

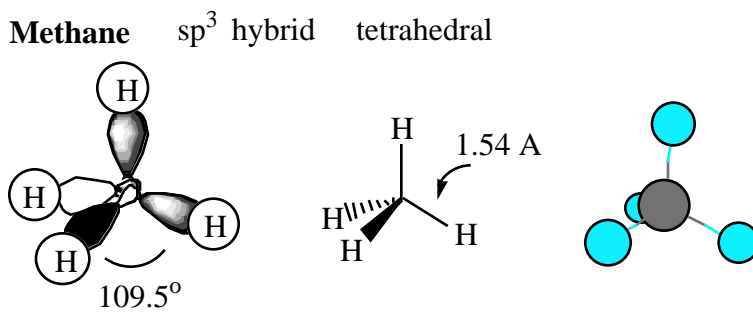
## CHAPTER 2 HYDROCARBONS

A hydrocarbon molecule contains only carbon and hydrogen. Hydrocarbons are further divided into several structural types called, alkanes, alkenes, alkynes and aromatics. The first three types are presented in this chapter, and aromatics are presented in a later chapter.

### 2.1 Alkanes

#### 2.1a Structure

A chain of carbon atoms that contains the maximum number of hydrogen atoms has the general formula  $C_nH_{2n+2}$  ( $n$  = number of carbon atoms). This type of hydrocarbon is called an alkane. Alkanes can exist in straight chains, chains with branching, and cycles. The carbon atom in an alkane has four  $sp^3$  hybridized and forms four single bonds that are equidistant from each other. The shape is referred to as tetrahedral with a C-C bond length of  $1.54 \text{ \AA}$  and bond angles of  $109.5^\circ$ .



#### 2.1b Nomenclature

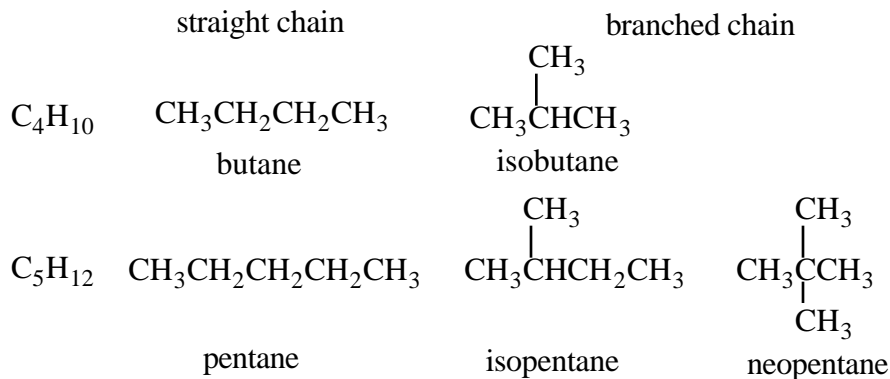
##### Hydrocarbon Chains

Knowledge about the names of alkanes is extremely important because the names of alkanes form the basis for the names of many other types of organic compounds. The names of the first ten alkanes are shown below. Alkane names always end with -ane.

Carbons	Structure	Name
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1	CH <sub>4</sub>	methane
2	CH <sub>3</sub> CH <sub>3</sub>	ethane
3	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	propane
4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	butane
5	C <sub>5</sub> H <sub>12</sub>	pentane
6	C <sub>6</sub> H <sub>14</sub>	hexane
7	C <sub>7</sub> H <sub>16</sub>	heptane
8	C <sub>8</sub> H <sub>18</sub>	octane
9	C <sub>9</sub> H <sub>20</sub>	nonane
10	C <sub>10</sub> H <sub>22</sub>	decane

Alkanes that contain four or more carbons can have different structures with the same formula that are known as **structural isomers**. The structural isomers of C<sub>4</sub>H<sub>10</sub> and of C<sub>5</sub>H<sub>12</sub> are shown below. The number of structural isomers increases with the number of carbon atoms. Butane, C<sub>4</sub>H<sub>10</sub>, has two structural isomers, pentane, C<sub>5</sub>H<sub>12</sub>, has three, but heptane, C<sub>7</sub>H<sub>14</sub>, has nine.

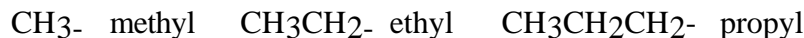


A systematic system of nomenclature for organic compounds has been developed by the International Union of Pure and Applied Chemistry (IUPAC). Names will be developed throughout the following chapters as the various compounds are encountered.

The parent IUPAC name of an alkane is derived from the length of the longest chain in the compound. The chain is named, as shown above, and the suffix -ane is added.

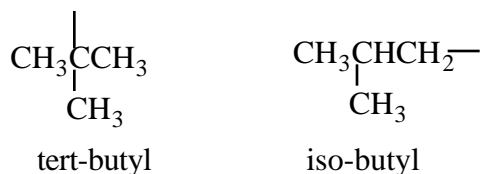
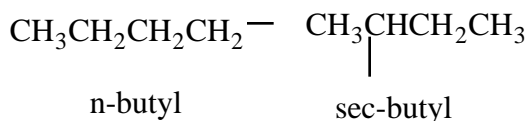
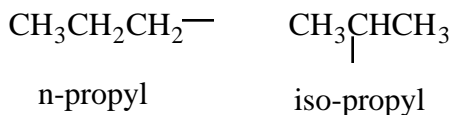
If alkane substituents are attached to the chain, they are named from their chain length by dropping the -ane and adding -yl. These are referred to as alkyl

substituents (alkane -ane + yl = alkyl). Three common alkyl groups are shown below.

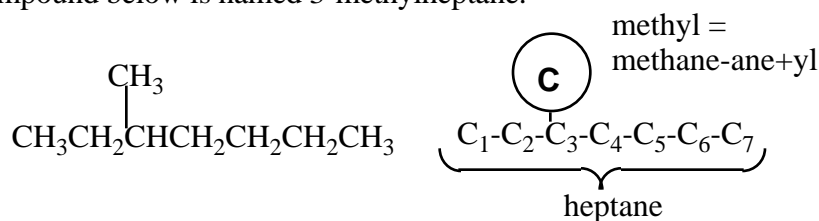


Structural isomers also exist in alkyl groups and are distinguished by a prefix added to the alkyl name.

prefixes are: n (normal straight chain), sec (secondary), iso, and tert (tertiary)

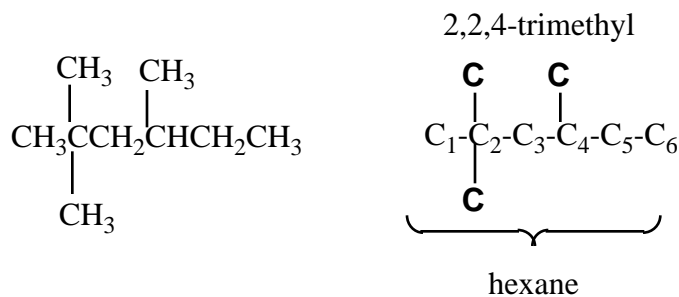


In an alkane that contains branching, the alkane main chain is numbered to give the attached alkyl group the lowest possible number. The final name has first the number of the branch position, then the alkyl group, then the parent alkane name. The compound below is named 3-methylheptane.

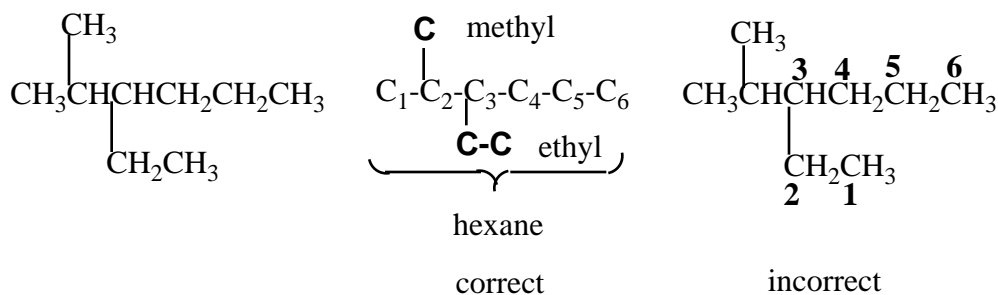


Often in a molecule there are several branched substituents that may or may not be identical. The identical substituents are grouped by first specifying the number of their positions, and then by adding a prefix to denote the number of groups: di for two, tri for three, tetra for four, penta for five, etc. The compound below is correctly named by IUPAC rules as 2,2,4-trimethylhexane. The numbers

must be separated by commas and followed by a hyphen.

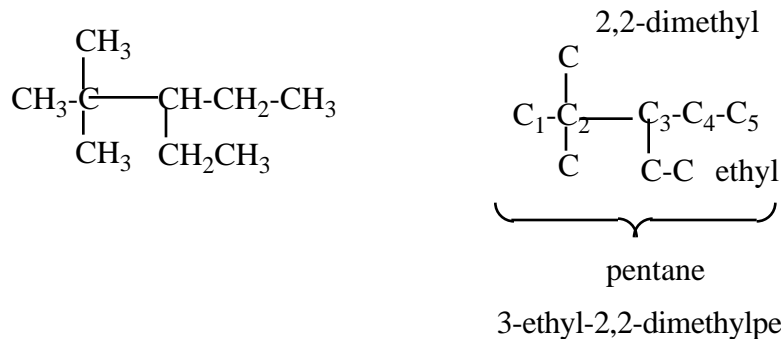


When the alkyl substituents are different, they are assigned the lowest numbers possible and named in alphabetical order. 3-Ethyl-2-methylhexane is the IUPAC name for the compound below.



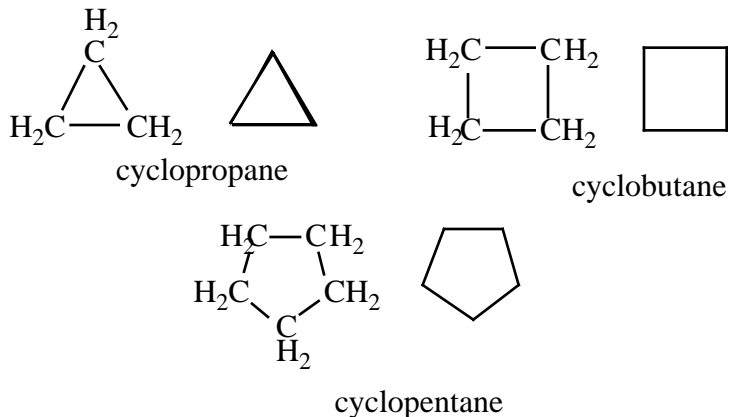
The compound above could be given another name because it contains a hexane parent chain. The alkyl substituent would be 3-isopropyl or 3-(1-methylethyl)-. The IUPAC system uses the chain with the greater number of substituents, thus using the wrong numbering gives a name with only one substituent.

In alphabetizing the alkyl groups the prefixes di-, tri-, tetra, etc., do not count, but the *i* of isopropyl does count. In the compound below the ethyl is named before methyl without regard to the di- in dimethyl. It is acceptable that the number 3 comes before the number 2 in the name; alphabetical order is all that counts.

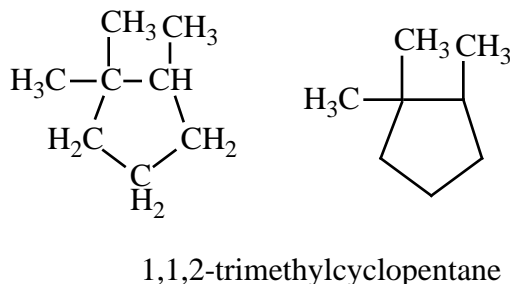


### Cyclic Hydrocarbons

Hydrocarbons can also exist with the carbon atoms forming a ring or cycle. The cycloalkanes are named by adding the prefix "cyclo" to the name of the alkane based on the number of carbon atoms. The condensed structure representation without C for carbon or H for hydrogen is convenient for writing cyclic alkanes.

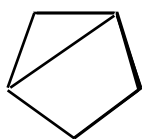


Alkyl groups attached to cycloalkanes are named alphabetically and given the lowest possible number.

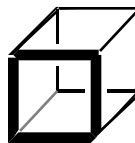


Cycloalkanes may also contain more than one ring, and their names are prefixed by the number of rings present, such as bicyclo[2.1.0]pentane. This is a cyclopentane but two rings are present. The names can become very complicated,

and the compounds are often given common names. The compound shaped like a cube is given the name cubane.



bicyclo[2.1.0]pentane



cubane

### 2.1c Naturally Occurring Hydrocarbons

The richest sources of hydrocarbons are coal and crude oil. The world has abundant supplies of these resources, but once they are consumed there is no natural way to replenish their supply.

Coal when used directly as a fuel does not furnish any useful hydrocarbons. Coal is heated at high temperature without oxygen in order to remove volatile materials and provide coke for furnaces in the iron industry. The volatile materials are called coal-gas and contain methane.

Methane, a valuable fuel, is found in several other natural sources also. Marsh gas, formed from decaying plants, contains methane, and methane is exhaled in the breath of cattle. Natural gases from pockets in the earth contain methane (80%) and ethane (10%) with the rest being higher gaseous alkanes.

Crude oil consists of a mixture of many hydrocarbon materials. The crude oil is sent to refineries where it is distilled to separate the different alkanes present. The fractions boiling under  $20^{\circ}$  contain methane, ethane, propane and butane. Fractions up to about  $70^{\circ}$  contain pentanes, hexanes and heptanes. Gasoline is obtained as a mixture of C5 to C11 hydrocarbons boiling from  $50$  to  $200^{\circ}$ ; kerosene is a mixture of C10 to C19 hydrocarbons boiling from  $170$  to  $350^{\circ}$ ; and diesel oil contains more than C16 and boils over  $280^{\circ}$ .

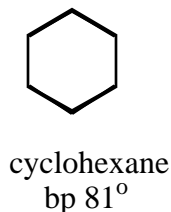
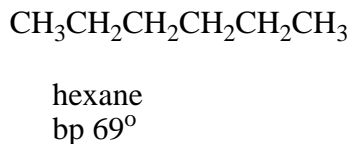
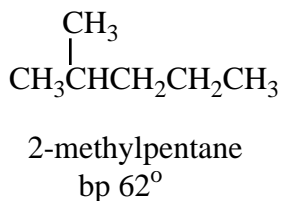
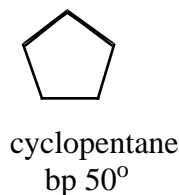
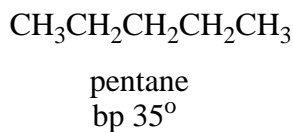
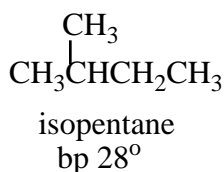
The tiger moth produces 2-methylheptadecane, a hydrocarbon sex attractant.

2-methylheptadecane  $C_{18}H_{38}$ 

Tiger moth sex attractant

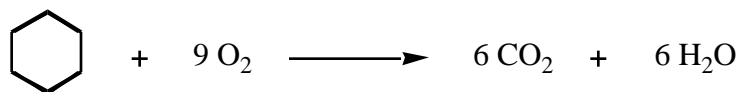
### 2.1d Physical Properties of Alkanes

Alkanes contain no electronegative atoms and thus are non-polar molecules that are useful as solvents for a wide range of organic substances. The boiling points of alkanes depend on the molecular mass and branching of the chain. Some general observations on boiling points are that branching decreases the boiling point, adding a  $CH_2$  or  $CH_3$  group increases the bp by  $20-30^\circ$ , and forming a ring increases the bp by  $10-20^\circ$ .



### 2.1d Reactions of Alkanes

Alkanes are relatively inert. Most reactions require specialized catalysts for breaking the carbon-carbon bonds. Burning, oxidation of alkanes, is a very important reaction in using alkanes as fuel. The fuels used in engines require additives to improve the combustibility for smooth and efficient burning.



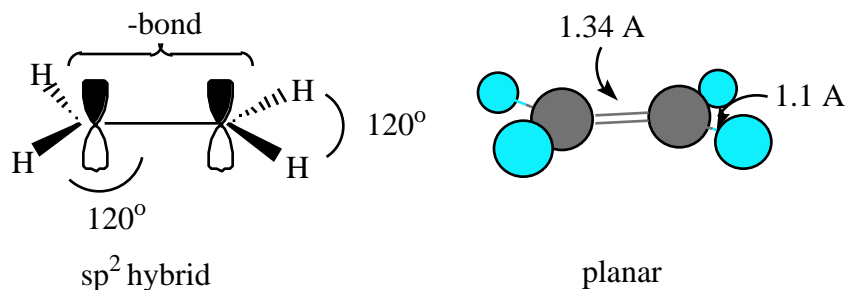
$$H = -950 \text{ kcal/mole}$$

## 2.2 Alkenes

### 2.2a Structure

Hydrocarbons can contain carbon bound to another carbon by a double bond made up of a sigma ( $\sigma$ ) bond and a pi ( $\pi$ ) bond. Compounds with double bonds are called alkenes and are considered unsaturated compounds, and an older system of terms calls them olefins. The general structure of an alkene in a chain is  $\text{C}_n\text{H}_{2n}$ , two hydrogens less than an alkane.

The alkene carbon atoms are  $\text{sp}^2$  hybridized and all of the single bonds are  $\text{sp}^2$  orbitals overlapped with orbitals from hydrogen or carbon. The unused p-orbitals in this hybridization join by side-to-side overlap to form a bond called a  $\pi$ -bond. The  $\pi$ -bond prevents rotation in the system and allows geometrical cis and trans isomers discussed in the stereochemistry chapter. The alkene is a planar structure with a C=C bond length of 1.34 Å and a C-H bond length of 1.1 Å. All bond angles are  $120^\circ$ .



### 2.2b Nomenclature

Alkenes are named from the corresponding alkane name by dropping the -ane and by adding -ene. The alkene function is a higher priority than an alkyl group and thus it is given the lowest number in the chain.

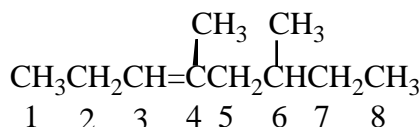


Alkene	IUPAC Name	Common Name
$\text{CH}_2=\text{CH}_2$	ethene	ethylene
$\text{CH}_2=\text{CHCH}_3$	propene	propylene
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	1-butene	butylene
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$	1-pentene	amylene

Both butene and pentene above can contain the double bond in another position. Thus numbering the position of the alkene becomes important. The numbering always goes across the double bond.

$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	1-butene	
$\text{CH}_3\text{CH}=\text{CHCH}_3$	2-butene	
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_2 = \text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$	2-methylpropene	isobutylene

Alkenes with alkyl substituents are named by establishing the parent name of the longest chain alkene and assigning the lowest number to the first double-bonded carbon of the alkene. The alkyl substituents are named in alphabetical order along with their position number.



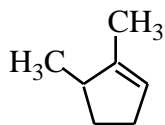
correct numbering with ene in 3 position

#### **4,6-dimethyl-3-octene**

Two common substituents also contain an alkene function, as shown.

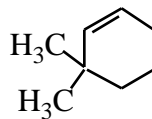


Cyclic alkenes are numbered from the alkene (and across the alkene) with the first carbon of the alkene assigned number one. The number one is written only when required to show the position of a substituent, not to show the position of the double bond that is assigned to position one.



1,5-dimethylcyclopentene

not 1,2-dimethylcyclopentene

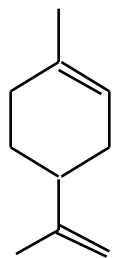


3,3-dimethylcyclohexene

not 1,1-dimethyl-2-cyclohexene

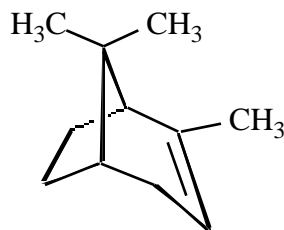
### 2.2c Naturally Occurring Alkenes

Alkene structures are also found in some interesting natural sources. Limonene is a natural substance found in lemon oil, and turpentine, a paint thinner, is found in pine trees.



limonene

found in lemon oil



turpentine

found in pine trees

The compound shaped like a soccer ball is not found in nature but is obtained by passing an electrical arc through pure carbon electrodes. It is named after Buckminster Fuller who proposed such structures. Thus the name is fullerene, but the compound is sometimes referred to as a Bucky Ball. Bucky Ball has the formula  $C_{60}$  and thus contains no hydrogen atoms.



$C_{60}$  fullerene

Bucky Ball

Low molecular weight alkenes are obtained by "cracking" or breaking down alkanes at high temperature with special catalysts. Ethene is obtained from ethane and some natural gas wells contain ethene, which is an important resource for the production of polyethylene used in plastic bags and toys.

**2.2d Physical properties of alkenes**

Alkenes, like alkanes, are non-polar materials with generally lower boiling points than the corresponding alkane. Alkenes also have strong odors, sometimes pleasant, sometimes not.



pentane

bp  $36^\circ$



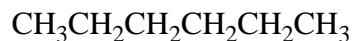
1-pentene

bp  $30^\circ$



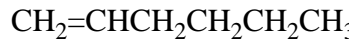
2-pentene

bp  $37^\circ$



hexane

bp  $69^\circ$



1-hexene

bp  $64^\circ$

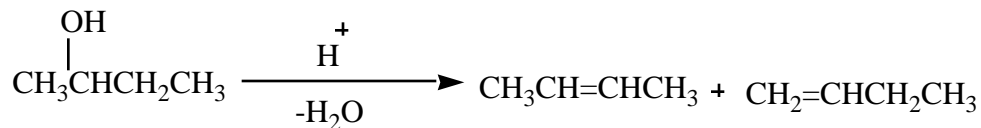
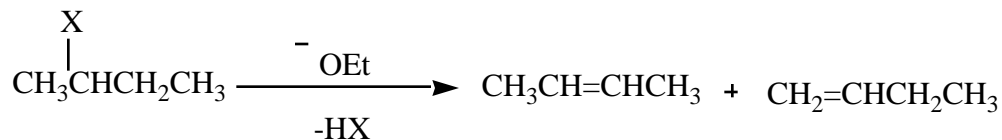
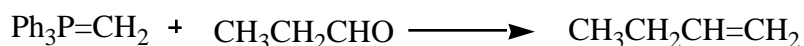


2-hexene

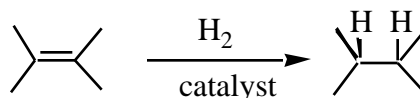
bp  $68^\circ$

**2.2e Preparation of Alkenes**

Alkenes are often prepared by removal of substituents from saturated precursors. Dehydration (loss of  $\text{H}_2\text{O}$ ) and dehydrohalogenation (loss of H and halogen) are two common elimination procedures for the preparation of alkenes. The Wittig reaction, which involves an aldehyde or ketone with an organophosphorus reagent is an extremely important alkene producing reaction. The reactions shown below all have very different reaction mechanisms that will be discussed in detail in later chapters.

**Preparation of Alkenes****Dehydration****Dehydrohalogenation****Wittig Reaction****2.2f Reactions of Alkenes****Hydrogenation and Alkene Stability**

A very important reaction of alkenes is the addition of hydrogen to the double bond. A catalyst is required and the reaction is called catalytic hydrogenation.



catalytic hydrogenation

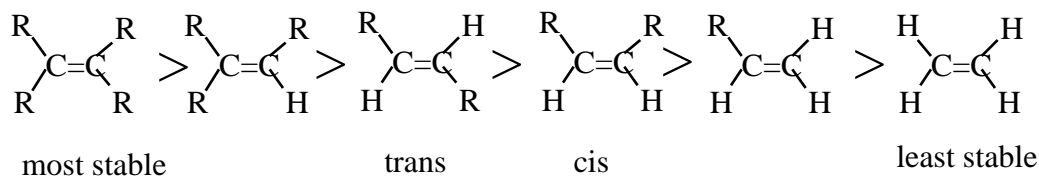
Catalytic hydrogenation provides alkanes in excellent yields and is an important and convenient reaction. Usually the alkene is reacted under pressure with hydrogen in the presence of a metal catalyst. Many catalysts are available for the process, but some common ones are 5% palladium on carbon (Pd/C), platinum oxide (PtO<sub>2</sub>), and nickel (Ni).

Measurement of the amount of heat given off, the heat of hydrogenation (ΔH), when an alkene is hydrogenated gives a measure of the stability of the alkene. The more stable alkenes give less heat.

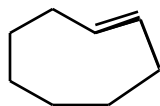
## Heats of Hydrogenation

Alkene	- H	kcal/mole
$\text{CH}_2=\text{CH}_2$		33
$\text{CH}_3\text{CH}=\text{CH}_2$		30
$\text{CH}_3\text{CH}=\text{CHCH}_3$	cis	29
	trans	28
$\text{CH}_3\underset{\text{CH}_3}{\text{C}}=\text{CHCH}_3$		26

A very important general trend in the stabilities of alkenes is found in these observations. Alkenes with more alkyl substituents are more stable. That means that an alkene with four alkyl groups attached to the alkene is more stable than one with four hydrogens attached. Later, many reactions will be observed to produce alkenes on the basis of the stability of the alkene. The listing shows relative alkene stability, it does not mean that ethylene is unstable, just is less stable than the others.

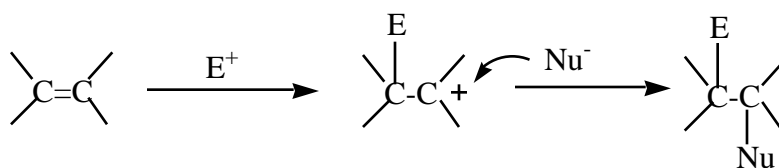


Cyclic alkenes are nearly always cis, but in some cases with increasing ring size, unstable trans alkenes are known. trans-Cyclooctene, shown below, is an example of a strained cyclic trans alkene.



### Electrophilic Addition

An important class of reaction with alkenes involves addition of an electrophile to the double bond in a process called electrophilic addition. The electrophile ( $\text{E}^+$ ) reacts with the alkene to produce a positively charged intermediate called a carbocation. A nucleophile reacts with the carbocation to complete the two-step addition process.



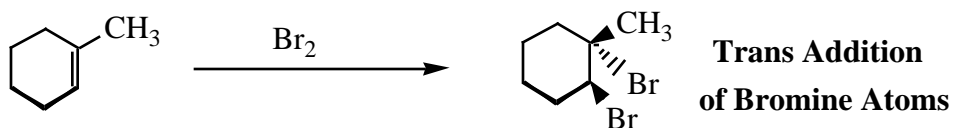
E = electrophile  $\text{Nu}^-$  = nucleophile of the reagent E-Nu

Unsymmetrical reagents follow a path in which the anion of the electrophilic reagent is bound to the more substituted carbon in the final product. This type of addition is called **Markovnikov addition**. Certain additions that do not occur by the electrophilic mechanism give products in which the opposite orientation is found, and are termed **anti-Markovnikov additions**. The orientation of the substituents in the product is a result of the reaction mechanism and will be discussed in detail in later chapters.

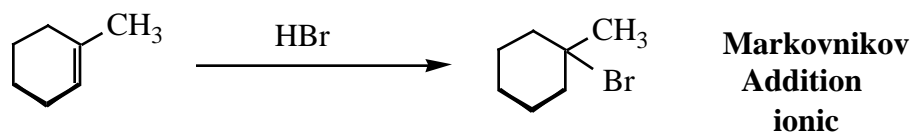
### Additions to Alkenes

#### Electrophilic Additions

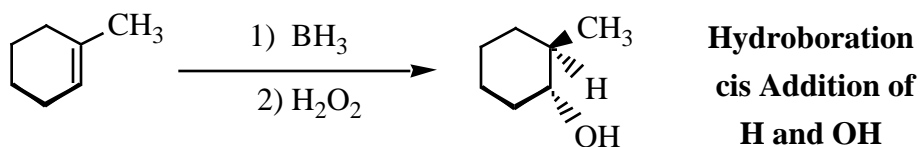
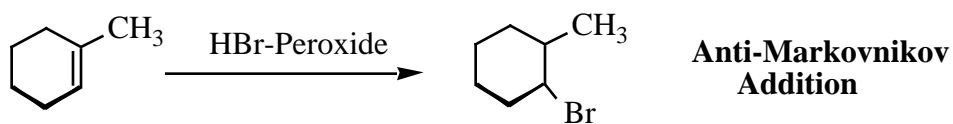
##### Symmetrical Additon



##### Unsymmetrical Additon



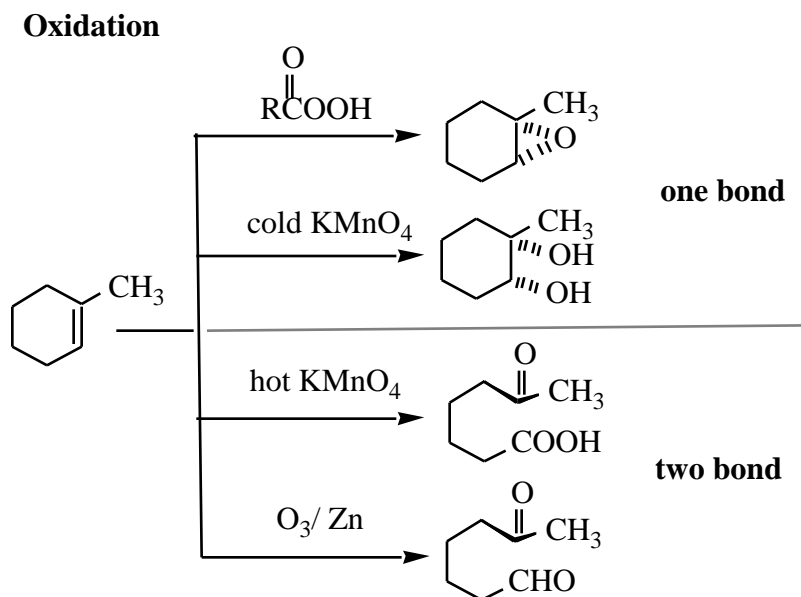
#### Non-Electrophilic Addition



Alkenes undergo oxidation with a wide variety of reagents. These reactions also fall into two categories: reactions that break both bonds of the alkene, and reactions that break only one bond of the alkene. The reactions are summarized below, and details about the reactions and mechanisms are given later.

### Oxidation of Alkenes

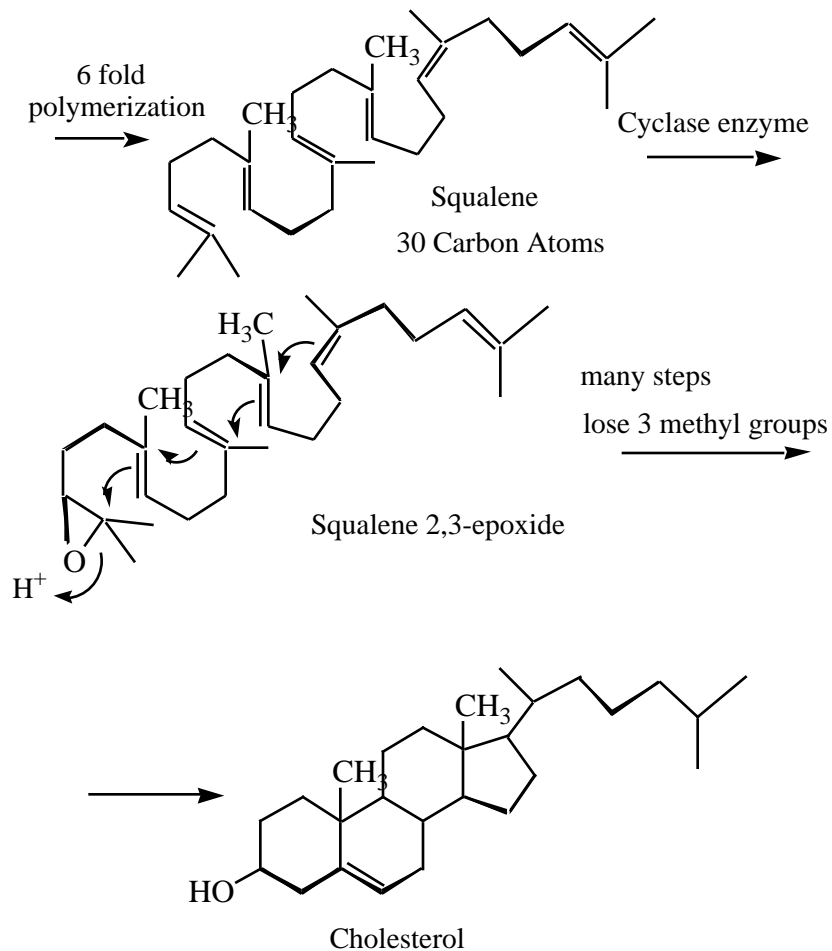
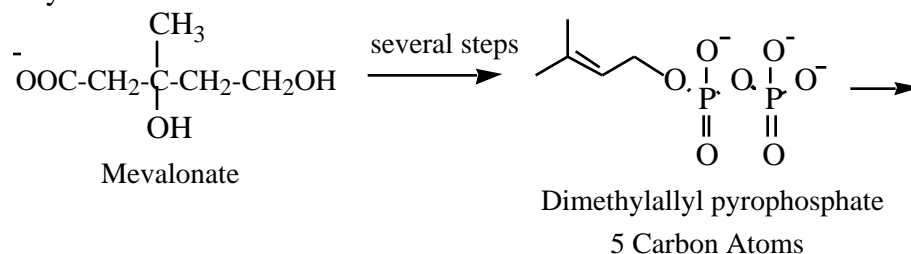
The double bond of alkenes is oxidized by a number of convenient reagents in synthetically useful processes. These reagents will oxidize only the pi bond (one bond oxidation) or both bonds of the alkene (two bond oxidation). The details of these reactions are given in chapters that discuss the functional groups produced.



### Biosynthesis of Alkenes and Cholesterol

The synthesis of compounds by the body is an area of biochemistry called biosynthesis. The body is capable of synthesizing many very complicated structures that are required for various life processes. Below is a short outline of the steps in the biosynthesis of cholesterol. Cholesterol is well known because of its implications in hardening of the arteries and heart disease. Serum levels over 300 mg/dL of cholesterol are considered high risk, and steps to reduce this level are commonly advised. Other compounds, called lipoproteins, are also closely related with heart disease. But for our purpose the biochemical marvel of converting a small molecule of mevalonate into a large poly-alkene called squalene can be appreciated. The squalene is converted into an epoxide in the body and is cyclized

by enzyme catalysis (enzymes are protein molecules). The epoxidation of an alkene and the reaction of an alkene with a proton are common reactions of alkenes found later in the chapter on alcohols. Finally, the biochemical marvel continues, as three methyl groups are lost and the molecule undergoes some rearrangement to produce cholesterol. The loss of methyl groups is not a common occurrence in organic chemistry.

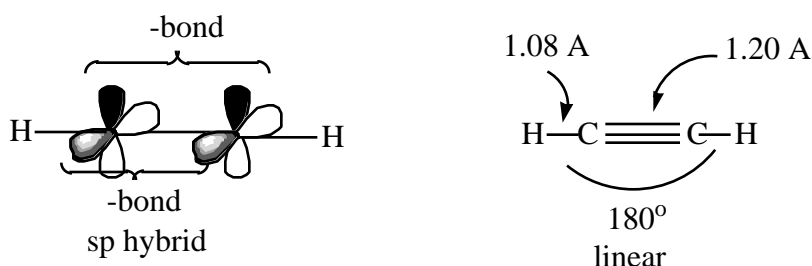




## 2.3 Alkynes

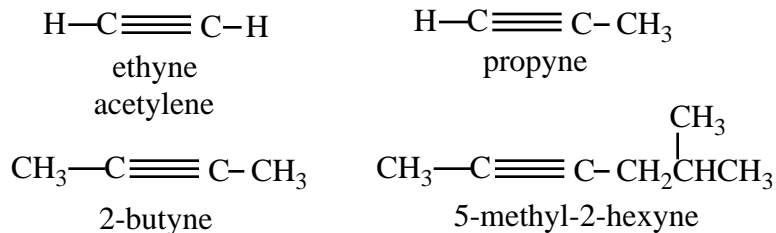
### 2.3a Structure

Alkynes, also called acetylenes, contain a structural unit in which carbon is bonded to another carbon with three bonds,  $C \equiv C$ . The double unsaturation gives rise to the general formula of  $C_nH_{2n-2}$  for alkynes. The carbon atoms in an alkyne are  $sp$  hybridized. The single bonds are made of  $sp$  hybridized carbon atoms overlapped with hydrogen or carbon. The remaining two unhybridized  $p$ -orbitals join in side-to-side overlap to make two orthogonal  $p$ -bonds. The overall alkyne structure is linear with a C-C bond length of 1.20 Å and C-H bond length of 1.08 Å.



### 2.3b Nomenclature

The IUPAC system of nomenclature derives an alkyne name from the corresponding alkane. The -ane is replaced by -yne and a number is used to give the location of the triple bond. Ethyne,  $C_2H_2$ , is the first alkyne and is also commonly known as acetylene. Alkynes are named by locating the parent name from the longest chain containing the triple bond. The alkyne is given the lowest possible number, and numbering proceeds across the triple bond. Substituents are given the lowest numbers possible and are named alphabetically.



### 2.3c Natural Alkynes

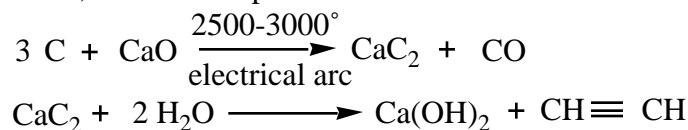
Many alkynes are found in small amounts in plant sources. The marigold flower contains the bithienyl compound below. The plant uses this material to kill small worms that attack the roots of the plant. Some gardeners grow marigolds along with other plants to take advantage of this natural protection.



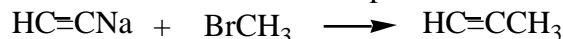
a bithienyl enyne isolated from marigold roots

### 2.3d Preparation of Alkynes

Most alkynes are synthesized from acetylene. Pure acetylene is obtained from calcium carbide, a substance produced from carbon and calcium oxide.



Acetylene can be converted to the sodium salt, sodium acetylide, that will displace the halogen atom in certain haloalkanes. The process is nucleophilic substitution and is discussed in detail in later chapters.



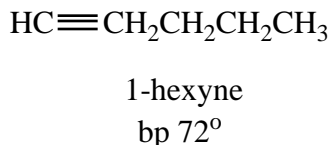
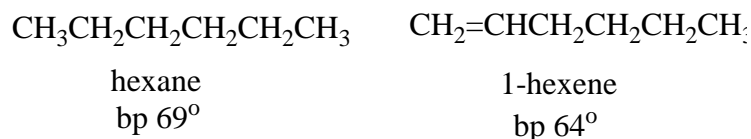
### 2.3e Physical Properties of Alkynes

Alkynes are low boiling materials that possess a high heat content. Thus a major use for alkynes, especially acetylene, is as a fuel for high temperature flames.

Acetylene is fairly unstable and detonates under pressure. Pure acetylene is not stored as a liquid or a gas under pressure. It is adsorbed onto carbon and kept in steel containers at about 10 atm of pressure.

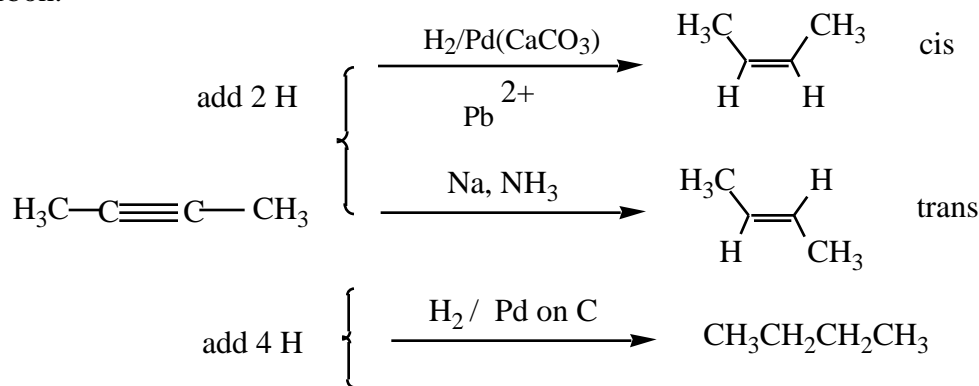
Although the thermal decomposition of acetylene to carbon and hydrogen does not involve any change in the volume of the gases, the reaction is extremely exothermic. A very sturdy apparatus must therefore be used for reactions of acetylene under pressure. The acetylene flame can burn at temperatures up to 2600°.

The boiling points of alkynes are somewhat higher than the boiling points of alkenes.



### 2.3f Reactions of Alkynes

Addition of hydrogen to alkynes can be controlled to add two hydrogen atoms and give an alkene as a product, or four hydrogen atoms can be added to give an alkane. Special methods are required to add just two hydrogen atoms. A catalyst of palladium on calcium carbonate containing lead ions (Lindlar catalyst) allows addition of one mole of hydrogen to give the cis-alkene, meaning the two substituents are on the same side of the double bond. Reductions with sodium in ammonia give the trans-alkene, which contains the two substituents on opposite sides of the double bond. Complete reduction of acetylenes to the hydrocarbon occurs easily on hydrogenation with a number of catalysts including palladium on carbon.

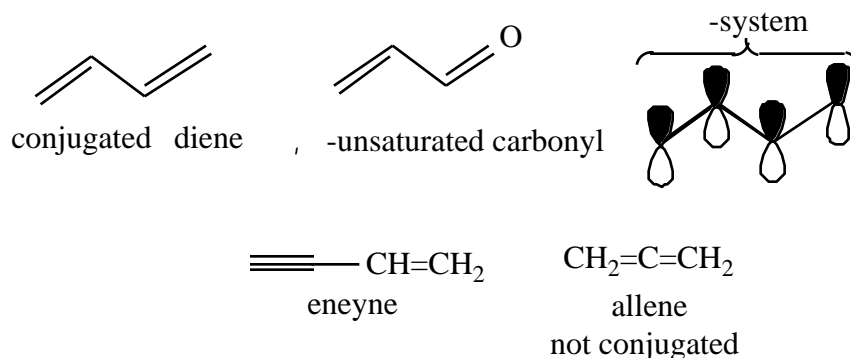


Alkynes react with a number of reagents to give addition products in a manner similar to alkenes. Those reactions will be discussed in the chapter on halogens.

### 2.4 Conjugated Alkenes

An organic molecule can possess more than one unsaturated system. When these systems are far apart from one another they behave as isolated functions. But

when they are separated by a single bond they are conjugated, and they behave as a unit instead of isolated systems. The orbital picture shows the electronic interaction of the systems. Several structures are shown below that are conjugated.



Some interesting dienes called allenes, but infrequently encountered, have two double bonds attached to one carbon. These systems are not conjugated.

## 2.5 Summary

Hydrocarbons are a class of organic compounds that contain only hydrogen and carbon. Hydrocarbons are divided into classes called *alkanes*, *alkenes* and *alkynes*.

Alkanes,  $C_nH_{2n+2}$ , are  $sp^3$  hybridized and have a tetrahedral shape. Usually volatile and found abundantly in oil and natural gas, alkanes are used widely as fuels. The *combustion of alkanes*, reaction with oxygen, produces carbon dioxide and water. Alkanes are systematically named, IUPAC rules, by adding an *ane* suffix to the term that designates the number of carbon atoms.

Alkenes,  $C_nH_{2n}$ , are  $sp^2$  hybridized and have a planar shape. Alkenes are prepared by *dehydration* and *dehydrohalogenation* reactions. Alkene chemistry is dominated by reactions of the double bond called a  $\pi$ -bond. The double bond undergoes *reduction*, *oxidation*, and *addition reactions*. Alkenes are named by replacing the alkane suffix, *ane*, with a new suffix *ene*. A number is assigned to the position of the double bond.

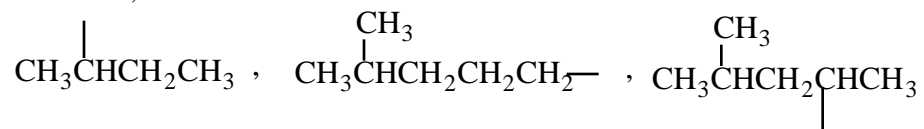
Alkynes,  $C_2nH_{2n-2}$ , are  $sp$  hybridized and are linear. Acetylene is well-known for its use in welding torches. The triple bond of alkynes can be *reduced* with hydrogen, or *oxidized* by a variety of reagents. Alkynes are named by replacing the *ane* suffix of the alkane with the *yne* suffix. The triple bond location is

designated by a number.

Alkenes and alkynes may be joined in compound to form extended unsaturated systems called *conjugated systems* such as that found in 1,3-butadiene.

## 2.6 Problem Set

2.1. Write the alkyl substituent names for ethane, octane, cyclohexane and the structures,



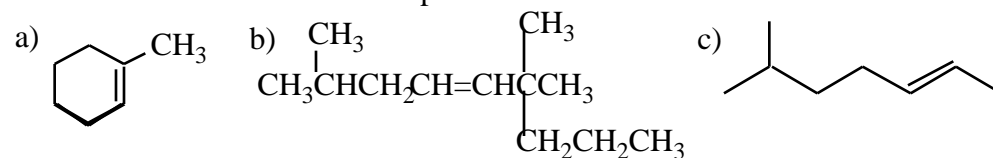
2.2. Write balanced equations for the complete combustion of propane and methylcyclopentane.

2.3. Draw and name all of the structural isomers of a) pentane and b) hexane.

2.4. Write structures, formulas, and formula weights for the following.

a) 3-isopropylnonane    b) cyclopropylcyclohexane    c) sec-butylcyclopentane

2.5. Provide names for each compound below.



2.6 Write structures that correspond to the names given.

- a) 1,2-pentadiene    b) 3-bromocyclopentene    c) 3,3-dichloro-1-pentyne  
d) cyclohexylethyne

2.7 Show the products from the reaction of 2-methyl-2-butene with a)  $\text{H}_2 / \text{Pt}$ , b) hot  $\text{KMnO}_4$ , c)  $\text{HBr}$ -peroxide, d)  $\text{HBr}$  (no peroxide), e)  $\text{Br}_2$ , f)  $\text{O}_3 / \text{Zn}$

2.8 Both Vitamin D and Cortisone contain significant hydrocarbon portions of their structure. Find their structures in a reference book (Merck Index) and list the function groups present in each molecule.