

## 20.2: Hydrocarbons

### Learning Objectives

- Explain the importance of hydrocarbons and the reason for their diversity
- Name saturated and unsaturated hydrocarbons, and molecules derived from them
- Describe the reactions characteristic of saturated and unsaturated hydrocarbons
- Identify structural and geometric isomers of hydrocarbons

The largest database<sup>1</sup> of organic compounds lists about 10 million substances, which include compounds originating from living organisms and those synthesized by chemists. The number of potential organic compounds has been estimated<sup>2</sup> at  $10^{60}$ —an astronomically high number. The existence of so many organic molecules is a consequence of the ability of carbon atoms to form up to four strong bonds to other carbon atoms, resulting in chains and rings of many different sizes, shapes, and complexities.

The simplest organic compounds contain only the elements carbon and hydrogen, and are called hydrocarbons. Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures. In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory. We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons. We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms. This leads to differences in geometries and in the hybridization of the carbon orbitals.

### 20.2.1: Alkanes

Alkanes, or saturated hydrocarbons, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has  $sp^3$  hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. The Lewis structures and models of methane, ethane, and pentane are illustrated in Figure 20.2.1. Carbon chains are usually drawn as straight lines in Lewis structures, but one has to remember that Lewis structures are not intended to indicate the geometry of molecules. Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) of the pentane molecule do not lie in a straight line. Because of the  $sp^3$  hybridization, the bond angles in carbon chains are close to  $109.5^\circ$ , giving such chains in an alkane a zigzag shape.

The structures of alkanes and other organic molecules may also be represented in a less detailed manner by condensed structural formulas (or simply, *condensed formulas*). Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule. These formulas have the appearance of a Lewis structure from which most or all of the bond symbols have been removed. Condensed structural formulas for ethane and pentane are shown at the bottom of Figure 20.2.1, and several additional examples are provided in the exercises at the end of this chapter.

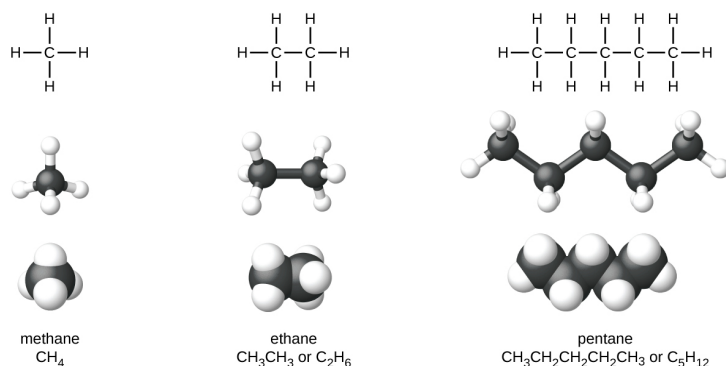


Figure 20.2.1: Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane.

A common method used by organic chemists to simplify the drawings of larger molecules is to use a skeletal structure (also called a line-angle structure). In this type of structure, carbon atoms are not symbolized with a C, but represented by each end of a line or

bond in a line. Hydrogen atoms are not drawn if they are attached to a carbon. Other atoms besides carbon and hydrogen are represented by their elemental symbols. Figure 20.2.2 shows three different ways to draw the same structure.

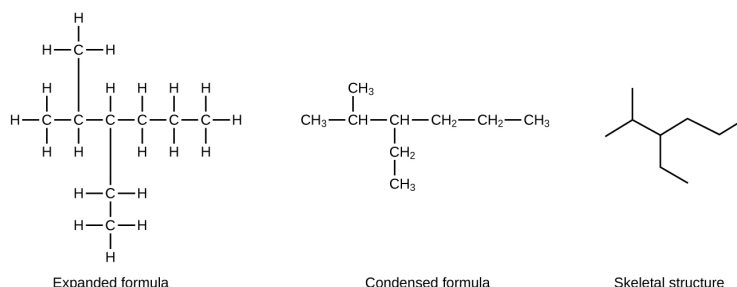
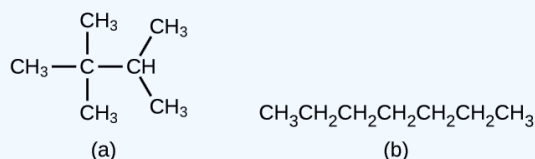


Figure 20.2.2: The same structure can be represented three different ways: an expanded formula, a condensed formula, and a skeletal structure.

### ✓ Example 20.2.1

**Drawing Skeletal Structures** Draw the skeletal structures for these two molecules:



### Solution

Each carbon atom is converted into the end of a line or the place where lines intersect. All hydrogen atoms attached to the carbon atoms are left out of the structure (although we still need to recognize they are there):

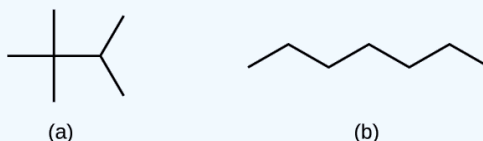


Figure a shows a branched skeleton structure that looks like a plus sign with line segments extending up and to the right and down and to the left of the rightmost point of the plus sign. Figure b appears in a zig zag pattern made with six line segments. The segments rise, fall, rise, fall, rise, and fall moving left to right across the figure.

### ? Exercise 20.2.1

Draw the skeletal structures for these two molecules:

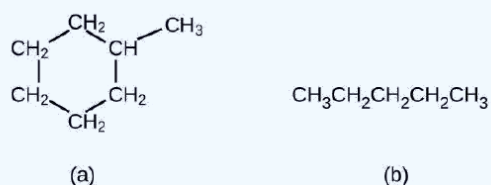
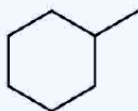


Figure a shows five  $\text{CH}_2$  groups and one  $\text{CH}$  group bonded in a hexagonal ring. A  $\text{CH}_3$  group appears above and to the right of the ring, bonded to the ring on the  $\text{CH}$  group appearing at the upper right portion of the ring. In b, a straight chain molecule composed of  $\text{CH}_3$   $\text{CH}_2$   $\text{CH}_2$   $\text{CH}_2$   $\text{CH}_3$  is shown.

### Answer



(a)

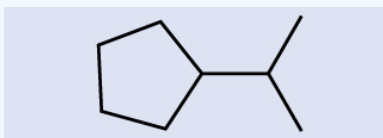


(b)

In a, a hexagon with a vertex at the top is shown. The vertex just to the right has a line segment attached that extends up and to the right. In b, a zigzag pattern is shown in which line segments rise, fall, rise, fall, and rise moving left to right.

### ✓ Example 20.2.2

Interpreting Skeletal Structures Identify the chemical formula of the molecule represented here:

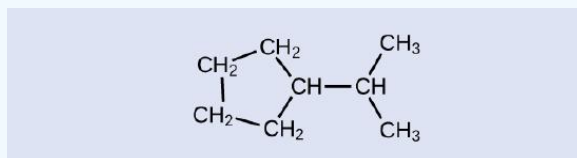


This figure shows a pentagon with a vertex pointing right, from which a line segment extends that has two line segments attached at its right end, one extending up and to the right, and the other extending down and to the right.

#### Solution

There are eight places where lines intersect or end, meaning that there are eight carbon atoms in the molecule. Since we know that carbon atoms tend to make four bonds, each carbon atom will have the number of hydrogen atoms that are required for four bonds. This compound contains 16 hydrogen atoms for a molecular formula of  $C_8H_{16}$ .

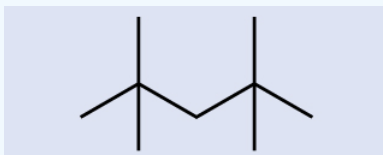
Location of the hydrogen atoms:



In this figure a ring composed of four  $CH_2$  groups and one  $CH$  group in a pentagonal shape is shown. From the  $CH$  group, which is at the right side of the pentagon, a  $CH$  is bonded. From this  $CH$ , a  $CH_3$  group is bonded above and to the right and a second is bonded below and to the right.

### ? Exercise 20.2.2

Identify the chemical formula of the molecule represented here:



A skeleton model is shown with a zigzag pattern that rises, falls, rises, and falls again left to right through the center of the molecule. From the two risen points, line segments extend both up and down, creating four branches.

#### Answer



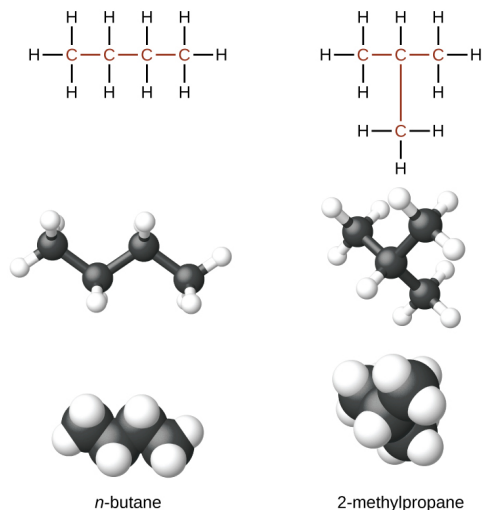
All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of  $C_nH_{2n+2}$ . The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the

molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table 20.2.1) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table 20.2.1: Properties of Some Alkanes

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP <sup>4</sup>	Number of Structural Isomers
methane	CH <sub>4</sub>	-182.5	-161.5	gas	1
ethane	C <sub>2</sub> H <sub>6</sub>	-183.3	-88.6	gas	1
propane	C <sub>3</sub> H <sub>8</sub>	-187.7	-42.1	gas	1
butane	C <sub>4</sub> H <sub>10</sub>	-138.3	-0.5	gas	2
pentane	C <sub>5</sub> H <sub>12</sub>	-129.7	36.1	liquid	3
hexane	C <sub>6</sub> H <sub>14</sub>	-95.3	68.7	liquid	5
heptane	C <sub>7</sub> H <sub>16</sub>	-90.6	98.4	liquid	9
octane	C <sub>8</sub> H <sub>18</sub>	-56.8	125.7	liquid	18
nonane	C <sub>9</sub> H <sub>20</sub>	-53.6	150.8	liquid	35
decane	C <sub>10</sub> H <sub>22</sub>	-29.7	174.0	liquid	75
tetradecane	C <sub>14</sub> H <sub>30</sub>	5.9	253.5	solid	1858
octadecane	C <sub>18</sub> H <sub>38</sub>	28.2	316.1	solid	60,523

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C<sub>4</sub>H<sub>10</sub>: They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:



The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used). Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2-methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms)

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in Figure 20.2.3 all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms.

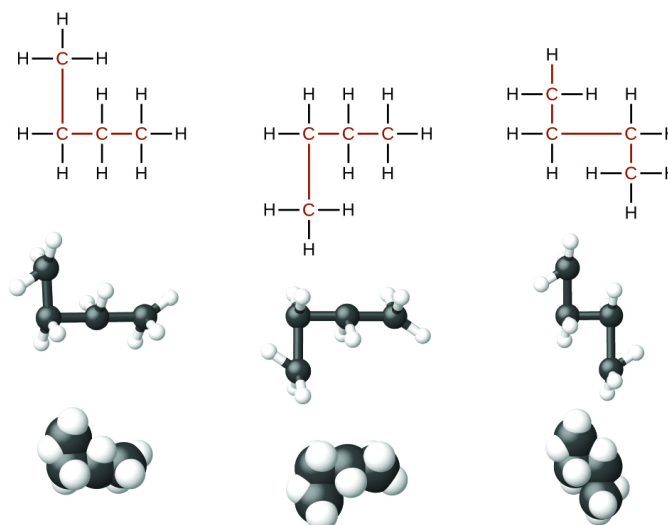
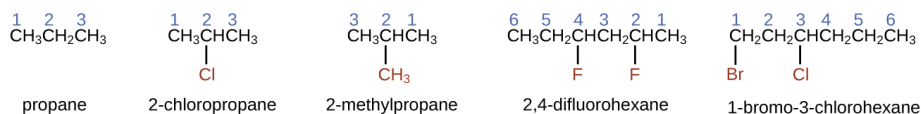


Figure 20.2.3: These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

## 20.2.2: The Basics of Organic Nomenclature: Naming Alkanes

The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

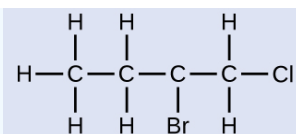
1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in Table 20.2.1.
2. Add prefixes to the name of the longest chain to indicate the positions and names of substituents. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.
- 3.



When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

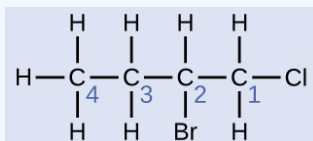
### ✓ Example 20.2.3: Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



This structure shows a C atom bonded to the H atoms and another C atom. This second C atom is bonded to two H atoms and another C atom. This third C atom is bonded to a Br atom and another C atom. This fourth C atom is bonded to two H atoms and a Cl atom.

### Solution

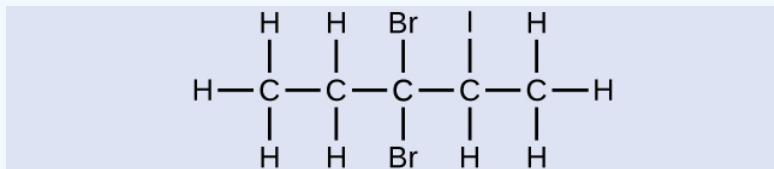


This structure shows a C atom bonded to the H atoms and another C atom. This second C atom is bonded to two H atoms and another C atom. This third C atom is bonded to an H atom, a Br atom, and another C atom. This fourth C atom is bonded to two H atoms and a Cl atom. The C atoms are numbered 4, 3, 2, and 1 from left to right.

The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

### ? Exercise 20.2.3

Name the following molecule:

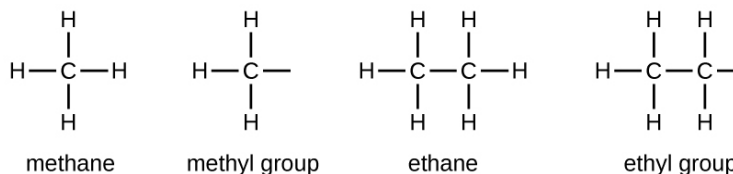


This figure shows a C atom bonded to three H atoms and another C atom. This second C atom is bonded to two H atoms and a third C atom. The third C atom is bonded to two Br atoms and a fourth C atom. This C atom is bonded to an H atom, and an I atom, and a fifth C atom. This last C atom is bonded to three H atoms.

### Answer

3,3-dibromo-2-iodopentane

We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an alkyl group is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:

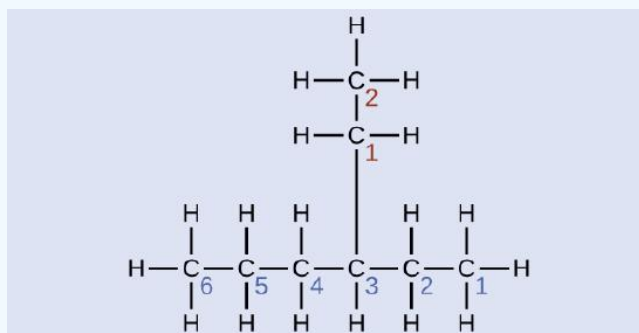


In this figure, methane is named and represented as C with four H atoms bonded above, below, to the left, and to the right of the C. The methyl group is shown, which appears like methane without the right most H. A dash remains at the location where the H was formerly bonded. Ethane is named and represented with two centrally bonded C atoms to which six H atoms are bonded; two above and below each of the two C atoms and to the left and right ends of the linked C atoms. The ethyl group appears as a similar structure with the right-most H atom removed. A dash remains at the location where the H atom was formerly bonded.

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

### ✓ Example 20.2.4 Naming Substituted Alkanes

Name the molecule whose structure is shown here:



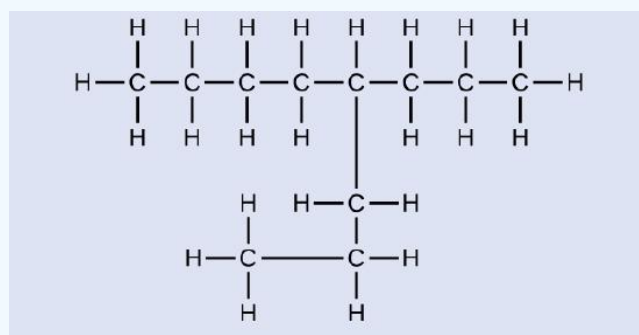
A chain of six carbon atoms, numbered 6, 5, 4, 3, 2, and 1 is shown. Bonded above carbon 3, a chain of two carbons is shown, numbered 1 and 2 moving upward. H atoms are present directly above, below, left and right of all carbon atoms in positions not already taken up in bonding to other carbon atoms.

#### Solution

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the blue numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in red)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

### ? Exercise 20.2.4

Name the following molecule:



This figure shows a C atom bonded to three H atoms and another C atom. This C atom is bonded to two H atoms and third C atom. The third C atom is bonded to two H atoms and a fourth C atom. The fourth C atom is bonded to two H atoms and a fifth C atom. This C atom is bonded to an H atom, a sixth C atom in the chain, and another C atom which appears to branch off the chain. The C atom in the branch is bonded to two H atoms and another C atom. This C atom is bonded to two H atoms and another C atom. This third C atom appears to the left of the second and is bonded to three H atoms. The sixth C atom in the chain is bonded to two H atoms and a seventh C atom. The seventh C atom is bonded to two H atoms and an eighth C atom. The eighth C atom is bonded to three H atoms.

#### Answer

4-propyloctane

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different “environments” in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models in Figure 20.2.3) Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent and removing any one of these hydrogen atoms produces an ethyl group. Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2-methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:

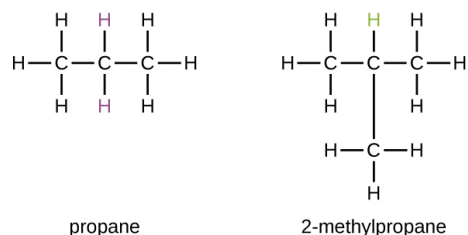
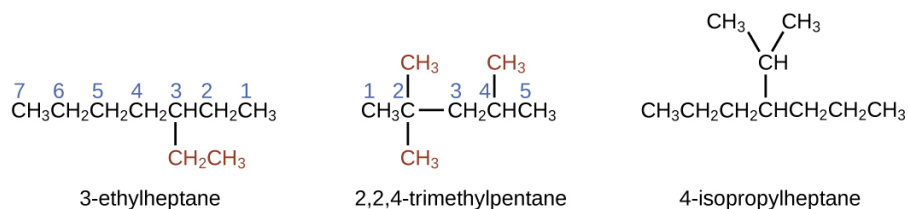


Figure 20.2.4.

Alkyl Group	Structure
methyl	$\text{CH}_3\text{—}$
ethyl	$\text{CH}_3\text{CH}_2\text{—}$
<i>n</i> -propyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$
isopropyl	$\begin{array}{c}   \\ \text{CH}_3\text{CHCH}_3 \end{array}$
<i>n</i> -butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
sec-butyl	$\begin{array}{c}   \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$
isobutyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{—} \\   \\ \text{CH}_3 \end{array}$
<i>tert</i> -butyl	$\begin{array}{c}   \\ \text{CH}_3\text{CCH}_3 \\   \\ \text{CH}_3 \end{array}$

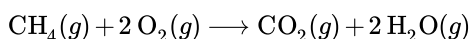
Figure 20.2.4: This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:





Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane,  $\text{CH}_4$ , is the principal component of natural gas. Butane,  $\text{C}_4\text{H}_{10}$ , used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure 20.2.5). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

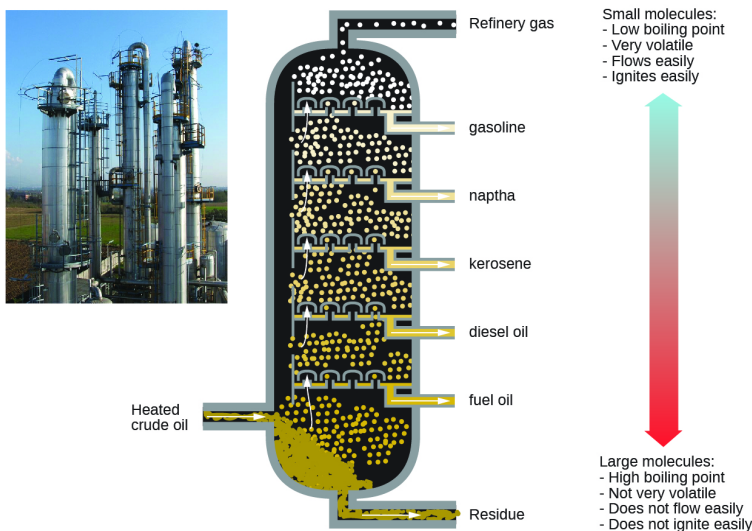
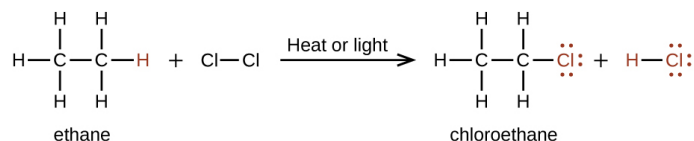


Figure 20.2.5: In a column for the fractional distillation of crude oil, oil heated to about  $425^\circ\text{C}$  in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

In a substitution reaction, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:



The C–Cl portion of the chloroethane molecule is an example of a functional group, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.

### 20.2.3: Alkenes

Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called alkenes. Carbon atoms linked by a double bond are bound together by two bonds, one  $\sigma$  bond and one  $\pi$  bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Ethene,  $\text{C}_2\text{H}_4$ , is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 20.2.6); the butene isomers follow in the series. Four carbon atoms in

the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

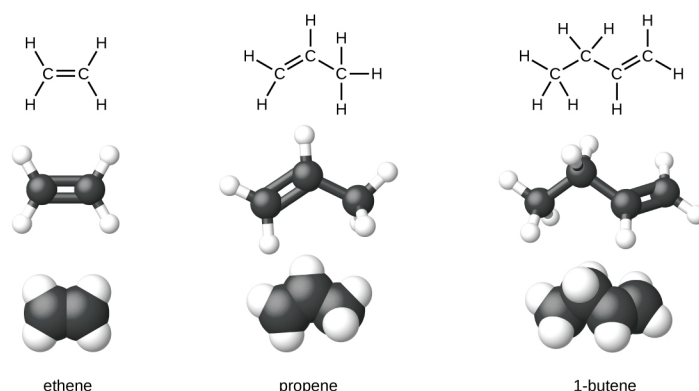


Figure 20.2.6: Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

### 20.2.4: Recycling Plastics

Polymers (from Greek words *poly* meaning “many” and *mer* meaning “parts”) are large molecules made up of repeating units, referred to as monomers. Polymers can be natural (starch is a polymer of sugar residues and proteins are polymers of amino acids) or synthetic [like polyethylene, polyvinyl chloride (PVC), and polystyrene]. The variety of structures of polymers translates into a broad range of properties and uses that make them integral parts of our everyday lives. Adding functional groups to the structure of a polymer can result in significantly different properties (see the discussion about Kevlar later in this chapter).

An example of a polymerization reaction is shown in Figure 20.2.7. The monomer ethylene (C<sub>2</sub>H<sub>4</sub>) is a gas at room temperature, but when polymerized, using a transition metal catalyst, it is transformed into a solid material made up of long chains of –CH<sub>2</sub>– units called polyethylene. Polyethylene is a commodity plastic used primarily for packaging (bags and films).

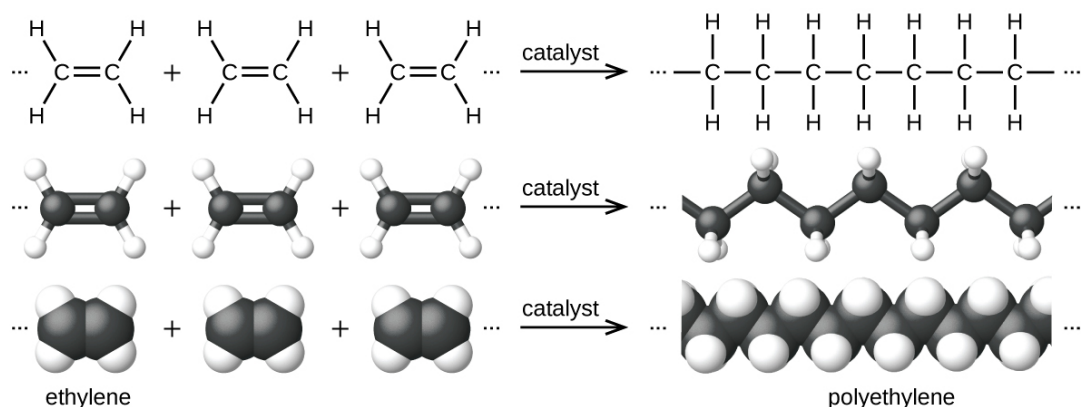


Figure 20.2.7: The reaction for the polymerization of ethylene to polyethylene is shown.

This diagram has three rows, showing ethylene reacting to form polyethylene. In the first row, Lewis structural formulas show three molecules of ethylene being added together, which are each composed of two doubly bonded C atoms, each with two bonded H atoms. Ellipses, or three dots, are present before and after the molecule structures, which in turn are followed by an arrow pointing right. On the right side of the arrow, the ellipses or dots again appear to the left of a dash that connects to a chain of 7 C atoms, each with H atoms connected above and below. A dash appears at the end of the chain, which in turn is followed by ellipses or dots. The reaction diagram is repeated in the second row using ball-and-stick models for the structures. In these representations, single bonds are represented with sticks, double bonds are represented with two parallel sticks, and elements are represented with balls. Carbon atoms are black and hydrogen atoms are white in this image. In the third row, space-filling models are shown. In these models, atoms are enlarged spheres which are pushed together, without sticks to represent bonds.

Polyethylene is a member of one subset of synthetic polymers classified as plastics. Plastics are synthetic organic solids that can be molded; they are typically organic polymers with high molecular masses. Most of the monomers that go into common plastics (ethylene, propylene, vinyl chloride, styrene, and ethylene terephthalate) are derived from petrochemicals and are not very biodegradable, making them candidate materials for recycling. Recycling plastics helps minimize the need for using more of the petrochemical supplies and also minimizes the environmental damage caused by throwing away these nonbiodegradable materials.

Plastic recycling is the process of recovering waste, scrap, or used plastics, and reprocessing the material into useful products. For example, polyethylene terephthalate (soft drink bottles) can be melted down and used for plastic furniture, in carpets, or for other applications. Other plastics, like polyethylene (bags) and polypropylene (cups, plastic food containers), can be recycled or reprocessed to be used again. Many areas of the country have recycling programs that focus on one or more of the commodity plastics that have been assigned a recycling code (Figure 20.2.8). These operations have been in effect since the 1970s and have made the production of some plastics among the most efficient industrial operations today.








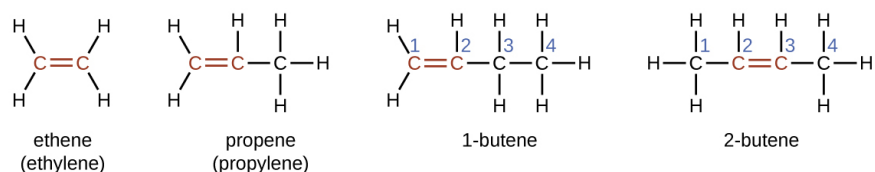
	<b>polyethylene terephthalate (PETE)</b>	Soda bottles and oven-ready food trays
	<b>high-density polyethylene (HDPE)</b>	Bottles for milk and dishwashing liquids
	<b>polyvinyl chloride (PVC)</b>	Food trays, plastic wrap, bottles for mineral water and shampoo
	<b>low density polyethylene (LDPE)</b>	Shopping bags and garbage bags
	<b>polypropylene (PP)</b>	Margarine tubs, microwaveable food trays
	<b>polystyrene (PS)</b>	Yogurt tubs, foam meat trays, egg cartons, vending cups, plastic cutlery, packaging for electronics and toys
	<b>any other plastics (OTHER)</b>	Plastics that do not fall into any of the above categories One example is melamine resin (plastic plates, plastic cups)

Figure 20.2.8: Each type of recyclable plastic is imprinted with a code for easy identification.

This table shows recycling symbols, names, and uses of various types of plastics. Symbols are shown with three arrows in a triangular shape surrounding a number. Number 1 is labeled P E T E. The related plastic, polyethylene terephthalate (P E T E), is used in soda bottles and oven-ready food trays. Number 2 is labeled H D P E. The related plastic is high-density polyethylene (H D P E), which is used in bottles for milk and dishwashing liquids. Number 3 is labeled V. The related plastic is polyvinyl chloride or (P V C). This plastic is used in food trays, plastic wrap, and bottles for mineral water and shampoo. Number 4 is labeled L D P E. This plastic is low density polyethylene (L D P E). It is used in shopping bags and garbage bags. Number 5 is labeled P P. The related plastic is polypropylene (P P). It is used in margarine tubs and microwaveable food trays. Number 6 is labeled P S. The related plastic is polystyrene (P S). It is used in yogurt tubs, foam meat trays, egg cartons, vending cups, plastic cutlery, and packaging for electronics and toys. Number 7 is labeled other for any other plastics. Items in this category include those plastic materials that do not fit any other category. Melamine used in plastic plates and cups is an example.

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:



Four structural formulas and names are shown. The first shows two red C atoms connected by a red double bond illustrated with two parallel line segments. H atoms are bonded above and below to the left of the left-most C atom. Two more H atoms are similarly bonded to the right of the C atom on the right. Beneath this structure the name ethene and alternate name ethylene are shown. The second shows three C atoms bonded together with a red double bond between the red first and second C atoms moving left to right across the three-carbon chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the middle C atom. Three more H atoms are bonded above, below, and to the right of the third C atom. Beneath this structure the name propene and alternate name propylene is shown. The third shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red first and second carbon in the chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the second C atom. H atoms are bonded above and below the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 1 dash butene is shown. The fourth shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red second and third C atoms in the chain. H atoms are bonded above, below, and to the left of the left-most C atom. A single H atom is bonded above the second C atom. A single H atom is bonded above the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 2 dash butene is shown.

### 20.2.5: Isomers of Alkenes

Molecules of 1-butene and 2-butene are structural isomers; the arrangement of the atoms in these two molecules differs. As an example of arrangement differences, the first carbon atom in 1-butene is bonded to two hydrogen atoms; the first carbon atom in 2-butene is bonded to three hydrogen atoms.

The compound 2-butene and some other alkenes also form a second type of isomer called a geometric isomer. In a set of geometric isomers, the same types of atoms are attached to each other in the same order, but the geometries of the two molecules differ. Geometric isomers of alkenes differ in the orientation of the groups on either side of a C = C bond.

Carbon atoms are free to rotate around a single bond but not around a double bond; a double bond is rigid. This makes it possible to have two isomers of 2-butene, one with both methyl groups on the same side of the double bond and one with the methyl groups on opposite sides. When structures of butene are drawn with 120° bond angles around the  $sp^2$ -hybridized carbon atoms participating in the double bond, the isomers are apparent. The 2-butene isomer in which the two methyl groups are on the same side is called a *cis*-isomer; the one in which the two methyl groups are on opposite sides is called a *trans*-isomer (Figure 20.2.9). The different geometries produce different physical properties, such as boiling point, that may make separation of the isomers possible:

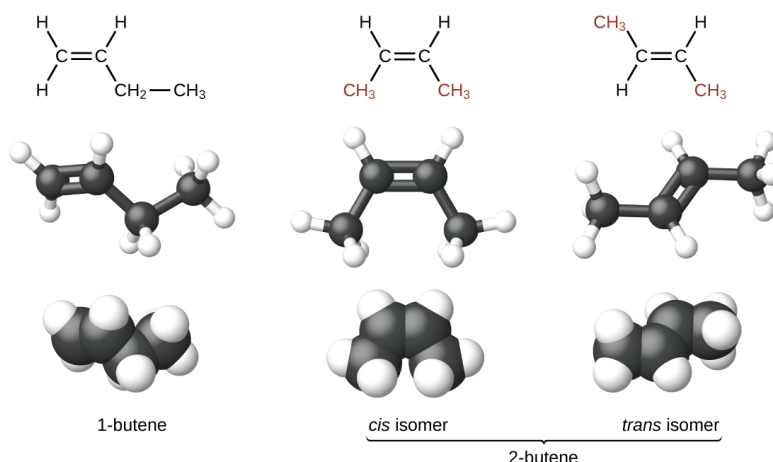
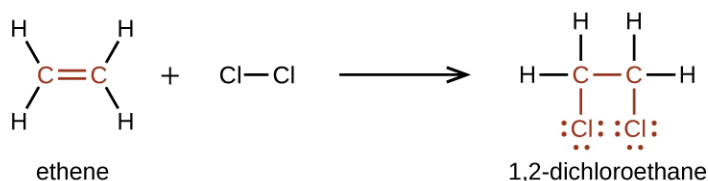


Figure 20.2.9: These molecular models show the structural and geometric isomers of butene.

The figure illustrates three ways to represent isomers of butene. In the first row of the figure, Lewis structural formulas show carbon and hydrogen element symbols and bonds between the atoms. The first structure in this row shows a C atom with a double bond to another C atom which is bonded down and to the right to C H subscript 2 which, in turn, is bonded to C H subscript 3. The first C atom, moving from left to right, has two H atoms bonded to it and the second C atom has one H atom bonded to it. The second structure in the row shows a C atom with a double bond to another C atom. The first C atom is bonded to an H atom up and to the left and C H subscript 3 down and to the left. The second C atom is bonded to an H atom up and to the right and C H subscript 3 down and to the right. Both C H subscript 3 structures appear in red. The third structure shows a C atom with a double bond to another C atom. The first C atom from the left is bonded up to a left to C H subscript 3 which appears in red. It is also bonded down and to the left to an H atom. The second C atom is bonded up and to the right to an H atom and down and to the left to C H subscript 3 which appears in red. In the second row, ball-and-stick models for the structures are shown. In these representations, single bonds are represented with sticks, double bonds are represented with two parallel sticks, and elements are represented with balls. C atoms are black and H atoms are white in this image. In the third row, space-filling models are shown. In these models, atoms are enlarged and pushed together, without sticks to represent bonds. In the final row, names are provided. The molecule with the double bond between the first and second carbons is named 1 dash butene. The two molecules with the double bond between the second and third carbon atoms is called 2 dash butene. The first model, which has both C H subscript 3 groups beneath the double bond is called the cis isomer. The second which has the C H subscript 3 groups on opposite sides of the double bond is named the trans isomer.

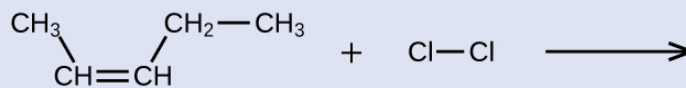
Alkenes are much more reactive than alkanes because the  $C = C$  moiety is a reactive functional group. A  $\pi$  bond, being a weaker bond, is disrupted much more easily than a  $\sigma$  bond. Thus, alkenes undergo a characteristic reaction in which the  $\pi$  bond is broken and replaced by two  $\sigma$  bonds. This reaction is called an addition reaction. The hybridization of the carbon atoms in the double bond in an alkene changes from  $sp^2$  to  $sp^3$  during an addition reaction. For example, halogens add to the double bond in an alkene instead of replacing hydrogen, as occurs in an alkane:



This diagram illustrates the reaction of ethene and C l subscript 2 to form 1 comma 2 dash dichloroethane. In this reaction, the structural formula of ethane is shown. It has a double bond between the two C atoms with two H atoms bonded to each C atom plus C l bonded to C l. This is shown on to the left of an arrow. The two C atoms and the double bond between them are shown in red. To the right of the arrow, the 1 comma 2 dash dichloroethane molecule is shown. It has only single bonds and each C atom has a C l with three pairs of electron dots bonded beneath it. The C and C l atoms, single bond between them, and electron pairs are shown in red. Each C atom also has two H atoms bonded to it.

#### ✓ Example 20.2.5: Alkene Reactivity and Naming

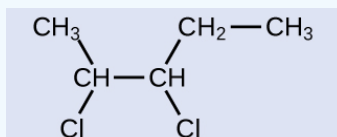
Provide the IUPAC names for the reactant and product of the halogenation reaction shown here:



The left side of a reaction and arrow are shown with an empty product side. On the left, C H subscript 3 is bonded down and to the right to C H which has a double bond to another C H. The second C H is bonded up and to the right to C H subscript 2 which is also bonded to C H subscript 3. A plus sign is shown with a C l atom bonded to a C l atom following it. This is also followed by a reaction arrow.

### Solution

The reactant is a five-carbon chain that contains a carbon-carbon double bond, so the base name will be pentene. We begin counting at the end of the chain closest to the double bond—in this case, from the left—the double bond spans carbons 2 and 3, so the name becomes 2-pentene. Since there are two carbon-containing groups attached to the two carbon atoms in the double bond—and they are on the same side of the double bond—this molecule is the *cis*-isomer, making the name of the starting alkene *cis*-2-pentene. The product of the halogenation reaction will have two chlorine atoms attached to the carbon atoms that were a part of the carbon-carbon double bond:

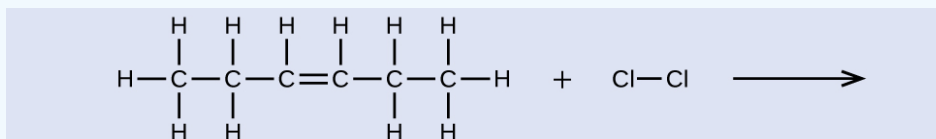


C H subscript 3 is bonded down and to the right to C H which is bonded down and to the left to C l. C H is also bonded to another C H which is bonded down and to the right to C l and up and to the right to C H subscript 2. C H subscript 2 is also bonded to C H subscript 3.

This molecule is now a substituted alkane and will be named as such. The base of the name will be pentane. We will count from the end that numbers the carbon atoms where the chlorine atoms are attached as 2 and 3, making the name of the product 2,3-dichloropentane.

### ? Exercise 20.2.5

Provide names for the reactant and product of the reaction shown:



This shows a C atom bonded to three H atoms and another C atom. This second C atom is bonded to two H atoms and a third C atom. This third C atom is bonded to one H atom and also forms a double bond with a fourth C atom. This fourth C atom is bonded to one H atom and a fifth C atom. This fifth C atom is bonded to two H atoms and a sixth C atom. This sixth C atom is bonded to three H atoms. There is a plus sign followed by a C l atom bonded to another C l atom. There is a reaction arrow. no products are shown.

### Answer

reactant: *cis*-3-hexene, product: 3,4-dichlorohexane

## 20.2.6: Alkynes

Hydrocarbon molecules with one or more triple bonds are called alkynes; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one  $\sigma$  bond and two  $\pi$  bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of  $180^\circ$ , giving these types of bonds a linear, rod-like shape.

The simplest member of the alkyne series is ethyne,  $\text{C}_2\text{H}_2$ , commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:



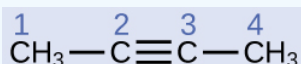
ethyne (acetylene)

The structural formula and name for ethyne, also known as acetylene, are shown. In red, two C atoms are shown with a triple bond illustrated by three horizontal line segments between them. Shown in black at each end of the structure, a single H atom is bonded.

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example,  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$  is called 1-butyne.

#### ✓ Example 20.2.6: Structure of Alkynes

Describe the geometry and hybridization of the carbon atoms in the following molecule:



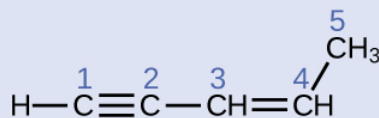
A structural formula is shown with C H subscript 3 bonded to a C atom which is triple bonded to another C atom which is bonded to C H subscript 3. Each C atom is labeled 1, 2, 3, and 4 from left to right.

#### Solution

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with  $sp^3$  hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as  $sp$  hybrids.

#### ? Exercise 20.2.6

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:



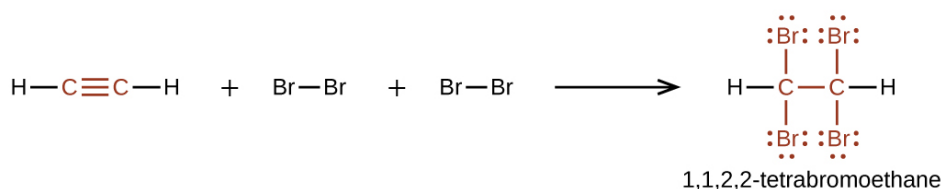
A structural formula is shown with an H atom bonded to a C atom. The C atom has a triple bond with another C atom which is also bonded to C H. The C H has a double bond with another C H which is also bonded up and to the right to C H subscript 3. Each C atom is labeled 1, 2, 3, 4, or 5 from left to right.

#### Answer

carbon 1:  $sp$ ,  $180^\circ$ ; carbon 2:  $sp$ ,  $180^\circ$ ; carbon 3:  $sp^2$ ,  $120^\circ$ ; carbon 4:  $sp^2$ ,  $120^\circ$ ; carbon 5:  $sp^3$ ,  $109.5^\circ$

Chemically, the alkynes are similar to the alkenes. Since the  $\text{C}\equiv\text{C}$  functional group has two  $\pi$  bonds, alkynes typically react even more readily, and react with twice as much reagent in addition reactions. The reaction of acetylene with bromine is a typical example:





This diagram illustrates the reaction of ethyne and two molecules of Br<sub>2</sub> to form 1,1,2,2-tetrabromoethane. In this reaction, the structural formula of ethyne, an H atom bonded to a red C atom with a red triple bond to another red C atom bonded to a black H atom, plus Br bonded to Br plus Br bonded to Br is shown to the left of an arrow. On the right, the 1,1,2,2-tetrabromoethane molecule is shown. It has an H atom bonded to a C atom which is bonded to another C atom which is bonded to an H atom. Each C atom is bonded above and below to a Br atom. Each Br atom has three pairs of electron dots. The C and Br atoms, single bond between them, and electron pairs are shown in red.

Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

### 20.2.7: Aromatic Hydrocarbons

Benzene, C<sub>6</sub>H<sub>6</sub>, is the simplest member of a large family of hydrocarbons, called aromatic hydrocarbons. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C<sub>6</sub>H<sub>6</sub>, are:

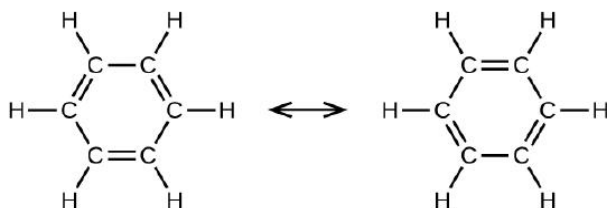


Figure 20.2.10.

This structural formula shows a six carbon hydrocarbon ring. On the left side there are six C atoms. The C atom on top and to the left forms a single bond to the C atom on the top and to the right. The C atom has a double bond to another C atom which has a single bond to a C atom. That C atom has a double bond to another C atom which has a single bond to a C atom. That C atom forms a double bond with another C atom. Each C atom has a single bond to an H atom. There is a double sided arrow and the structure on the right is almost identical to the structure on the left. The structure on the right shows double bonds where the structure on the left showed single bonds. The structure on the right shows single bonds where the structure on the left showed double bonds.

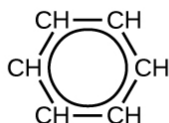
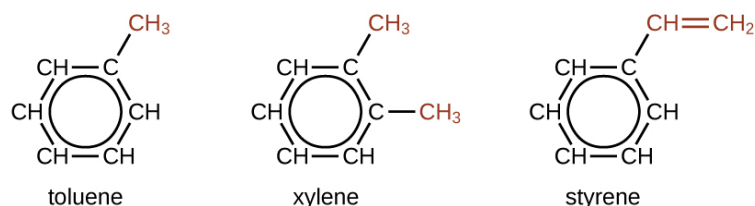


Figure 20.2.10: This condensed formula shows the unique bonding structure of benzene.

A six carbon hydrocarbon ring structural formula is shown. Each C atom is bonded to only one H atom. A circle is at the center of the ring.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:



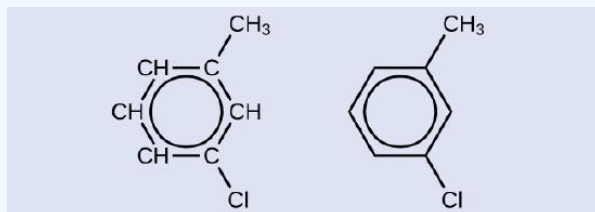


Three structural formulas are shown. The first is labeled toluene. This molecule has a six carbon hydrocarbon ring in which five of the C atoms are each bonded to only one H atom. At the upper right of the ring, the C atom that does not have a bonded H atom has a red C H subscript 3 group attached. A circle is at the center of the ring. The second is labeled xylene. This molecule has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and right of the ring, the two C atoms that do not have bonded H atoms have C H subscript 3 groups attached. These C H subscript 3 groups appear in red. A circle is at the center of the ring. The third is labeled styrene. This molecule has a six carbon hydrocarbon ring in which five of the carbon atoms are each bonded to only one H atom. At the upper right of the ring, the carbon that does not have a bonded H atom has a red C H double bond C H subscript 2 group attached. A circle is at the center of the ring.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

### ✓ Example 20.2.7: Structure of Aromatic Hydrocarbons

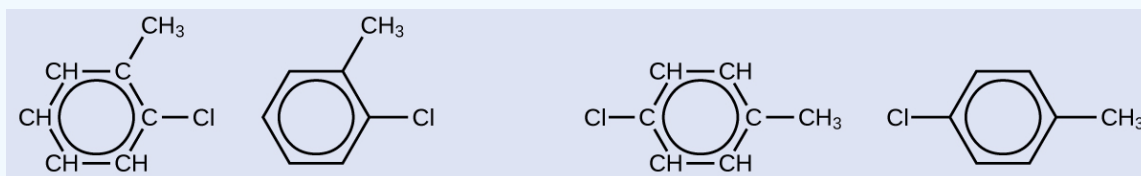
One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



Two structural formulas are shown. The first has a six carbon hydrocarbon ring in which four of the carbon atoms are each bonded to only one H atom. At the upper right of the ring, the carbon that does not have a bonded H atom has a C H subscript 3 group attached. The C to the lower right has a C l atom attached. A circle is at the center of the ring. The second molecule has a hexagon with a circle inside. From a vertex of the hexagon at the upper right a C H subscript 3 group is attached. From the vertex at the lower right, a C l atom is attached.

### Solution

Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:

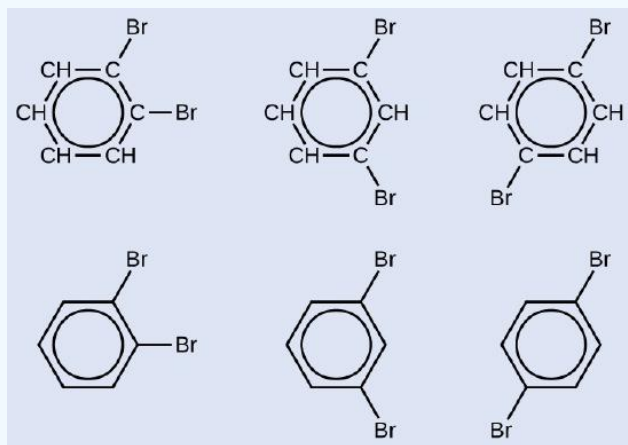


Two pairs of structural formulas are shown. The first has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right of the ring, the C atom that does not have a bonded H atom has a C H subscript 3 group attached. The C atom to the right has a C l atom attached. A circle is at the center of the ring. The second molecule in the first pair has a hexagon with a circle inside. From a vertex of the hexagon at the upper right a C H subscript 3 group is attached. From the vertex at the right, a C l atom is attached. The second pair first shows a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. A C l atom is attached to the left-most C atom and a C H subscript 3 group is attached to the right-most C atom. A circle is at the center of the ring. The second molecule in the pair has a hexagon with a circle inside. A C H subscript 3 group is attached to a vertex on the right side of the hexagon and to a vertex on the left side, a C l atom is bonded.

## ? Exercise 20.2.7

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

**Answer**



Three pairs of structural formulas are shown. The first has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and right of the ring, the two C atoms that do not have bonded H atoms have one Br atom bonded each. A circle is at the center of the ring. Beneath this structure, a similar structure is shown which has a hexagon with a circle inside. From vertices of the hexagon at the upper right and right single Br atoms are attached. The second has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and lower right of the ring, the two C atoms that do not have bonded H atoms have a single Br atom bonded each. A circle is at the center of the ring. Beneath this structure, a similar structure is shown which has a hexagon with a circle inside. From vertices of the hexagon at the upper right and lower right single Br atoms are attached. The third has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and lower left of the ring, the two C atoms that do not have bonded H atoms have Br atoms bonded. A circle is at the center of the ring. Beneath this structure, a similar structure is shown which has a hexagon with a circle inside. From vertices of the hexagon at the upper right and lower left, single Br atoms are attached.

## Summary

Strong, stable bonds between carbon atoms produce complex molecules containing chains, branches, and rings. The chemistry of these compounds is called organic chemistry. Hydrocarbons are organic compounds composed of only carbon and hydrogen. The alkanes are saturated hydrocarbons—that is, hydrocarbons that contain only single bonds. Alkenes contain one or more carbon-carbon double bonds. Alkynes contain one or more carbon-carbon triple bonds. Aromatic hydrocarbons contain ring structures with delocalized  $\pi$  electron systems.

## Footnotes

1. This is the Beilstein database, now available through the Reaxys site ([www.elsevier.com/online-tools/reaxys](http://www.elsevier.com/online-tools/reaxys)).
2. Peplow, Mark. "Organic Synthesis: The Robo-Chemist," *Nature* 512 (2014): 20–2.
3. Physical properties for  $C_4H_{10}$  and heavier molecules are those of the *normal isomer*, *n*-butane, *n*-pentane, etc.
4. STP indicates a temperature of 0 °C and a pressure of 1 atm.

## Glossary

### addition reaction

reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.

### alkane

molecule consisting of only carbon and hydrogen atoms connected by single ( $\sigma$ ) bonds

**alkene**

molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

**alkyl group**

substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

**alkyne**

molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

**aromatic hydrocarbon**

cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

**functional group**

part of an organic molecule that imparts a specific chemical reactivity to the molecule

**organic compound**

natural or synthetic compound that contains carbon

**saturated hydrocarbon**

molecule containing carbon and hydrogen that has only single bonds between carbon atoms

**skeletal structure**

shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

**substituent**

branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

**substitution reaction**

reaction in which one atom replaces another in a molecule

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