ALKANES

These are hydrocarbons which form a homologous series of saturated nature with a general formula C_nH_{2n+2}. Successive members differ in composition by a methylene group.

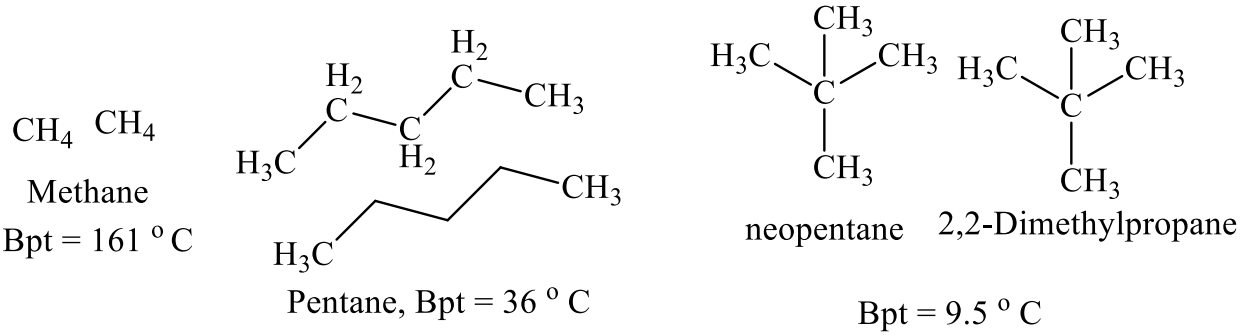
The main sources of Alkanes include:

- Natural gas which mainly contains methane with low amounts or propane and butane
- Petroleum products which are separated by fractional distillation during a process of refining

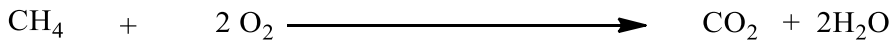
PHYSICAL PROPERTIES OF ALKANES

Other things being equal, the more carbon atoms, the higher the boiling point of an alkane. As can be seen from the table of straight chain alkanes, boiling points rise steadily from CH_4 which has a boiling point of -162 ^{o}C to $C_{10}H_{22}$ which has a boiling point of 174 ^{o}C as each additional CH_2 group is added to the chain.

The reason for this rise is an increase in the intermolecular forces. As shown in the following figure below, larger molecules can make close contact with each other over a much larger surface area than can smaller molecules. The total force exerted between the two is thus greater. In the same way we can also explain why branched-chain hydrocarbons boil at lower temperatures than straight-chain compounds. The branched molecules are more compact and provide less area over which intermolecular forces can act.



The alkanes are rather unreactive and do not combine readily with other substances. When heated sufficiently, however, they burn in air, a process known as combustion. Combustion releases large quantities of heat; not surprisingly, the most important use of alkanes is as fuels. Natural gas is mainly (approximately 85 percent) methane.



ΔH_m = - 890.4 kJ mol^{-1}

Propane or liquefied petroleum gas sold in tanks for portable use is usually a mixture of both propane and butane. Though both are gases at ordinary temperature and pressure, they liquefy under pressure in the tank. Gasoline is a more complex mixture of alkanes having 5 to 12 carbon atoms. Better-quality gasoline usually contains a higher percentage of branch-chain alkanes than the regular grade. Kerosene contains C_{10} to C_{16} alkanes, while heating oil usually involves the C_{12} to C_{18} range. Even longer-chain alkanes are found in lubricating oil, C_{15} to C_{25} and paraffin wax (used for candles and waxed paper), C_{23} to C_{29}.

The variation of boiling point with chain length in the alkanes provides a simple method for partially separating them from each other in petroleum. When petroleum is heated, the shorter-chain compounds begin to boil off initially. These can be collected by cooling the vapor until it recondenses to a liquid. As boiling proceeds, the temperature rises and longer and longer-chain compounds boil off.

Finally, only the very long chain compounds are left and such a process is called fractional distillation. Fractional distillation plays an important role in petroleum refining, which is a series of physical and chemical processes by which the most valuable and useful components are obtained from natural crude oil.

The alkanes are typical examples of nonpolar compounds. The electronegativities of carbon and hydrogen are 2.5 and 2.1, respectively, and so the C—H bond has almost no polarity. Consequently, even the most unsymmetrical hydrocarbon molecules have very small dipole moments. We can therefore take the boiling-point behavior of the alkanes to be representative of other nonpolar substances. Simple molecules are gases, while medium-sized molecules are liquids, and only quite large molecules are solids.

Summary:

i. Alkanes are colourless and odourless.

ii. They possess weak Van Der Waals forces of attraction.

iii. Alkanes having 1-4 carbon atoms are gases, then from 5-17 carbon atoms are liquids and those having 18 or more carbon atoms are solid at 298K.

iv. **Structure of alkanes**. All the carbon atoms are sp^3 hybridized which means they form four sigma bonds with either carbon or hydrogen atoms. The bond angle between them is 109.5 ^{o} C and they exhibit tetrahedral geometry.

v. **Melting and boiling points**. Shorter chain alkanes have low melting and boiling points but as the number of carbon atoms in the chain increases, melting and boiling points rise.

Boiling point: it increases with the increasing molecular weight as the Van Der Waals force increases with increasing molecular weight. Straight chain alkanes have higher boiling point than their structural isomers.

Melting point: it also increases with increasing molecular weight because it is difficult to break the intermolecular forces of attraction between higher alkanes as they are generally solids. Even- numbered alkanes have a better packing in the solid phase than the odd ones as they form a well- organized structure which is difficult to break hence even- numbered alkanes have a higher boiling point than odd- numbered alkanes.

Alkane	**Formula**	**Bpt [°C]**	**Mpt [°C]**	**Density [kg/m3] (at 25 °C)**	**Isomers**
Methane	CH_4	−162	−182	0.656 (gas)	1
Ethane	C_2H_6	−89	−183	1.26 (gas)	1
Propane	C_3H_8	−42	−188	2.01 (gas)	1
Butane	C_4H_{10}	0	−138	2.48 (gas)	2

Pentane	C_5H_{12}	36	−130	626 (liquid)	3
Hexane	C_6H_{14}	69	−95	659 (liquid)	5
Heptane	C_7H_{16}	98	−91	684 (liquid)	9
Octane	C_8H_{18}	126	−57	703 (liquid)	18
Nonane	C_9H2_0	151	−54	718 (liquid)	35
Decane	$C_{10}H_{22}$	174	−30	730 (liquid)	75
Undecane	$C_{11}H_{24}$	196	−26	740 (liquid)	159
Dodecane	$C_{12}H_{26}$	216	−10	749 (liquid)	355
Tridecane	$C_{13}H_{28}$	235	−5.4	756 (liquid)	802
Tetradecane	$C_{14}H_{30}$	253	5.9	763 (liquid)	1858
Pentadecane	$C_{15}H_{32}$	270	10	769 (liquid)	4347
Hexadecane	$C_{16}H_{34}$	287	18	773 (liquid)	10,359
Heptadecane	$C_{17}H_{36}$	303	22	777 (solid)	24,894
Octadecane	$C_{18}H_{38}$	317	28	781 (solid)	60,523
Nonadecane	$C_{19}H_{40}$	330	32	785 (solid)	148,284
Icosane	$C_{20}H_{42}$	343	37	789 (solid)	366,319
Triacontane	$C_{30}H_{62}$	450	66	810 (solid)	4,111,846,763
Tetracontane	$C_{40}H_{82}$	525	82	817 (solid)	62,481,801,147,341
Pentacontane	$C_{50}H_{102}$	575	91	824 (solid)	1,117,743,651,746,953,270
Hexacontane	$C_{60}H_{122}$	625	100	829 (solid)	2.21587345357704×1022
Heptacontane	$C_{70}H_{142}$	653	109		

vi. Solubility: alkanes are soluble in organic solvents rather than polar solvents like water.

vii. Alkanes have a lower density than water, they float on water. Density increases with an increase in molecular mass.

viii. Apart from weak Van Der Waals forces, London forces, Dispersion forces, weak intermolecular forces act between the molecules of alkanes.

Cracking

This is the breaking down of long chain organic molecules (hydrocarbon) into two or small molecules which are useful products. Cracking can be done using a catalyst (catalytic cracking) or by using high temperature (thermal cracking.

NOMENCLATURE/NAMING OF ALKANES

Naming of alkane

The names of all alkanes end with ***-ane***. Whether or not the carbons are linked together end-to-end in a ring (called cyclic alkanes or cycloalkanes) or whether they contain side chains and branches, the name of every carbon-hydrogen chain that lacks any double bonds or functional groups will end with the suffix ***-ane.***

Alkanes with unbranched carbon chains are simply named by the number of carbons in the chain. The first four members of the series (in terms of number of carbon atoms) are named as follow:

CH_4 = methane

C_2H_6 = ethane

C_3H_8 = propane

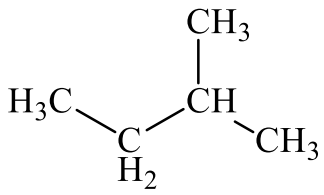
C_4H_{10} = butane

Alkanes with five or more carbon atoms are named by adding the suffix ***-ane*** to the appropriate numerical multiplier, except the terminal -a is removed from the basic numerical term. Hence, C_5H_{12} is called pentane, C_6H_{14} is called hexane, C_7H_{16} is called heptane and so forth.

Straight-chain alkanes are sometimes indicated by the prefix n- (for normal) to distinguish them from branched-chain alkanes having the same number of carbon atoms. Although this is not strictly necessary, the usage is still common in cases where there is an important difference in properties between the straight-chain and branched-chain isomers: e.g., n-hexane is a neurotoxin while its branched-chain isomers are not.

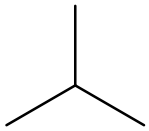
Using Common Names with Branched Alkanes

Certain branched alkanes have common names that are still widely used today. These common names make use of prefixes, such as ***iso-, sec-, tert-***, and ***neo-***. The prefix ***iso-***, which stands for **isomer**, is commonly given to *2-methyl alkanes*. In other words, if there is methyl group located on the second carbon of a carbon chain, we can use the prefix iso-. The prefix will be placed in front of the alkane name that indicates the total number of carbons. Examples: isopentane which is the same as 2-methylbutane,



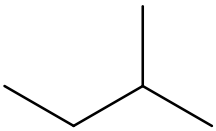
iso- Pentane

isobutane which is the same as 2-methylpropane

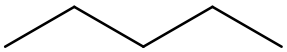


iso- Butane

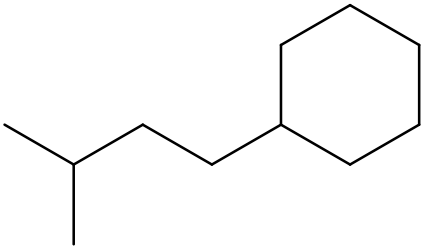
To assign the prefixes ***sec-***, which stands for secondary, and ***tert-***, for tertiary, it is important that we first learn how to classify carbon molecules. If a carbon is attached to only one other carbon, it is called a primary carbon. If a carbon is attached to two other carbons, it is called a secondary carbon. A ***tertiary carbon*** is attached to three other carbons and last, a **quaternary** carbon is attached to four other carbons. Examples:



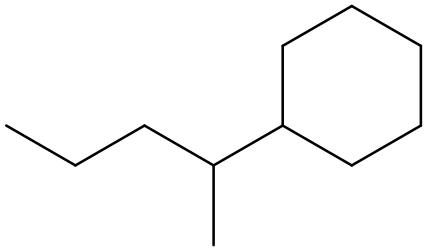
iso-Pentane



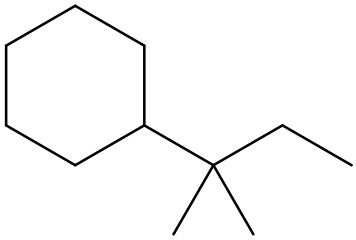
Pentane



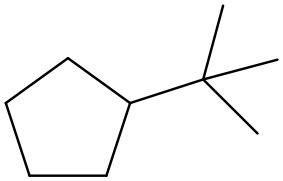
isopentylcyclohexane



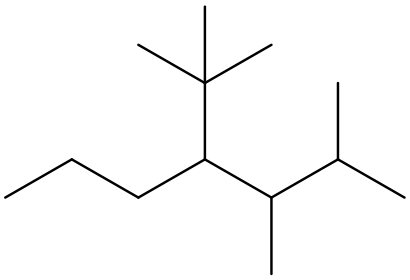
sec-pentylcyclohexane



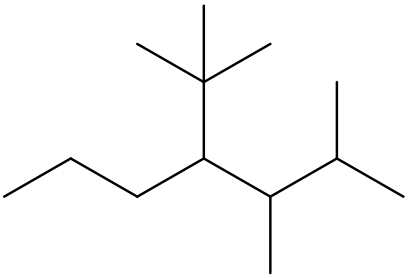
tert-pentylcyclohexane



tert-Butylcyclopentane

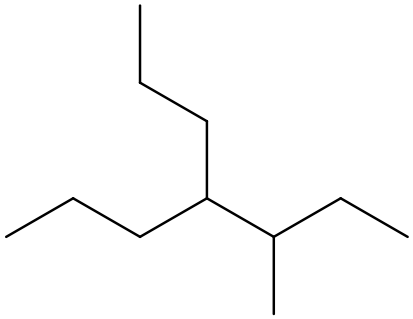


4-tert-Butyl-5-isopropylhexane

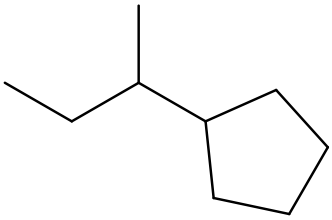


3-tert-Butyl-2-isopropylhexane

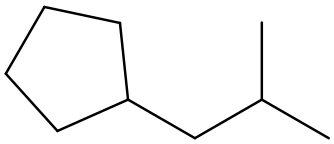
3-tert-Butyl-2-isopylhexane is the correct name.



4-sec-Butylheptane

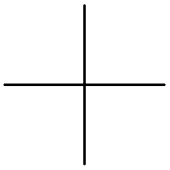


sec-Butylcyclopentane

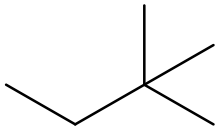


iso-Butylcyclopentane

The prefix ***neo-*** refers to a substituent whose second-to-last carbon of the chain is trisubstituted (has three methyl groups attached to it). A neo-pentyl has five carbons total. Examples:



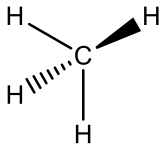
Neopentane



Neohexane

Drawing Hydrocarbons

Recall that when carbon makes four bonds, it adopts the tetrahedral geometry. In the tetrahedral geometry, only two bonds can occupy a plane simultaneously. The other two bonds point in back or in front of this plane. In order to represent the tetrahedral geometry in two dimensions, solid wedges are used to represent bonds pointing out of the plane of the drawing toward the viewer, and dashed wedges are used to represent bonds pointing out of the plane of the drawing away from the viewer. Consider the following representation of the molecule methane:

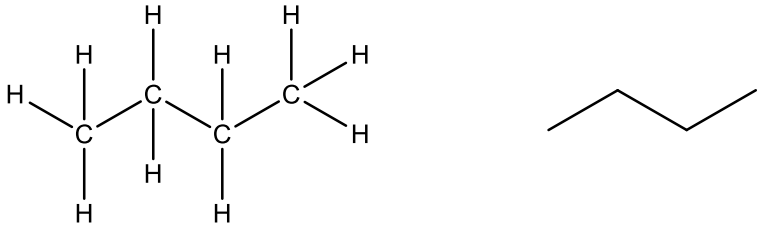


In the above drawing, the two hydrogens connected by solid lines, as well as the carbon in the center of the molecule, exist in a plane (specifically, the plane of the computer monitor / piece of paper, etc.). The hydrogen connected by a solid wedge points out of this plane toward the viewer, and the hydrogen connected by the dashed wedge points behind this plane and away from the viewer.

In drawing hydrocarbons, it can be time-consuming to write out each atom and bond individually. In organic chemistry, hydrocarbons can be represented in a shorthand notation called a **skeletal structure**. In a skeletal structure, only the bonds between carbon atoms are represented. Individual carbon and hydrogen atoms are not drawn, and bonds to hydrogen are not drawn.

In the case that the molecule contains just single bonds (sp3 bonds), these bonds are drawn in a "zig-zag" fashion. This is because in the tetrahedral geometry all bonds point as far away from

each other as possible, and the structure is not linear. Consider the following representations of the molecule propane:



Full structure of propane and skeletal structure of propane

Only the bonds between carbons have been drawn, and these have been drawn in a "zig-zag" manner. Note that there is no representation of hydrogens in a skeletal structure. Since, in the absence of double or triple bonds, carbon makes four bonds total, the presence of hydrogens is implicit. Whenever an insufficient number of bonds to a carbon atom are specified in the structure, it is assumed that the rest of the bonds are made to hydrogens. For example, if the carbon atom makes only one explicit bond, there are three hydrogens implicitly attached to it. If it makes two explicit bonds, there are two hydrogens implicitly attached, etc. Note also that two lines are sufficient to represent three carbon atoms. It is the bonds only that are being drawn out, and it is understood that there are carbon atoms (with three hydrogens attached!) at the terminal ends of the structure.

Alkyl Groups

Alkanes can be described by the general formula C_nH_{2n+2}. An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula CnH2n+1. The removal of this hydrogen results in a stem change from ***-ane to -yl.*** Take a look at the following examples.

Three Principles of Naming

1. Choose the longest, most substituted carbon chain containing a functional group.

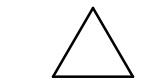
2. A carbon bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substituent present must have the lowest possible number.

3. Take the alphabetical order into consideration; that is, after applying the first two rules given above, make sure that your substituents and/or functional groups are written in alphabetical order.

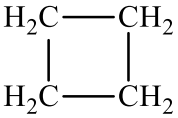
Cycloalkanes

Cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbons atoms that make up the ring are single bonded to other atoms (no double or triple bonds). There are also polycyclic alkanes, which are molecules that contain two or more cycloalkanes that are joined, forming multiple rings.

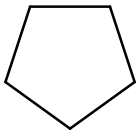
Many organic compounds found in nature or created in a laboratory contain rings of carbon atoms with distinguishing chemical properties; these compounds are known as cycloalkanes. Cycloalkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds, but in cycloalkanes, the carbon atoms are joined in a ring. The smallest cycloalkane is cyclopropane.



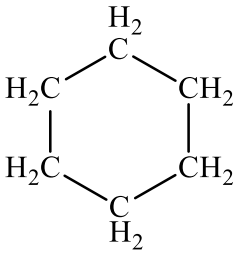
Cyclopropane



Cyclobutane

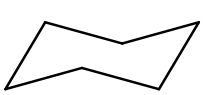


Cyclopentane



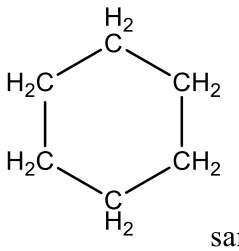
Cyclohexane

If you count the carbons and hydrogens, you will see that they no longer fit the general formula $C_nH_{2n+2.}$ By joining the carbon atoms in a ring, two hydrogen atoms have been lost. The general formula for a cycloalkane is $CnH_{2n.}$ Cyclic compounds are not all flat molecules. All of the cycloalkanes, from cyclopentane upwards, exist as "puckered rings". Cyclohexane, for example, has a ring structure that looks like this:

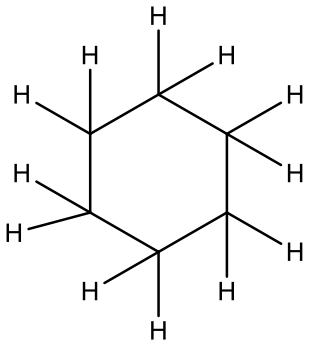


Although polycyclic compounds are important, they are highly complex and typically have common names accepted by IUPAC. However, the common names do not generally follow the basic IUPAC nomenclature rules. The general formula of the cycloalkanes is C_nH_{2n}, where n is the number of carbons. The naming of cycloalkanes follows a simple set of rules that are built upon the same basic steps in naming alkanes. Cyclic hydrocarbons have the prefix "***cyclo-***".

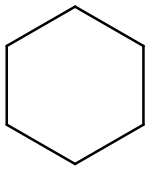
For simplicity, cycloalkane molecules can be drawn in the form of skeletal structures in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens.



same as



same as



IUPAC Rules for Nomenclature

1) Determine the cycloalkane to use as the parent chain. The parent chain is the one with the highest number of carbon atoms. If there are two cycloalkanes, use the cycloalkane with the higher number of carbons as the parent chain.

2) If there is an alkyl straight chain that has a greater number of carbons than the cycloalkane, then the alkyl chain must be used as the primary parent chain. Cycloalkane acting as a substituent to an alkyl chain has an ending "***-yl***" and, therefore, must be named as a ***cycloalkyl***. Replace the "***-ane***" with "***-yl***".

3) Determine any functional groups or other alkyl groups.

4) Number the carbons of the cycloalkane so that the carbons with functional groups or alkyl groups have the lowest possible number. A carbon with multiple substituents should have a lower number than a carbon with only one substituent or functional group. One way to

make sure that the lowest number possible is assigned is to number the carbons so that when the numbers corresponding to the substituents are added, their sum is the lowest possible.

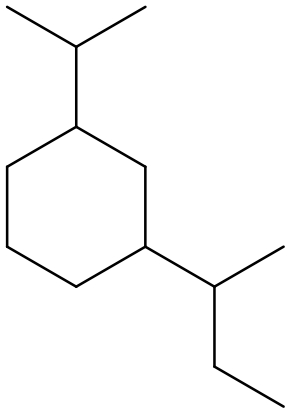
5) When naming the cycloalkane, the substituents and functional groups must be placed in alphabetical order.

6) Indicate the carbon number with the functional group with the highest priority according to alphabetical order. A dash"-" must be placed between the numbers and the name of the substituent. After the carbon number and the dash, the name of the substituent can follow. When there is only one substituent on the parent chain, indicating the number of the carbon atoms with the substituent is not necessary.

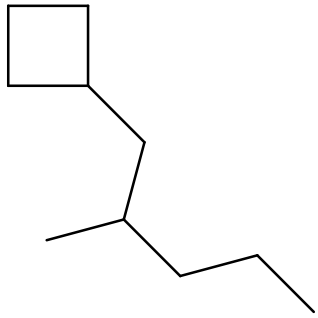
7) If there is more than one of the same functional groups on one carbon, write the number of the carbon two, three, or four times, depending on how many of the same functional group is present on that carbon. The numbers must be separated by commas, and the name of the functional group that follows must be separated by a dash. When there are two of the same functional group, the name must have the prefix "di". When there are three of the same functional group, the name must have the prefix "tri". When there are four of the same functional group, the name must have the prefix "tetra". However, these prefixes cannot be used when determining the alphabetical priorities. There must always be commas between the numbers and the dashes that are between the numbers and the names.

8) If the substituents of the cycloalkane are related by the cis or trans configuration, then indicate the configuration by placing "cis-" or "trans-" in front of the name of the structure

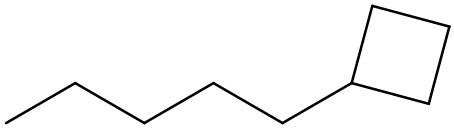
9) After all the functional groups and substituents have been mentioned with their corresponding numbers, the name of the cycloalkane can follow.



1-(*sec*-butyl)-3-isopropylcyclohexane

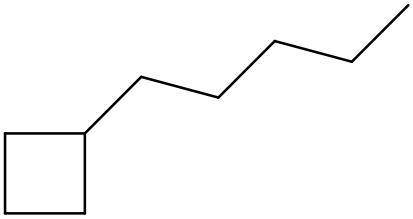


(2-methylpentyl)cyclobutane

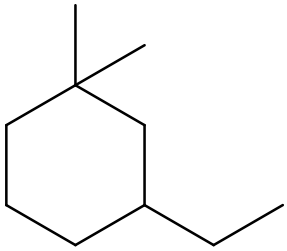


1-Cyclobutylpentane

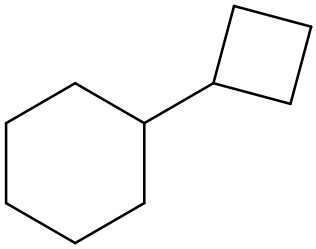
Not



pentylcyclobutane



3-ethyl-1,1-dimethylcyclohexane



cyclobutylcyclohexane

ISOMERISM IN ALKANES

Alkanes possess structural isomers of class chain isomers.

Example

A hydrocarbon Q has a vapour density of 36 with empirical formula C_5H_{12}.

(a) Determine the molecular formula of Q

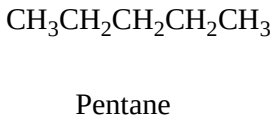
(b) Write down the possible isomers of Q and their IUPAC names

Soln:

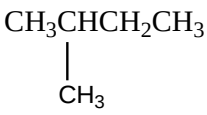
(a) *Molecular mass = 36x2 = 72g*

$(C_5H_{12})_n = 72 \Rightarrow 72n = 72 \therefore n = 1$ *M.F of Q is C_5H_{12}*

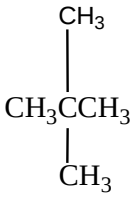
(b)



Pentane



2-methylbutane



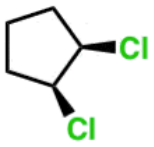
2,2-dimethylpropane

cis– and _trans_- Isomerism ("Geometrical Isomerism") In Rings

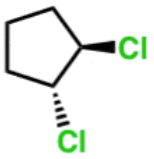
Small rings can't be turned "inside out" without breaking bonds. One of the most important consequences of this is that it can lead to the existence of *stereoisomers* – molecules which share the same molecular formula and the same connectivity but have a different arrangement of atoms in space.

These two versions of 1,2 dichlorocyclopentane, (shown below) are an example. They have the same connectivity – both are 1,2-dichlorocyclopentane – but have different arrangements of their atoms in space. The chlorines are on the same side of the ring in the left-hand isomer (both "wedges", coming out of the page) and on the opposite sides (one wedged, one dashed) on the right-hand isomer.

Review: Cis and trans isomers ("geometrical isomers") in rings



cis-1,2-dichlorocyclopentane



trans-1,2-dichlorocyclopentane

- In the cis isomer the two groups point in the same direction relative to the plane of the ring. In the trans isomer they point in opposite directions.
- They have different physical properties (e.g. melting points, boiling points)
- They are stereoisomers: specifically, diastereomers.
  cis-trans isomers are sometimes called geometric isomers (a subset of diastereomers)
- Geometrical isomers are only possible because there is no free rotation in small rings.

These two molecules **cannot be interconverted through rotation of the C-C bond without rupturing the ring**. They are therefore *isomers.* Molecules which have the **same connectivity but different arrangement in space** are known as ***stereoisomers***.

Specifically, the relationship between the two molecules above is that of *diastereomers:* stereoisomers which are not mirror images of each other. These two molecules have different physical properties – different boiling points, melting points, reactivities, spectral characteristics and so on.

NB. The other subclass of stereoisomer is "enantiomers". We apply this to two stereoisomers which are (non-superimposable) mirror images of each other. Also: keep in mind that the terms "diastereomer" and "enantiomer" denote comparative relationships, like the term's "brother" or "cousin".

Use of *cis*- And *trans*- Notation in Rings

The terms cis- and *trans*– are used to denote the *relative* configuration of two groups to each other in situations where there is restricted rotation.

[Side note: the "restricted rotation" is how cis- and trans- subtly differs from syn and anti, which we use in cases where there is free rotation, such as the orientation of methyl groups in "eclipsed" and "staggered" butane. Bottom line: ***syn and anti forms can generally be interconverted through bond rotation: cis and trans forms cannot****.]*

In nomenclature, "*cis*" is used to distinguish the isomer where **two identical groups** (e.g., the two chlorines in 1,2-dichlorocyclopentane) are pointing in the **same** direction from the plane of the

ring, and *trans* to distinguish the isomer where they point in **opposite** directions. [*You might also hear organic chemists say, "the chlorines are cis to each other" or "the hydrogens are trans to one another".*]

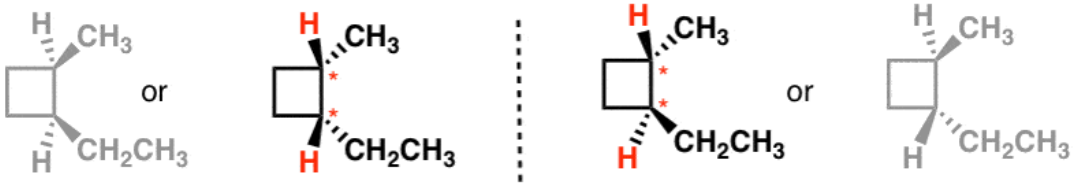
In order for *cis*- *trans*- isomerism to exist in rings, we need two conditions:

- two (and only two) carbons **each** bearing non-identical substituents above and below the ring
- the two carbons have *at least* one of those substituents in common

In 1,2-dichlorocyclopentane we saw that C-1 and C-2 each had non-identical substituents (H and Cl) above and below the ring, and they each had at least one substituent in common (in fact they have two substituents in common: H and Cl).

Here's another example: *cis*- and *trans*– 1-ethyl-2-methylcyclobutane. Note that they **each** have two carbons which **each** bear non-identical substituents above and below the ring (H and CH_3; H and CH_2CH_3). They also have at least one substituent in common (**H**). So, we can refer to *cis*-1-ethyl-2-methylcyclohexane as the isomer where the two hydrogens are pointing in the same direction, and *trans* where they point in opposite directions.

We can use *cis*- and *trans*- so long as the two carbons have at least one identical substituent above/below the ring (in this case, H)



cis-1-ethyl-2-methyl cyclobutane *trans*-1-ethyl-2-methyl cyclobutane

[Note if you've covered chirality: note that each molecule contains two chiral centers: the *cis*- and *trans*- forms exist as a pair of enantiomers [one of each is greyscaled]

cis- and *trans*- thus refers to the "relative" configuration of the two identical groups. The "absolute" configuration is denoted by the *(R)/(S)* system.

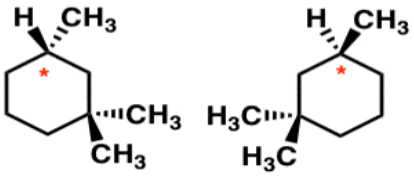
If you've covered chirality, you might also note an interesting fact: there are two ways to draw each of the *cis*- and *trans*– isomers, and they can't be superimposed on each other. These are *enantiomers*, by the way.

So *cis*- and *trans*- doesn't specify which enantiomer (it can be applied to either). It's just describing the *relative* configuration of the two groups (**H** in this case). If we want to specify a particular enantiomer, we need to use the Cahn-Ingold-Prelog (CIP) system of assigning *R* and *S* configurations, which provides us with the "absolute" configuration. In that

case, *cis*– and *trans*- is redundant. Because *cis*– and *trans*– is relative, it doesn't work if the two carbons don't share a common substituent. In that case you also have to use *(R)/(S)*. Looking at 2 examples where "cis" and trans" doesn't work in rings and leave it there.

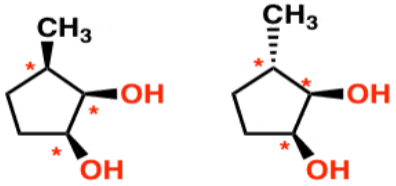
2 Cases where *cis-trans* isomerism is *not* possible in rings:

Only 1 carbon with two different groups above & below the plane:



Same molecule, just rotated

Three or more carbons with 2 different substituents above/ below the plane:



Too many possibilities:
(cis- trans- only allows for 2)

Use (R)/(S) instead

PREPARATION OF ALKANES

1. HYDROGENATION OF ALKENES AND ALKYNES

This method provides one of the most suitable methods for preparing Alkanes. It used to deduce the number of the double or triple bond in the unsaturated hydrocarbon.

The method requires catalyst such as Nickel, Platinum or Palladium. Nickel requires an elevated temperature of 150^{o}C whereas Platinum and Palladium requires ordinary temperature.

This reaction is used to determine the molecular mass of the Alkanes or Alkenes or Alkynes based upon the stoichiometry of the reaction

$$C_nH_{2n} + H_2 \xrightarrow[150^oC]{Ni} C_nH_{2n+2}$$

e.g.

$$CH_3CH{=}CHCH_3 \xrightarrow[150^oC]{H_2 / Ni} CH_3CH_2CH_2CH_3$$

Or

$$C_nH_{2n-2} + 2H_2 \xrightarrow[150^oC]{Ni} C_nH_{2n+2}$$

e.g.

$$CH_3C{\equiv}CCH_3 \xrightarrow[150^oC]{2H_2 / Ni} CH_3CH_2CH_2CH_3$$

Example

2.24dm^3 of Hydrogen gas at s.t.p reacts with 8.4g of hydrocarbon Q as represented by the equation below:

$$RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3$$

(a) Identify the functional group in the hydrocarbon Q

(b) Determine the molecular mass of Q hence that of R

(c) Write the:

(i) Molecular formula of Q

(ii) Possible isomers of Q and their IUPAC names

(1 mole of a gas occupies 22.4dm^3)

Soln:

(a) Alkenes

(b) Moles of Hydrogen gas reacted = $\frac{2.24}{22.4} = 0.1$

$\Rightarrow$*Moles of the Alkenes = 0.1 (since the mole ratio is 1: 1) hence the RFM = 0.1x8.4 = 84*

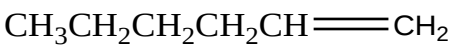
Molecular mass of Q = 84g

$\Rightarrow$ *R + 2(12) + 3(1) = 84 thus R = 57g*

(c) (i) From the general formula of Alkenes C_nH_{2n}

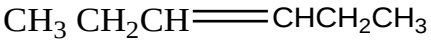
$\Rightarrow n(12) + 2n(1) = 84$ *or* $n = 6$ $\therefore$ *M.F of Q is* C_6H_{12}

(ii)

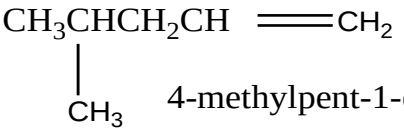


Hex-1-ene

Hex-2-ene

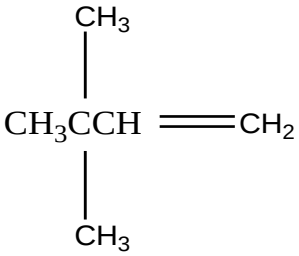


Hex-3-ene



and

4-methylpent-1-ene



3,3-dimethylpropene

2. KOLBE'S SYNTHESIS

When aqueous solution of sodium salt of the carboxylic acid is electrolyzed, an alkane is liberated at the anode and carbon dioxide at the cathode.

This is suitable for preparing symmetrical alkane of the R-R.

i.e.

$$2\ RCOO^- \longrightarrow R\text{-}R + 2CO_2 + 2e$$

e.g.

$$CH_3COO^- \longrightarrow CH_3CH_3 + CO_2 + 2e$$

3. DECARBOXYLATION METHOD

The sodium salt of the carboxylic acid is heated with soda lime, which contains sodium hydroxide and calcium oxide.

This reaction decreases the carbon chain by one carbon

$$RCOONa \xrightarrow[Heat]{Sodalime} RH + Na_2CO_3$$

$$CH_3COONa \xrightarrow[Heat]{NaOH\ (s)} CH_4$$

4. FROM ALKYL HALIDES

Reduction of alkyl halides also generates Alkanes. This can be done by using Zinc-Copper couple in ethanol or using lithium aluminum hydride in dry ether.

i.e.

$$RX \xrightarrow[Dry\ Ether]{LiAlH_4} RH + LiAlX_4$$

$$RX + 2H^+ \xrightarrow[Ethanol]{Zn\text{-}Cu\ Couple} RH + Zn^{2+} + X^-$$

e.g.

$$CH_3CH_2Br \xrightarrow[Dry\ Ether]{LiAlH_4} CH_3CH_3$$

Hydrolysis of Grignard reagent also gives rise to alkane

$$RX + Mg \xrightarrow{\text{Dry Ether}} RMgX \quad \text{(Alkyl magnesium halide)}$$

$$RMgX + H_2O \xrightarrow[\text{or } H_2SO_4]{HCl} RH + Mg(OH)X$$

e.g.

$$CH_3MgCl \xrightarrow[H_2SO_4]{H_2O} CH_4$$

5. WURTZ REACTION

Haloalkanes react with metallic sodium in dry ether to yield Alkanes of higher molecular mass and the carbons atoms are in even numbers.

Greater yield is obtained when the alkane has a higher molecular mass.

i.e.

$$2RX + 2\,Na \xrightarrow{\text{Dry ether}} R\text{-}R + 2NaX$$

e.g.

$$CH_3CH_2CH_2Br \xrightarrow[\text{Dry ether}]{Na} CH_3CH_2CH_2CH_2CH_2CH_3$$

$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[\text{Dry ether}]{Na} CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCHCH_3 \quad (CH_3 \text{ on } CH_3)$$

FOR METHANE

Hydrolysis of Aluminum carbide with hot water or dilute mineral acids form methane

$$Al_4C_3 + 12\,HCl \longrightarrow 3CH_4 + 4AlCl_3$$

N.B. The diagonal carbide can also be used i.e., Beryllium carbide

REACTIONS OF ALKANES

Alkanes are generally unreactive compared to alkenes and alkynes.

Reasons:

- The C-C and C-H bonds are strong therefore unless heated to higher temperatures or subjected to ultraviolet light.
- Carbon and Hydrogen have nearly the same electronegativity value therefore the bonds are slightly polarized.
- There are no lone pairs of electrons in Alkanes therefore Alkanes are not attacked by acids.

However, under certain conditions, some of the reactions of Alkanes (paraffins) include:

1. COMBUSTION

Alkane's burn in excess oxygen to form carbon dioxide and water, the reaction is exothermic and it can be used to determine the molecular formula of the Alkanes.

$$C_nH_{2n+2} + (3n+1)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

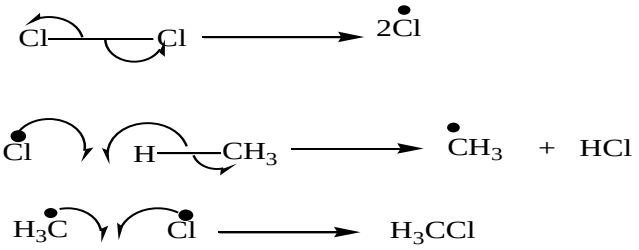
2. CHLORINATION OR BROMINATION

Alkanes react with halogens when heated at 250-400^oC or in presence of Ultraviolet light to form a mixture of products which are difficult to separate.

The reactivity is the order of Fluorine> Chlorine> Bromine> Iodine. Iodine does not react with Alkanes while Fluorine reacts explosively.

$$CH_4 \xrightarrow[\text{U.V.light}]{Cl_2} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

Mechanism



N.B. The reaction mechanisms repeat to generate the rest of the products.

3. NITRATION REACTION

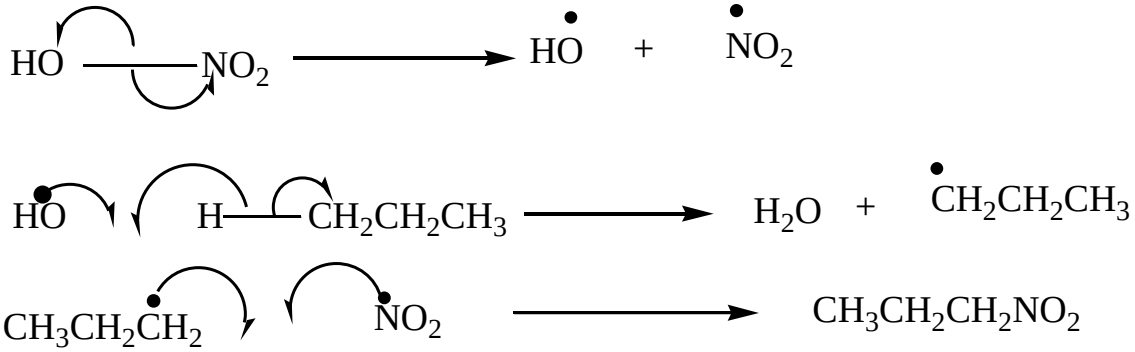
Alkanes react with nitric acid at about 400^{o}C via free radical mechanism to form nitroalkane

$$RH \xrightarrow[400^{o}C]{HNO_3} RNO_2 + H_2O$$

e.g.

$$CH_3CH_2CH_3 \xrightarrow[400^{o}C]{HNO_3} CH_3CH_2CH_2NO_2$$

Mechanism

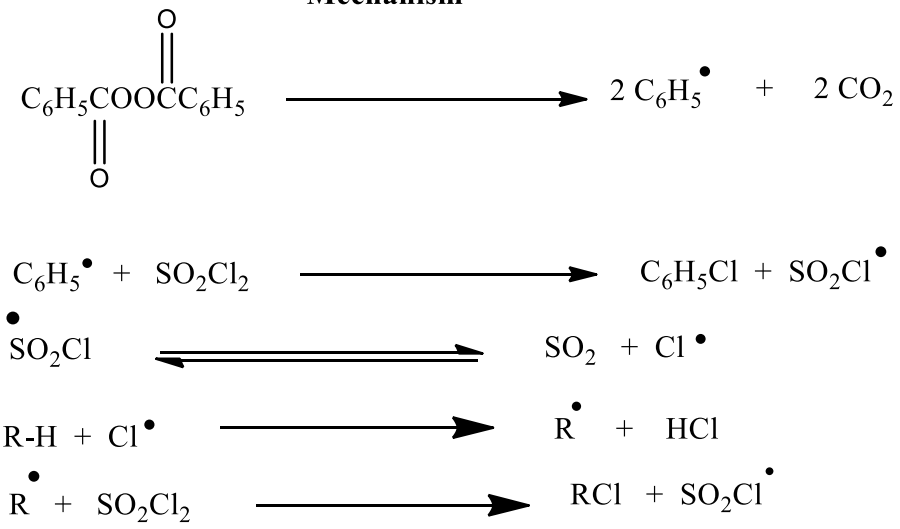


4. HALOGENATION USING SULPHURYL CHLORIDE

An organic peroxide is used as an initiator.

$$R\text{-}H + SO_2Cl_2 \xrightarrow[\text{UV light}]{ROOR} R\text{-}Cl + SO_2 + HCl$$

Mechanism


C6H5COOCC6H5
2 C6H5•
+
2 CO2
C6H5• + SO2Cl2
C6H5Cl + SO2Cl•
•SO2Cl
SO2 + Cl•
R-H + Cl•
R• + HCl
R• + SO2Cl2
RCl + SO2Cl•