

Jagiellonian University Medical College
School of Medicine in English

Organic Chemistry GUIDE

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ORGANIC CHEMISTRY

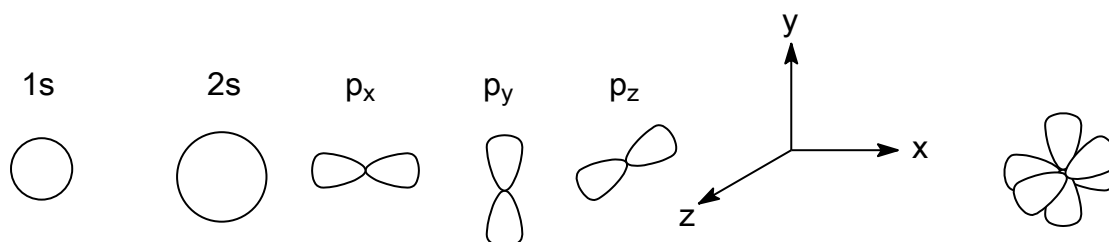
1. Structure and bonding in organic chemistry

Chemistry is everywhere around, and it is this branch of science that impacts our everyday life to the greatest extent. Organic chemistry in particular – it is absolutely vital for future physicians to understand what is actually going on in our organisms.

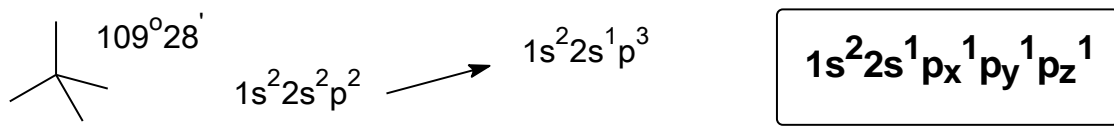
The number of recognized chemical compounds has steadily grown over the years – in 2013 there were over 75 million. Vast majority of them are organic compounds discovered or isolated from nature by chemists. In order to better appreciate this rather complex world we shall start off our guided tour from the carbon atom.

1.1. Hybridization and molecular shapes

Electron configuration of a carbon atom ${}_6\text{C}^{12}$: $1s^2 2s^2 2p^2$ shows that its four valence electrons occupy orbitals 2s (paired electrons) and 2p. What are the orbitals? Quantum mechanics says that the probability of encountering the electrons within the space limited by an orbital is much greater than outside it. The s orbitals remain balls with the radius greater for 2s than for 1s and the p orbitals resemble number 8 rotating along the axis. There are three possible p orbitals along x, y and z axes.

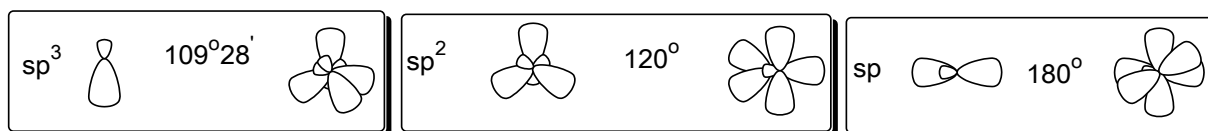


We know from praxis that carbon atoms are tetravalent and they form a tetrahedral structure with four equivalent bonds. It is the result of a promotion of one electron from 2s orbital to 2p orbital as their difference in energy is very small. According to Hund's rule the occupation of valence orbitals will be then $2s^1 2p_x^1 2p_y^1 2p_z^1$.



To explain the tetrahedral structure we should assume the so called hybridization (mixing) of orbitals. The first type of hybridization sp^3 hybridization happens in the 3D space ($sp_x p_y p_z$) so it is easy to imagine that the electrons as the negatively charged particles would prefer to be as far from each other as possible. Hence the axes of sp^3 orbitals will form the tetrahedral structure with the angle between each two of them equal to $109^\circ 28'$. But other types of hybridization are also possible. For sp^2 hybridization (e.g. $sp_x p_y$) three axes of hybrid orbitals

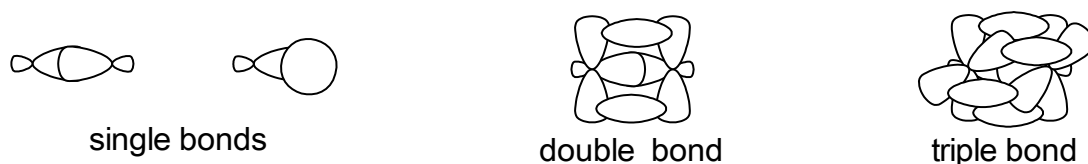
will be directed on a plane to the tops of a triangle. The angle between any two of them is then equal to 120° . But remember that there is still one non-hybrid orbital – in this case p_z with the axis perpendicular to this plane. Another possibility is sp hybridization (e.g. sp_x) with two axes of hybrid orbitals placed along the line in the opposite directions. The angle between them is then 180° and there are still two non-hybrid orbitals – in this case p_y and p_z with axes perpendicular to them and to each other.



Such an image of hybridization allows us to understand the spatial structure of organic molecules and the stability of bonds. Covalent bonds, most popular in organic molecules, are formed by electron pairs common for the two partner atoms. Those could well be the carbon atoms, building up the chain or ring structures, or the atoms of other elements like hydrogen, oxygen, nitrogen, sulfur, phosphorus, to name only those most popular in organic chemistry. But nowadays almost the entire Mendelejev's table can be built into organic structures. For example organometallic compounds have recently grown more significant in organic synthesis.

1.2. Carbon skeletons with single and multiple bonds, structural and skeleton formulas of organic compounds, homologous series

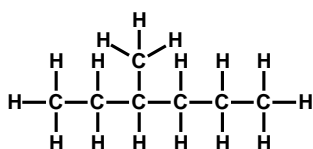
There are several types of bonds in organic molecules. Single bonds are formed when orbitals of two atoms overlap along their axes (molecular orbitals) so the electron pairs are formed. As shown below, this can happen through overlapping of the carbon sp^3 orbital with the s orbital of hydrogen (C-H bond) or through overlapping of the two sp^3 orbitals of the carbon atoms (C-C bond). Single bonds are called the σ bonds. The same can take place with the two sp^2 orbitals of the two carbon atoms. But then, apart from a single C-C bond formed, a side-by-side overlapping of the two non-hybrid p orbitals of both carbon atoms in the plane perpendicular to the plane of a single bond, is possible. In this way a double bond, called the π bond, is formed. Likewise with the sp hybrid orbitals. Two carbon atoms can make use of them to form a single bond. Additionally by the side overlapping of the two, perpendicular to each other, the non-hybrid orbitals can form two π bonds perpendicular to each other. It is then called a triple bond.



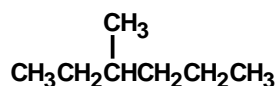
What may actually be inferred from this image is that the atoms connected by a single bond can rotate freely, whereas in the case of a double or a triple bond the rotation is impossible (as otherwise the overlapping would be broken up). When single, double or triple bonds are formed between the carbon atoms which results in the chain or ring molecules and when we add on the possibility of a single bond formation with hydrogen, oxygen, sulfur, nitrogen and other atoms as well as the double bond formation between carbon and oxygen, sulfur, nitrogen or other atoms (in the case of nitrogen also a triple bond formation is possible), we obtain the endless number of molecular structures, which only goes to demonstrate overall richness of organic chemistry.

Chemists order the organic compounds in series called the homologous series. The members of such series differ by $-\text{CH}_2-$ (methylene) group and usually have similar chemical properties, but their physical properties change proportionally to the number of atoms in the molecule. The simplest organic compounds are hydrocarbons composed exclusively of carbon and hydrogen. They form several homologous series of saturated hydrocarbons (with single bonds exclusively) called alkanes and unsaturated hydrocarbons (with double or triple bonds between the carbon atoms) called alkenes or alkynes, respectively. It goes without saying that other, more unsaturated hydrocarbons, are also feasible (e.g. with two or more multiple bonds in the molecule). How can we depict the structure of a hydrocarbon or the other organic molecules? By virtue of a molecular formula that shows the composition of the compound e.g. C_7H_{16}

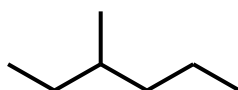
or by a structural formula that shows all the bonds present in the molecule:



or by a condensed structural formula - some groups of atoms appear without showing the bonds:

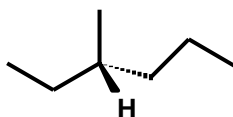


or by a line-angle (skeleton) formula showing precisely the carbon skeleton. At the end of each line the carbon atoms appear and all carbon atoms are connected with the corresponding



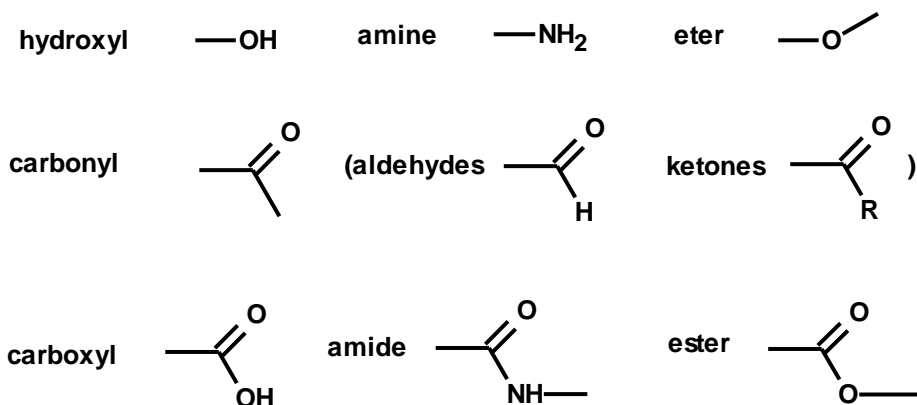
number of hydrogen atoms:

or the most advanced stereochemical formula that shows a 3D space arrangement of atoms:

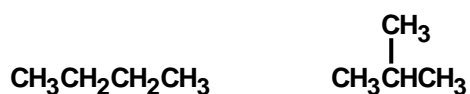


1.3. Functional groups, isomerism

The chemical properties of organic molecules depend not only on their carbon skeleton but also and mainly on the so called functional groups formed by the atoms other than carbon and hydrogen. Further below the key functional groups are shown:



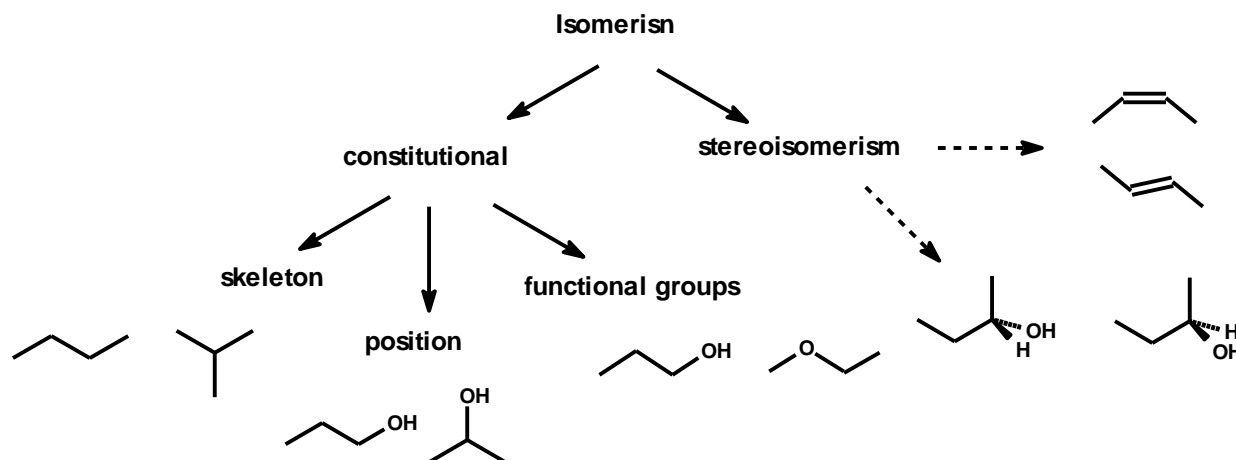
The atoms or the groups of atoms that replace the hydrogen atoms along the carbon skeleton are called substituents. Very often various halogens also play a role of substituents. The variety of organic compounds can be explained by isomerisms: the same molecular formula can correspond to various structural formulas. This possibility of isomerism is augmented by the introduction of functional groups into molecules. When testing the saturated hydrocarbons we can see that that the first members of homologous series of alkanes do not have isomers. But already in the case of butane C_4H_{10} we can draw the straight carbon chain as well as a branched one:



Usually the bulk physical properties of the compound depend strongly on the structure of their molecules. Essential is the space distance of particular atoms in the molecule. More compact molecules (here those with the branched chain) are usually more volatile due to a lower boiling point.

The picture below show various types of isomerism feasible in organic molecules. When we introduce a substituent into an organic molecule the constitutional isomerism starts already at the three carbons skeleton, as this substituent may be attached to side carbon atom or to the

carbon atom in the middle. A special type of isomerism occurs when we take into consideration a spatial arrangement of the atoms in the molecule (see Stereochemistry).

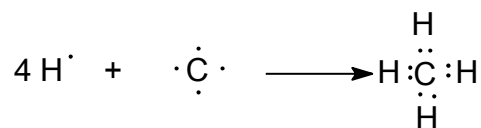


1.4. Lewis structures, formal charges, resonance

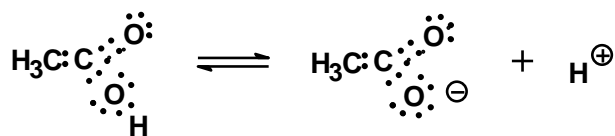
Sometimes Lewis formulas are used to depict the structure of organic molecules. These formulas show all the valence electrons of all atoms comprised within a molecule, depicted as single dots. These formulas are particularly important for showing some ionic structures and reactions. Let us consider these examples:



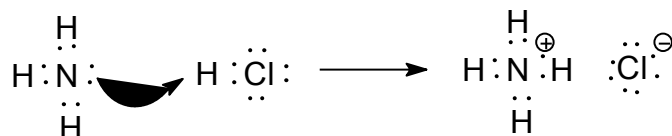
By comparing of usual number of valence electrons with the actual number of electrons in a given structure one can derive the so called formal charge of the atom. Please note that from a single bond between the atoms one electron is allocated to one partner and the other one to another partner. A question: would a carbon atom in a simplest hydrocarbon methane molecule possess any formal charge, then?



No, because from each bond one electron is allocated to the hydrogen atom and the other one to the carbon atom, so four electrons belong to carbon and this number is equal to the original number of carbon valence electrons. Some heteroatoms (different from carbon and hydrogen) very often possess lone electron pairs which are crucial for some reactions, as it can be seen in the example of carboxylic acid dissociation:

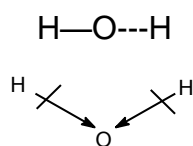


When we treat gaseous ammonia with gaseous hydrogen chloride we obtain a solid: ammonium chloride. This reaction is depicted below showing the formal charges: positive on the nitrogen atom (only four electrons instead of five) and negative on the chlorine atom (eight electrons instead of seven):



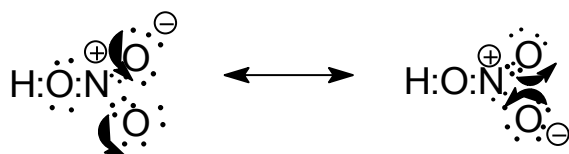
Movement of electrons is usually marked by curly arrows.

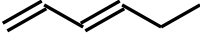
Formal charges are not the same as partial charges. Usually covalent σ -bonds connecting atoms of different elements are polarized depending on electronegativity of these atoms. The σ -bond is then slightly shifted toward more electronegative atom. These partial charges formed in this way are marked usually by δ^+ on more electropositive atom and δ^- on more electronegative atom as in water molecule: $\delta^+ \delta^- \delta^+$



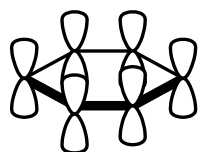
It can be also marked by $\overset{+}{\rightarrow}$ that shows a tendency in electron density. Summing up these effects in space tell us whether a particular molecule is polar or not.

The structure of some molecules cannot be depicted by a single formula, e.g. nitric acid:

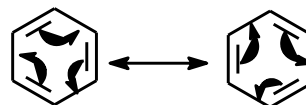


We call it resonance i.e. the electrons in this molecule are delocalized. There exists only one molecule but we are unable to express its properties by a single formula – we need at least two formulas for this purpose. This is characteristic for the compounds with the conjugated electron systems: double bonds separated by a single bond (or an atom with a lone electron pair separated from a multiple bond by a single bond), e.g.  The same story goes for with an unsaturated aromatic hydrocarbon benzene C_6H_6 with the three double bonds in a conjugated system:

Delocalized electrons in benzene



Kekulé structures

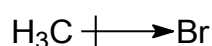


The electrons in this cyclic planar hydrocarbon form a delocalized electron cloud. The proof of this is provided by physicochemical data showing e.g. bond length absolutely equal for all carbon-carbon bonds, when usually a double bond is shorter than a single one. Resonance or mesomeric structures are usually linked by the following arrow: \leftrightarrow and specific properties of a molecule are presented by all of them together. Molecules represented by resonance structures are usually very stable. In order to destroy a resonance system, extra energy is required. That is why such molecules prefer certain types of reactions e.g. substitution predominates addition.

2. Classification and properties of organic compounds

2.1. Hydrocarbons (alkanes, alkenes, alkynes, aromatic compounds), alkyl halides

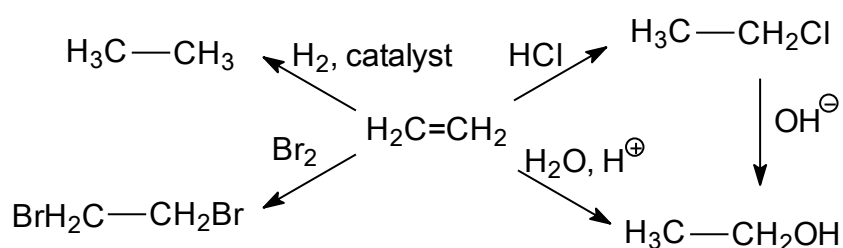
Alkanes represent a homologous series of saturated hydrocarbons C_nH_{2n+2} . The first four members: methane, ethane, propane and butane are gaseous under standard conditions, further are liquids and, starting from C_{17} - solids. They can be encountered in nature as natural gas and crude petroleum. Higher homologues can appear as open chain or branched hydrocarbons. The chains in saturated hydrocarbons may be straight then we have to deal with normal alkanes, in other words n -alkanes, or with the branched alkanes. Similar class form cycloalkanes C_nH_{2n} cyclic saturated hydrocarbons. Alkanes are chemically and biologically inert. They react practically with oxygen only (this is a combustion leading to CO_2 and H_2O or CO and H_2O or even to C in a form of soot and H_2O , depending on the amount of oxygen used) and halogens under irradiation to give various haloalkanes (alkyl halides). These derivatives are very important because having highly polarised carbon-halogen bond they are very reactive and can undergo substitution with electron rich molecules. The big difference in electronegativity of carbon and halogen leads to the formation of partial negative charge on the halogen atom and partial



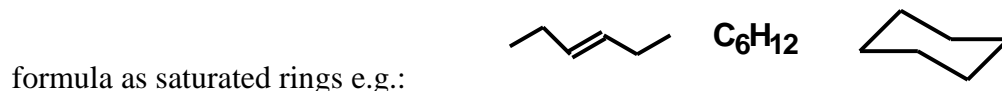
positive charge on the carbon atom and accounts for its susceptibility to the attack of negatively charged species, so substitution may occur.

In contrast to alkanes, unsaturated hydrocarbons with one double bond – alkenes C_nH_{2n} and with one triple bond – alkynes C_nH_{2n-2} are far more reactive. Both classes of compounds form

homologous series in which the physical properties, as usual, change gradually according to the growing number of carbon atoms. Also in this group of unsaturated compounds exist other homologous series of compounds with the branched chains and with more multiple bonds. The multiple bonds give these compounds their chemical character - there are unsaturated because double or triple bonds are susceptible to addition. The π bond between two carbon atoms can open easily and two new substituents are attached to both carbon atoms. At the same time their hybridization changes from sp^2 or sp to sp^3 so saturated derivative is formed. This is the addition reaction. Usually hydrogen, hydrogen halide, halide or water molecules are added to a multiple bond. Alkanes, haloalkanes, more substituted haloalkanes, or alcohols are formed, respectively as it is shown for ethene molecule:



As we have seen the unsaturated hydrocarbons with one double bond have the same general



And unsaturated hydrocarbons with one triple bond have the same general formula as those



So it is the high time to define the elements of unsaturation: a double bond = one element of unsaturation; a ring = one element of unsaturation; a triple bond = two elements of unsaturation. This definition is more general (it concerns also compounds with nitrogen, oxygen...). What is more, we can calculate the elements of unsaturation S of a compound on the basis of its molecular formula:

$$S = \frac{2 + 2x(\text{IV}) + 1xm(\text{III}) - 1xn(\text{I})}{2}$$

where l means the number of tetravalent atoms, m means the number of trivalent atoms, and n means

the number of monovalent atoms (usually hydrogen but also halogens) in the molecule.

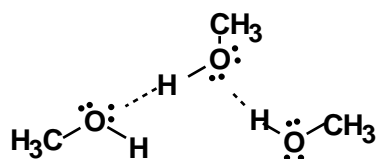
2.2. Alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids and their derivatives

As a result of the substitution of the halogen atom in haloalkanes by hydroxyl group $-\text{OH}$ or by the addition of water molecule to the double bond in alkenes a new class of compounds with hydroxyl functional group is formed: alcohols. Among the possible isomeric alcohols

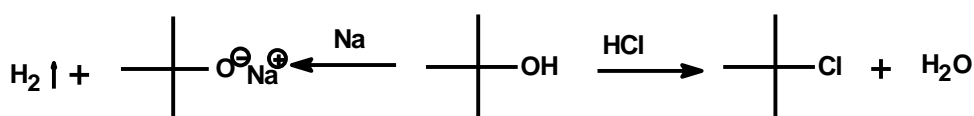
primary $\text{—CH}_2\text{—OH}$ secondary $\begin{array}{c} \text{OH} \\ | \\ \text{—CH—} \end{array}$ or tertiary $\begin{array}{c} \text{OH} \\ | \\ \text{—C—} \\ | \end{array}$ alcohols can be enumerated.

Most popular alcohols are liquid and are used as solvents. In the homologous series of alcohols the physical properties are changed gradually but surprisingly enough the boiling points of these compounds are much higher than those of the hydrocarbons of similar molecular weight. It is the result of association of the alcohol molecules caused by hydrogen bonding. Highly polarized O-H bond is responsible for that phenomenon. Partial negative charge and additionally lone electron pairs on oxygen atom can attach the positively charged

hydrogen of the neighbouring molecule.

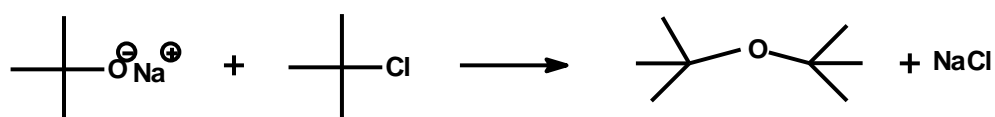


The polarisation of both C-O and O-H bonds in the molecules of alcohols are also responsible for their chemical properties. They are weak acids, react with alkali metals under anhydrous conditions, causing hydrogen evolution. The hydroxyl group in alcohols can also be substituted e.g. by the halogens:



Special class of compounds possessing hydroxyl functional group constitute phenols. In this case hydroxyl group is attached to aromatic ring e.g. $\text{C}_6\text{H}_5\text{OH}$. Phenols, having molecular mass bigger than popular alcohols are usually solids. From a chemical point of view they are much more acidic than alcohols, and very often also show toxic and corrosive properties.

Alcohols can be treated as the derivatives of water: a carbon skeleton of a hydrocarbon has replaced one hydrogen atom in a water molecule. When this happens twice a new class of compounds is formed i.e. ethers. They are usually obtained by the reaction of haloalkanes with alkali metal salts of alcohols:

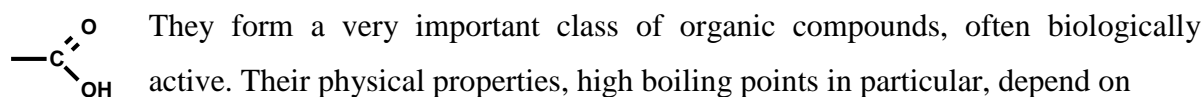


Ethers are volatile, unreactive compounds, very useful in organic synthesis as excellent and inert solvents.

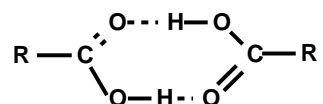
Alcohols can be treated as the first stage of hydrocarbon oxidation. Further oxidation of alcohols (subtraction of hydrogen molecule from hydroxyl group and the neighbouring carbon

atom) provides carbonyl functional group $>C=O$ possessing double bond between carbon and oxygen atom. When the carbonyl group is attached to at least one hydrogen atom the functional group of aldehydes is formed and when it is attached to the two carbon skeletons then it results in ketones. These series of compounds are very important both from a practical point of view (e.g. aldehydes used as fragrances or ketones used as solvents) and in an organic synthesis. Aldehydes are more reactive than ketones. Due to the highly polarised $C=O$ bond both aldehydes and ketones are susceptible for addition of water, alcohols (the formation of hemiacetals and acetals and ketals) and amines. They can either be reduced to alcohols, or oxidized to carboxylic acids.

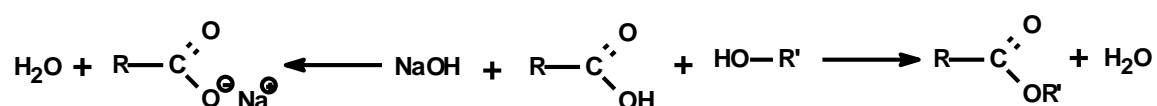
Oxidation of aldehydes, sometimes spontaneous and occurring under the influence of oxygen from the air produces carboxylic acids that possess a carboxyl functional group:



strong hydrogen bonds and double “head to tail” association of the molecules:

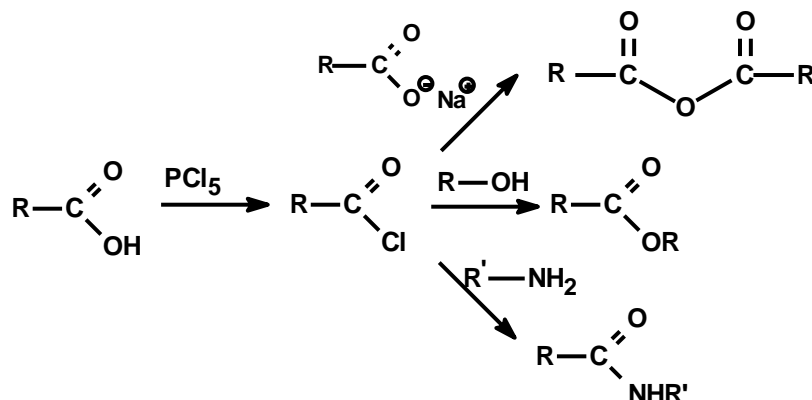


They form several homologous series depending on the number of carboxylic groups or other substituents (e.g. halogens or a hydroxyl group) in the molecule. Polarisation of bonds within carboxylic group prompts its high reactivity. As acids, these compounds can react both with active metals and metal hydroxides to produce salts. They also react with alcohols providing esters. In this condensation a water molecule is also produced:



Substitution of hydroxyl within carboxylic group gives numerous derivatives of acids of higher reactivity than the carboxylic acid itself. Acid chlorides are the result of $-\text{OH}$ replacement by $-\text{Cl}$. Acid amides are the results of $-\text{OH}$ replacement by $-\text{NH}_2$ (primary amides) or by $-\text{NHR}$ (secondary amides) or by $-\text{NR}^1\text{R}^2$ (tertiary amide) where R means the carbon skeleton of a hydrocarbon. The growing order of reactivity of acid derivatives is structured as follows: carboxylic acid, acid amide, ester, acid anhydride, acid halide. Therefore to carry out any reaction in acid derivatives it is useful to transform the acid by

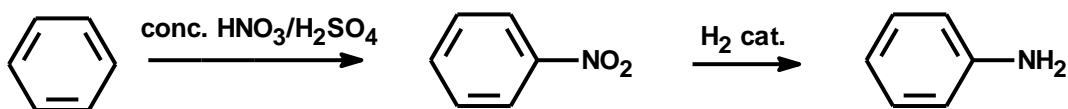
means of phosphorus (V) chloride into acid chloride and then use the corresponding reagents to secure a proper result:



2.3. Amines, nitro compounds, amino acids

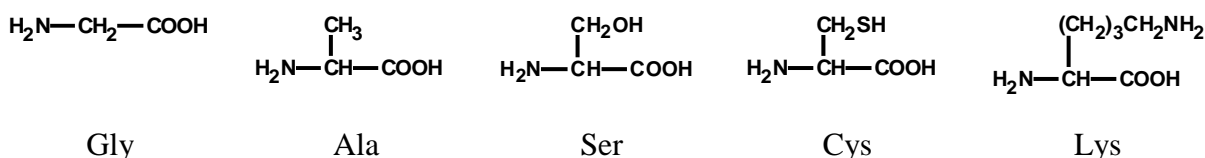
In analogy to alcohols, derived from water, amines are the organic derivatives of ammonia. Since in this case maximum three hydrogen atoms can be replaced by the carbon skeletons, it becomes feasible to obtain three classes of compounds: primary amines $\text{R}-\text{NH}_2$, secondary amines $\text{R}^1\text{R}^2\text{NH}$ and tertiary amines $\text{R}^1\text{R}^2\text{R}^3\text{N}$ where R means the carbon skeleton of hydrocarbon. Amines are relatively volatile compounds, more volatile than alcohols of similar molecular mass (weaker hydrogen bonds). They are usually toxic, yet many of them are biologically active, and are characterised by pungent smell. From a chemical point of view they represent organic bases, able to form salts with acids. This is owed to the lone electron pair of nitrogen atom that can bind a proton, that leads to ammonium cation. The basicity of amines is growing in the following order: primary < secondary < tertiary amines with R representing a saturated carbon skeleton. An opposite situation is represented by the aromatic amines with R representing an unsaturated ring skeleton with the delocalized electrons. Then the lone electron pair of nitrogen is involved in this delocalization (resonance), being a weaker electron donor for a proton from acid. So the aromatic amines are weaker bases. Still they are vital in the organic synthesis and in numerous industrial applications. The most popular aromatic amine – aniline (phenylamine) $\text{C}_6\text{H}_5\text{NH}_2$ is obtained by the reduction of nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$.

Nitro compounds, the other important class of organic compounds that possess $-\text{NO}_2$ functional group bound to a carbon skeleton can be treated as the starting materials for amines, aromatic ones in particular. Nitro compounds are usually obtained by a nitration reaction, when aromatic hydrocarbon (e.g. benzene) is treated with a mixture of conc. sulphuric and conc. nitric acids:



Amino acids form a homologous series of compounds possessing two different functional groups, in this particular case an amino group and a carboxyl group. So their properties are dictated by this fact and they are then both basic and acidic. Consequently, they can form salts both with acids and with bases. Furthermore, their functional groups can react within the

same molecule which then results in a zwitterionic form e.g.: $\text{H}_3\text{N}^{\oplus}\text{—CH}_2\text{—COO}^{\ominus}$ (in the case of amino acids with one amino group and one carboxylic group it is an isoelectric point – the molecule as a whole has no electric charge). The presence of highly polar groups in the structure of amino acids prompts the formation of strong hydrogen bonds; in fact, amino acids are usually high melting solids, well soluble in water. Amino acids play a vital role in all living organisms. They are the building blocks of peptides and proteins (α - amino acids having an amino group at the carbon next to carboxyl group). There are twenty of them, basic and acidic ones also among them, with more than one functional group. They can contain also the functional groups other than amino and carboxyl groups, e.g. serine or cysteine. They are usually marked off by abbreviated names, e.g. Gly from glycine, Ala from alanine, Lys from lysine, Ser from serine, Cys from cysteine and so on.



Human body is well capable of synthesizing some of them, but the other ones must be provided with a routine dietary intake (essential amino acids).

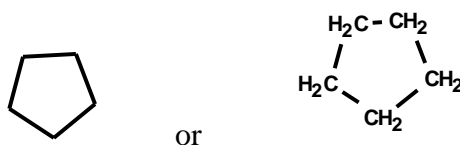
3. Nomenclature of organic compounds

3.1. Hydrocarbons of various classes

The presented variety of organic compounds prompt the question: how chemists can communicate with each other having so many compounds to deal with? The importance of naming them is obvious. Who is responsible for the nomenclature of organic compounds? IUPAC – International Union of Pure and Applied Chemistry. According to IUPAC rules alkanes are named as follows (first four of them with common names and starting from five carbon atoms in the molecule the names with the ending –ane are derived from the numerals):

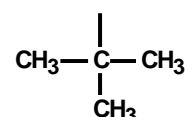
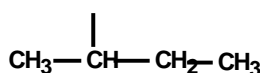
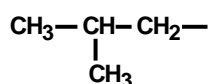
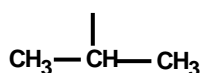
Name	Molecular formula	Condensed molecular formula
Methane	CH ₄	CH ₄
Ethane	C ₂ H ₆	CH ₃ -CH ₃
Propane	C ₃ H ₈	CH ₃ -CH ₂ -CH ₃
Butane	C ₄ H ₁₀	CH ₃ -CH ₂ -CH ₂ -CH ₃ or CH ₃ -(CH ₂) ₂ -CH ₃
Pentane	C ₅ H ₁₂	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₃ or CH ₃ -(CH ₂) ₃ -CH ₃
Hexane	C ₆ H ₁₄	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃ or CH ₃ -(CH ₂) ₄ -CH ₃
Heptane	C ₇ H ₁₆	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃ or CH ₃ -(CH ₂) ₅ -CH ₃

Cyclic alkanes have similar names beginning with the prefix cyclo- e.g. cyclopentane:



In the case of branched hydrocarbons various substituents occur in the main carbon chain. Before we start naming them, though, we should set out to define primary, secondary, tertiary and quaternary carbon atoms. Primary carbon atom is connected with one neighbouring carbon atom only, the secondary with two, the tertiary with three and quaternary with four carbon atoms. The smaller part of a chain connected with longer part of a chain are the alkyl groups (usually marked as R). Alkyl is an alkane from which one hydrogen atom is dragged away so its general formula is C_nH_{2n+1}. The most important alkyl groups are listed below:

methyl -CH₃ ethyl -CH₂-CH₃ propyl -CH₂-CH₂-CH₃ butyl -CH₂-CH₂-CH₂-CH₃



isopropyl

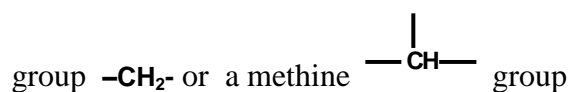
isobutyl

sec-butyl

tert-butyl

(The names isopropyl and isobutyl come from isomeric propyl or isomeric butyl, respectively, the names *sec*-butyl and *tert*-butyl come from connections at secondary or tertiary carbon atoms, respectively). Prefixes separated by a dash are written in italics and prefix iso is written together with the name of an alkane.

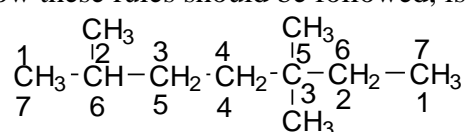
Also more hydrogen atoms may be split off from an alkane as in the case of a methylene



Very strict and precise nomenclature rules for the branched hydrocarbons, according to IUPAC rules, are as follows:

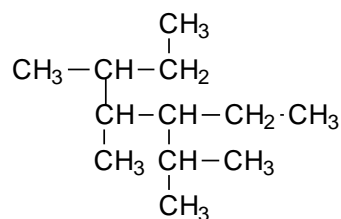
- Choose the longest chain (the more branched out, the better)
- Give numbers to the carbon atoms along the main chain [the smaller are the numbers of carbon atoms with substituents (compare one by one!) the better]
- Put the substituents in an alphabetical order
- Give separate number to each substituent
- Do not include in an alphabetical order neither the prefixes written in italics (e.g. *sec*, *tert*) nor the prefixes showing repeated number of substituents (2 = di, 3 = tri, 4 = tetra...)
- Connect the successive components of the name by the dashes and separate the numbers by the commas

An example of how these rules should be followed, is shown below:



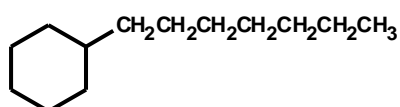
The sequence of numbered carbon atoms with substituents: either 2,5,5 (from the left to the right) or 3,3,6 (from the right to the left) [not the sum of these numbers! which in both cases is equal to 12]. The proper name is: 2,5,5-trimethylheptane

What is the proper name for the following compound?



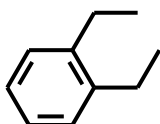
3-ethyl-2,4,5-trimethylheptane

The naming of the ring compounds is done very much in the same way, but when the combination of a ring and a chain is concerned then the main carbon skeleton is the one with the bigger number of carbon atoms so the following compound is named cyclohexylheptane (it could be 1-cyclohexylheptane but please note that in obvious cases like this one, number 1

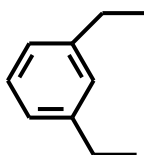


can be skipped).

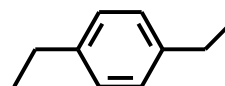
With regard to the aromatic compounds, benzene in particular, a special convention to naming their double substituted derivatives applies:



1,2-diethylbenzene
ortho-diethylbenzene



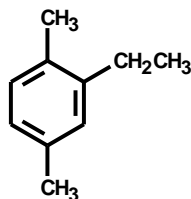
1,3-diethylbenzene
meta-diethylbenzene



1,4-diethylbenzene
para-diethylbenzene

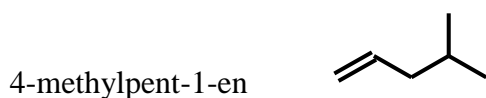
they are, however, usually written as *o*-diethylbenzene, *m*-diethylbenzene, *p*-diethylbenzene.

For more complicated benzene derivatives the numbering of a ring carbon atoms follows along the shortest possible route, e.g.: 2-ethyl-1,4-dimethylbenzene.



The names of monofunctional derivatives of alkanes are derived from the name of an alkane carbon skeleton, while the suffix (ending) shows which functional group is encountered in the derivative. So:

Alkenes i.e. hydrocarbons with a double bond have the names with the suffix –en and the numbering of carbon atoms in a chain starts off from the end next to the double bond. Its presence is shown in the name by the number of the first carbon atom of a double bond in the direction of counting and this number is put just before the –en suffix. The example:



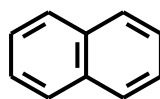
More unsaturated hydrocarbons are named likewise e.g. hexa-1,3,5-triene

Alkynes i.e. hydrocarbons with a triple bond have the names ending with –yne and the analogous rules of numbering. Also here the numbering according to the triple bond is more important than the numbering according to the substituents.

Arenes i.e. aromatic hydrocarbons have no suffix in their names. Examples:



benzene

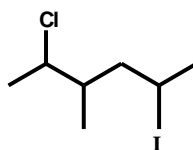


naphthalene

3.2. Compounds with one functional group

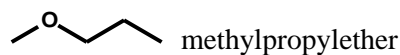
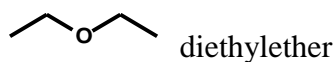
Halogen derivatives of hydrocarbons have no suffix in their names and halogens are marked as prefixes e.g. iodomethane, 2-bromopropane.

The numbering follows common rules and both alkyls and halogens are put in an alphabetical order e.g.: 2-chloro-5-iodo-3-methylhexane

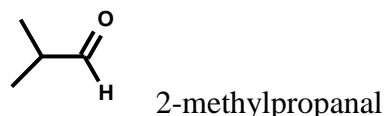
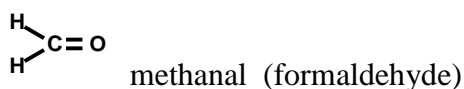


Alcohols i.e. hydrocarbons with hydroxyl functional group have the names ending with –ol and conform to similar numbering rules with the preference of -OH numbering e.g.: 4-methylpentan-2-ol. Simple alcohols are named: methanol, ethanol, propanol...

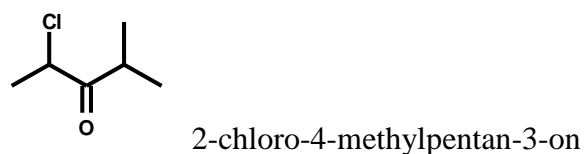
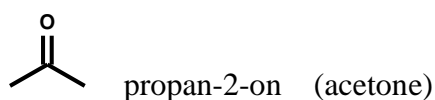
Ethers have no suffix and are named as follows:



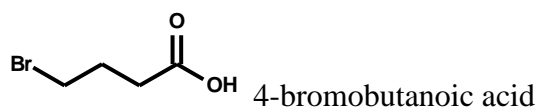
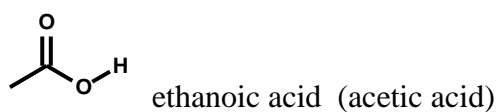
Aldehydes with a carbonyl functional group at the end of a hydrocarbon chain have the names ending with –al and the same rules regarding any substituents apply. The numbering always starts off with the carbon of a functional group e.g.:



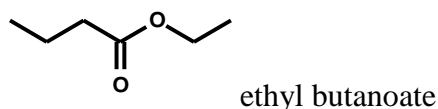
Ketones with a carbonyl functional group connected with the two carbon skeletons have the names ending with -on derived from the longest carbon skeleton including a carbonyl group. The numbering starts off from the end of the chain closest to the carbonyl and the rules regarding any substituents are the same, e.g. propan-2-on (2- can be skipped, as there is here no other possibility), 2-chloro-4-methylpentan-3-on.



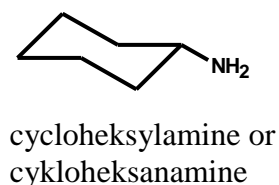
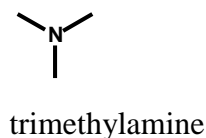
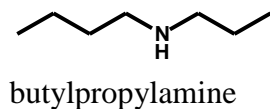
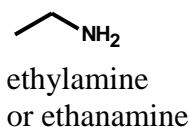
Carboxylic acids with a carboxyl functional group always at the end of a chain, are named as the acids after the longest hydrocarbon name ending with –oic. The numbering always starts off with the carbon of a carboxyl group e.g. :



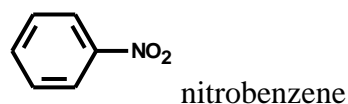
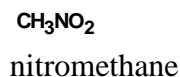
Esters are the derivatives of carboxylic acids and alcohols so their names are made up of two parts: they start off from an alkyl rest of alcohol followed by the name of an acid ending with -oate e.g.:



Amines have the names derived from hydrocarbon names ending with –amine. For secondary or tertiary amines the names of the carbon chains or rings are put in an alphabetical order e.g.:



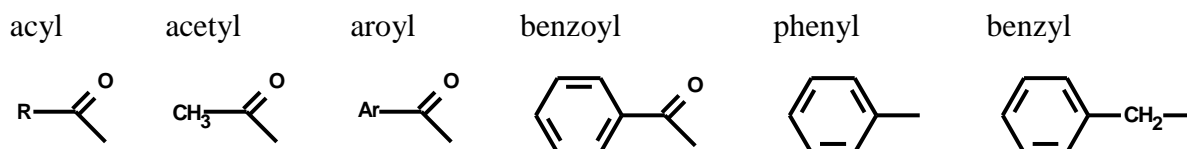
Nitro compounds with a functional group $-\text{NO}_2$ have the names with the prefix nitro- ending with the name of the hydrocarbon to which a functional group is attached, e.g.:



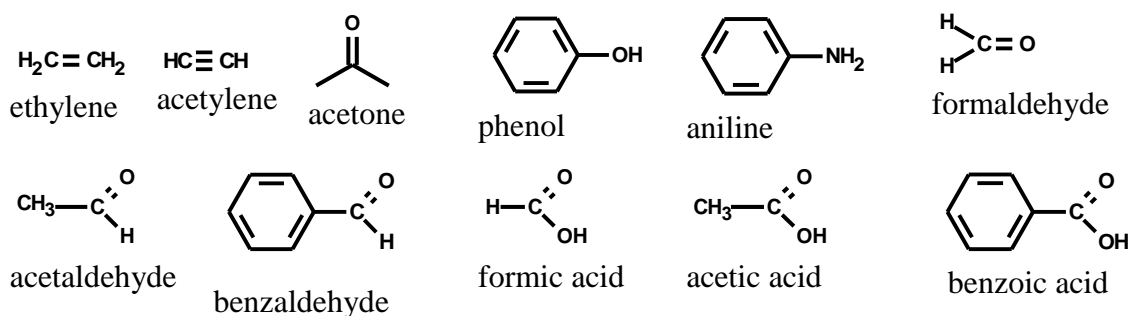
3.3. Compounds with more functional groups, preferences in naming

There are many organic compounds that possess more than one functional group. Then the problem of preference in naming arises. Generally speaking, the more oxidized functional groups are preferred in naming. The current preference of certain classes of compounds in naming is: acid > ester > aldehyde > ketone > alcohol > amine > alkene > alkyne > alkane > ether > halogen derivatives

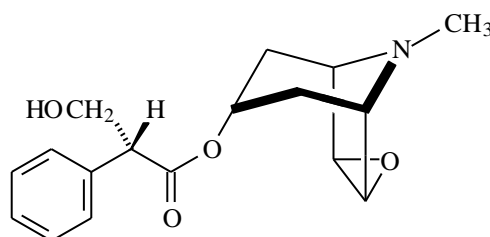
It is also quite useful to know the common names of some substituents (acyl derived from acid, acetyl derived from acetic acid, and aroyl derived from aromatic acid) like:



Having devised such precise rules of naming the organic compounds organic chemists still used many common names of various compounds, in particular, the organic acids e.g.:



Sometimes the names of organic compounds are so complicated that it is simply more convenient to use then a common name as in case of the alkaloid *Scopolamine*

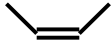


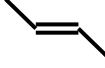
4. Stereochemistry

4.1. Conformations

The distance between single atoms in the molecule influences the bulky properties of a substance built of these molecules. Therefore the spatial structure of molecules is essential. When we look at a simple molecule of ethane with single bond between carbon atoms we can assume numerous various structures resulting from free rotation around this single bond. They are called conformations and one conformation is going into another one very quickly. Therefore what is observed is just an average state of the molecule.

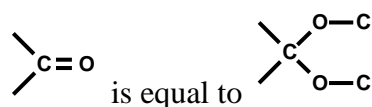
4.2. Z/E stereoisomers

A different situation takes place when the double bond is present in the molecule. Then the free rotation is impossible what results in *cis/trans* or *Z/E* stereoisomers. Already in but-2-en two methyl groups can be found on the same side of a double bond (the shorter distance between their carbon atoms) → *cis* or *Z* isomer  or on the opposite sides of a double

bond (the longer distance between their carbon atoms) → *trans* or *E* isomer. 

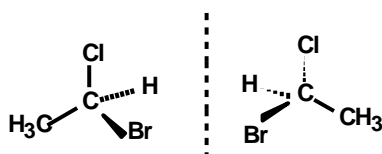
Cis/trans isomers can occur also in saturated ring compounds with two substituents on the same side of the ring or on the opposite sides of the ring. The problem appears, when e.g. four different substituents are placed around the double bond. The *cis/trans* convention is not sufficient in this case. Therefore Cahn-Ingold-Prelog (CIP rules for priority) convention, basing on comparison of atomic numbers of substituents, was introduced. The bigger atomic number the more preference for the substituent. How does it work? We should divide the molecule into two parts with the line perpendicular to the double bond. Then we should compare the preference of both substituent on one side choosing number one on this side and then we use the same procedure for the second side of the molecule. At the end we compare the prior substituents on both sides and state whether they are on the same side of a double bond (*Z* isomer) or on the opposite sides (*E* isomer). Remember that *E* and *Z* isomers differ in physical (sometimes also in chemical) properties.

Sometimes the usage of Cahn Ingold Prelog rules is more complicated when the substituents have the same atomic number e.g. CH₃ and C₂H₅. Comparison of carbon atom with the carbon atom does not bring the answer therefore we should go to the "second sphere" and concern the atoms in a distance of one more bond, comparing the substituents one by one starting from the prior one up to the moment when the right answer is found. In case of double or triple bonds within the substituents we change them mentally to single bonds e.g.



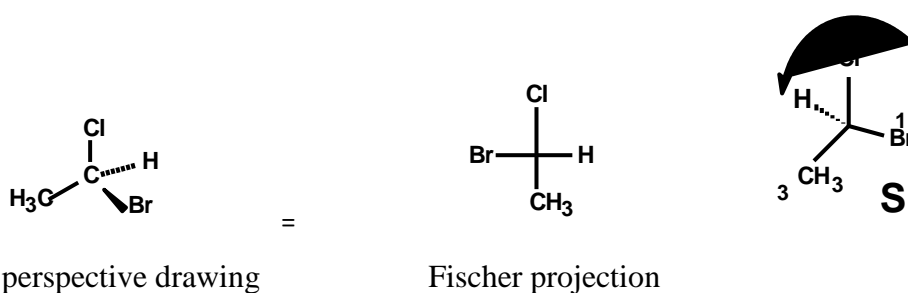
4.3. Enantiomers and diastereomers

Architecture of the molecules is also crucial in the case of optically active compounds. Some saturated compounds show a remarkable feature. They change in solutions an angle of polarised light. It is due to the fact that molecules of this compound are chiral. They show two forms of molecular structure being as an object and its mirror image (optical isomers). The reason for that is the presence of a stereogenic centre in the molecule. It is a carbon atom with four different substituents (chiral carbon atom).



For such chiral carbon atom the spatial arrangement of substituents is given by absolute configuration *R* (from rectus = right) or *S* (from sinister = left). This can be investigated by physicochemical methods and it is in agreement with *R* or *S* configuration elucidated with the help of Cahn Ingold Prelog preference rules. For showing the spatial arrangement of a molecule the Fischer projection may be used. In this convention:

- the longest carbon chain is written in a perpendicular manner
- each stereogenic centre is marked by a cross (without the C symbol in a centre)
- around each cross perpendicular substituents are going behind the plane of a drawing
- vertical substituents are going in front of the drawing plane

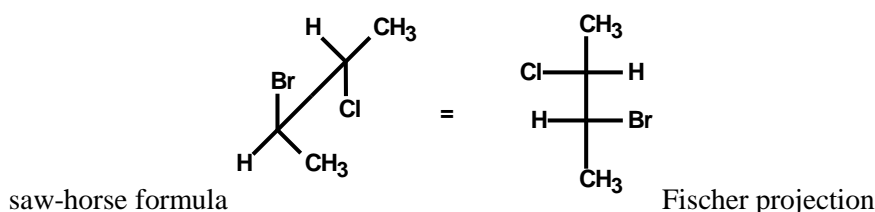


To find the absolute configuration we have to prescribe the order of preference to each of four substituent around the stereogenic centre (No 1 the most prior...no 4 the least prior, according to CIP rules). Then we should arrange the molecule in that way that the least preferred substituent is going behind the plane and the three remaining substituents are in front of us. Then we examine the direction of movement from 1 through 2 up to 3. When it is clockwise we do with *R* configuration and when is anticlockwise the configuration is *S*.

For molecules with one stereogenic centre two enantiomers are possible. They differ only in the ability to shift the angle of plane polarised light as (+) or (-). Other physical and chemical properties for enantiomers are the same. But there are some molecules that have more than one stereogenic centre. Already for two chiral carbon atoms four possibilities are possible: *R,R* or *S,S* or *R,S* or *S,R*. Two of them are enantiomers in pairs: *R,R* and *S,S* as well as *R,S* and *S,R*. But e.g. *R,R* and *R,S* or *S,S* and *S,R* are in pairs diastereomers. They differ also in other physical properties. For n stereogenic centres in the molecule the number of stereoisomers is 2^n . The stereochemistry of organic molecules plays an essential role in their biological activity (e.g. for enzymes, proteins, sugars or medicines).

4.4. Models and notations to represent stereoisomers

Except Fischer projection there are other possible representations of spatial structure of molecules on the plane e.g. saw-horse formulas or perspective drawings.



To study stereochemistry very useful is also the usage of various molecular models. The most popular are ball-and-stick models that are available in some bookshops or can be even constructed at home from matches and plasticine.

5. Organic reactions

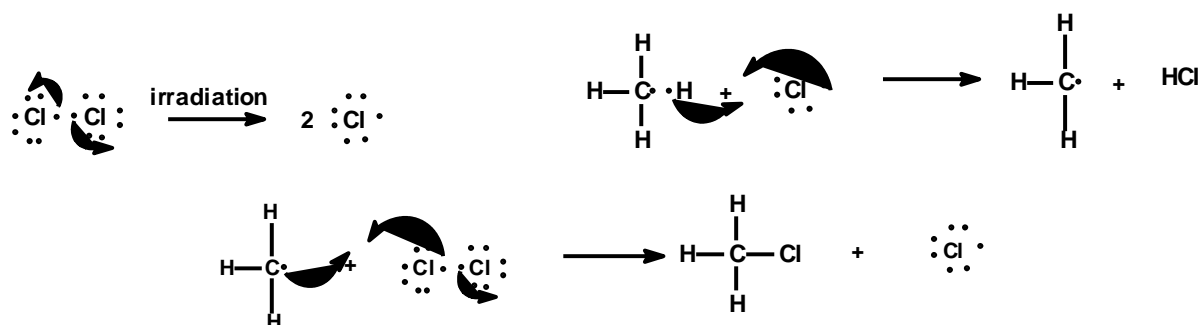
5.1. Acids and bases in organic chemistry

To understand how the acidity or basicity of organic compounds is connected with their structure it is very useful to define electron withdrawing groups (halogens X, carbonyl, carboxyl group, nitro group) that can lower the electron density of the adjacent atoms and electron donors (alkyl, hydroxyl, amino group) that can enhance the electron density of the adjacent atoms. That influence is either of inductive or resonance origin. Inductive effect based on the difference in electronegativity of the elements and polarization of bonds drops very quickly with the distance (according to Coulomb's law). So it is easy to foresee that e.g. 2-fluoroacetic acid is stronger than 2-chloroacetic acid. That one is stronger acid than 3-chloropropanoic acid and all of them are stronger acids than acetic acid. Taking electrodons into consideration it is easy to foresee that e.g. trimethylamine is stronger base than ammonia. There are numerous acidic compounds (carboxylic acids, phenols, alcohols) as well as organic bases (primary, secondary and tertiary amines) in organic chemistry. Amides i.e. derivatives of carboxylic acids, where hydroxyl group is replaced by an amine group, are less

basic than amines, because the resonance between the lone electron pair of nitrogen and double bond of carbonyl and the electron withdrawing effect of a carbonyl group lower the electron density of nitrogen, hence its ability to bind a proton. Amino acids are both acidic and basic (amphoteric) but depending on the number of carboxyl and amino groups they can be either acidic or basic.

5.2. Mechanisms of organic reactions, radicals, nucleophiles and electrophiles

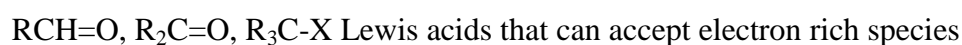
What happens when the organic reaction takes place? Some bonds are cleaved and some new bonds are formed. In the simplest case it may concern one bond only. The bond can be cleaved in such a way that one electron is remaining with one partner and the other one with the second fragment (homolytic cleavage) – then the very reactive species with unpaired electrons, called radicals, are formed and they try to find immediately a partner to form the new bond. The movement of single electrons is marked by a hook as shown below:



These single steps of the reaction (in this case a radical chlorination of methane) provide the mechanism of the reaction. Sometimes it is not easy to elucidate the mechanism of a reaction and it needs long investigations and precise proofs. Radical reactions, however more and more popular in organic chemistry, are not as common as polar mechanisms. In this case the bond electron pair is shifted to one partner only (homolytic cleavage) so anions and cations are involved in the stepwise mechanism. To understand it better we have to define nucleophiles, species which likes nucleus, hence having either lone electron pair (pairs) or a negative charge, as well as electrophiles, species that like electrons, hence have positive charge. Typical nucleophiles (usually Lewis bases) :

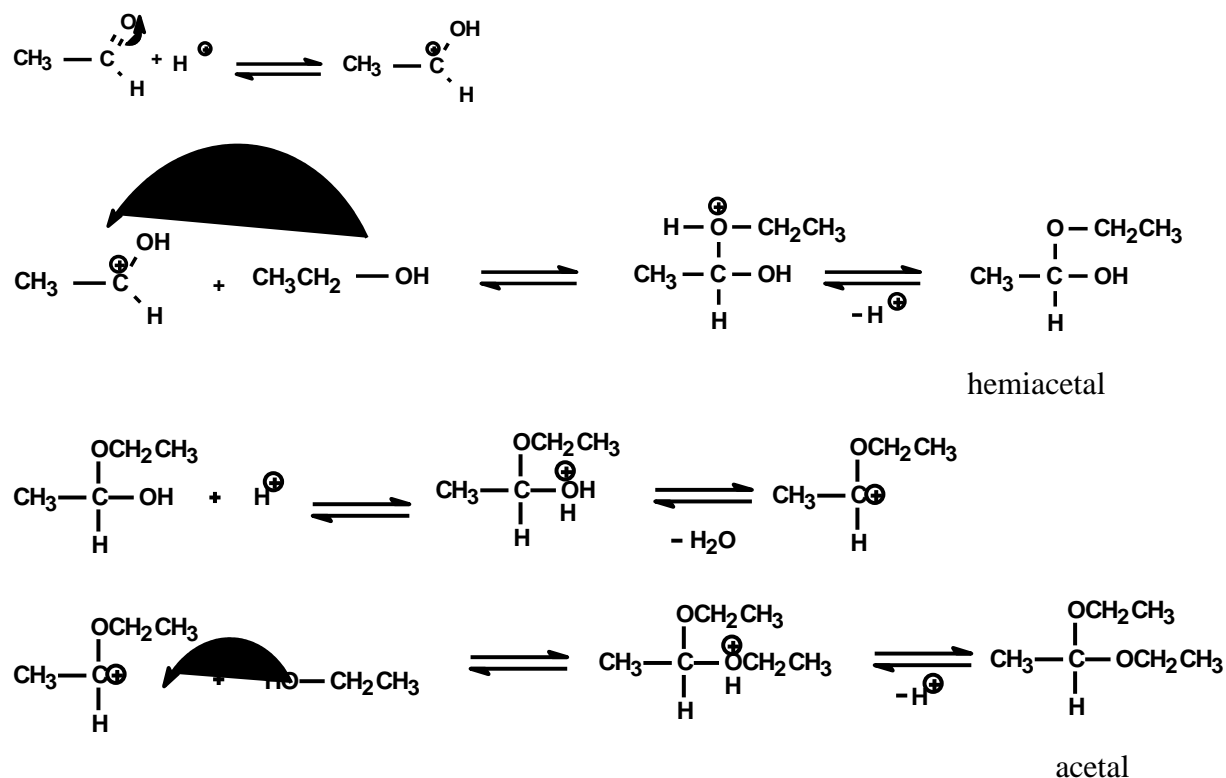


Typical carbon electrophiles:



Practically all polar reactions in organic chemistry are reactions between a nucleophile and an electrophile. So we can e.g. ask whether aldehydes react with alcohols. As alcohol is a typical nucleophile and the aldehyde shows a partial positive charge on carbon atom the answer is

yes. The mechanism of the reaction of hemiacetal and acetal (the names of products) formation from ethanal and ethanol is shown below:

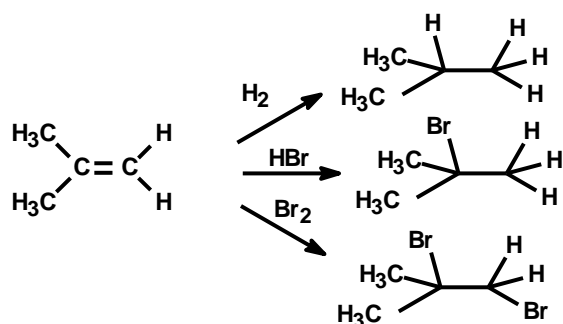


The process is reversible under acidic conditions.

5.3. The main types of organic reactions

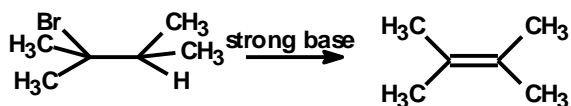
What are the main types of organic reactions?

Addition, when one molecule is added to the other and the only product is formed that way:

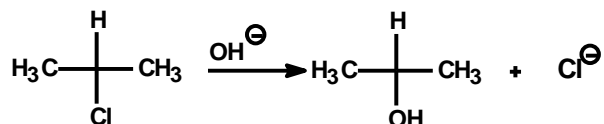


Addition is characteristic for double and triple bonds and it may be represented by e.g. hydrogenation, halogenation, hydrohalogenation or hydration of multiple bonds under influence of acids.

The reverse reaction is **elimination**. In this case by splitting off a smaller molecule the double (or triple) bond can be formed as shown below:

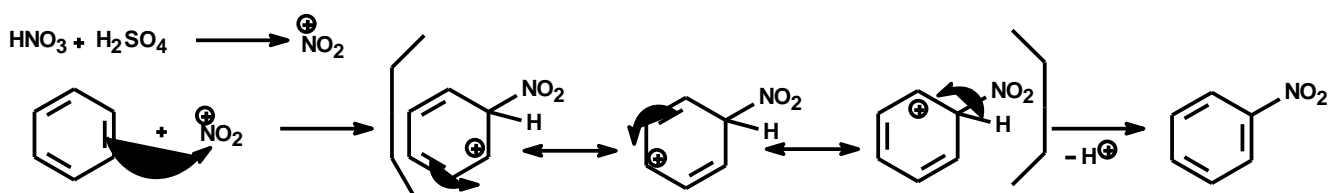


Substitution takes place when one substituent is replaced by another one as e.g. in nucleophilic substitution of haloalkanes by hydroxide ion:

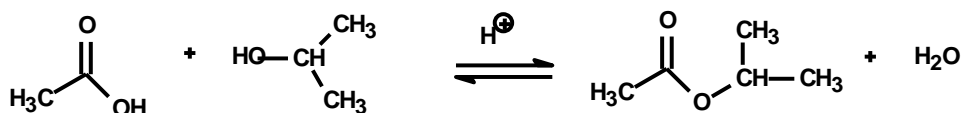


The mechanism of this reaction depends strongly on the ability of a starting material to form carbocation (it is stable with electondonating substituents) and on the character of the leaving group (the less polar the bond between carbon atom and the leaving group the more easy it detaches e.g. I is a better leaving group than Cl⁻). There are two possible mechanisms of nucleophilic substitution: S_N1 (like this described) and S_N2 a simultaneous process when the reagent is attacking a carbon atom and the leaving group abandons the carbon atom. From kinetics point of view the rate of the reaction depends in the case of S_N1 reaction on the concentration of a starting material only whereas in the case of S_N2 on the concentration of both starting material and attacking reagent. Substitution and elimination are often concurrent reactions.

In aromatic compounds **electrophilic substitution** predominates over addition, because they are electron rich compounds that tend to preserve their aromaticity. The example of such reaction is nitration of benzene shown below:

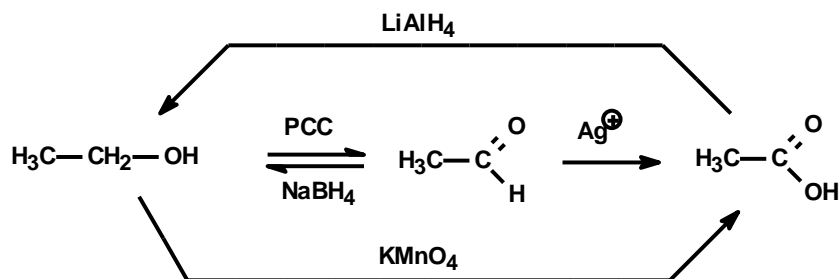


Condensation is a reaction in which a small molecule (usually water or ammonia) is splitted off parallel to the formation of the product. Typical example of condensation is the synthesis of esters from carboxylic acids and alcohols. The process needs acidic catalysis and is reversible. The excess of acidic catalyst may cause decomposition of the ester formed (acidic hydrolysis) therefore after the reaction the traces of acids should be thoroughly removed. The following reaction of isopropyl ethanoate formation is an example of typical condensation (esterification):



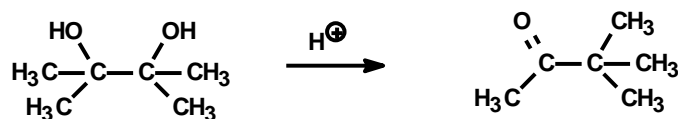
The hydrolysis of esters can occur also under alkaline condition and is then irreversible.

Very important group of reactions are **redox (reduction/oxidation)** reactions. Depending on the selective reagents they make possible the syntheses of various classes of organic compounds as in the following scheme:

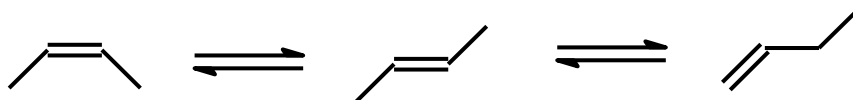


(PCC is pyridinium chlorochromate)

The reaction proceeding with the change of a carbon skeleton (sometimes atoms of other elements may be also involved) are called **rearrangements**:



Similar process occurs also in **isomerization**:



6. Some important applied organic compounds

6.1 Fats are esters of fatty acids (acids with the long hydrophobic hydrocarbon chain) and

a specific alcohol – glycerol: 1,2,3-propanetriol: $\text{HO}-\text{CH}_2-\overset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{OH}$ The fatty acids, most popular in nature, are palmitic acid $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ and stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$. The fats obtained from these acids are solids. But very important in the nutrition are liquid fats (oils) which are derived from monounsaturated fatty acids like e.g. *cis*-oleic acid $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ or polyunsaturated fatty acids.

6.2 Lipids comprise not only fats but also waxes, some vitamins, sterols, phospholipids and others.

6.3 Waxes are esters of fatty acids with long-chain alcohols. Beeswax is e.g. a mixture of various esters with the main component $\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_2(\text{CH}_2)_{28}\text{CH}_3$.

6.4 Soaps are salts of fatty acids and some metals, usually sodium or potassium, e.g. $\text{CH}_3(\text{CH}_2)_{14}\text{COO}^- \text{Na}^+$. As the other synthetic surfactants they have a long hydrophobic hydrocarbon chain ended with the highly polar group. Therefore they can help to remove e.g. fatty spots from fabrics by formation of micelles: hydrophobic hydrocarbon chains showing affinity to fat molecules surround them to leave hydrophilic carboxylic groups outside. That enables their hydrogen bond formation with water molecules thus removal of spots by water.

6.5 Polymers are macromolecules formed from single molecules (mers) usually by addition or condensation. Their production makes nowadays a very important branch of chemical industry. And biopolymers like starch, cellulose or proteins play a vital role in life processes.

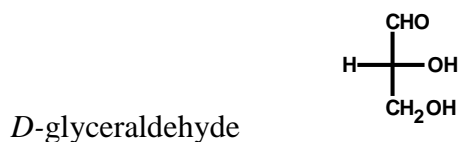
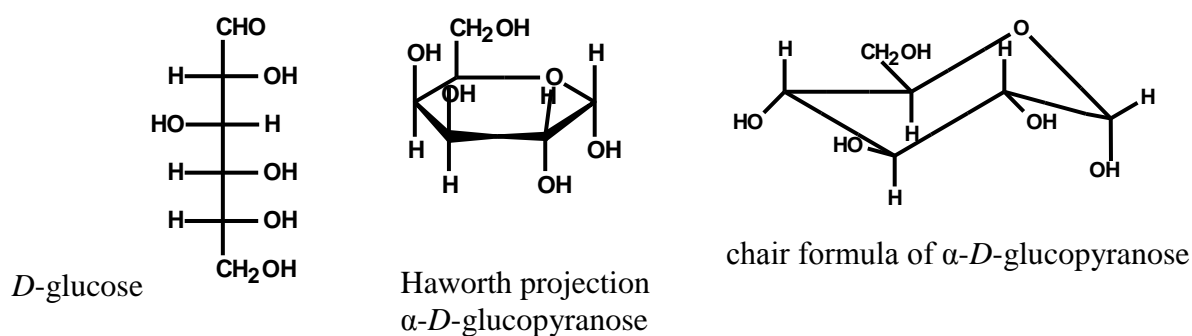
7. Some biologically active organic compounds

7.1 Peptides are biologically active molecules formed in the reaction of amino acids molecules. In this condensation so called peptide bond is formed and the water molecule is removed. This means in fact the formation of an amide. In nature this is an enzymatic process but in laboratory when acidic carboxylic group of one amino acid (called C-terminal) reacts with the basic amino group of the second amino acid (called N-terminal) the salt is formed. To make this condensation possible some special methods are used, e.g. the carboxylic group of one amino acid is transferred into acid chloride and then it reacts smoothly with the amino group of the second amino acid. The remaining functional groups should be then protected (blocked) to obtain the proper result. Nowadays such condensation of two (or more amino acids) is also possible directly by using special agents like DCC (dicyclohexylcarbodiimide). It can happen also with the help of special techniques on solid support - resins (Merrifield method).

7.2 Proteins are macromolecular polypeptides showing not only a proper sequence of amino acids bound in a chain (primary structure) but also much more complicated structures connected by hydrogen bonds (α -helix, β -sheet – secondary structure) and other forces influencing their spatial arrangement - folding (tertiary structure). The formation of complexes by several polypeptide chains is called quaternary structure.

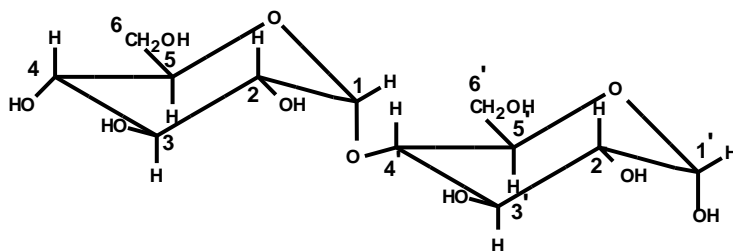
7.3 Carbohydrates are well known compounds of general formula $\text{C}_n\text{H}_{2m}\text{O}_m$. They have usually one carbonyl functional group as aldehyde group (aldoses) or ketone group (ketoses) and many hydroxyl groups. So they are at the same time polyalcohols. Simple molecules (monosaccharides) are called depending on the number of carbon atoms in their molecules: trioses, tetroses, pentoses, hexoses and so on. Because of the presence of many stereogenic centres saccharides show a great variety of stereoisomers. The representative of hexose group

is glucose. It belongs, as majority of sugars to *D*-sugars. It is connected historically with the configuration of last by one carbon atom in the molecule compared with arbitrary assumed *D*-configuration of *D*-glyceraldehyde. Now we know that this is, according to Cahn Ingold Prelog rule, absolute *R*-configuration. Monosaccharides, being polyhydroxyaldehydes or ketones occur in solutions both in an open-chain form as well as in a ring form. The closure of the ring is possible by the hemiacetal formation. In this way a six membered heterocyclic ring is formed (with the name pyranose) or in the case of fructose (being ketohexose) a five membered ring is formed (with the name furanose). The ring formation leads to a new stereogenic centre (anomeric carbon atom) having two possible configurations: α - with hydroxyl group oriented on the opposite side of the ring towards $-\text{CH}_2\text{OH}$ substituent and β - with both these substituents on the same side of the ring. The stereoisomers of glucose or other sugars can be presented as Fischer projections (for open chain form) or as Haworth or chair formulas:

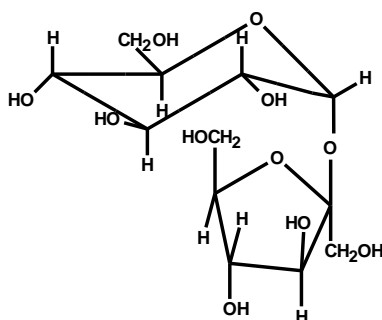


Monosaccharides can react with each other and in such condensation disaccharides (e.g. lactose, maltose, sucrose) are formed. During this reaction water molecule is splitted off from two hydroxyl groups of a monosaccharide. At least one of them must be a more reactive hemiacetal hydroxyl group as e.g. in:



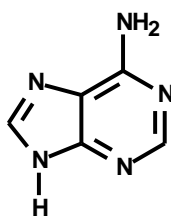


Also two hemiacetal groups of both monosaccharides can take part in this reaction. But then the come back to the open chain form is no more possible. Such disaccharides cannot show the reactions characteristic for aldehydes e.g. reduction of silver oxide and they are called non-reducing sugars as e.g. Sucrose i.e. α -D-glucopyranosyl- β -D-fructofuranose

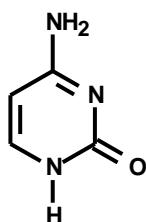


Polycondensation can lead to more complicated carbohydrates: oligosaccharides (with 3 – 9 monosaccharide units) and polysaccharides (with more than 9 monosaccharide units). The representatuive of polysaccharides are starch and cellulose.

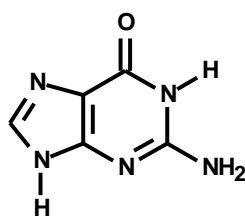
7.4 Heterocyclic bases belong to the wide class of heterocyclic compounds containing rings including an atom or atoms different than carbon. Heterocyclic compounds make up more than the half of all organic compounds and are very popular among biologically active compounds. Heterocyclic bases contain nitrogen atom (or atoms) as a heteroatom. There are the following heterocyclic bases present in nucleic acids:



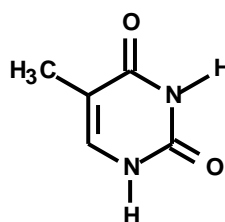
adenine (A)



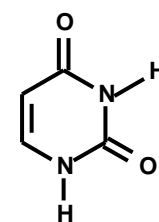
cytosine (C)



guanine (G)



thymine (T)



uracil (U)

7.5 Nucleic acids are biopolymers, essential in life processes. They carry genetic information, are responsible for synthesis of proteins. These macromolecules are constructed of nucleotides

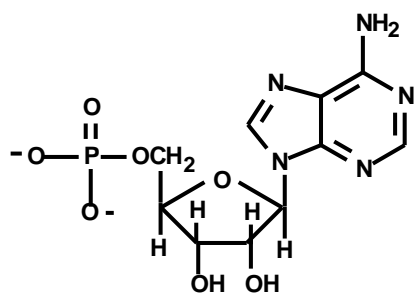
7.6 Nucleotides are building blocks of nucleic acids DNA (deoxyribonucleic acid) and RNA (ribonucleic acid). Nucleotides are composed of three parts:

nucleobase (adenine, cytosine, guanine and thymine in case of DNA and adenine, cytosine, guanine and uracil in case of RNA)

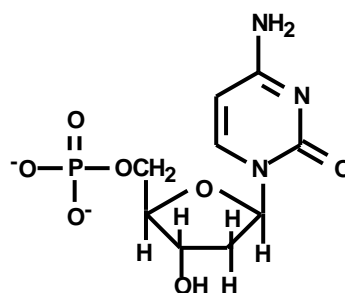
monosaccharide – pentose: ribose in RNA and deoxyribose (one hydroxyl in the sugar moiety is replaced by hydrogen) in DNA

phosphate moiety

Nucleic base is bound with sugar by *N*-glycosidic bond and sugar forms ester with phosphoric acid.



Example of nucleotide in RNA



Example of nucleotide in DNA

DNA is double-stranded and these strands coil around each other forming a double-helix held by hydrogen bond formation of complementary bases: A-T and C-G. RNA is usually single-stranded but shows complicated space arrangements held by hydrogen bonds of complementary bases: A-U and C-G. There is a relationship between the sequence of amino acids in proteins synthesized in cells and a sequence of bases in DNA (genetic code).

Key words:

Organic chemistry:

Isomers; sp³, sp² and sp hybridization; homologous series; tetravalent carbon; single, double and triple bonds; conjugated systems of multiple bonds; resonance; aromaticity; hydrocarbons; alkanes, alkenes, alkynes, substituents, heteroatoms, alkyl halides; alkyl group; primary, secondary and tertiary alcohols and amines; aldehydes and ketones; carbonyl group; carboxyl group; acids; esters; amides; anhydrides; nitro compounds; conformers; Z/E stereoisomers; enantiomers; diastereomers; Fischer projections; nucleophiles, electrophiles, reaction mechanisms; carbocation; radical; leaving group;

addition; substitution; elimination; reduction; oxidation; rearrangement; biomolecules; fatty acids; lipids; soaps; waxes; micelles; mono-, oligo- and polysaccharides; triose; tetrose; pentose; hexose; aldose; ketose; hemiacetals; acetals; pyranose; furanose; amino acids;