INTRODUCTION TO ORGANIC NOMENCLATURE

ALKANES, HYDROCARBONS, and FUNCTIONAL GROUPS. All organic compounds are made up of at least carbon and hydrogen. The most basic type of organic compound is one made up exclusively of ***sp^3* carbons** covalently bonded to other carbons and hydrogens through **sigma bonds only**. The generic name for this family of compounds is **alkanes**. Alkanes are part of a more general category of compounds known as **hydrocarbons**. Some hydrocarbons such as alkenes and alkynes contain *sp^2* or *sp*-hybridized carbon atoms.

Alkanes are of great importance to the different classification systems and the naming of organic compounds because they consist of a carbon chain that forms the main structural unit of all organic substances. When an alkane carbon chain is modified in any way, even by the mere introduction of an *sp^2* carbon or a heteroatom (atoms other than carbon and hydrogen), is is said to be **functionalized**. In other words, a **functional group** has been introduced and a new class of organic substances has been created.

A functional group is a specific arrangement of certain atoms in an organic molecule that becomes the **center of reactivity**. That is, it is the portion of the structure that **controls the reactivity of the entire molecule and much of its physical properties**. An entire classificaton system of functional groups is based on atom hybridization. Some of these functional groups are presented on page 2. They are the most commonly studied in introductory organic chemistry courses.

ALKANE NOMENCLATURE. Since alkanes are the most fundamental types of organic compounds, their structural features (a basic carbon chain, or skeleton) provide the basis for the nomenclature of all organic compounds. The earliest nomenclature systems followed almost no systematic rules. Substances were named based on their smell, or their natural source, etc. Many of those names are still in use today and are collectively known as **common names**. As organic chemistry developed and structures became more complex, a systematic method for naming organic compounds became necessary. The *International Union of Pure and Applied Chemistry* (IUPAC) is the organism that sets the rules for nomenclature of organic compounds today. Names that follow IUPAC rules are known as **systematic names**, or **IUPAC names**.

According to IUPAC rules, the first four alkanes are called ***methane**, **ethane**, **propane**, and **butane***. They contain one, two, three, and four carbon atoms respectively, in a linear arrangement. Beginning with the fifth member of the series, ***pentane***, the number of carbons is indicated by a greek prefix (penta, hexa, hepta, etc.). Most organic chemistry textbooks contain tables of at least the first ten members of the series, along with their structures and physical properties. Thus, the first two and most elementary rules for naming alkanes are to identify the length of the carbon chain, start the name with the appropriate greek prefix, and end the name with the suffix -*ane*. All this is obvious from the examples just given. Other rules are discussed next.

OVERVIEW OF FUNCTIONAL GROUPS BASED ON ATOM HYBRIDIZATION

I. HYDROCARBONS - Substances containing only carbon and hydrogen.

ALKANES	C—C	Only sp^3 carbon present (technically not a functional group)
ALKENES	C=C	At least one π-bond between two sp^2 carbons present
ALKYNES	C≡C	At least one triple bond between two sp carbons present

II. ALKYL HALIDES, OR HALOALKANES - Substances containing at least one C-X bond, where X=F, Cl, Br, or I.

ALKYL FLUORIDES	C—F	ALKYL CHLORIDES	C—Cl
ALKYL BROMIDES	C—Br	ALKYL IODIDES	C—I

III. GROUPS CONTAINING OXYGEN - Both carbon and oxygen can be sp^3 or sp^2 hybridized, or a combination of both.

ALCOHOLS C—OH and ETHERS C—O—C sp^3 Oxygen

ALDEHYDES —C(=O)—H and KETONES C—C(=O)—C sp^2 Oxygen

CARBOXYLIC ACIDS —C(=O)—OH, ESTERS —C(=O)—O—C, and ANHYDRIDES —C(=O)—O—C(=O)—

These functional groups contain both sp^3 and sp^2 oxygen.

ACID, OR ACYL HALIDES —C(=O)—X The most common halogens used are chlorine and bromine.

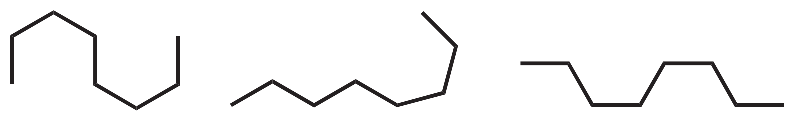
IV. GROUPS CONTAINING NITROGEN - They may also contain other elements. For example amides also contain oxygen.

AMINES C—N (sp^3 Nitrogen), AMIDES —C(=O)—N, and NITRILES —C≡N (sp Nitrogen)

Before proceeding, it is important to emphasize that beginning organic chemistry students must get used to seeing alkane chains from different angles, perspectives, and positions, as shown below using line-angle formulas for **linear alkanes**.

Hexane

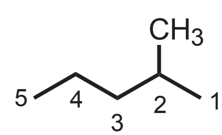
Octane



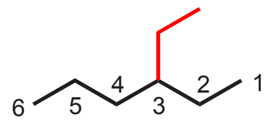
BRANCHED ALKANES and ALKYL GROUPS. When naming branched alkanes by IUPAC rules, identify and name the **longest continuous carbon chain** first. Then identify the branch, or branches. The branches are called **alkyl groups**. For example, a one carbon branch is called a methyl group. The names of alkyl groups are the same as those of analogous alkanes, except that their names end in ***-yl***, instead of *-ane*. The following are examples of the most common alkyl groups encountered in introductory organic chemistry courses. Alky groups never exist by themselves. In alkanes they are always attached to a higher priority chain and are therefore sometime called **substituents**. The point of attachement is indicated by a dash.

CH_3-	CH_3CH_2-	$CH_3CH_2CH_2-$	$CH_3\overset{\vert}{C}HCH_3$
Methyl	Ethyl	*n*-propyl	isopropyl
$CH_3CH_2CH_2CH_2-$	$CH_3-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-$	$CH_3\overset{\vert}{C}HCH_2CH_3$	$CH_3\underset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}CH_3$
n-butyl	isobutyl	*sec*-butyl	*t*-butyl

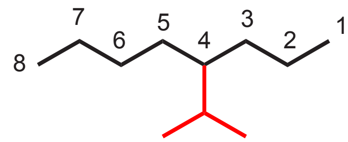
In the following example, the longest continuous carbon chain has five carbons. Therefore the parent alkane is **pentane**. There is a **methyl** group attached to this chain. The molecule is then named *methylpentane*. Finally, the exact position of the methyl group is specified by numbering the main chain from the end closest to the methyl group. The complete IUPAC name for this alkane is ***2-methylpentane***.



In the following examples the alkyl groups are shown in red. Students must get used to line-angle formulas as early as possible.

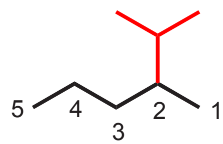


3-Ethylhexane

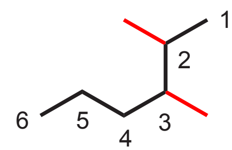


4-Isopropyloctane

Make sure you've identified the longest continuous carbon chain correctly. Otherwise you might end up with the wrong name. The longest continuous carbon chain doesn't always have to be a horizontal row of carbons. It can take twists and turns. That's why one must get used to visualize molecules from different angles and perspectives. The following example illustrates the correct name and an incorrect name based on a horizontal row of carbons.



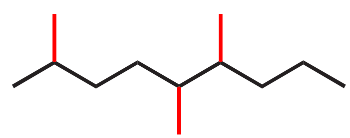
INCORRECT: 2-Isopropylpentane



CORRECT: 2,3-Dimethylhexane

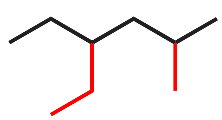
The correct name above illustrates what's done when there are several substituents of the same kind. First identify their positions, then use the prefixes *di-, tri-, tetra-*, etc. to indicate how many are present.

2,4-Dimethylpentane

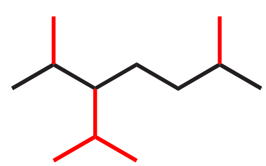


2,5,6-Trimethylnonane

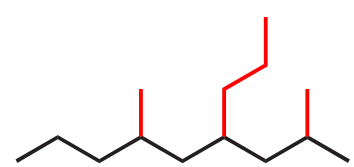
If there are substituents of different kinds present, name them in alphabetical order (e.g. ethyl before methyl). Prefixes such as *di-, tri-, tetra-*, etc. are ignored when alphabetizing.



4-**E**thyl-2-**m**ethylhexane



3-**I**sopropyl-2,6-di**m**ethylheptane

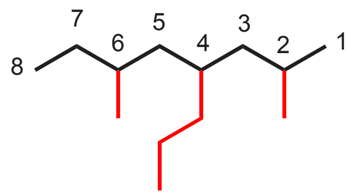


2,6-Di**m**ethyl-4-**p**ropylnonane

If there are several options for choosing the longest continuous carbon chain, choose the one that yields the simplest name. That means:

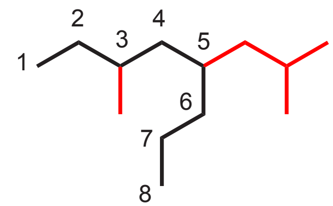
(a) The longest continuous carbon chain has the greatest number of substituents, and
(b) The name has the lowest set of numbers indicating the substituent positions.

CORRECT: 2,6-Dimethyl-4-propyloctane



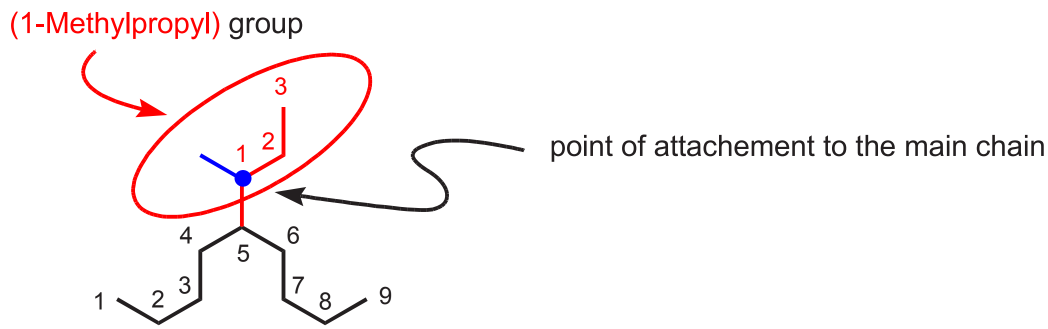
3 substituents of simpler structure, and a lower set of position numbers

INCORRECT: 5-Isobutyl-3-methyloctane



2 substituents of more complex structure, and a greater set of position numbers

Complex alky groups (those which are branched themselves) are named as if they were alkanes, but the name ends in ***-yl*** and is enclosed in parenthesis. The carbon from which the substituent atttaches to the main chain is automatically number 1.

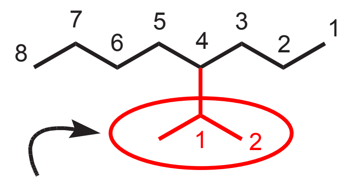


5-(1-Methylpropyl) nonane

Although common alkyl group names such as *isopropyl* and *t-butyl* are commonly used as part of IUPAC names, strict IUPAC rules call for naming them as complex substituents. Common names are used because they are easier to say, shorter, and save paper and ink in scientific publications when they have to be used repeatedly in manuscripts.

4-Isopropyloctane

Acceptable and commonly used name



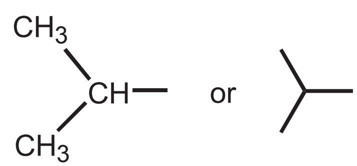
4-(1-Methylethyl) octane

Correct IUPAC name, but cumbersome for routine use

COMMON NAME: Isopropyl group
IUPAC NAME: (1-Methylethyl)

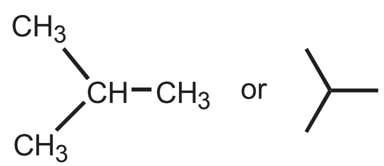
ALKANES: COMMON NAMES. Like alkyl groups, alkanes can also have common names. Common, or "trivial" names are rarely used for straight chain alkanes, but are frequently used for branched alkanes. The following pages contain some terminology that organic chemistry students must memorize or become familiar with, due to the fact that it is widely used in textbooks and in the chemical literature.

ISOALKANES and ISOALKYL GROUPS. The ***iso*** structural unit consists of two methyl groups attached to a common carbon. When this unit is present in an alkane or alky group, the common name starts with the prefix ***iso***.

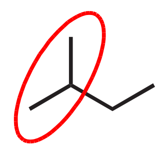


The ***iso*** structural unit

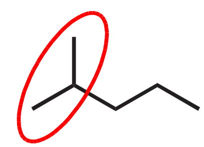
When this unit is present in alkanes, the molecule is named according to the **total number of carbon atoms present**, but the name starts with the prefix *iso*. The smallest possible isoalkane is then ***isobutane***.



Isobutane - four carbons total

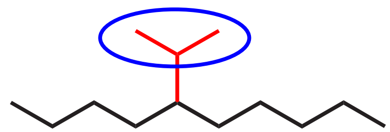


Isopentane - five carbons total

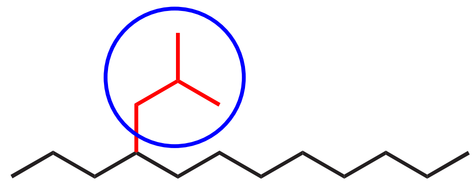


Isohexane - six carbons total

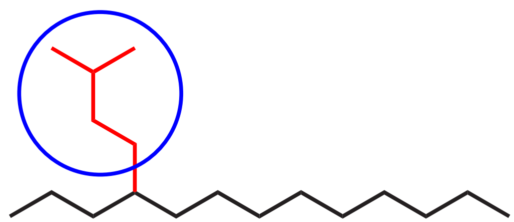
The same rules apply to isoalkyl groups, but their names end in ***-yl***. The smallest possible isoalky group is the ***isopropyl*** group, because alkyl groups are always attached to another carbon chain.



The isopropyl group, or (1-Methylethyl)

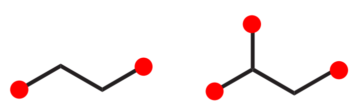


The isobutyl group, or (2-Methylpropyl)



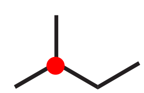
The isopentyl group, or (3-Methylbutyl)

PRIMARY, SECONDARY, AND TERTIARY CARBONS. Another bit of terminology associated with common names refers to the connectivity of sp^3 carbons in alkanes and alkyl groups. A **primary carbon** is one that is covalently attached to only one other carbon. A **secondary carbon** is one attached to two other carbons. A **tertiary carbon** is attached to three other carbons. This definition implies that methane cannot have any such carbons, since it consists of only one carbon atom. Likewise, **this terminology applies only to sp^3 carbons**. Other types are not defined in this way. In the following examples the carbons in question are indicated as dots.

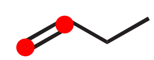


primary (1^o) carbons

secondary (2^o) carbons

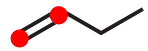


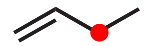
tertiary (3^o) carbons

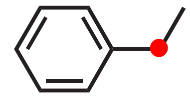


undefined

The carbon atoms directly engaged π-bonding in alkenes are referred to as **vinylic**. An sp^3 carbon directly attached to a vinylic carbon is referred to as **allylic**. Finally, an sp^3 carbon directly attached to a benzene ring is referred to as **benzylic**.

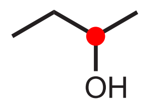

vinylic carbons


allylic carbon

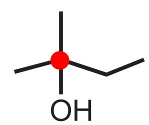

benzylic carbon

Although it is emphasized that this is terminology used in common names, it is widely used and therefore important. It constitutes the basis for characterizing not only alkanes, but also other types of compounds where the main functionality is attached to a carbon that belongs to one of the types described. Thus we can have **primary alcohols**, **secondary chlorides**, **allylic hydrogens**, etc. based on the type of carbon to which they are attached.

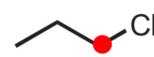
primary alcohol



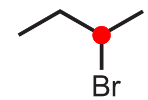
secondary alcohol



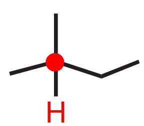
tertiary alcohol



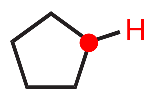
primary chloride



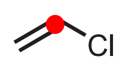
secondary bromide



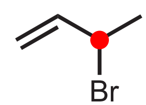
tertiary hydrogen



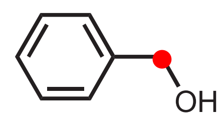
secondary hydrogen



vinyl chloride

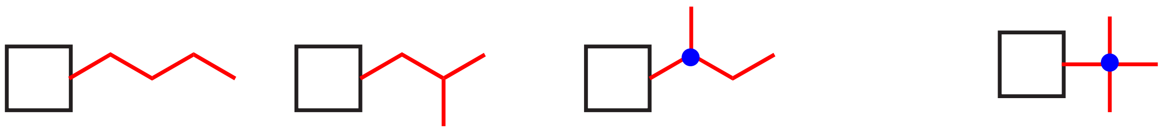


allyilic bromide



benzyl alcohol

This terminology is also used to identify the point of attachment of certain alkyl groups to the main chain of a molecule, based on the type of carbon from which the alkyl group connects to the main chain. For example four different butyl groups are possible, depending on their structure and their point of attachemnt to the main carbon chain. Two of them are named ***sec*-butyl** and ***tert*-butyl** (or ***t*-butyl**) because they connect to the main chain from a secondary and a tertiary carbon respectively.



n-butyl group

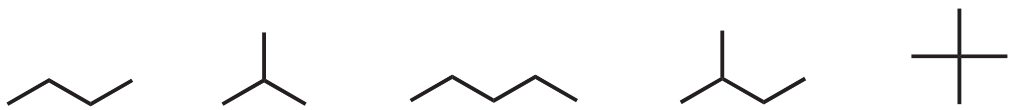
isobutyl group

sec-butyl group
the point of attachment
is a secondary carbon

t-butyl or *tert*-butyl group
the point of attachment is
a tertiary carbon

The square represents the main carbon chain of a molecule

While there are four possible butyl groups, only two possible butanes exist. They are *n*-butane and isobutane (once again, these are **common** names). Likewise, there are three possible pentanes called *n*-pentane, isopentane, and neopentane.



n-butane

isobutane

n-pentane

isopentane

neopentane

The nomenclature concepts presented in the previous sections also apply to cycloalkanes. Please consult your organic chemistry textbook for examples and additional practice exercises.

ORGANIC NOMENCLATURE, PART II
HALOALKANES, OR ALKYL HALIDES

Like alkanes, alkyl halides, called ***haloalkanes*** by IUPAC rules, can have common names as well as systematic names. Common names are widely used because they are short and easy to say and write. Once you know what chloroform is, it's easier to refer to it as such, rather than as trichloromethane.

COMMON NAMES - Most common names refer to the main carbon frame as an alkyl group, and then add the halogen name, ending in *-ide*. Names such as isopropyl, or sec-butyl are extensively used. Likewise, primary halides have the halogen attached to a primary carbon, secondary halides have the halogen attached to a secondary carbon, etc. Refer to chapter 6 in your textbook. Examples are:

CH_3Cl

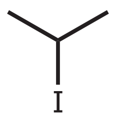
Methyl chloride

CH_3CH_2Br

Ethyl bromide

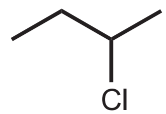
$Cl-CH_2-Cl$

Methylene chloride (CH_2Cl_2)

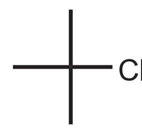


Isopropyl iodide

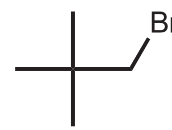
n-butyl chloride



sec-butyl chloride

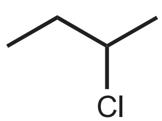


t-butyl chloride

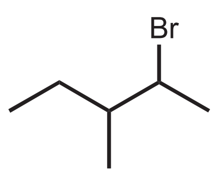


Neopentyl bromide

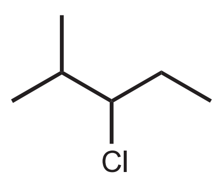
IUPAC NAMES - The systematic naming of haloalkanes follows the same basic principles as that of alkanes. Find the longest carbon chain and number it trying to obtain the lowest set of numbers. Follow the alphabetical rule in naming the substituents, whether they are alkyl groups or halogens. Use prefixes such as *di-*, *tri*, as needed. The following examples illustrate these points.



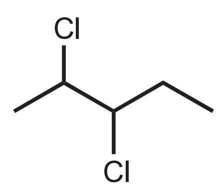
2-Chlorobutane



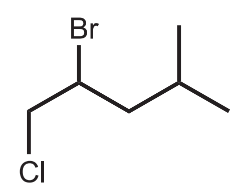
2-Bromo-3-methylpentane



3-Chloro-2-methylpentane

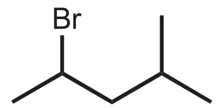


2,3-Dichloropentane



2-Bromo-1-chloro-4-methylpentane

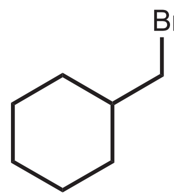
If two substituents are equally far from either end, number the chain according to alphabetical order.



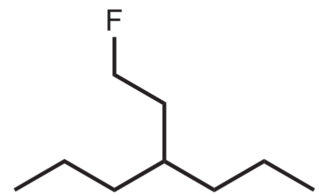
2-Bromo-4-methylpentane,

NOT: 2-Methyl-4-bromopentane

Name complex substituents using parenthesis and the guidelines discussed before for alkanes.



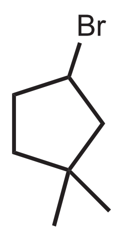
Bromomethylcyclohexane



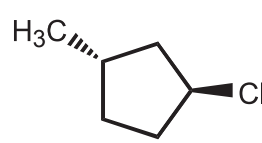
4-(2-Fluoroethyl)heptane

All these rules apply only if the substituents on the main carbon chain are alkyl groups and/or halogens. Other functional groups have different priorities, depending on their nature.

To name cyclohaloalkanes that contain halogen and alky substituents, number from the carbon bearing the halogen. Remember to indicate *cis* or *trans* when applicable.



1-Bromo-2,3-dimethylcyclopentane



trans-1-Chloro-3-methylcyclopentane