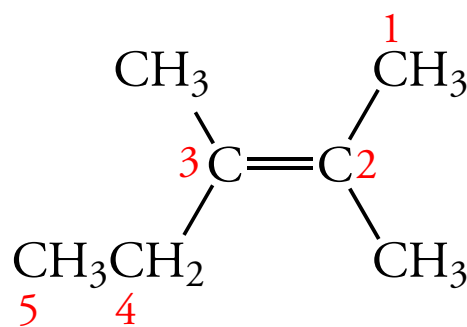
3. Number the carbon atoms in the longest continuous chain starting from the end of the chain nearer the first branch.



This is a substituted 3-heptene, not a substituted 4-heptene.

### Rule 4

4. Alkyl groups and other substituents are named, and their positions on the chain are identified, according to the numbering established by rule 3. Names and numbers are prefixed to the parent name.

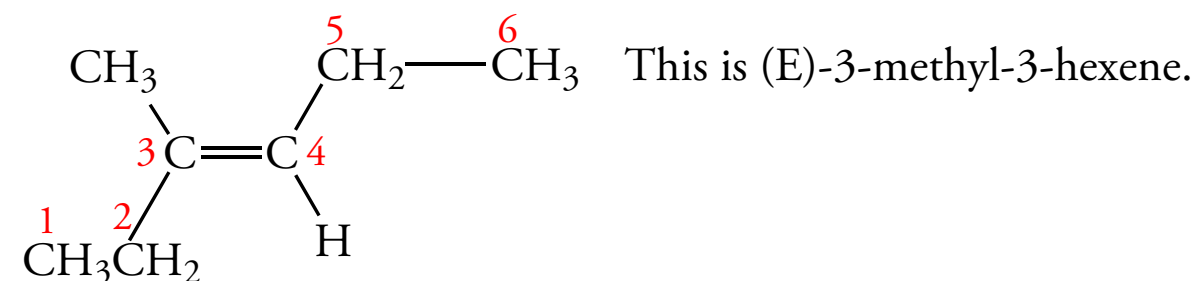


This is 2,3-dimethyl-2-pentene, not 3,4-dimethyl-3-pentene.

## 5.6 NOMENCLATURE OF ALKENES

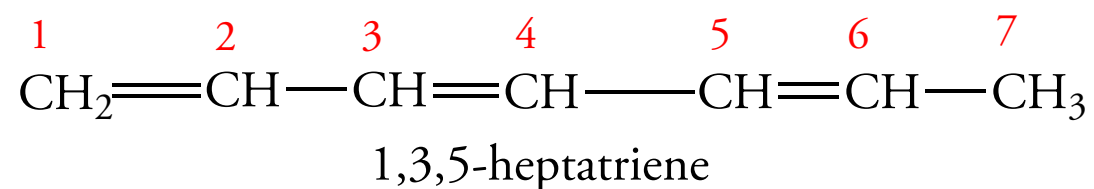
### Rule 5

5. If the compound can exist as an E or Z isomer, the appropriate prefix followed by a hyphen is placed within parentheses in front of the name.



### Rule 6

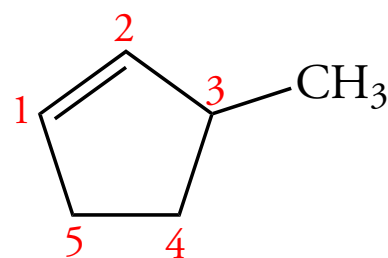
6. If the compound contains more than one double bond, specify the location of each double bond by a number. A prefix to *-ene* indicates the number of double bonds.



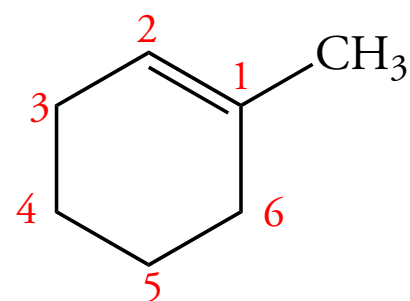
## 5.6 NOMENCLATURE OF ALKENES

### Rule 7

7. Name cycloalkenes by numbering the ring to give the double-bonded carbon atoms the numbers 1 and 2. Choose the direction of numbering so that the first substituent on the ring receives the lower number. The position of the double bond is not given because it is known to be between the C-1 and C-2 atoms.



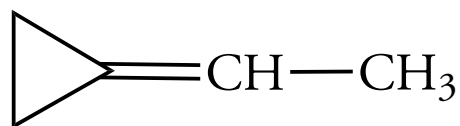
3-methylcyclopentene



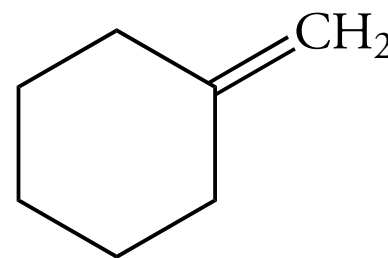
1-methylcyclohexene

### Rule 8

8. Compounds with a carbon-carbon double bond positioned between a ring carbon atom and a substituent on the ring are named using **-ylidene** to name the group as a substituent. However, the ( $=\text{CH}_2$ ) group is named methene rather than methyldene.



ethylidene cyclopropane



methylenecyclohexane



## 5.7 PHYSICAL PROPERTIES OF ALKENES

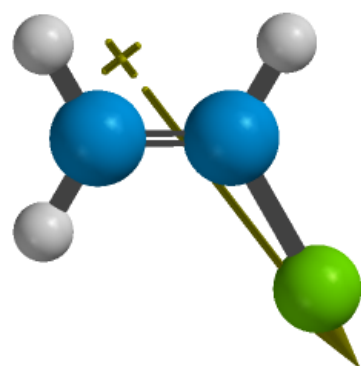
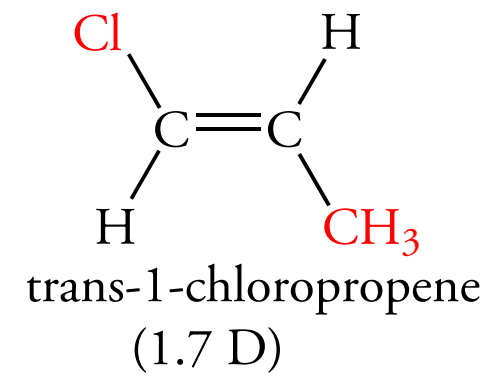
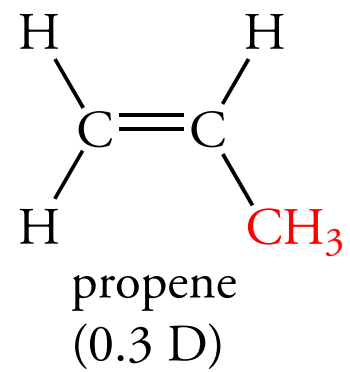
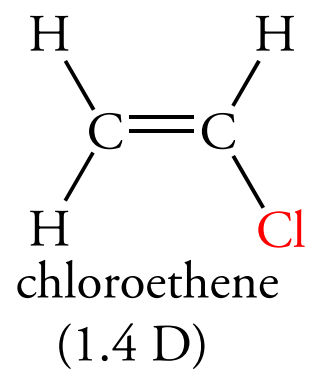
### Density of Alkenes

**Table 5.2 Densities of Alkenes**

Alkene	Density $d^{20}$ (g cm <sup>-3</sup> )
1-pentene	$2.6 \times 10^{-5}$
cis-2-pentene	$8.5 \times 10^{-5}$
trans-2-pentene	$2.6 \times 10^{-4}$
2-methyl-2-butene	$7.8 \times 10^{-4}$
3-methyl-1-butene	0.648
1-hexene	0.675
2,3-dimethyl-2-butene	0.705
1-heptene	0.698
1-octene	0.716
1-nonene	0.731
1-decene	0.743

## 5.7 PHYSICAL PROPERTIES OF ALKENES

### Polarity of Alkenes

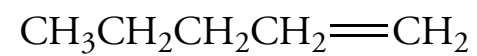


## 5.7 PHYSICAL PROPERTIES OF ALKENES

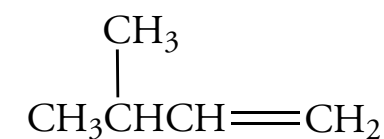
### Boiling Points of Alkenes

**Table 5.3**  
Boiling Points of Alkenes

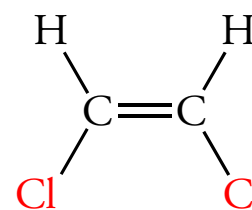
Alkene	Boiling Point (°C)
ethene	-103.7
propene	-47.4
1-butene	-6.3
2-methylpropene	-6.9
<i>cis</i> -2-butene	+3.7
<i>trans</i> -2-butene	0.9
1-pentene	30.0
<i>cis</i> -2-pentene	36.9
<i>trans</i> -2-pentene	36.4
1-hexene	63.5
1-heptene	93
1-octene	122.5
1-nonene	146
1-decene	171



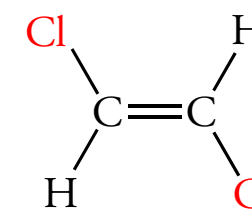
1-pentene  
(bp 30 °C)



3-methyl-1-butene  
(bp 25 °C)



*cis*-1,2-chloroethene  
(bp 60 °C)



*trans*-1,2-chlorodichloroethene  
(bp 47 °C)

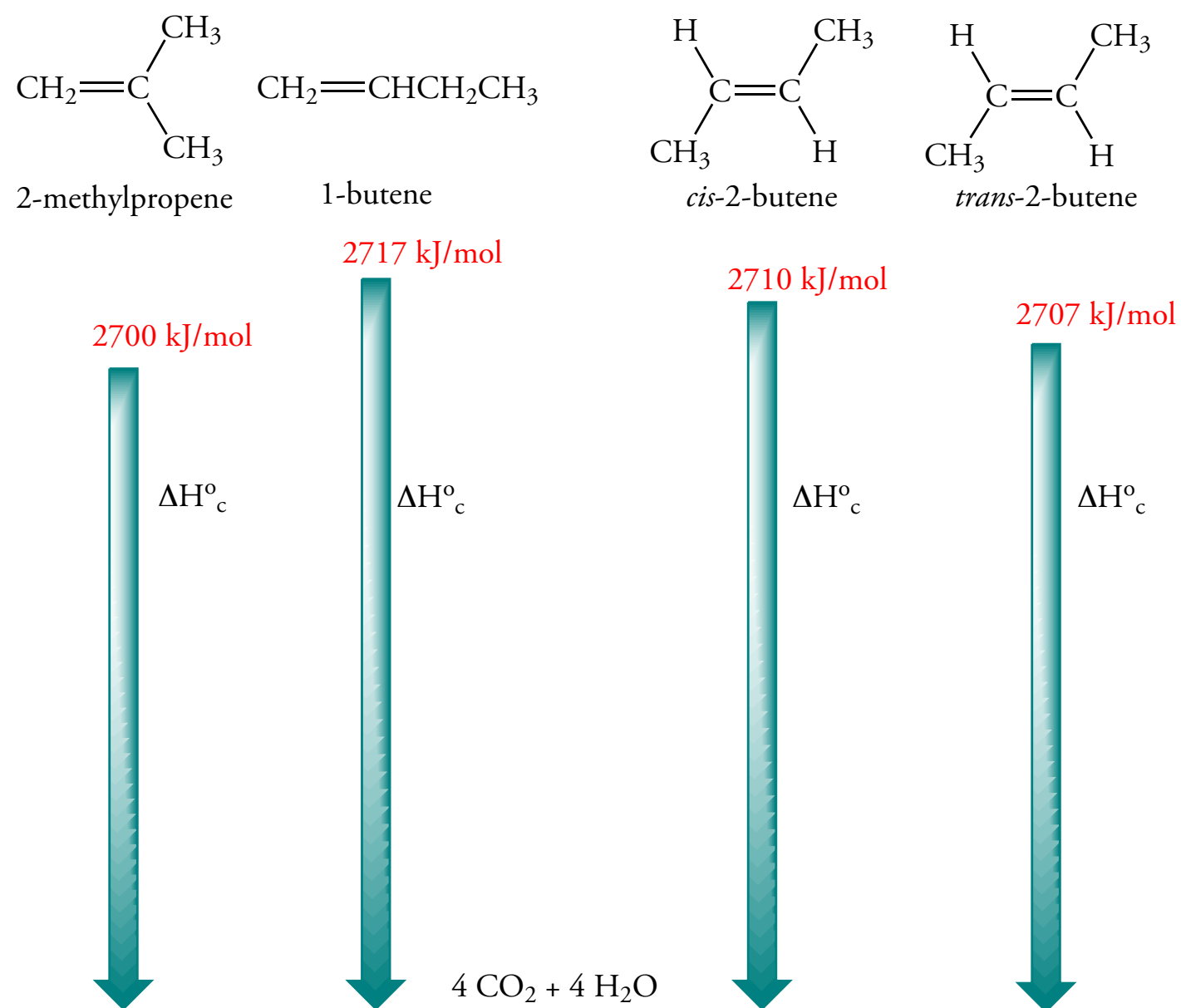
## 5.8 STABILITY OF ALKENES

1-butene < *cis*-2-butene < *trans*-2-butene < 2-methylpropene

————— increasing stability (decreasing  $\Delta H_c^\circ$ ) —————>

### Figure 5.4 Heats of Combustion of Isomeric Butenes

The heats of combustion of the isomeric butenes are plotted on the vertical axis in  $\text{kJ mole}^{-1}$ . All compounds are at higher energy than the common products, carbon dioxide and water.

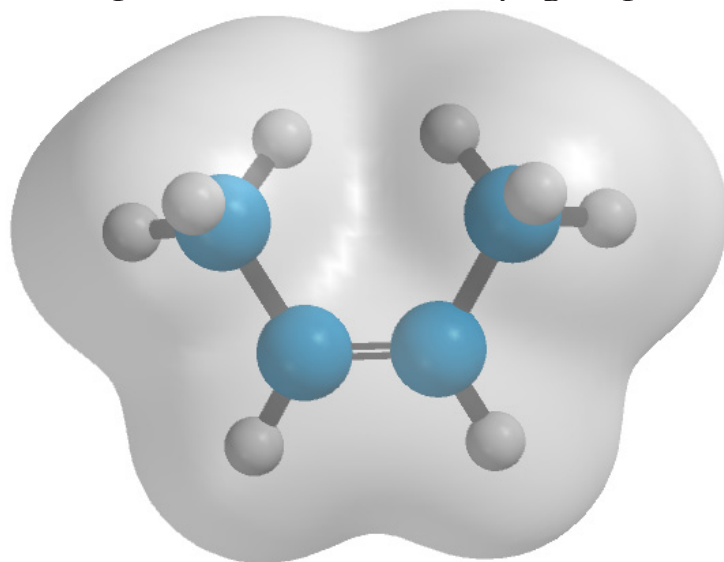


## 5.8 STABILITY OF ALKENES

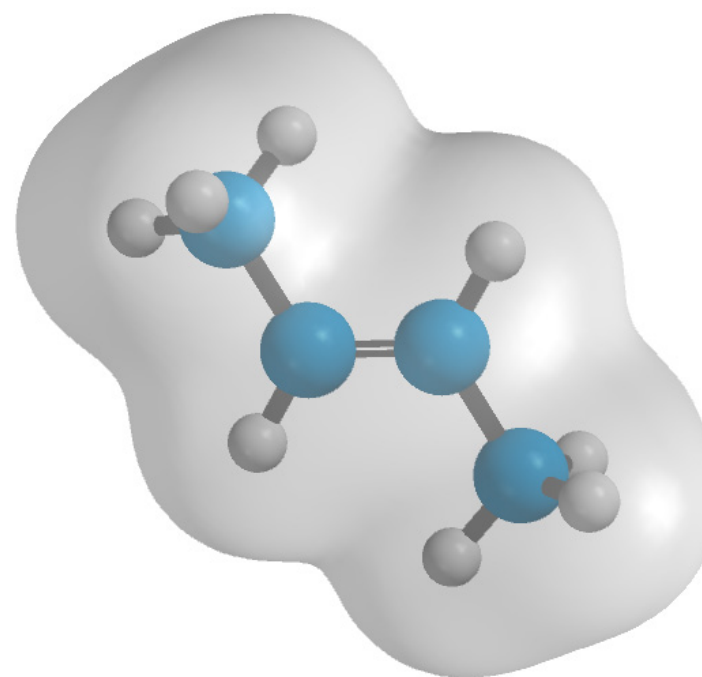
### Figure 5.5 Steric Effects and Stability of Alkenes

Some of the hydrogen atoms of the two methyl groups in *cis*-2-butene are within their van der Waals radii. These atoms are in a 1,6 relationship, and they sterically interfere with each other. There is no steric effect in the *trans* isomer.

Steric repulsion between methyl groups.

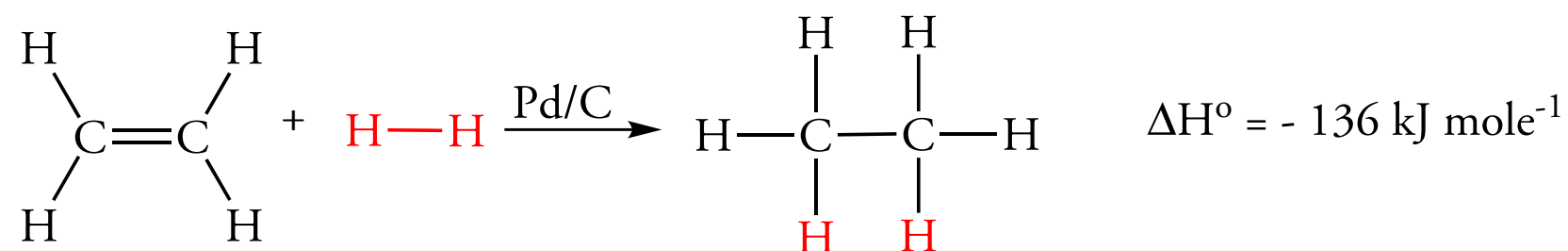


*cis*-2-butene

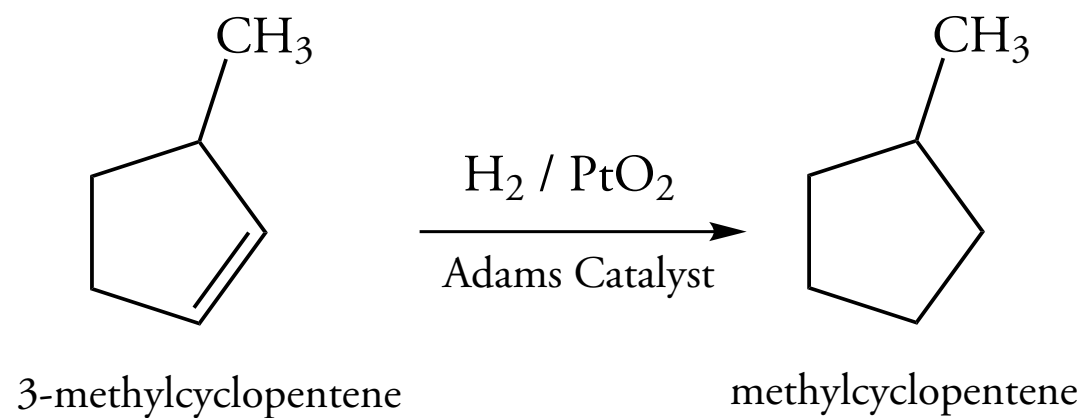
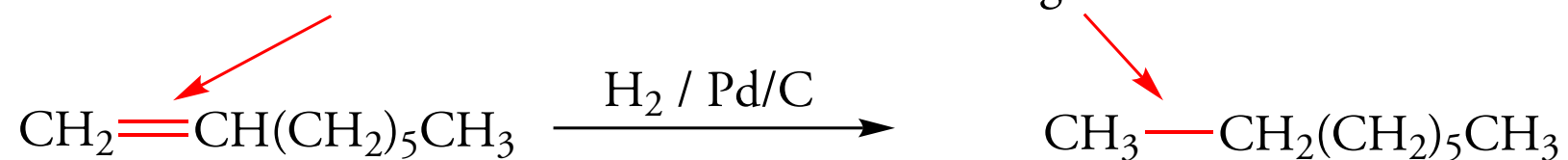


*trans*-2-butene

## 5.9 REDUCTION OF ALKENES

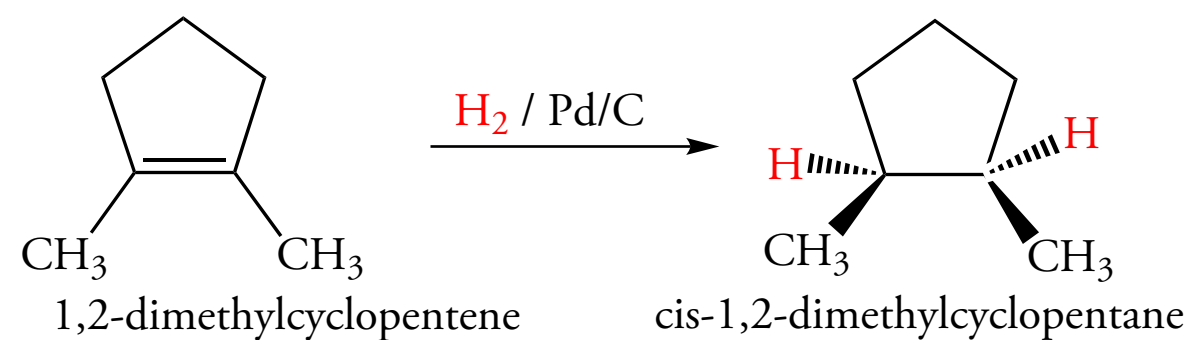


The double bond is converted to a single bond.

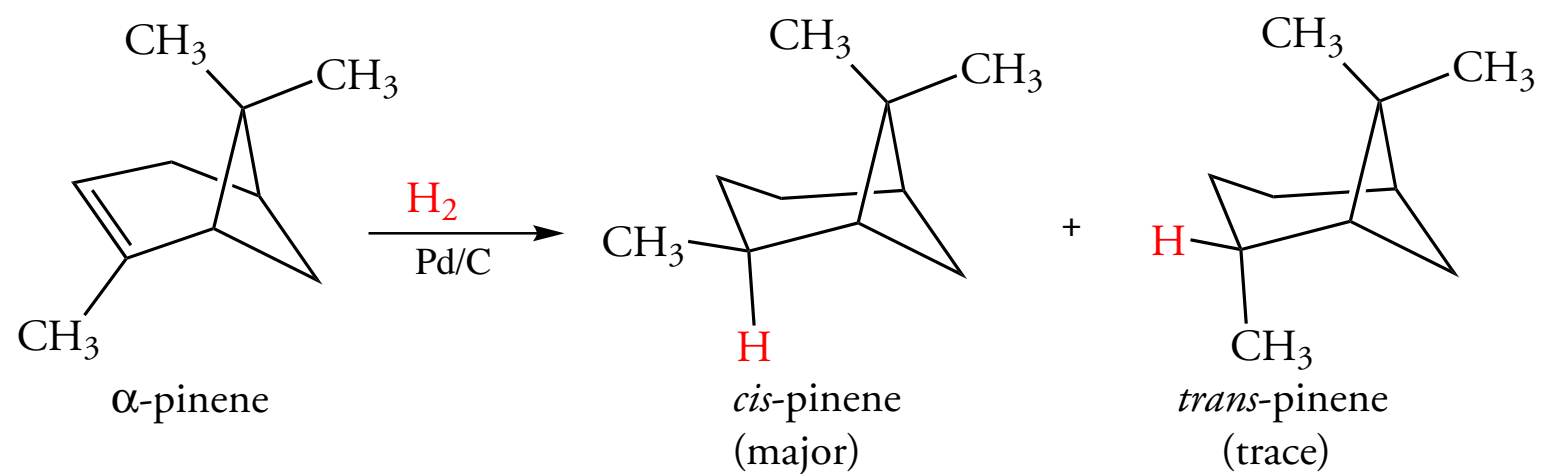


## 5.10 MECHANISM OF CATALYTIC HYDROGENATION

### Stereochemistry of Hydrogenation



### Stereoselectivity of Hydrogenation



## 5.10 HEATS OF HYDROGENATION OF ALKENES

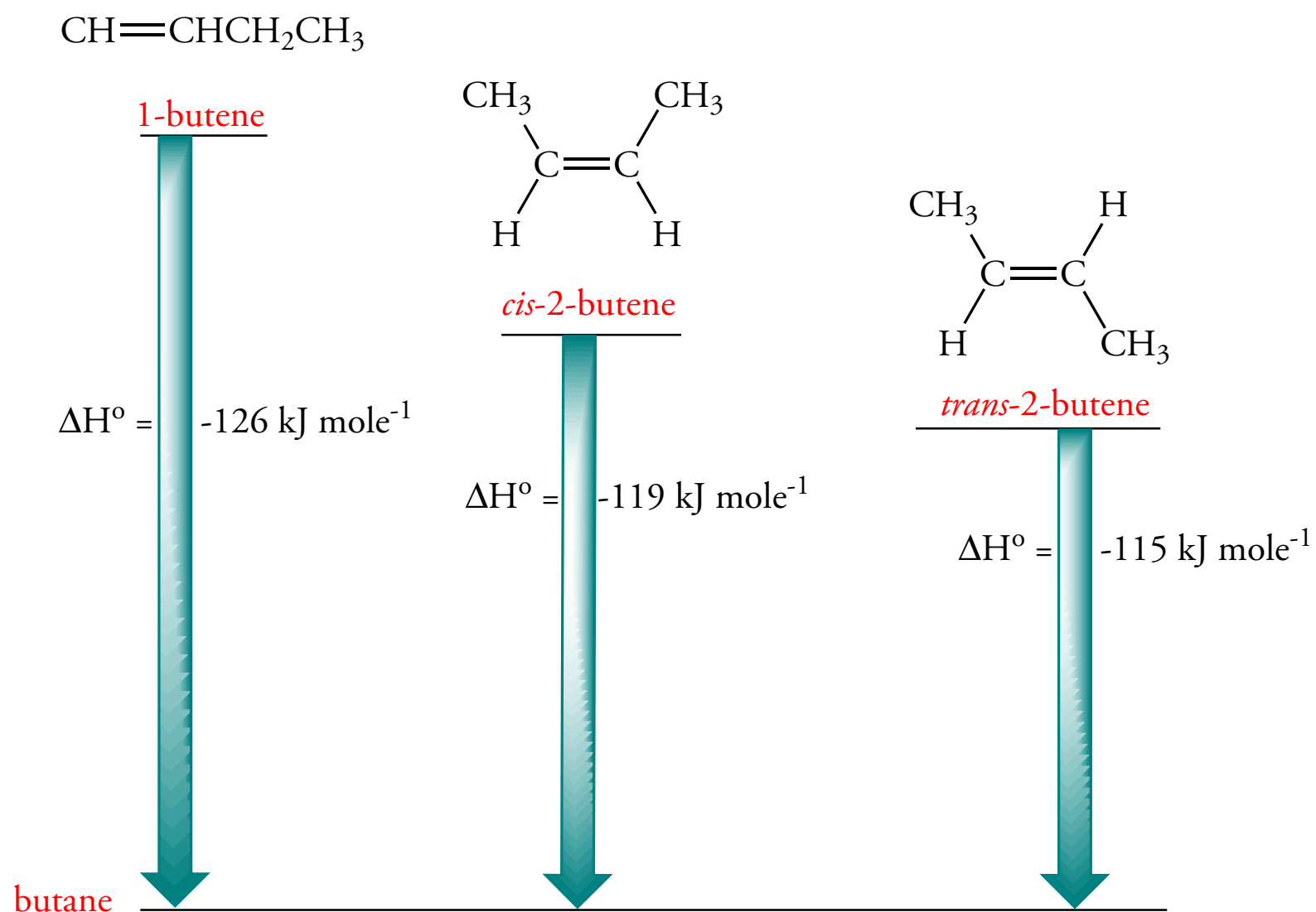
### Structural Effects on Heats of Hydrogenation



$\Delta H^\circ_{\text{hydrogenation}}$  : monosubstituted > disubstituted > trisubstituted > tetrasubstituted

### Figure 5.6 Heats of Hydrogenation of Isomeric Butenes

The positions of three isomeric butenes show their relative heats of formation.





**Table 5.4**  
**Heats of Hydrogenation of Alkenes**

<i>Alkene</i>	$\Delta H^\circ_{\text{hydrogenation}}$ kJ mole <sup>-1</sup>	<i>Alkene</i>	$\Delta H^\circ_{\text{hydrogenation}}$ kJ mole <sup>-1</sup>
<i>Unsubstituted</i>		<i>Internal Disubstituted</i>	
ethene	136	<i>cis</i> -2-butene	119
<i>Monosubstituted</i>		<i>trans</i> -2-butene	115
propene	125	<i>cis</i> -2-pentene	117
1-butene	126	<i>trans</i> -2-pentene	114
1-hexene	126	<i>cis</i> -4,5-dimethyl-2-hexene	118
3-methyl-1-butene	127	<i>trans</i> -4,5-dimethyl-2-hexene	113
<i>Terminal disubstituted</i>		<i>Trisubstituted</i>	
2-methylpropene	117	2-methyl-2-pentene	112
2-methyl-1-butene	118	2,3-dimethyl-3-hexene	114
2,3-dimethyl-1-butene	116	<i>Tetrasubstituted</i>	
2,3-dimethyl-1-hexene	117	2,3-dimethyl-2-butene	110
		2,3-dimethyl-2-hexene	106