Organic chemistry – alkane crib notes

Alkanes

Structure & bonding

All alkanes contain only single C – C bonds.

All alkanes have sp^3 hybridised orbitals. This is where an electron from the Carbon $2s^2$ orbital is promoted (moved) to the empty 2p orbital. This reduces the energy between s and p orbitals giving 4 equivalent sp orbitals. They are all sigma (σ) bonds.

The C-C bond is formed by a "side on" overlap of one of these orbitals. The other three sp^3 orbitals bond with other groups.

The C – C bond is electronically neutral – it has no charge making it unreactive. As there is no charge on the C – C bond, it is also insoluble in polar solvents (such as water).

The bond angle between C and H in the simplest alkane is 109º23'. At this angle, the 4 hydrogens are as far away from each other as possible. This is known as being sterically favourable.

Boiling point

The longer the carbon chain, the higher the boiling point. At room temperature, anything with a length less than 5 carbons will be a gas, between 5 and 40 are liquids with above 40 being solid (called waxes)

Naming and formulae

The formulae of pure hydrocarbons follows the C_nH_{2n+2} rule (for every carbon in the chain there are twice that number + 2 hydrogens)

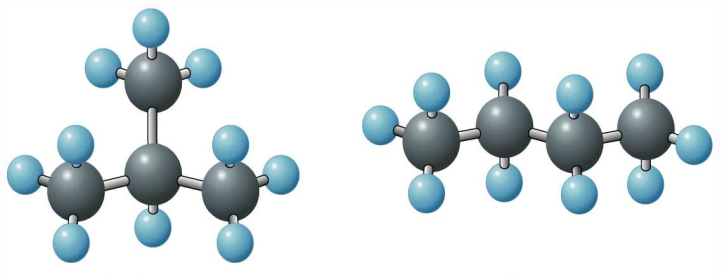
Name	Number of C
Methane	1
Ethane	2
Propane	3
Butane	4
Pentane	5

Name	Number of C
Hexane	6
Heptane	7
Octane	8
Nonane	9
Decane	10

Isomerism

Isomerism means “same formula, different structure”. Alkanes have structural isomers. Butane has a formula of C_4H_{10}, 2-methyl propane also has the same formula but will have different chemical properties.

For example



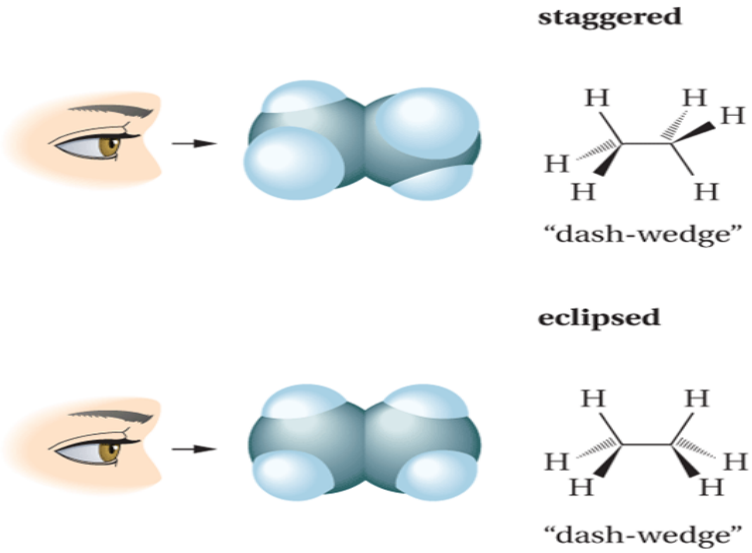
2-methyl propane
C_4H_{10}

Butane
C_4H_{10}

Optical isomerism

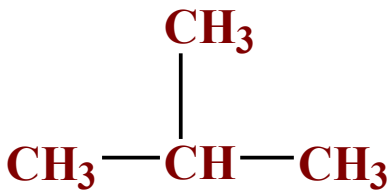
Optical means “to look at”. This is a form of stereoisomerism (the other type is not seen in alkanes – that is geometric). There are two ways to draw an optical isomer – staggered or eclipsed.

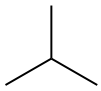
An alkane will have completely free rotation around each C-C bond which means the hydrogens (or other substituted groups) can be anywhere at any time. In practice, they are not – the H (or groups) will always try to be as far away as possible from each other at all times which is why there are two ways to draw an optical isomer.



Drawing an alkane

There are two ways of drawing any organic structure; skeletal and non-skeletal.





Non-skeletal form. It is usual to exclude the H as it is assumed that if nothing is drawn next a C, it will be H.

Skeletal form. A carbon is at the end of each line or at a point. There are 4 carbons here.

Naming system for alkanes

For simple hydrocarbons

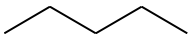
1. Find the longest line of carbons – this does not have to be in a straight line, so be careful! This will give the "skeletal" name
2. Add "ane" to the end of the skeletal name

Skeletal names

Number of C	Skeletal name
1	Meth
2	Eth
3	Prop
4	But
5	Pent

Number of C	Skeletal name
6	Hex
7	Hept
8	Oct
9	Non
10	Dec

e.g.

 This has 5 carbons (one on each end and one on each point). This will give a skeletal name of "Pent". As all of the bonds are single bonds, "ane" is added onto the end of the skeletal name. It is called "Pentane".

Hydrocarbons with a branch

A branch is something which comes off the longest carbon chain. Anything that comes off the longest chain is known as a "group"

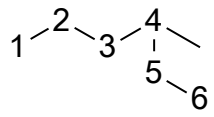
A group substitutes a hydrogen.

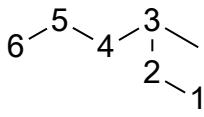
Group names

For just a hydrocarbon group, count the number of carbons (gives a skeletal name) and add "yl" after the skeletal part.

The position of the group is also important. To find the position, count from the end of the chain until the carbon with the branch on is reached. Do the same from the other end. Whichever is the smaller number is the position of the chain

e.g.

(a) 



(b)

The longest chain length here is 6 carbons (notice that it is not the longest straight line). This will give a skeletal name of “hex”. As they are all single bonds, it is an alkane, therefore it will be hexane.

There is also a group coming off the chain. As there is nothing else written on that group, it is safe to say it is a carbon (remember for skeletal diagrams unless it says otherwise the end and points are ALWAYS carbon).

In both (a) and (b) there is a one carbon branch giving a skeletal name of “meth”. As it comes off the chain, it is a group so it is a “methyl” group.

If the carbons are counted from the left, the methyl group will be on the 4th carbon. If the carbons are counted from the right, it is on the 3rd carbon. As 3 is smaller than 4, the group is said to be on the “3 carbon”. This gives a full name of

3-methyl-hexane

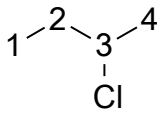
Non-carbon groups

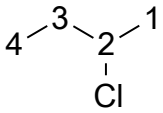
It is not uncommon for an alkane to contain group VII elements (halides).

Element	**Symbol**	**Group name**
Fluorine	F	Fluoro
Chlorine	Cl	Chloro

Element	**Symbol**	**Group name**
Bromine	Br	Bromo
Iodine	I	Iodo

The same naming rules apply.





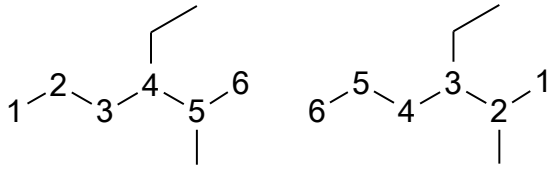
Longest C chain contains 4 carbons, gives a skeletal name of “But”
All bonds are single, so it is an alkane, gives the full chain name of “Butane”
There is a branch. It is a chlorine , so will have the group name “chloro”
Count from the left, the group is on the 3rd carbon.
Count from the right, the group is on the 2nd carbon.
Name is 2-chloro-butane

Chains with multiple branches

An chain may contain multiple branches – they need to be named correctly and this is done by “order of priority”.

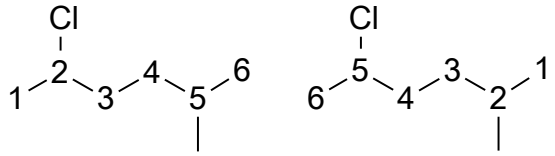
Lowest order are hydrocarbons with the higher the weight, the lower the priority
Halides have a higher priority in naming than hydrocarbons with the heavier halides having a higher priority than the lighter halides

e.g.



Longest carbon chain = 6 C, skeletal name = “Hex”
All bonds are single on the chain, ending is “ane”, full chain = “hexane”
There are two branches, a methyl and ethyl. From the left, ethyl is on the 4 carbon and methyl on the 5 carbon, from the right methyl is on the 2 carbon, ethyl is on the 3.
According to the priority rules, methyl is more important than ethyl, so must have the smaller number
Name is therefore 2-methyl, 3-ethylhexane

e.g.



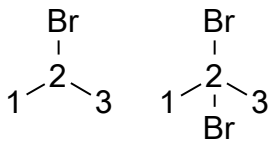
Longest carbon chain = 6C, skeletal name = “Hex”
All bond are single on the chain, ending is “ane”, full chain = “hexane”
There are two branches, a chloro and a methyl. From the left, chloro is on the 2C and methyl is on the 5C, from the right methyl is on the 2C and chloro is on the 5C
According to the priority rules, halides are more important than alkyl groups so must have the smaller number
Name is 2-chloro, 5-methylhexane

When there are more than one of the same group on the same carbon

Again, the name of the carbon chain is the same as before
Again, the number of the carbon with the substitutions is given the same as before

The difference now is that a “multiplier” has to be added before the name of the group

e.g.



Chain has 3 carbons, all with a single bond = propane
The first propane has a single group on the 2C so is called 2-bromopropane

The second propane has two groups on the 2C that are the same so is called 2,2-dibromopropane

Number of substitutions with the same group	Multiplier prefix
2	di
3	tri
4	tetra

Note though that as the carbon has been substituted twice the number has to be given twice. If a carbon is substituted three times, the number would be given 3 times.

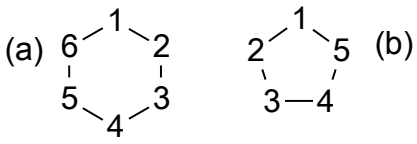
When there are more than one group on the same carbon

Name the longest chain, find the substituted carbon, name the substitutions alphabetically (priority is not important here as the substitution is on the same carbon). Remember that the substituted carbon number has to be given for each group (e.g. 2-fluoro-2-chloropropane and not 2-fluoro-chloropropane. This second example would indicate that the chloro is a “terminal” group. Terminal means “at the end”)

Cyclo compounds

A cyclic compound is one where the carbons are in a ring. The naming rules for the pure hydrocarbon cyclo-compounds are the same for the non-cyclic compounds. Count the number of carbons for the skeletal name, add “ane” to the end if they are all single bonds.

The difference now is that the name is prefixed with “cyclo”



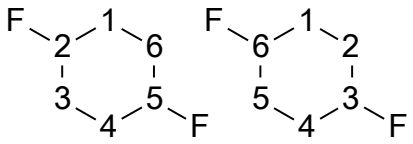
e.g. (a) has 6 carbons = hex, all single bonds = ane. As they are in a ring, the name is preceded by cyclo. Name = cyclohexane

(b) has 5 carbons = pent, all single bonds = ane. As they are in a ring, the name is preceded by cyclo. Name = cyclopentane

Cyclo compounds under 5 carbons will form, but are energetically unfavourable; the angle between each C is much lower than 100º (roughly 60º for cyclopropane and 90º for cyclobutane). When the C-C bonds break in these, a large amount of energy is released.

With cyclo compounds containing 5C, the bond angle between each C is around 100º and is much more stable with cyclohexane (6C) being about 108º (almost the same as for a standard non-cyclic alkane)

Naming of the substituted cyclo alkanes have the same rules as for non-cyclic alkanes with one important difference. As the chain is in a ring, the numbering can go clockwise or anti-clockwise. To tell if the numbering goes clockwise or anti-clockwise the “missing C” rule can be used.



These are the same molecule, but can be called 2,5-fluoro-cyclohexane or 3,6-fluoro-cyclohexane.

To decide which one, the “missing C” rule can be used. This rule says to look for the substitution with the least number of non-substituted carbons. If C1 is taken as the top carbon, the one on the left has no missing carbon carbons going anti-clockwise, but one missing carbon going clockwise. The numbering therefore goes anti-clockwise. It is therefore 2,5-fluoro-cyclohexane

Reactions of alkanes

As there is no charge on the C-C chain, alkanes are fairly unreactive. The only important ones to understand are the reactions with halides and oxygen.

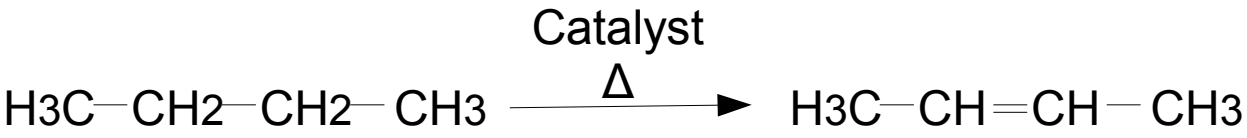
With oxygen

The reaction with oxygen is known as a combustion reaction (they molecule is burned). There are two types of combustion reaction : complete and incomplete.

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ (complete – carbon dioxide is formed)
$C_3H_8 + 3½\ O_2 \rightarrow 3CO + 4H_2O$ (incomplete – carbon monoxide is formed)

Dehydration

An alkane is reacted at high temperature over a suitable catalyst to form an alkene and H_2. An alkene is a carbon chain with one (or more) double bonds.



Alkenes are far more useful chemically.

Halogenation (reactions with halides)

This is the replacement of a hydrogen with a group VII element and is usually performed via a “free radical mechanism”.

A free radical is a highly reactive, uncharged element which are formed by exposing the halide to light.

Free radical mechanisms follow a three step mechanism

1. Initiation (the formation of the free radical)
2. Propagation (formation of more radicals and new compounds)

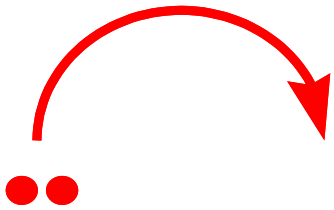
3. Termination (all of the reactants have been used up)

Free radical mechanisms are difficult to control and moreover, are considered wasteful as the final product is not always the product that is required.

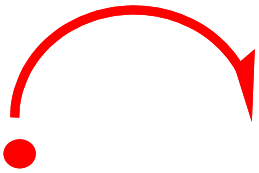
Curly arrows

Curly arrows indicate the direction that electrons move in. As electrons are negative, they will ALWAYS go to a positive charge.

There are two types of curly arrow



2 electrons move = full arrow



1 electron moves = ½ arrow

For most of the time, the double headed arrow is used. During free radical mechanisms, the single arrow is normally used.

Take the reaction between methane (CH_4) and chlorine (Cl_2).

1. Initiation

Here the Cl-Cl bond is broken to form 2 Cl radicals (written $Cl^{\bullet}$). The shared electrons in the bond have been broken. It is important to remember that ions have not formed, but the Cl in the p^5 state (electronically neutral, but very reactive) have.

This process is light initiated (Cl_2 is exposed to normal sunlight)

2. Propagation

The $Cl^{\bullet}$ are introduced into a reaction vessel containing methane. As the radicals are highly reactive, if they come into contact with methane, the radical will replace a hydrogen to form the stable chloromethane product.

A hydrogen radical is released.

If the $H^{\bullet}$ and $Cl^{\bullet}$ come into contact, they will form HCl.

The problem though is that a methyl radical can also be formed and there is nothing to stop further replacement of H with either $Cl^{\bullet}$, $CH_3^{\bullet}$ or even $H^{\bullet}$. The final mixture can (and will) contain lots of products and not just the intended product.

3. Termination

When all of the radicals (not just the $Cl^{\bullet}$ from the initiation step) have all reacted, or the source of $Cl^{\bullet}$ is removed or the reaction vessel is cooled sufficiently to stop further reactions, the reaction is said to have terminated.

As there can be a large number of products, it will cost a lot to separate out and obtained the desired compound. It is considered wasteful economically and energetically.