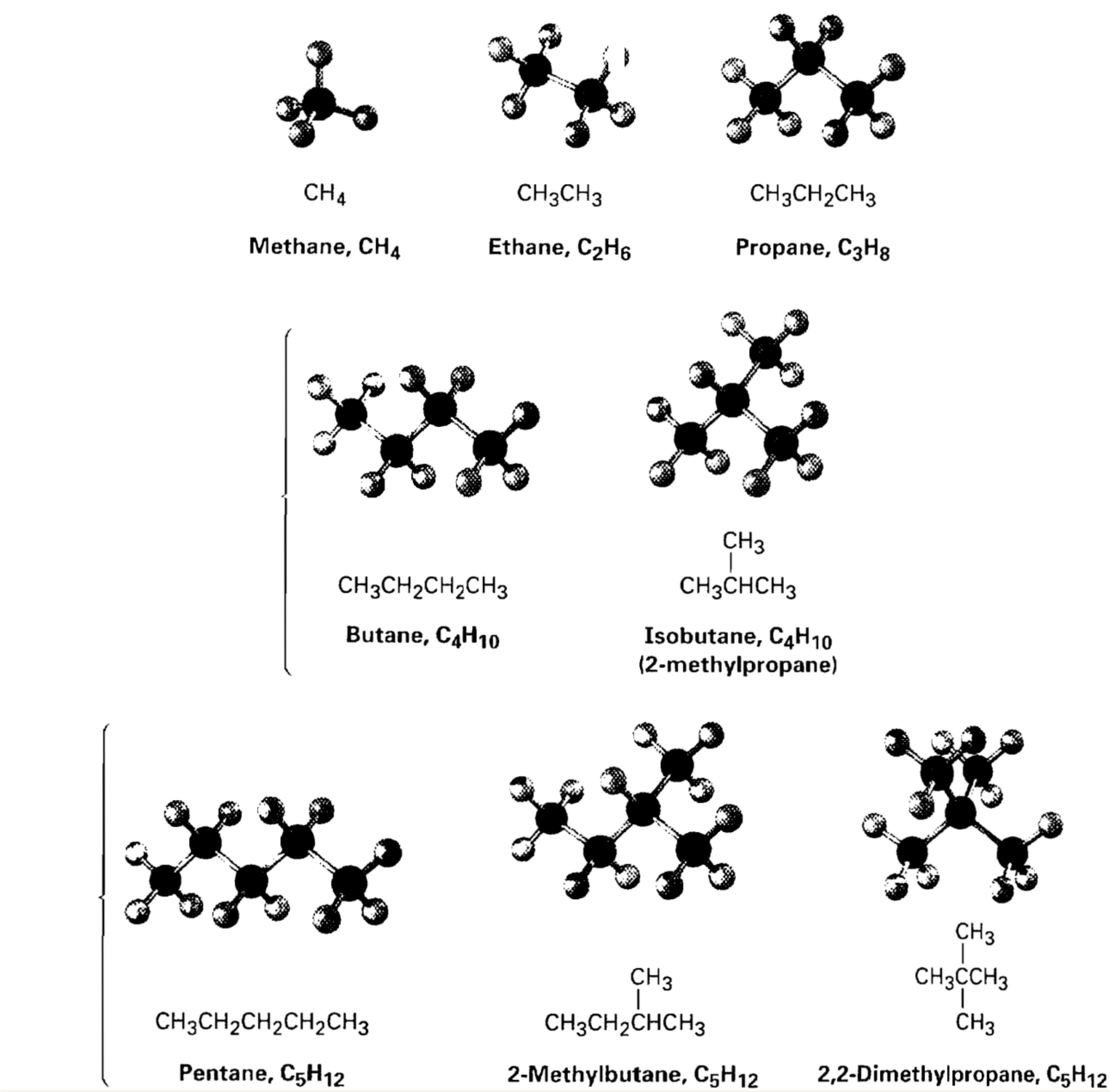
Alkanes: The Nature of Organic Compounds

Alkanes and Alkyl group: Isomers

Alkanes are often described as *saturated hydrocarbons:* **hydrocarbons** because they contain only carbon and hydrogen atoms; **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*n*H2*n*+2, where *n* is any integer. Alkanes are also occasionally called **aliphatic** compounds, a word derived from the Greek *aleiphas,* meaning "fat."

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 possible combination of two carbons with six hydrogens (ethane, CH3CH3) and only one possible combination of three carbons with eight hydrogens (propane, $CH_3CH_2CH_3$). If larger numbers of carbons and hydrogens combine, more than one kind of molecule can form. For example, there are two ways that molecules with the formula C_4H_{10} can form: the four carbons can be in a row (butane), or they can be branched (isobutane). Similarly, there are three ways in which C_5H_{12} molecules



Compounds like butane, whose carbons are connected in a row, are called **straight-chain alkanes, or normal (*n*) alkanes**, whereas compounds with branched carbon chains, such as isobutane (2-methylpropane), are called **branched chain alkanes**.

Compounds like the two C_4H_{10} molecules and the three C_5H_{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** 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**.

Straight-chain alkanes are named according to the number of carbon atoms they contain, With the exception of the first four compounds—methane, ethane, propane, and butane—whose names have historical origins, the alkanes are named based on Greek numbers, according to the number of carbons. The suffix -*ane* is added to the end of each name to identify the molecule as an alkane. Thus, pent*ane* is the five-carbon alkane, hex*ane* is the six-carbon alkane, and so on.

Names of straight chain alkane					
The number of carbon	Name	Formula (C_nH_{2n+2})	The number of carbon	Name	Formula (C_nH_{2n+2})
1	Methane	CH4	9	Nonane	C9H20
2	Ethan	C2H6	10	Decane	C10H22
3	Propane	C3H8	11	Undecane	C11H24
4	Butane	C4H10	12	Dodecane	C12H26
5	Pentane	C5H12	13	Tridecane	C13H28
6	Hexane	C6H14	20	Icosane	C20H42
7	heptane	C7H16	30	Triacontane	C30H62
8	Octane	C8H18			

If a hydrogen atom is removed from an alkane, the partial structure that remains is called an **alkyl group**. Alkyl groups are named by replacing the *-ane* ending with an *-yl* ending. For example, removal of a hydrogen atom from methane, CH4, generates a *methyl group*, _ CH3, and removal of a hydrogen atom from ethane, CH3CH3, generates an *ethyl group*, _ CH2CH3. Similarly, removal of a hydrogen atom from the end carbon of any *n*-alkane gives the series of *n*-alkyl groups shown below:

Some Straight-Chain Alkyl Groups

Alkane	Name	Alkyl group	Name	(abbreviation)
CH4	Methane	_CH3	Methyl	(Me)
CH3CH3	Ethane	_CH2CH3	Ethyl	(Et)
CH3CH2CH3	Propane	_CH2CH2CH3	Propyl	(Pr)
CH3CH2CH2CH3	Butane	_CH2CH2CH2CH3	Butyl	(Bu)
CH3CH2CH2CH2CH3	Pentane	_CH2CH2CH2CH2CH3	Pentyl, or amyl	

One further word about naming alkyl groups: the prefixes *sec*- (for secondary) and *tert*- (for tertiary),so 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.

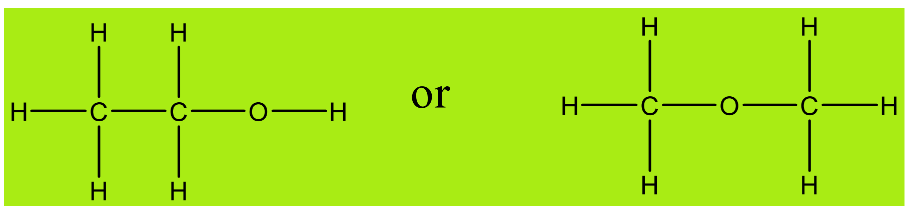
The R group can be methyl, ethyl, or any of a multitude of others. You might think of **R** as representing the **R**est of the molecule

Example Drawing Isomeric Structures

Propose structures for two isomers with the formula C_2H_6O.

Strategy We know that carbon forms four bonds, oxygen forms two, and hydrogen forms one. Put the pieces together.

Solution There are two possibilities:



Naming branched- chain alkane

The system of naming (*nomenclature*) that we'll use is devised by the International Union of Pure and Applied Chemistry (IUPAC,usually spoken as **eye-you-pac**).
A chemical name typically has four parts in the IUPAC system of nomenclature: prefix, parent, locant, and suffix.

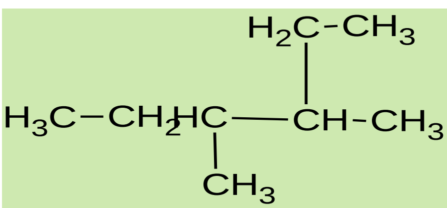
Prefix	**Parent**	**Locant**	**Suffix**
Where and what are the substitution	**How many carbons**	**where is the primary functional group**	**what is the primary functional group**

named by following four steps.

STEP 1 Find the parent hydrocarbon.

(a) Find the longest continuous carbon chain in the molecule and use the name of that chain as the parent name.

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



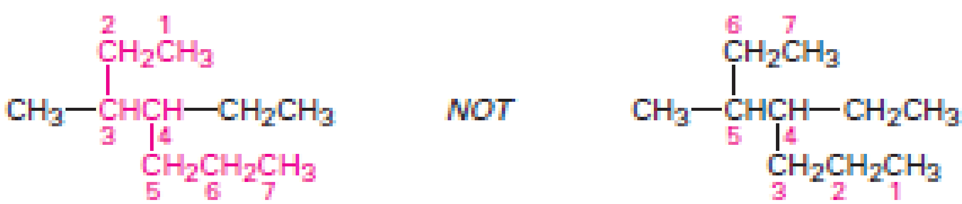
named as hexan with tow sustitution

Not

named as hexan with one sustitution

STEP 2 Number the atoms in the main chain.

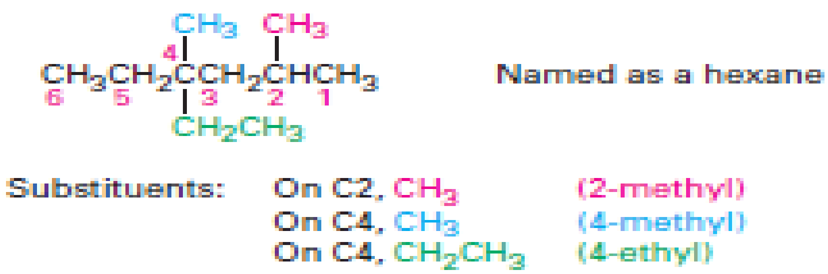
Beginning at the end nearer the first branch point, number each carbon atom in the parent chain.



The first branch occurs at C3 in the proper system of numbering but at C4 in the improper system.

STEP 3 Identify and number the substituents.

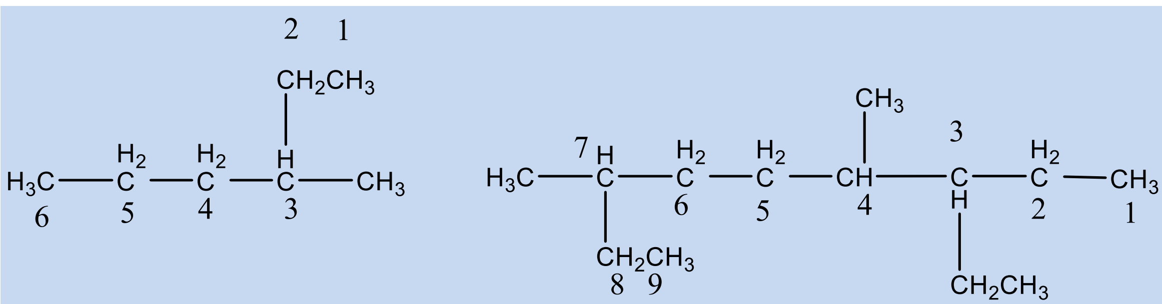
Assign a number, called a *locant*, to each substituent to specify its point of attachment to the parent chain. If there are two substituents on the same carbon, assign them both the same number. There must always be as many numbers in the name as there are substituents.



STEP 4 Write the name as a single word.

Use hyphens to separate the various prefixes and commas to separate numbers.

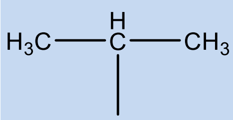
If two or more different side chains are present, cite them in alphabetical order. If two or more identical side chains are present, use the appropriate multiplier prefixes *di*-, *tri*-, *tetra*-, and so forth. Don't use these prefixes for alphabetizing, though. Full names for some examples follow:

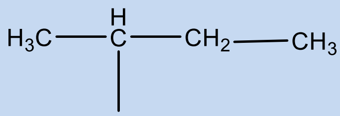


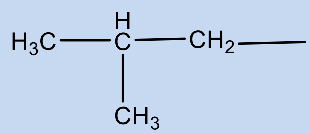
3-methyl hexane

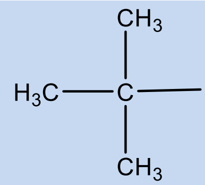
3-Ethyl-4,7-dimethylnonane

For historical reasons, a few simple branched-chain alkyl groups also have nonsystematic, common names.


Isopropyl (i-Pr)

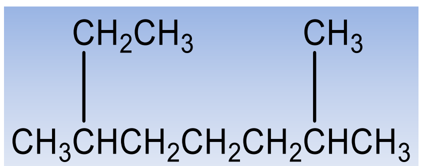

sec-Butyl
(sec-Bu)


Isobutyl


tert-Butyl
(t-Butyl or t-Bu)

Example Naming an Alkane

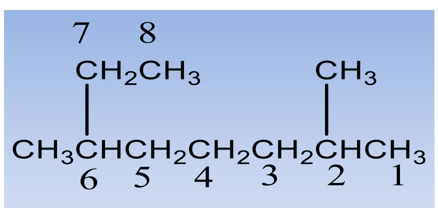
What is the IUPAC name of the following alkane?



Strategy The molecule has a chain of eight carbons (octane) with two methyl substituents.

Numbering from the end nearer the first methyl substituent indicates that the methyls are at C2 and C6.

Solution


2,6-Dimethyloctane

Properties of Alkanes

Alkanes are sometimes referred to as *paraffins*, a word derived from the Latin *parum affinis*, meaning “slight affinity.” This term aptly describes their behavior, for alkanes show little chemical affinity for other substances and are inert to most laboratory reagents. They do, however, react under appropriate conditions with oxygen, chlorine, and a few other substances.

The reaction of an alkane with O_2 occurs during combustion in an engine or furnace when the 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 reacts with oxygen according to the equation:

$$CH4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O + 890\ kJ\ (213\ kcal)$$

The reaction of an alkane with Cl_2 occurs when a mixture of the two is irradiated with ultraviolet light (denoted *hυ*, where *υ* is the lowercase Greek letter nu). Depending on the relative amounts of the two reactants and on the time allowed for reaction, a sequential replacement of the alkane hydrogen atoms by chlorine occurs, leading to a mixture of chlorinated products. Methane, for instance, reacts with chlorine to yield a mixture of chloromethane(CH_3Cl), dichloromethane(CH_2Cl_2), trichloromethane ($CHCl_3$), and tetrachloromethane (CCl4).

$$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$$

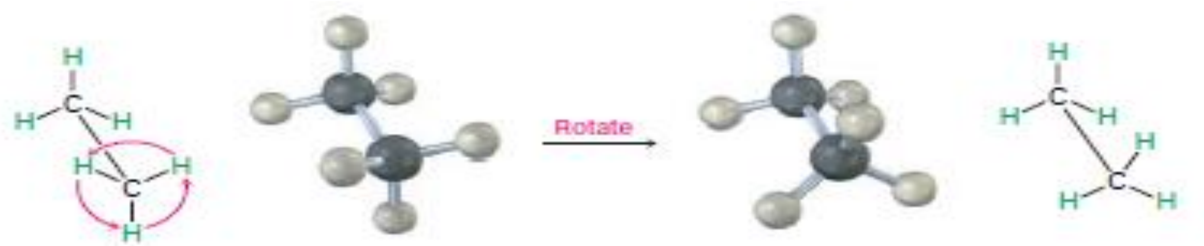
$$CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 + HCl$$

$$CHCl_3 \xrightarrow{Cl_2} CCl_4 + HCl$$

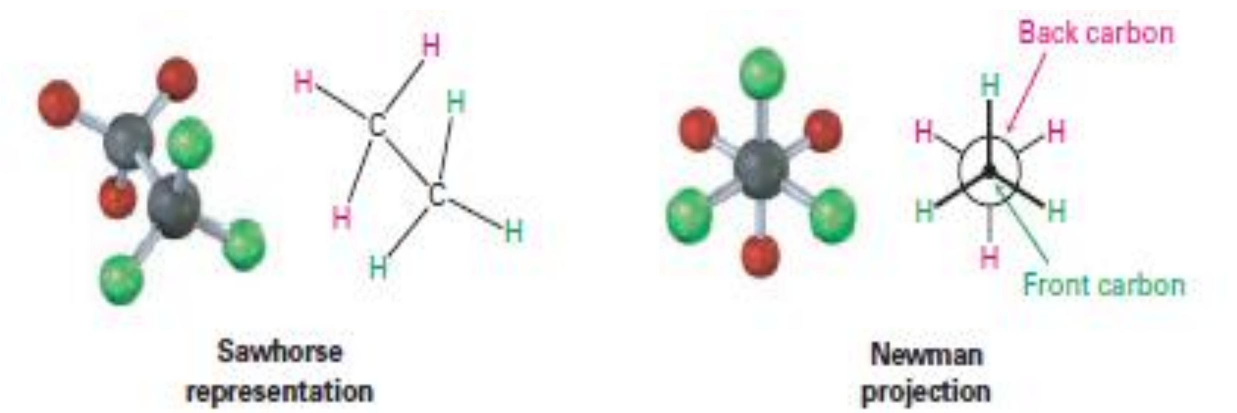
Conformation of Ethane

We know that a carbon–carbon single bond results from the head-on overlap of two atomic orbitals. Because the amount of this orbital overlap is the same regardless of the geometric arrangements of other atoms attached to the carbons, *rotation* is possible around carbon–carbon single bonds. In ethane, for instance, rotation around the C - C bond occurs freely, constantly changing the geometric relationships between the hydrogens on one carbon and those on the other. The different arrangements of atoms that result from bond rotation are called **conformations**, and molecules that have different arrangements are called conformational isomers, or *conformers*. Unlike constitutional isomers, however, different conformers can't usually be isolated because they interconvert too rapidly.

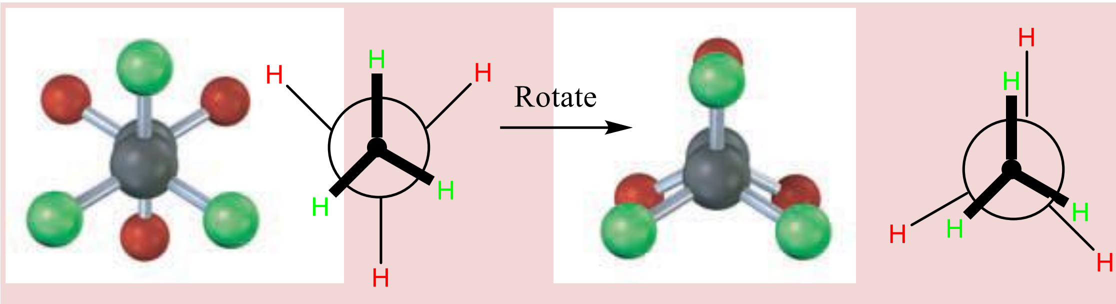


Chemists represent different conformations in two ways, as shown in the above Figure.

A **sawhorse representation** views the C-C bond from an oblique angle and indicates spatial relationships by showing all the C-H bonds. A **Newman projection** views the C - C bond directly end-on and represents the two carbon atoms by a circle. Bonds attached to the front carbon are represented by lines to a dot in the center of the circle, and bonds attached to the rear carbon are represented by lines to the edge of the circle.



The lowest-energy, most stable conformation is the one in which all six C - H bonds are as far away from one another as possible (**staggered** when viewed end-on in a Newman projection). The highest-energy, least stable conformation is the one in which the six C - H bonds are as close as possible (**eclipsed** in a Newman projection). At any given instant, about 99% of ethane molecules have an approximately staggered conformation, and only about 1% are close to the eclipsed conformation



Ethane—staggered conformation

Ethane—eclipsed conformation

What is true for ethane is also true for propane, butane, and all higher alkanes.

Example **Drawing a Newman Projection**

Sight along the C1 - C2 bond of 1-chloropropane and draw Newman projections of the most stable and least stable conformations.

Strategy The most stable conformation of a substituted alkane is generally a staggered one in which large groups are as far away from one another as possible. The least stable conformation is generally an eclipsed one in which large groups are as close as possible.

Solution

Most stable (staggered)

Least stable (eclipsed)