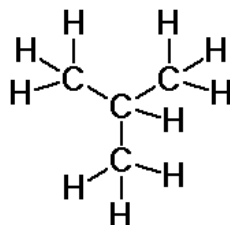


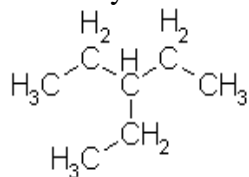
## 2.2 Naming of Alkanes

Frequently we will be looking at large, complicated organic molecules and we will want to refer to a small portion of that molecule by name without referring to the whole molecule. To take a simple example, let's look at the branched isomer of butane:



We can regard this molecule as being a chain propane molecule with a  $\text{CH}_3$  group being substituted on the middle carbon atom and providing a branch point. Note that this  $\text{CH}_3$  group is almost but not quite a methane molecule. There is one less H atom so that the  $\text{CH}_3$  group can be bonded by its fourth bond to the propane chain. We call this  $\text{CH}_3$  group a **methyl** group.

Similarly in the molecule:



We have a  $-\text{CH}_2\text{CH}_3$  group being branching off of the middle C atom of a pentane molecule. Again the  $-\text{CH}_2\text{CH}_3$  group is almost an ethane molecule except that one hydrogen has been removed so that the bond can be used to attach the group to the main chain. The  $-\text{CH}_2\text{CH}_3$  group is called an **ethyl group**.

These are names for alkyl groups for any given number of carbons, but we will be concerned only with the names for chains ranging from 1-10 carbon atoms.

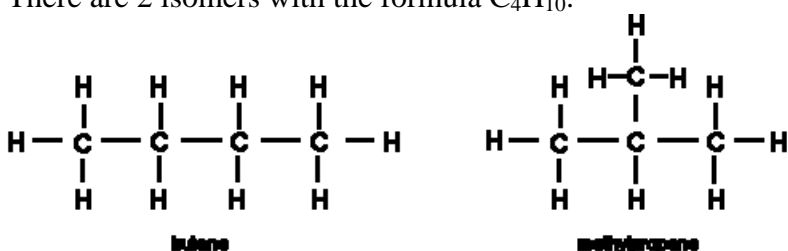
<u>Number of C Atoms</u>	<u>Name</u>
1	methyl
2	ethyl
3	propyl
4	butyl
5	pentyl

6	hexyl
7	heptyl
8	octyl
9	nonyl
10	decyl

The first four names (which are by far the most common) can be remembered by the mnemonic device:

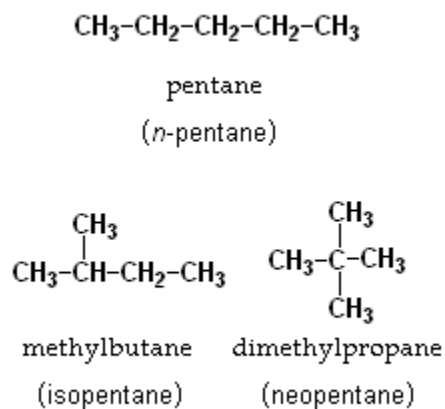
Methyl, ethyl  
 Propyl, butyl  
 After that,  
 It's all futile!

There are 2 isomers with the formula  $C_4H_{10}$ :



The unbranched chain isomer is called butane as indicated by the rules given above. The branched chain isomer was originally called isobutane, because it was an isomer of butane.

For the formula  $C_5H_{12}$  there are 3 isomers as shown below. The first molecule is the unbranched chain pentane; the second molecule has a methyl ( $-CH_3$ ) branch off of a 4-C chain, and the third has 2 methyl ( $CH_3$ ) groups coming off the middle C atom of the 3 carbon chain:



The first molecule is called pentane as before; the second isomer was called isopentane, and the third isomer was called neopentane because it was a new isomer (neo-is the Latin for new).

If we look at the table below however, we see that naming these isomers by simply putting prefixes in front of the name of the straight chain isomer will not be a very easy task for organic molecules containing a large number of C atoms. We will simply run out of names.

<u>Chemical Formula</u>	<u>Number of Isomers</u>
$C_6H_{14}$	5
$C_7H_{16}$	9
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4347
$C_{40}H_{82}$	62,500,000,000,000

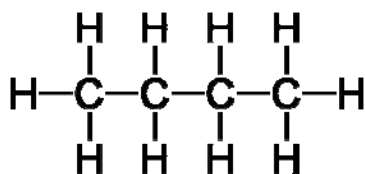
Clearly a more systematic way of naming molecule is necessary and organic chemists have developed such a system, called IUPAC nomenclature (International Union of Pure and Applied Chemistry). We will present the rules necessary to name alkanes in this unit, and will present additional rules for naming other functional groups in subsequent units. Although systematic names are used by professional chemists, it should be noted that most drug and food molecules are referred to by common non-systematic names. These names must simply be memorized.

### **Rules of Systematic Nomenclature**

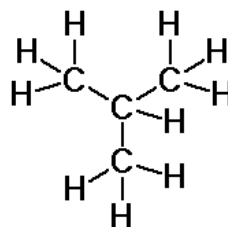
1. Name the longest (straight) unbranched carbon chain in the structure.
2. Preceding the name of the longest chain, write down in alphabetical order the names of each of the alkyl groups which are attached to the main chain.
3. If there are several groups of the same kind, list the group only once, using appropriate prefix: di- for 2, tri- for 3, tetra- for 4, penta- for 5, hexa- for 6, hepta- for 7, octa- for 8 to indicate how many of the groups there are.
4. Assign a number, as a prefix, to each of the alkyl groups in the name to indicate the position of the group on the main chain. Start numbering from whichever end of the main chain results in the lowest sum of numbers.

#### **.Examples: Draw and name**

**2 isomers of butane ( $C_4H_{10}$ )**

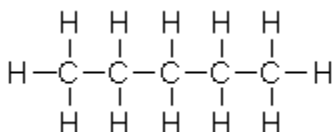


butane (as before)

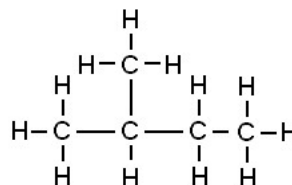


2-methylpropane

### 3 isomers with the formula (C<sub>5</sub>H<sub>12</sub>)

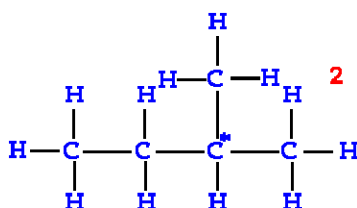


pentane (as before)



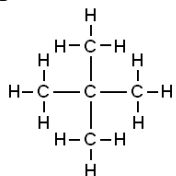
2-methylbutane

longest chain is 4 C's, so name compound as a derivative of butane with a methyl group hanging on 2nd C from the end



We might draw

as still another isomer and name it 3-methylbutane. Closer inspection shows that if we simply flip the molecule over from left to right we will have 2-methylbutane, which is the preferred name, since it has a smaller number.

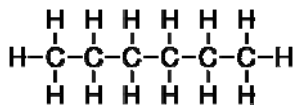


2,2-dimethylpropane

longest "straight" chain is 3C's so name it propane; two methyl groups hanging off second C so we have 2,2-dimethylpropane

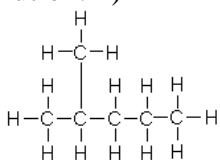
Note that IUPAC rules require that the number 2 be repeated to make it absolutely clearly that both methyl groups are on #2 C of the unbranched chain.

### Draw 4 isomers with formula C<sub>6</sub>H<sub>14</sub>



Solution: 1)

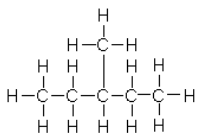
hexane



2)

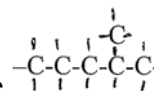
2-methyl pentane. (We want to start numbering from left to right to keep the numbering as small as possible.)

If we move the branch down one C on the main chain we have:



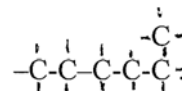
The name of this molecule is 3-methyl pentane and it does not matter from which end of the molecule we start the numbering.

If we move the methyl group down another C on the main chain we have



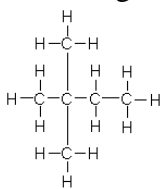
You might initially think this is a new isomer, 4-methylpentane, but closer inspection should make you realize this molecule is the same as 2-methylpentane, just flipped from left to right.

If we move the methyl branch 1 C further down the chain we have

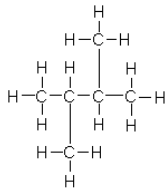


Careful inspection of this conformation should reveal that it is NOT a branched isomer at all. It is just a different conformation of an unbranched 6 C hexane chain. It may be easier to visualize this if you take a pencil (or pen) and start from left to right. You can cover all 6 C atoms in one continuous stroke of the pencil.

4) There are however two more isomers of  $\text{C}_6\text{H}_{14}$  which have two methyl groups branching off a 4 C unbranched chain.

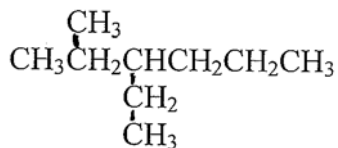


2,2 dimethylbutane



2,3 dimethylbutane

Additional naming practice:



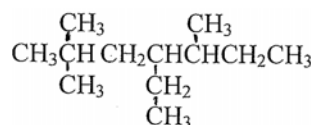
a)

The longest straight chain is 6 C's so name it hexane; add the branching chains in alphabetical order: ethyl and methyl. We still need to indicate where the ethyl and methyl groups are hooked on and that's where the numbers come in. Numbering from left to right we obtain:

3-ethyl-2-methylhexane Sum of numbers is 5

Numbering from right to left: 4-ethyl-5-methylhexane. The sum of the numbers is 9, so numbering from left to right is preferred.

Draw the line-bond notation for the above molecule.



b)Name:

Longest straight chain, ignoring branches, is 7 carbons.

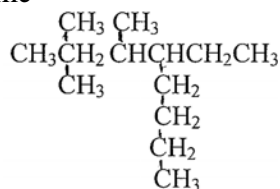
We have 3 methyl groups and one ethyl group branching off the main chain so our in front we have ethyl trimethyl

Now add the numbers, try starting from either end (then add the sum of the numbers).

Numbering from left to right we get 4-ethyl-2,2,5-trimethylheptane. Sum of #'s is 13

Numbering from the right to left we have 4-ethyl-3,6,6-trimethylheptane. Sum of #'s is 19  
First answer is correct name because the sum of numbers is smaller.

c)Name



At first glance it might appear that the longest chain(reading straight across) has 6 C, but look again and notice there is a 4 C branch on C #4 (from the left). This "branch" is longer than the 2 C chain continuing horizontally. Since free rotation allows putting the chain in whichever direction we wish, the longest unbranched chain contains 8 C atoms

Numbering from left to right we have:

4-ethyl-2,2,3-trimethyloctane. Sum of numbers is 11

Number from right to left we have

5-ethyl-6,7,7 trimethyloctane. Sum of numbers is 25

First name is the correct one.

## Naming alkanes with halogens

In naming a molecule which contain halogens (F,Cl,Br, and I) we treat the halogen just like an alkyl group and indicate its presence with the following names:

fluoro	for	F
chloro	for	Cl
bromo	for	Br
iodo	for	I

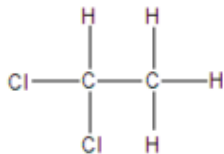
Older common names for simple halogenated compounds often use the ionic form of the halogen name i.e. fluoride, chloride, bromide, and iodide even though no ionic bond is present.

CH<sub>3</sub>Cl is named chloromethane. The older name is methyl chloride.

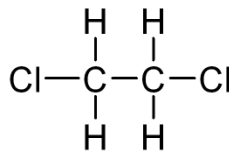
CH<sub>3</sub>Br is named bromomethane. The older name is methyl bromide

Let's look at some examples:

a) Two molecules with which we introduced the concept of structural isomers:



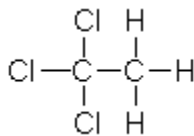
1,1-dichloroethane



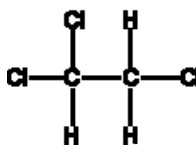
1,2-dichloroethane

The longest carbon chain in both cases is ethane and in both cases there are two chlorine atoms so name them both dichloroethane. However in the first case both Cl atoms are on the same C atom so call it 1,1-dichloroethane. In the second molecule the Cl atoms are on different carbon atoms so we indicate that as 1,2-dichloroethane.

b) Two isomers with the formula C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>

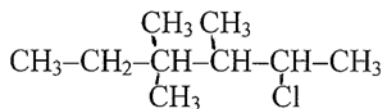


1,1,1-trichloroethane  
(not 2,2,2-trichloroethane  
and not 1-trichloroethane)



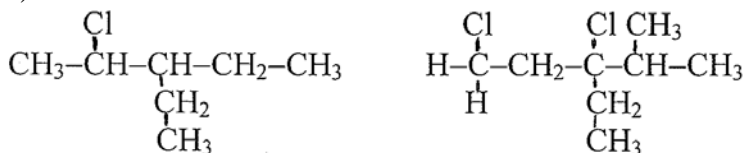
1,1,2-trichloroethane  
(not 1,2,2-trichloroethane)

c) A molecule with both alkyl and halogen groups



Numbering from left to right: 5-chloro-3,3,4 trimethylhexane Sum of numbers is 15  
 Numbering from right to left: 2-chloro-3,4,4-trimethylhexane Sum of number is 13.  
 Numbering from right to left gives the correct name.

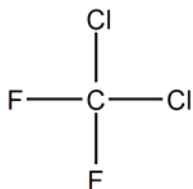
d)



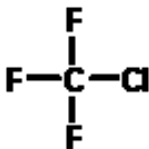
2-chloro-3-ethylpentane    1,3-dichloro-3-ethyl-4-methylpentane  
 What would the numbering be if we numbered from right to left?

### Examples with practical uses:

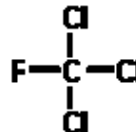
#### Freons



Dichlorodifluoromethane  
(Freon12)

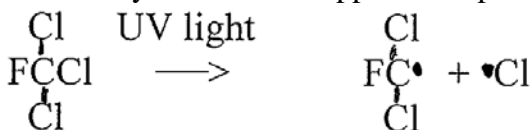


chlorotrifluoromethane  
(Freon13)



trichlorofluoromethane  
(Freon 11)

Freon 12 and other Freons have been used as the gases in refrigerators and air conditioners, but when they escape to the upper atmosphere, UV radiation can break the C-Cl bond and produce Cl free radicals (molecules with unpaired electrons) which can then destroy ozone in the upper atmosphere.



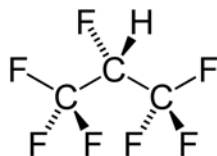
Chlorofluorocarbons(CFC's) were phased out in developed countries for spray cans in 1978, for refrigerators and air conditioners in 1995, and for medical inhalers (**metered dose inhalers** or MDI's for inhaled drugs such as **albuterol**) as of 2008. They have been replaced with hydrofluoroalkanes (HFAs) 134a and 227 which are *less* damaging to the ozone layer. (The hydrofluoroalkanes are less damaging to the ozone layer because the C-F bond is not as susceptible breakage by UV radiation as the C-Cl bond.)





HFA 134a has the structure and the systematic name 1,1,1,2-tetrafluoroethane

HFA 227 has the wedge and dash structure



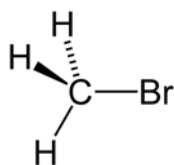
and the systematic name 1,1,1,2,3,3,3-heptafluoropropane.

Notice that both of these molecules contain only F halogen atoms and no Cl atoms. The C-F bond is much more resistant to UV light than the C-Cl bond. The substitution of HFAs for CFCs is more complicated than you might think and has required extensive research in the last two decades. The HFAs are more expensive to produce and large scale testing of efficacy and toxicity of the newly reformulated inhalers was required by the FDA. The cost of metered dose inhalers (MDIs) using HFAs are substantially more expensive than the old inhalers using CFCs.



Two albuterol inhalers reformulated with HFAs.

### Bromomethane (Methyl bromide)

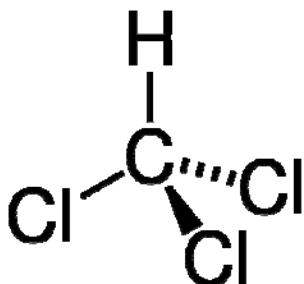


IUPAC: bromomethane

Common: methylbromide

Bromomethane (methyl bromide) has been used as a specialized soil fumigant, especially for growing strawberries. It is extremely toxic and great care must be taken in applying it. Methyl bromide is also a very potent ozone destroyer and there have been calls for taking it off the market for many years.

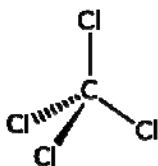
### Trichloromethane(chloroform)



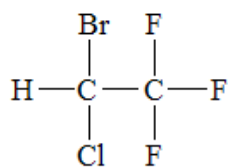
Trichloromethane (chloroform) was one of the earliest general anesthetics ( a molecule which induces sleep as well as analgesia). It was administered by breathing the vapors of liquid chloroform and was first used during childbirth in 1847. It competed strongly with ether for the next 60 years as the general surgical anesthetic of choice. It has a sweet smell and is much less flammable and less irritating than ether, but the risk of putting the patient to sleep permanently is higher than for ether. Lethal overdose with chloroform was all too frequent and it could cause cardiac arrhythmias. Accumulated data published in 1934 showed that deaths from chloroform anesthesia were over four times as frequent as those with ether anesthesia (about 1 in 3000 for chloroform vs 1 in 14,000 for ether anesthesia). It is no longer use as an anesthetic.

It continued to be used in some cough suppressants and toothpastes and other cosmetics until such use was banned in 1976 based on data from rats that it could cause birth defects and liver cancer. Current exposure in the US is very small, primarily from chlorinated water reacting with organic compounds in the water to form trace amounts of chloroform in drinking water.

### Tetrachloromethane(carbon tetrachloride)



Tetrachloromethane(carbon tetrachloride) was commonly used as a drycleaning solvent in the first half of the twentieth century to remove grease and dirty from clothes.. It was also used in the synthesis of the Freon gases for refrigerators and air conditioners. Exposure to CCl<sub>4</sub> was associated with neurological, liver, and kidney damage and it was replaced as a dry cleaning solvent. Like the Freon molecules, CCl<sub>4</sub> can cause ozone depletion and its use has dropped dramatically.



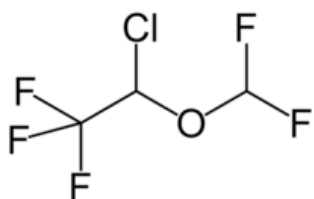
IUPAC: 2-bromo-2-chloro 1,1,1-trifluoroethane

Common: halothane

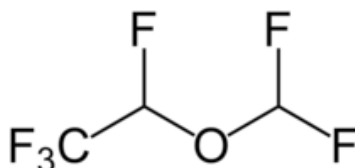
This molecule has the common name of **halothane** (suggest why!). It came on the market in 1956 and replaced ether as the anesthetic of choice because it was less irritating to the airway and it was not flammable. It did however have some adverse effects including cardiac depression (slowing of the heart rate) and rare (1 in 35,000) cases of hepatitis. It gradually lost "market share" to safer anesthetics.

### Current inhalation anesthetics:

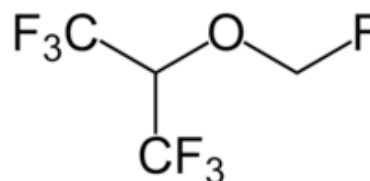
The current most commonly used inhalation anesthetics are halogenated ethers shown below which eliminate the flammability problem of ether and are generally less irritating to the airway than ether.



**Isoflurane**



**Desflurane**

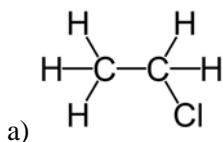


**Sevoflurane**

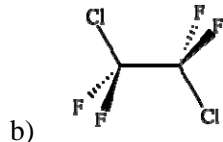
The mechanism of action of general anesthetics is poorly understood, is very complex, and probably involves many different factors. They appear to inhibit movement of the action potential along neurons as well as activating or inactivating a wide variety of neuronal receptors.

### Topical anesthetics that work by chilling the skin surface

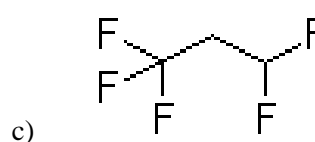
Name the following three molecules:



1 chloroethane  
ethyl chloride



1,2-dichloro-1,1,2,2-tetrafluoroethane



1,1,1,3,3-pentafluoropropane

a) The first molecule has the common name ethyl chloride and has been used as a mild topical anesthetic while doing minor surgeries (e.g. removing a deep splinter). It has a low boiling point (12 °C) and boils off the skin (at 37°C), lowering the skin temperature in the process and decreasing pain sensation. It is occasionally used as a recreational inhalant. Its use is decreasing..

b) The second molecule, 1,2-dichloro-1,1,2,2-tetrafluoroethane, is marketed under the trade name, Frigiderm, works by a similar mechanism. It has a boiling point of 4°C.

c) The third molecule, 1,1,1,3,3-pentafluoropropane, is marketed under the name Gebauer's Spray and Stretch. It is marketed for reducing pain of sprains. (Boiling point = 14°C)



**Perfluoroalkanes** (completely fluorinated C chains) are liquids which dissolve large amounts of oxygen while remaining biologically inert. Such fluids were the basis for the oxygenated liquid in the movie *The Abyss*. Perfluoroalkanes have been investigated for filling the lungs of premature infants with respiratory distress syndrome. Clinical trials of one such liquid (Liquivent) were disappointing and it was not approved for market. Perfluorochemicals are also accumulating in the environment due to their inertness, albeit in small concentrations. They can accumulate in the fat of animals (including humans). Although their short-term toxicity appears to be low, long term data is minimal and there is increasing concern about the long term biological effects of perfluorochemicals accumulating in the body.



Perfluorochemicals have also been investigated for their use as artificial blood which could be used instead of real blood for blood transfusions. Perfluorochemicals would have the advantage of not having to match blood types and would not require testing for viral contamination with HIV and hepatitis which are necessary for blood transfusions. More recent research has been done on an emulsion of perfluorochemical, water, and lecithin) with the trade name Oxygent™. There is definitely a demand for a blood substitute, but that product has not yet been widely marketed.