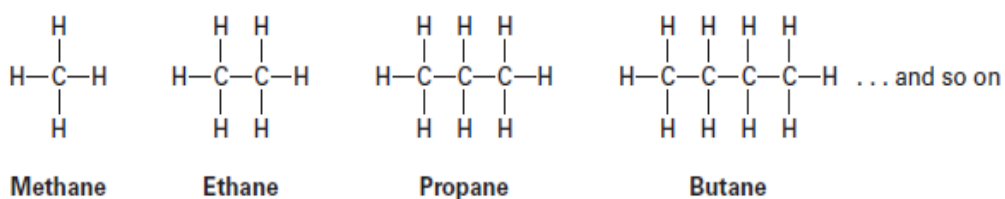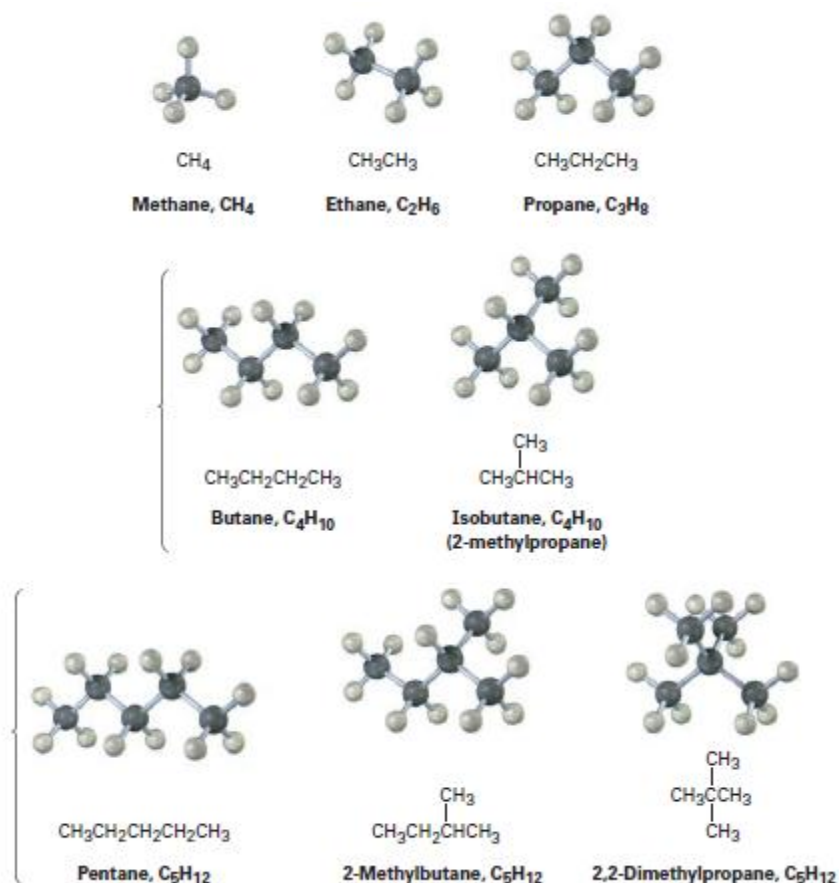# Alkanes

Alkanes are simplest family of molecules that contain the carbon– carbon single bond results from σ (head-on) overlap of carbon sp^3 hybrid orbitals.

Alkanes are often described as *saturated hydrocarbons:* **hydrocarbons** because they contain only carbon and hydrogen; **saturated** because they have only C-C and C-H single bonds and thus contain the maximum possible number of hydrogens per carbon. They have the general formula C_nH_{2n+2}, where n is an integer. Alkanes are also occasionally called **aliphatic** compounds.

Methane   Ethane   Propane   Butane

Think about the ways that carbon and hydrogen might combine to make alkanes. With one carbon and four hydrogens, only one structure is possible: methane, CH_4. Similarly, there is only one combination of two carbons with six hydrogens (ethane, CH_3CH_3) and only one combination of three carbons with eight hydrogens (propane, $CH_3CH_2CH_3$). When larger numbers of carbons and hydrogens combine, however, more than one structure is possible.

For example, there are *two* substances with the formula C_4H_{10}: the four carbons can all be in a row (butane), or they can branch (isobutane). Similarly, there are three C_5H_{12} molecules, and so on for larger alkanes.

CH$_4$

Methane, CH$_4$

CH$_3$CH$_3$

Ethane, C$_2$H$_6$

CH$_3$CH$_2$CH$_3$

Propane, C$_3$H$_8$

CH$_3$CH$_2$CH$_2$CH$_3$

Butane, C$_4$H$_{10}$

CH$_3$CHCH$_3$ with CH$_3$ branch

Isobutane, C$_4$H$_{10}$
(2-methylpropane)

CH$_3$CH$_2$CH$_2$CH$_2$CH$_3$

Pentane, C$_5$H$_{12}$

CH$_3$CH$_2$CHCH$_3$ with CH$_3$ branch

2-Methylbutane, C$_5$H$_{12}$

CH$_3$CCH$_3$ with two CH$_3$ branches

2,2-Dimethylpropane, C$_5$H$_{12}$

Compounds like butane and pentane, whose carbons are all connected in a row, are called **straight-chain alkanes**, or *normal alkanes*. Compounds like 2-methylpropane (isobutane), 2-methylbutane, and 2,2-dimethylpropane, whose carbon chains branch, are called **branched-chain alkanes**.

Compounds like the two C$_4$H$_{10}$ molecules and the three C$_5$H$_{12}$ molecules, which have the same formula but different structures, are called *isomers,* from the Greek *isos + meros,* meaning "made of the same parts." **Isomers** are compounds that have the same numbers and kinds of atoms but differ in the way the atoms are arranged. Compounds like butane and isobutane, whose atoms are connected differently, are called **constitutional isomers**.
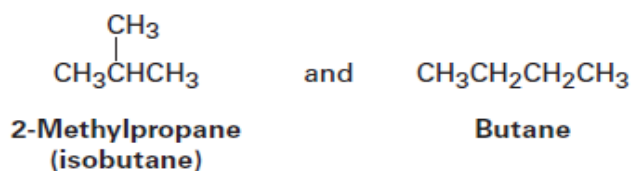
We'll see shortly that other kinds of isomers are also possible, even among compounds whose atoms are connected in the same order. As Table 3-2 shows, the number of possible alkane isomers increases dramatically with the number of carbon atom
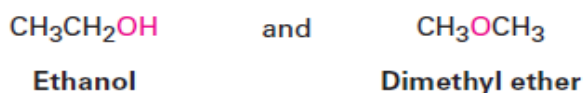
TABLE 3-2 Number of Alkane Isomers

Formula	Number of isomers
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4347
$C_{20}H_{42}$	366,319
$C_{30}H_{62}$	4,111,846,763

Constitutional isomerism is not limited to alkanes it occurs widely throughout organic chemistry. Constitutional isomers may have different carbon skeletons (as in isobutane and butane), different functional groups (as in ethanol and dimethyl ether), or different locations of a functional group along the chain (as in isopropylamine and propylamine). Regardless of the reason for the isomerism, constitutional isomers are always different compounds with different properties but with the same formula.
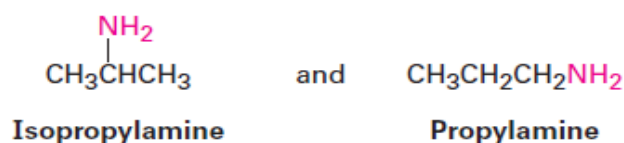
Different carbon skeletons C_4H_{10}

$$CH_3CHCH_3 \quad (CH_3) \quad \text{and} \quad CH_3CH_2CH_2CH_3$$

2-Methylpropane (isobutane)   Butane

Different functional groups C_2H_6O

$$CH_3CH_2OH \quad \text{and} \quad CH_3OCH_3$$

Ethanol   Dimethyl ether

Different position of functional groups C_3H_9N

$$CH_3CHCH_3 \quad (NH_2) \quad \text{and} \quad CH_3CH_2CH_2NH_2$$

Isopropylamine   Propylamine

A given alkane can be drawn in many ways. For example, the straight chain, four-carbon alkane called butane can be represented by any of the structures shown in **Figure 3-2**. These structures don't imply any particular three-dimensional geometry for butane; they indicate only the connections among atoms. In practice, chemists rarely draw all the bonds in a molecule and usually refer to butane by the condensed structure, $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$. Still more simply, butane can be represented as $n\text{-}C_4H_{10}$, where n denotes *normal* (straight-chain) butane.

$$CH_3—CH_2—CH_2—CH_3 \qquad CH_3CH_2CH_2CH_3 \qquad CH_3(CH_2)_2CH_3$$
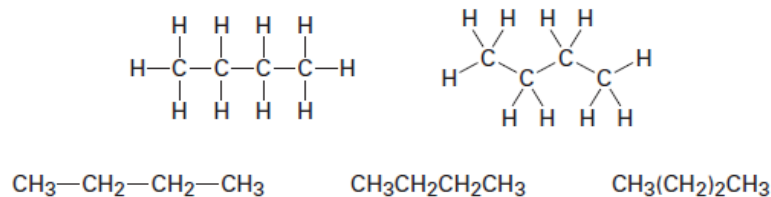
Figure 3-2 some representations of butane, C_4H_{10}. The molecule is the same regardless of how it's drawn. These structures imply only that butane has a continuous chain of four carbon atoms; they do not imply any specific geometry.

Straight-chain alkanes are named according to the number of carbon atoms they contain, as shown in **Table 3-3**. With the exception of the first four compounds (methane, ethane, propane, and butane) whose names have historical roots, the alkanes are named based on Greek numbers. The suffix *-ane* is added to the end of each name to indicate that the molecule identified is an alkane. Thus, pent*ane* is the five-carbon alkane; hex*ane* is the six carbon alkane, and so on. We'll soon see that these alkane names form the basis for naming all other organic compounds, so at least the first ten should be memorized.

TABLE 3-3 Names of Straight-Chain Alkanes

Number of carbons (n)	Name	Formula (C_nH_{2n+2})	Number of carbons (n)	Name	Formula (C_nH_{2n+2})
1	Methane	CH_4	9	Nonane	C_9H_{20}
2	Ethane	C_2H_6	10	Decane	$C_{10}H_{22}$
3	Propane	C_3H_8	11	Undecane	$C_{11}H_{24}$
4	Butane	C_4H_{10}	12	Dodecane	$C_{12}H_{26}$
5	Pentane	C_5H_{12}	13	Tridecane	$C_{13}H_{28}$
6	Hexane	C_6H_{14}	20	Icosane	$C_{20}H_{42}$
7	Heptane	C_7H_{16}	30	Triacontane	$C_{30}H_{62}$
8	Octane	C_8H_{18}			

Alkyl Groups

If you imagine removing a hydrogen atom from an alkane, the partial structure that remains is called an **alkyl group**. Alkyl groups are not stable compounds themselves; they are simply parts of larger compounds. Alkyl groups are named by replacing the -*ane* ending of the parent alkane with an -*yl* ending.

For example, removal of hydrogen from methane, CH_4, generates a *methyl* group, -CH_3, and removal of hydrogen from ethane, CH_3CH_3, generates an *ethyl* group, -CH_2CH_3. Similarly, removal of a hydrogen atom from the end carbon of any straight-chain alkane gives the series of straight-chain alkyl groups shown in **Table 3-4**.

Combining an alkyl group with any of the functional groups listed earlier makes it possible to generate and name many thousands of compounds. For example:
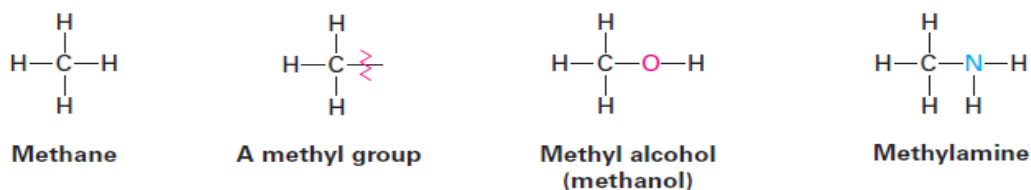

Methane   A methyl group   Methyl alcohol   Methylamine
                                          (methanol)

TABLE 3-4 Some Straight-Chain Alkyl Groups

Alkane	Name	Alkyl group	Name (abbreviation)
CH_4	Methane	$-CH_3$	Methyl (Me)
CH_3CH_3	Ethane	$-CH_2CH_3$	Ethyl (Et)
$CH_3CH_2CH_3$	Propane	$-CH_2CH_2CH_3$	Propyl (Pr)
$CH_3CH_2CH_2CH_3$	Butane	$-CH_2CH_2CH_2CH_3$	Butyl (Bu)
$CH_3CH_2CH_2CH_2CH_3$	Pentane	$-CH_2CH_2CH_2CH_2CH_3$	Pentyl, or amyl

Just as straight-chain alkyl groups are generated by removing hydrogen from an end carbon, branched alkyl groups are generated by removing a hydrogen atom from an internal carbon. Two 3-carbon alkyl groups and four 4-carbon alkyl groups are possible **(Figure 3-3)**.
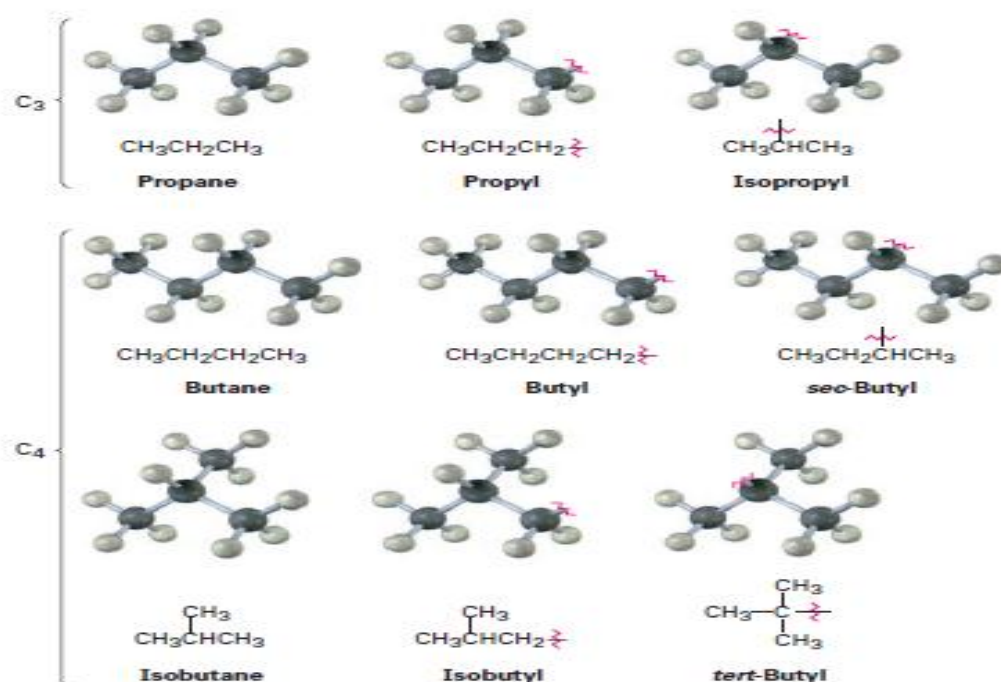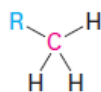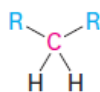

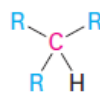**Figure 3-3 Alkyl groups generated from straight-chain alkanes.**

One further comment about naming alkyl groups: the prefixes *sec-* (for secondary) and *tert-* (for tertiary) used for the C4 alkyl groups in Figure 3-3 refer to *the number of other carbon atoms attached to the branching carbon atom.* There are four possibilities: primary (1°), secondary (2°), tertiary (3°), and quaternary (4°).
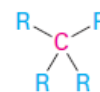
Primary carbon (1°) is bonded to one other carbon.   Secondary carbon (2°) is bonded to two other carbons.   Tertiary carbon (3°) is bonded to three other carbons.   Quaternary carbon (4°) is bonded to four other carbons.
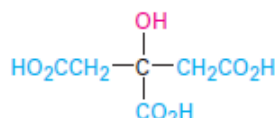
The symbol **R** is used here and throughout organic chemistry to represent a *generalized* organic group. The R group can be methyl, ethyl, propyl, or any of a multitude of others. You might think of **R** as representing the **R**est of the molecule, which isn't specified.

The terms *primary, secondary, tertiary,* and *quaternary* are routinely used in organic chemistry, and their meanings need to become second nature. For example, if we were to say, "Citric acid is a tertiary alcohol," we would mean that it has an alcohol functional group (-OH) bonded to a carbon atom that is itself bonded to three other carbons.
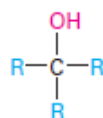

General class of tertiary alcohols, R_3COH Citric acid—a specific tertiary alcohol

In addition, we also speak of hydrogen atoms as being primary, secondary, or tertiary. Primary hydrogen atoms are attached to primary carbons (RCH_3), secondary hydrogens are attached to secondary carbons (R_2CH_2), and tertiary hydrogens are attached to tertiary carbons (R_3CH). There is, of course, no such thing as quaternary hydrogen.

Primary hydrogens (CH_3)
Secondary hydrogens (CH_2)
A tertiary hydrogen (CH)
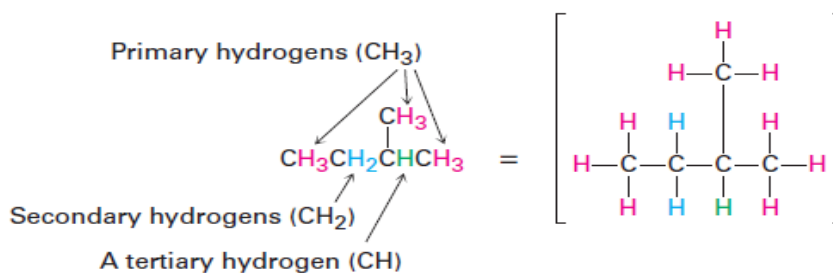
Naming Alkanes

A chemical name typically has four parts in the *IUPAC system of nomenclature*: prefix, parent, locant, and suffix. The prefix identifies the various **substituent** groups in the molecule, the parent selects a main part of the molecule and tells how many carbon atoms are in that part, the locants give the positions of the functional groups and substituents, and the suffix identifies
the primary functional group.

6

Locant — Prefix — Parent — Suffix

Where are the substituents and functional groups? — What are the substituents? — How many carbons? — What is the primary functional group?
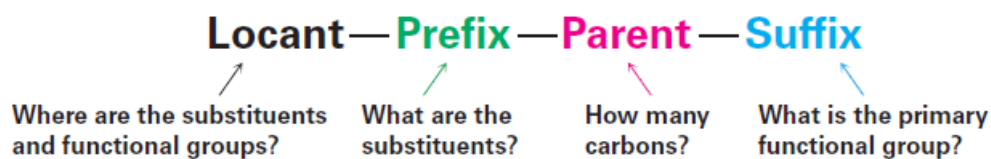
Step 1

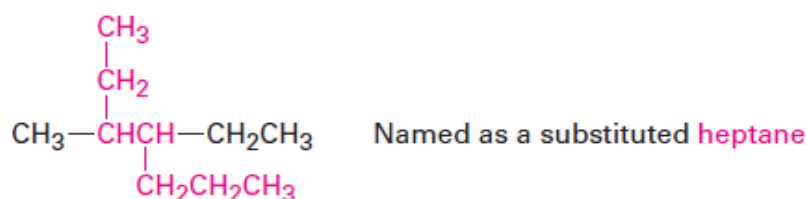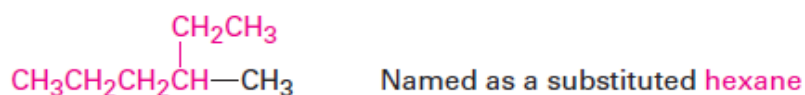**Find the parent hydrocarbon.**

(a) Find the longest continuous chain of carbon atoms in the molecule, and use the name of that chain as the parent name. The longest chain may not always be apparent from the manner of writing; you may have to "turn corners."

$$CH_2CH_3$$
$$CH_3CH_2CH_2\overset{|}{C}H\!-\!CH_3 \qquad \text{Named as a substituted hexane}$$

$$CH_3$$
$$\overset{|}{C}H_2$$
$$CH_3\!-\!\overset{|}{C}HCH\!-\!CH_2CH_3 \qquad \text{Named as a substituted heptane}$$
$$\overset{|}{C}H_2CH_2CH_3$$

(b) If two different chains of equal length are present, choose the one with the larger number of branch points as the parent.

$$CH_3$$
$$CH_3\overset{|}{C}HCHCH_2CH_2CH_3$$
$$\overset{|}{C}H_2CH_3$$

Named as a hexane with *two* substituents

NOT

$$CH_3$$
$$CH_3\overset{|}{C}H\!-\!CHCH_2CH_2CH_3$$
$$\overset{|}{C}H_2CH_3$$

as a hexane with *one* substituent

Step 2

Number the atoms in the longest chain.

(a) Beginning at the end nearer the first branch point, number each carbon atom in the parent chain.

$$\overset{2\;\;\;1}{CH_2CH_3}$$
$$CH_3\!-\!\overset{3}{C}H\overset{}{C}H\!-\!\overset{}{C}H_2CH_3$$
$$\overset{5\;\;6\;\;7}{CH_2CH_2CH_3}$$

NOT

$$\overset{6\;\;\;7}{CH_2CH_3}$$
$$CH_3\!-\!\overset{5}{C}H\overset{4}{C}H\!-\!CH_2CH_3$$
$$\overset{3\;\;2\;\;1}{CH_2CH_2CH_3}$$

The first branch occurs at C3 in the proper system of numbering, not at C4.

(b) If there is branching an equal distance away from both ends of the parent chain, begin numbering at the end nearer the second branch point.
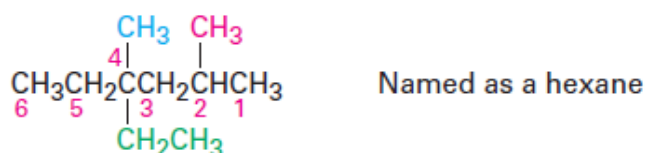
Step 3

Identify and number the substituents.

(a) Assign a number, or *locant,* to each substituent to locate its point of attachment to the parent chain.
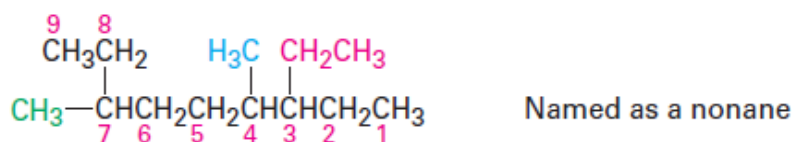
(b) If there are two substituents on the same carbon, give both the same number. There must be as many numbers in the name as there are substituents.

Step 4

Write the name as a single word.

Use hyphens to separate the different prefixes, and use commas to separate numbers. If two or more different substituents are present, cite them in alphabetical order. If two or more identical substituents are present on the parent chain, use one of the multiplier prefixes *di-*, *tri-*, *tetra-*, and so forth, but don't use these prefixes for alphabetizing. Full names for some of the examples we have been using are as follows:

$$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH}-\underset{1}{CH_3}$$ with $\underset{2}{CH_2}\underset{1}{CH_3}$ branch

3-Methylhexane

$$CH_3-\underset{7}{CH}\underset{6}{CH_2}\underset{5}{CH_2}\underset{4}{CH}-\underset{3}{CH}\underset{2}{CH_2}\underset{1}{CH_3}$$
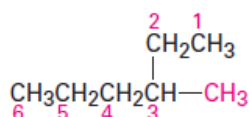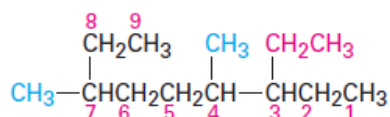
3-Ethyl-4,7-dimethylnonane

$$\underset{1}{CH_3}\underset{2}{CH}\underset{3}{CH}\underset{4}{CH_2}\underset{5}{CH_2}\underset{6}{CH_3}$$

3-Ethyl-2-methylhexane

$$CH_3\underset{3}{CH}\underset{4}{CH}CH_2CH_3$$

4-Ethyl-3-methylheptane

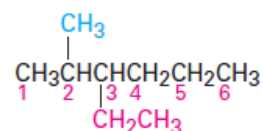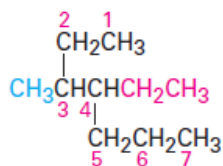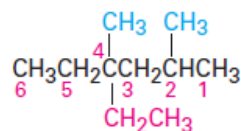$$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{C}\underset{3}{CH_2}\underset{2}{CH}\underset{1}{CH_3}$$

4-Ethyl-2,4-dimethylhexane

Step 5

Name a branched substituent as though it were itself a compound.

In some particularly complex cases, a fifth step is necessary. It occasionally happens that a substituent on the main chain is itself branched. In the following case, for instance, the substituent at C6 is a three-carbon chain with a methyl group. To name the compound fully, the branched substituent must first be named.

$$\underset{1}{CH_3}\underset{2}{CH}\underset{3}{CH}\underset{4}{CH_2}\underset{5}{CH_2}\underset{6}{CH}-CH_2CHCH_3$$
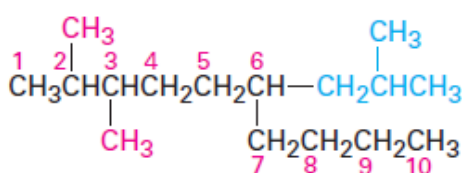
Named as a 2,3,6-trisubstituted decane

$$\left[-CH_2\underset{2}{CH}CH_3\right]$$
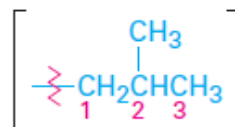
A 2-methylpropyl substituent

Number the branched substituent beginning at the point of its attachment to the main chain, and identify it—in this case, a 2-methylpropyl group.

The substituent is treated as a whole and is alphabetized according to the first letter of its complete name, including any numerical prefix. It is set off in parentheses when naming the entire molecule.

$$\underset{1}{CH_3}\underset{2}{CH}\underset{3}{CH}\underset{4}{CH_2}\underset{5}{CH_2}\underset{6}{CH}-CH_2CHCH_3$$
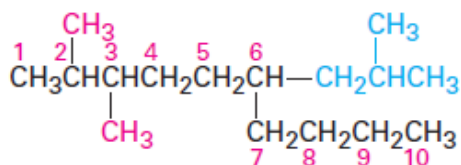
2,3-Dimethyl-6-(2-methylpropyl)decane

9

As a further example:
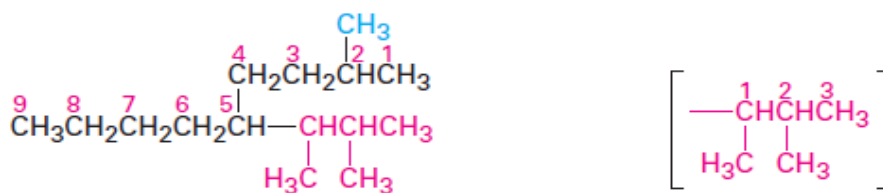
5-(1,2-Dimethylpropyl)-2-methylnonane   A 1,2-dimethylpropyl group

For historical reasons, some of the simpler branched-chain alkyl groups also have nonsystematic, common names, as noted earlier.

Isopropyl (*i*-Pr)

3-Carbon
alkyl group

sec-Butyl
(sec-Bu)   Isobutyl   tert-Butyl
(*t*-butyl or *t*-Bu)

4-Carbon
alkyl groups

Isopentyl, also called
isoamyl (*i*-amyl)   Neopentyl   tert-Pentyl, also called
tert-amyl (*t*-amyl)

5-Carbon alkyl groups

The common names of these simple alkyl groups are so well entrenched in the chemical literature that IUPAC rules make allowance for them. Thus, the following compound is properly named either 4-(1-methylethyl) heptane or 4-isopropylheptane. There's no choice but to memorize these common names; fortunately, there are only a few of them.
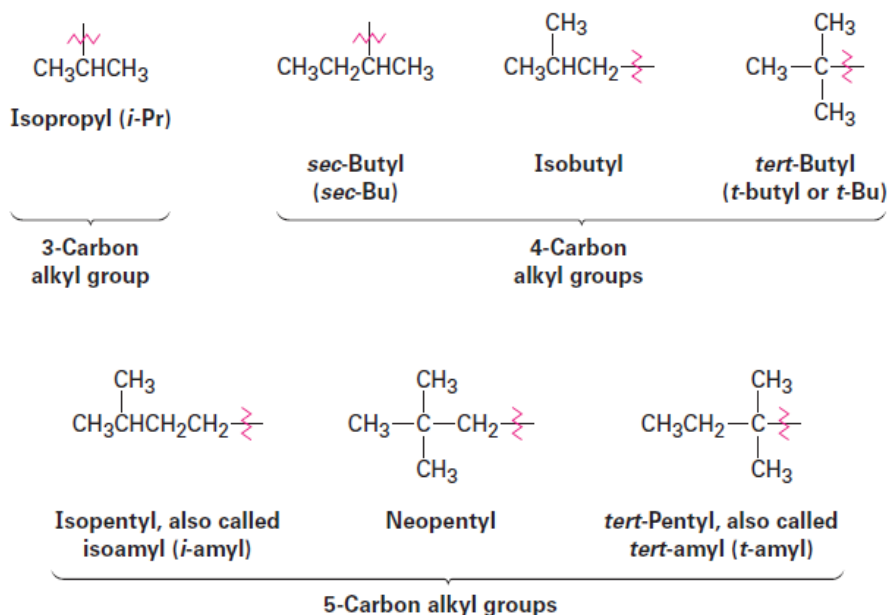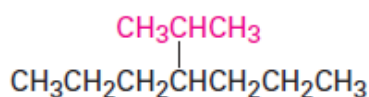

4-(1-Methylethyl)heptane   or   4-Isopropylheptane

When writing an alkane name, the non-hyphenated prefix iso- is considered part of the alkyl-group name for alphabetizing purposes, but the hyphenated and italicized prefixes *sec-* and *tert-* are not. Thus, isopropyl and isobutyl are listed alphabetically under *i,* but *sec*-butyl and *tert*-butyl are listed under *b*

Physical Properties of Alkanes

Alkanes are sometimes referred to as *paraffins,* a word derived from the Latin *parum affinis,* meaning "little affinity." This term aptly describes their behavior, for alkanes

show little chemical affinity for other substances and are chemically inert to most laboratory reagents. They are also relatively inert biologically and are not often involved in the chemistry of living organisms.

Alkanes are used primarily as fuels, solvents, and lubricants. Natural gas, gasoline, kerosene, heating oil, lubricating oil, and paraffin "wax" are all composed primarily of alkanes, with different physical properties resulting from different ranges of molecular weights.

1. Solubilities and Densities of Alkanes

Alkanes are nonpolar, so they dissolve in nonpolar or weakly polar organic solvents. Alkanes are said to be **hydrophobic** ("water hating") because they do not dissolve in water. Alkanes are good lubricants and preservatives for metals because they keep water from reaching the metal surface and causing corrosion.

Alkanes have densities around 0.7 g/mL, compared with a density of 1.0 g/mL for water. Because alkanes are less dense than water and insoluble in water, a mixture of an alkane (such as gasoline or oil) and water quickly separates into two phases, with the alkane on top.

2. Boiling point and melting point

Alkanes show regular increases in boiling point and melting point as molecular weight increases **(Figure 3-4)**. Only when sufficient energy is applied to overcome these forces does the solid melt or liquid boil. As you might expect, dispersion forces increase as molecule size increases, accounting for the higher melting and boiling points of larger alkanes.
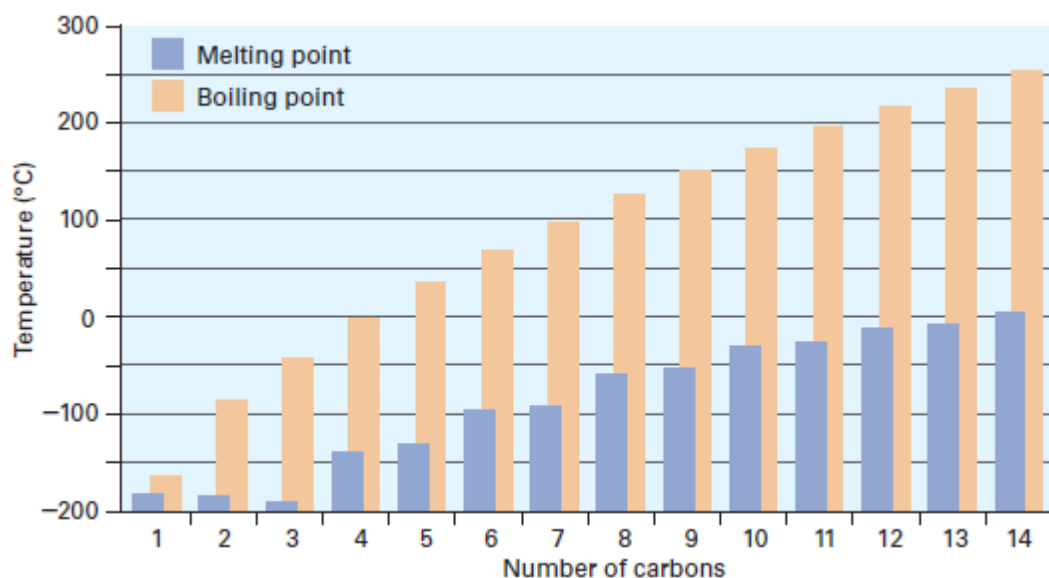
**Figure 3-4 A plot of melting and boiling points versus number of carbon atoms for the C1–C14 straight-chain alkanes. There is a regular increase with molecular size.**

Another effect seen in alkanes is that increased branching lowers an alkane's boiling point. Thus, pentane has no branches and boils at 36.1 °C, isopentane (2-methylbutane) has one branch and boils at 27.85 °C, and neopentane (2,2-

dimethylpropane) has two branches and boils at 9.5 °C. Similarly, octane boils at 125.7 °C, whereas isooctane (2,2,4-trimethylpentane) boils at 99.3 °C. Branched-chain alkanes are lower-boiling because they are more nearly spherical than straight-chain alkanes, have smaller surface areas, and consequently have smaller dispersion forces.
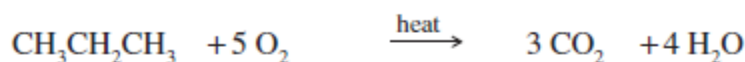
Reactions of Alkanes

Alkanes do, however, react with oxygen, halogens, and a few other substances under appropriate conditions. Reaction with oxygen occurs during combustion in an engine or furnace when an alkane is used as a fuel. Carbon dioxide and water are formed as products, and a large amount of heat is released. For example, methane (natural gas) reacts with oxygen according to the equation

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + \text{890 kJ/mol (213 kcal/mol)}$$
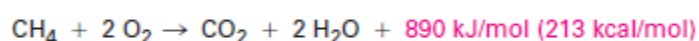
1. **Combustion** is a rapid oxidation that takes place at high temperatures, converting alkanes to carbon dioxide and water. Little control over the reaction is possible, except for moderating the temperature and controlling the fuel/air ratio to achieve efficient burning.

$$C_nH_{(2n+2)} + \text{excess } O_2 \xrightarrow{\text{heat}} n\,CO_2 + (n+1)\,H_2O$$

Example

$$CH_3CH_2CH_3 + 5\,O_2 \xrightarrow{\text{heat}} 3\,CO_2 + 4\,H_2O$$

2. **Cracking and Hydrocracking** catalytic **cracking** of large hydrocarbons at high temperatures produces smaller hydrocarbons. The cracking process usually operates under conditions that give the maximum yields of gasoline. In **hydrocracking,** hydrogen is added to give saturated hydrocarbons; cracking without hydrogen gives mixtures of alkanes and alkenes.

Catalytic hydrocracking

Catalytic cracking

3. **Halogenation** Alkanes can react with halogens (F_2, Cl_2, Br_2, I_2) to form alkyl halides. For example, methane reacts with chlorine to form chloromethane (methyl chloride), dichloromethane (methylene chloride), trichloromethane (chloroform), and tetrachloromethane (carbon tetrachloride).

The reaction of an alkane with Cl_2 occurs when a mixture of the two is irradiated with ultraviolet light (denoted *hy,* where *y* is the Greek letter *nu*). Depending on the time allowed and the relative amounts of the two reactants, a sequential substitution of the alkane hydrogen atoms by chlorine occurs, leading to a mixture of chlorinated products. Methane, for instance, reacts with Cl_2 to yield a mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4.

A radical is highly reactive because it contains an atom with an odd number of electrons (usually seven) in its valence shell, rather than a stable, noble gas octet. A radical can achieve a valence-shell octet in several ways. For example, the radical might abstract an atom and one bonding electron from another reactant, leaving behind a new radical. The net result is a radical substitution reaction.

An example of an industrially useful radical reaction is the chlorination of methane to yield chloromethane. This substitution reaction is the first step in the preparation of the solvents dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$).


Methane   Chlorine   Chloromethane
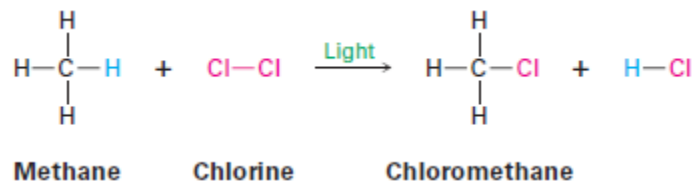
Like many radical reactions in the laboratory, methane chlorination requires three kinds of steps: *initiation, propagation,* and *termination.*

Initiation Irradiation with ultraviolet light begins the reaction by breaking the relatively weak Cl-Cl bond of a small number of Cl_2 molecules to give a few reactive chlorine radicals.
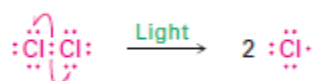
Propagation Once produced, a reactive chlorine radical collides with a methane molecule in a propagation step, abstracting a hydrogen atom to give HCl and a methyl radical ($\cdot CH_3$). This methyl radical reacts further with Cl_2 in a second propagation step to give the product chloromethane plus a new chlorine radical, which cycles back and repeats the first propagation step. Thus, once the sequence has been initiated, it becomes a self-sustaining cycle of repeating steps (a) and (b), making the overall process a *chain reaction.*
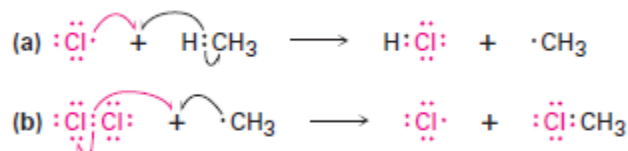
Termination Occasionally, two radicals might collide and combine to form a stable product. When that happens, the reaction cycle is broken and the chain is ended. Such termination steps occur infrequently, however, because the concentration of radicals in the reaction at any given moment is very small. Thus, the likelihood that two radicals will collide is also small.

Possible termination steps