

Chemistry course
ACME Faculty, EHVE course
B.Sc. Studies, I year, I semester
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Organic chemistry, part 2:
Hydrocarbons, halogen derivatives,
basics of practical organic chemistry

Alkanes

- **Alkanes** are the most simple hydrocarbons. They consist of, as the name suggests, carbon and hydrogen atoms. Atoms in alkanes can be connected only with single bonds, thus they are called saturated hydrocarbons (they can not be hydrogenated further).
- They can form linear **carbon skeletons** (straight-chains), branched (open-chain) or closed, *i.e.* rings (cyclic compounds), rings with branches, polycyclic compounds, *etc.* If alkane carbon chain is forming ring(s), it is called **cycloalkane**.

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Alkanes

Depending on carbon atoms number in alkane, main part of its name is changing:

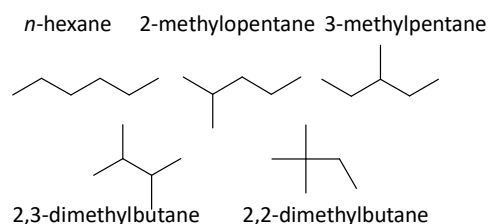
1 – methane (CH ₄)	9 – nonane	
2 – ethane (C ₂ H ₆)	10 – decane (C ₁₀ H ₂₂)	
3 – propane (C ₃ H ₈)	11 – undecane (C ₁₁ H ₂₄)	
4 – butane (C ₄ H ₁₀)	12 – dodecane	$\text{H}_3\text{C}-(\text{CH}_2)_{10}-\text{CH}_3$
5 – pentane (C ₅ H ₁₂)	13 – tridecane (C ₁₃ H ₂₈)	
6 – hexane (C ₆ H ₁₄)	14 – tetradecane (C ₁₄ H ₃₀)	
7 – heptane (C ₇ H ₁₆)	15 – pentadecane (in 16-19 first part as in 6-9)	
8 – octane (C ₈ H ₁₈)	20 – icosane (C ₂₀ H ₄₂)	

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Alkanes' isomers

Alkanes with straight (no branches) carbon chain are called *n*-alkanes. Their isomers can be branched as follows:

Gasoline is a mixture of branched alkanes C₅-C₈



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Alkanes' properties

- Methane, ethane, propane and butane have **no smell** – the smell of (natural) gas from cooker or gas cylinder is a **thiol** smell (methanethiol, ethanethiol, *tert*-butylthiol, thiophene, itd.). Thiol is added on purpose, for easier organoleptic detection of gas leaks/escape.
- Alkanes are colorless (possible color is caused usually by impurities).
- Alkanes do not mix with water, but they can be mixed with each other without limitations.
- Initial compounds of the **homologous series** of *n*-alkanes C₁-C₄ are gaseous, C₅-C₁₅ are liquid (gasoline, gas oils) and C₁₆ and above are solid (paraffins, waxes).

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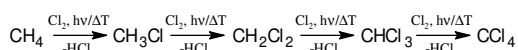
Alkanes' reactivity

- Alkanes are of a low reactivity, because both C-C and C-H bonds are stable and almost unpolarized.
- Apart from combustion (oxidation), alkanes can be a subject to **halogenation** reaction, that is substitution of halogen for hydrogen atom (F, Cl, Br, I).

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Halogenation

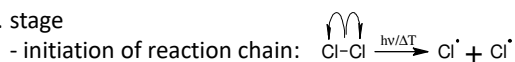
- It is a **substitution** reaction (exchange of one atom/group for another) with **radical mechanism** (reaction proceeds with radicals formation as intermediate products). Reaction with fluorine proceeds rapidly in standard conditions. Reaction with chlorine and bromine occurs upon reaching high temperatures (300°C) or during UV-light irradiation (hv). General notation:



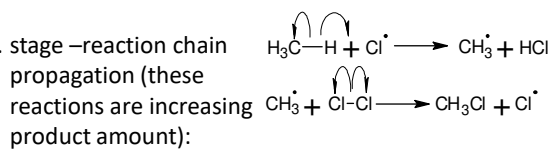
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Halogenation

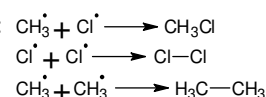
1. stage



2. stage –reaction chain



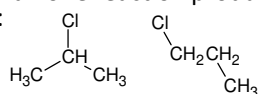
3. stage – termination:



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Halogenation

- As one can see, it is possible to form longer alkanes as a result of halogenation reaction, as well as their halogenation products.
- Halogenation of longer alkanes is looking similarly, but there is more than one reaction product, in case of propane:



- Due to higher radicals stability if they are formed at tertiary (secondary) carbons, there is a bigger chance for halogenation products formation if the halogen atom would be placed at higher-order carbons.

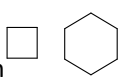
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Halogenation

- Example: in propane there are 6 hydrogen atoms at primary carbons, 2 hydrogens at secondary carbons, thus one should await product ratio of 6:2 (3:1) (if there would be the same chance to detach hydrogen by chlorine radical from each carbon). However, hydrogens' reactivity is various, depending on carbon order to which they are bound. During chlorination reactivity ratio is 1 (primary): 3.8 (secondary) : 5 (tertiary). Thus the product ratio in this case is 6 : 7.6 (6x1 : 2x3.8).
- In case of bromination, that proceeds analogically to chlorination, product formation ratio is 1:80:1600. Thus bromination is a very **specific** reaction (there is usually only one product and its yield is ca. 99%).

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Cycloalkanes

- Cycloalkanes do have similar molecular structure to alkanes, but their carbon chain forms a ring. Their names are formed like in case of alkanes, although "cyclo" prefix is added, e.g. 4-carbon cycloalkane is cyclobutane and 6-carbon cycloalkane is called cyclohexane. 
- Cycloalkanes are subject to halogenation and combustion identically to alkanes. Also, with prominent exception of cyclopropane (that is a subject to reactions in a way of alkenes), they are not subject to any reactions other than alkanes are.

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Combustion of organic compounds

Combustion of hydrocarbons with enough oxygen amount always leads to carbon dioxide CO₂ (from carbon atoms) and water H₂O (from hydrogen atoms) formation. If there is a shortage of oxygen, H₂O is formed together with CO and CO₂, or even CO alone (carbon monoxide).

In oxygen-free conditions and high temperature, longer hydrocarbons are shortened. Shorter ones are subject to complex transitions leading to cyclic and polycyclic compounds. Eventually, they form different forms of coal (tars, coke/carbon black) and gas – mixture of methane, hydrogen and other gases.

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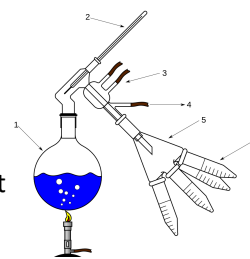
Techniques of organic compounds separation

To identify compound of unknown origin or to confirm structure of compound obtained through synthesis, one has to be sure, that this compound is pure (that it is only one compound). For that reason, one has to separate compound(s) from impurities. The same compound separation techniques are also used for separating compound classes from each other.

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Separation techniques

Distillation – liquid mixtures can be separated by use of differences between their boiling points. That method is giving poor results in case of low volatile/non-volatile compounds, mixtures of compounds with close boiling points and some mixtures that are vaporizing together (in spite of different boiling points).



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Separation techniques

Crystallization – bases on dissolving the mixture (impure compound) in a solvent in which impurities dissolving easily (one compound) and the main one (or second compound) is not dissolving easy. They are dissolved at high temperature. During cooling down the crystals of worse dissolving substance are crystallizing slowly. Crystallization can obtain product of high purity.

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Separation techniques

Chromatography is a technique that utilize differences between substances in their migration through different adsorbents (usually materials of high porosity that binds selected compounds classes on their surface). Depending on medium and shape of adsorbent bed, we can distinguish:

- column chromatography
- thin-layer chromatography
- gas chromatography

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Separation techniques

In **column chromatography** we use alumina (Al_2O_3) or silica gel (SiO_2) bed. One pours concentrated solution of a mixture on bed and slowly runs mixture through the bed with additions of a solvent. Depending on interactions strength between mixture components and bed, components are moving through bed with different speed and that is allowing to separate them. This technique can be used as analytical method (less-frequent nowadays) and for purification of reaction mixtures.

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Separation techniques

This-layer chromatography (TLC) is a commonly used analytical method. It differs from column chromatography mainly with the form of adsorbent bed – thin layer of alumina (Al_2O_3) is coated on a plate (glass, aluminum). Plate is put into a beaker with some analyzed solution on the bottom, which moves through the plate upwards (lifted by capillary forces).

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Separation techniques

Gas chromatography is based on passing gaseous mixtures (diluted with inert gas) through a very long capillary (0.1 mm diameter, meter order length). Its walls are covered with thin layer of semi-liquid polymer (usually) – so-called **stationary phase**. Gases are multiple times dissolving and vaporizing from the polymer. They do it at different rates (they interact differently with stationary phase) and as a result components are passing through the capillary after different times.

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Analysis/identification techniques

Methods of compound identification:

- Elemental analysis (EA)
- Mass spectrometry (MS)
- Nuclear Magnetic Resonance (NMR)
- Spectroscopy techniques (IR, Raman, UV-Vis, AES, AAS)
- Chromatographic techniques
- Classical methods (use of selective/specific reactions, that occurs only for one class of compounds/one compound)

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Analysis/identification techniques - EA

Elemental analysis consists in combustion of material sample in very high temperature. Subsequently apparatus analyses how much given compound has formed: water (thus, how much hydrogen was there initially in the sample), carbon dioxide (carbon), nitrogen oxides (nitrogen), sometimes (depending on apparatus) also sulfur oxides (sulfur) and some halogen oxides are analyzed as well, as well as initial amount of oxygen. Thus, if the sample consisted of one compound, it is possible to define its molecular formula with high precision (e.g. $C_{14}H_{15}N_6F_3$).

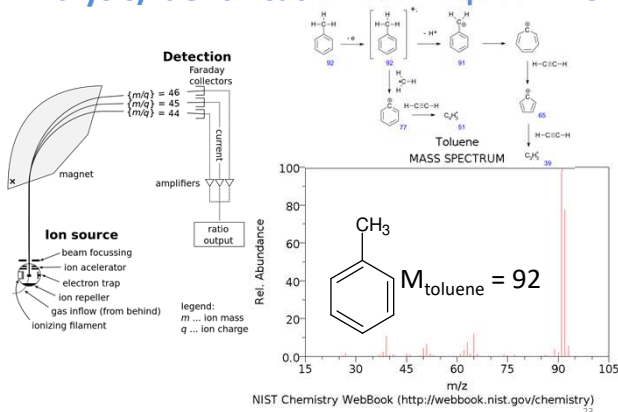
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Analysis/identification techniques - MS

Mass spectrometry is based on ionization of a molecule and (depending on apparatus and analyzed compound) breaking down this molecule into smaller parts. There are various techniques for their analysis. For instance, magnetic field bends path of ion, and change of path depends on ions' mass (and also its charge, if it is different than ± 1). Thus, it hits the sensor in different places depending on its mass. That allows for precise molecular mass determination – even up to ± 0.001 u in small compounds – up to 1000 u (so the molecular formula of the compound can be determined – different atoms have different deviations from integer weight values). In techniques utilizing molecule fragmentation, those smaller ions are formed of functional groups, chains, rings, so it is possible to determine whole structural parts of the initial compound.

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Analysis/identification techniques - MS



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

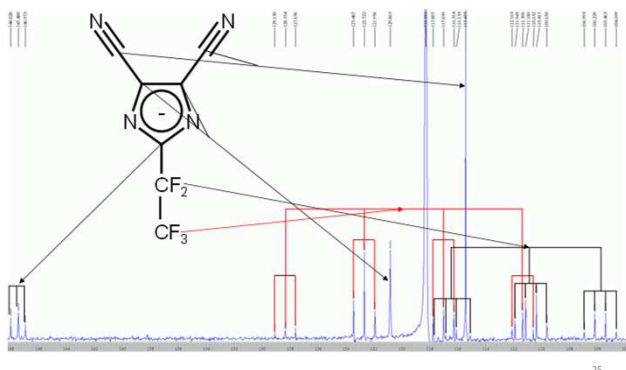
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Analysis/identification techniques - NMR

NMR is analytical technique of atomic nucleus and its interactions with fast changing magnetic field. Atomic nuclei, depending on with what atoms (how many, which elements) they are forming bonds (or what atoms are near to it), they interact differently with magnetic field. NMR can distinguish those interactions and identify those atoms in the neighborhood or bonded (or even functional groups, up to 2-3 atoms away), although for identification the model samples are required (for unambiguous statement, if it is the same compound, or if it is pure).

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Analysis/identification techniques - NMR



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Analysis/identification techniques – spectroscopic methods

Spectroscopic methods are based on interactions between electromagnetic waves and atoms or bonds (electrons). As atoms forming bonds do have energy levels, they can absorb and emit quanta of energy (e.g. electromagnetic radiation). Depending on what type of energy is absorbing those quanta – vibrational, rotation, electrons (excitation), those are different wavelength ranges. For instance, vibrations are best “seen” through interactions with infrared wavelengths and electronic energy level through interactions with UV and visible (UV-Vis) wavelengths.

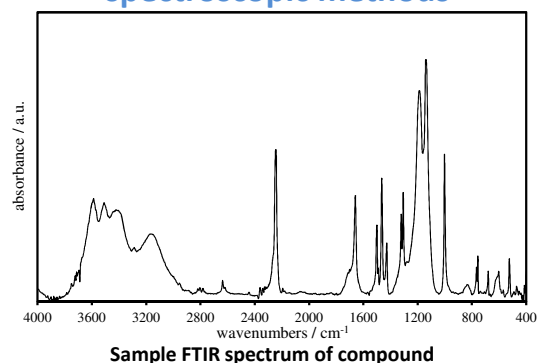
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Analysis/identification techniques – spectroscopic methods

Spectroscopic methods can obtain information on bond types are present in the investigated compound, so one can get to know what fragments it consists of (e.g. bonds C=O, C-H, C-C, C=C, C≡C, C≡N, C=N, O-H, presence of hydrogen bonds), and even distinguish from each other different carbon-oxygen bond types - C-O-H, C-O-C and C=O. Also C-C, C=C and aromatic bonds differ from each other.

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Analysis/identification techniques – spectroscopic methods



Sample FTIR spectrum of compound

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Analysis/identification techniques

By combining different analytical methods, one can determine exact structure of molecule not known before, confirm that synthesis succeeded (one got proper product) or determine level and type of impurities (and if there are any). Knowing molecular formula (MS, EA), bond types and presence of functional groups/atomic groups (Raman, IR, NMR), it is easy to reverse-engineer structure of even very complicated molecules.

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Analysis/identification techniques - chromatography

Group of chromatography (liquid, gas) techniques work on different principle than spectroscopic ones. These techniques base their operation on interactions between compounds and adsorbent bed (stationary phase) – each compound goes through the given amount and type of adsorbent in different (but repeatable) time. If one has a standard of compound, it is possible to confirm or deny presence of a given compound even in very sophisticated sample.

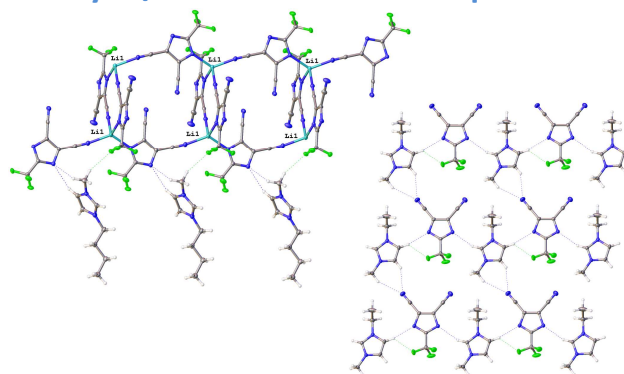
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Analysis/identification techniques - XRD

Non-standard analytical technique is XRD – X-ray diffraction, which can visualize exact atomic position, type and arrangement in space for the given compound. Unfortunately, it is required to have very pure form of compound and obtain big single crystal of it (modern diffractometers require crystal sizes above 0.1mm). These requirements severely limit applications of this method to solid, easy crystallizing substances (apart from other factors like apparatus cost, long measurement time - much higher and longer than for other techniques).

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Analysis/identification techniques - XRD



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Alkenes

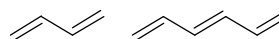
Alkenes are hydrocarbons in which there is at least one double bond (and no triple or aromatic bonds). Double bond is stronger than single one, bond length is shorter. Double bond means more electrons and local negative charge (denser electron cloud). Thus, it is more attractive for electrophiles (cations, local positive charges in highly polarized molecules). π electrons (all electrons above single bond) have priority in reaction with electrophile.

Alkenes with closed ring of carbon chain are cycloalkenes.

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Alkenes

Alkenes are called the same way as alkanes (stemmed from main carbon chain length), but with **-en** suffix. Thus instead of ethane - ethene (usually called ethylene), propane – propene, *etc.* In case of longer backbone double bond position is added to compound name: but-1-ene or but-2-ene. If there is more than one double bond, corresponding numeral prefix is added (di, tri, *etc.*) and their positions in carbon chain: buta-1,3-diene, hexa-1,3,5-triene.



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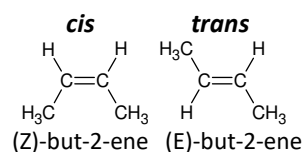
Alkenes and *cis-trans* isomerism

- Carbons that form double bond has sp^2 configuration, so all their bonds are in one plane. Thus, there is easy access to those carbons from two sides (no substituents blocking the way).
- Molecule parts are not rotating around the axis of double bond, like they do in case of each single bond. If carbon atoms forming the bond do have different substituents, they can form two **diastereoisomers** (called *cis* and *trans*).

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Alkenes and *cis-trans* isomerism

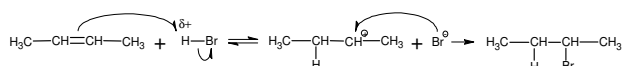
For instance, in case of but-2-ene: there is a **configuration** of compound, in which backbone chain is on the same side of the double bond (*cis*) and there is a configuration in which it is positioned diagonally (*trans*). One can call them *cis*-but-2-ene, but short name is (Z)-but-2-en (*cis*) or (E)-but-2-en (*trans*). Diastereoisomers do have different properties: melting points, boiling points, different reactivity, or even density (*e.g.* due to different packing in crystalline structure).



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Alkenes (olefins)

Incorporation of electrophiles to alkenes through attack on double bond is called an **addition**. There are two new bonds forming (added elements are not necessarily from the same molecule) at the cost of double bond. Alkenes reactions are mostly additions, e.g. HBr addition:



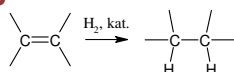
Bromine always will bond with the higher order carbon (as intermediate higher order carbocation is always more stable – the one of lower order would regroup to it anyway). Thus:



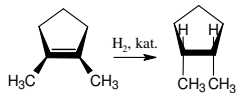
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Alkenes

- Hydrogenation to alkane:



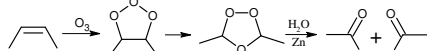
As H₂ molecule can approach from one side at a time (catalyst holds/coordinate the hydrogen molecule and thus it is weakening its bond, activating it for reaction this way), so hydrogenation of cycloalkane is leads to *cis* isomer, so it is stereoselective (reaction in which two parts of the same molecule are connected to the same other molecule from one side is called **syn-addition**):



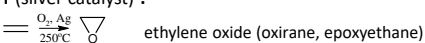
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Alkenes

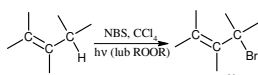
- with permanganate (at high temperature):
- with ozone (and then with water in zinc presence):



- with oxygen (silver catalyst):



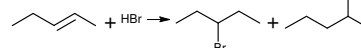
- with organic peroxides (radical mechanism, causing bromine to substitute at the lower order carbon atom):
- with N-bromosuccinimide (NBS) (substitutes bromine at so-called allyl position – the next carbon to double bond forming carbon):



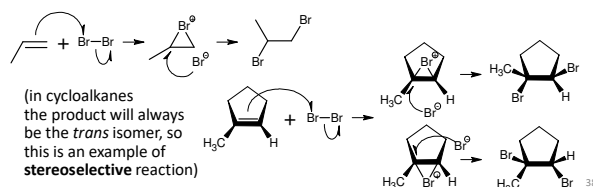
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Alkenes

- If two carbon atoms have the same order, then two reaction products are forming in the similar amounts (normally, side-products form as well, but in small amounts):



- Bromine addition is an example of **anti-addition** (bromine atoms are connecting to the opposite sides of the molecule):

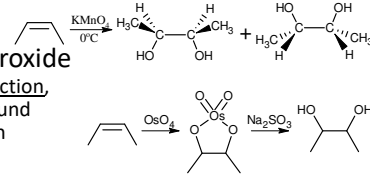


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Alkenes

Other alkenes reactions:

- with water (in acid presence):
- with borohydride (and hydrolysis in acidic environment or oxidation in alkali presence):
- with permanganate (at low temperature):
- with osmium tetroxide (so-called **group protection**, it forms stable compound decomposed only with sodium sulfite):

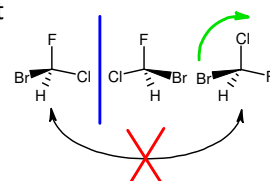


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Stereoisomerism

Left and right glove are mirror images of each other but they are not the same (not superimposable). That type of similarity (non-identity of mirror images) is called **chirality**. Objects, which mirror images are identical (superimposable) are called **achiral**.

CHBrClF molecule is chiral, as its mirror image is not superimposable with the original one, regardless of how it will be rotated. At least one atom of carbon in the molecule has to have four different substituents, in order to be the **chiral center** (*) (**asymmetric carbon**).

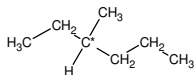


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Stereoisomerism

Enantiomers are stereoisomers of the same chiral molecule (mirror images of each other). Enantiomers have almost identical properties (such as melting point, boiling point, density, color, reactivity with achiral compounds, heat capacity, etc.).

Racemate is mixture two enantiomers in 1:1 ratio.



Polarized light do have polarization plane. After transition of such light through such optically active substance, that plane is turned. Enantiomers of one substance can turn it to left **(-)** (left-handed) or to right **(+)** (right-handed enantiomer). Racemate is not turning polarization plane **(±)** (thus the name optical isomerism).

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Stereoisomerism

Enantiomers are reacting differently (reaction rate, activation energy) with each of the enantiomers of optically active compounds. That is a reason, why a lot of compounds do have different biological effects (biochemical), e.g. left-handed can be an excellent cure (e.g. fits to some protein) and right-handed is a poison (e.g. blocks active site of enzyme).

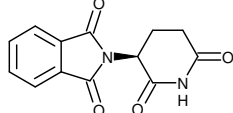
Most of compounds in our organisms are optically active – sugars, proteins, enzymes, DNA, RNA, etc. Moreover, most of these compounds are existing in natural form only as one enantiomer (the case of aminoacids, sugars, etc.). Artificial synthesized (those “other”) enantiomers of naturally occurring compounds are usually toxic (the best case is they are neutral, because cannot react with anything – not fits to anything).

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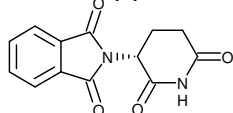
Stereoisomerism

The most infamous case of inequality of enantiomers in bioactivity terms was Thalidomide (under different brand names) – over-the-counter drug used as sedative, against nausea and morning sickness for pregnant women (50s and 60s in Germany, Sweden, and multiple other countries). Active form was racemate, but, as it was found out later, R enantiomer had healing properties, while S enantiomer was highly teratogenic (fetus damage). Up till now, few thousand people are living with disabilities caused by that drug.

(S)-thalidomide



(R)-thalidomide



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Alkynes

Alkynes are hydrocarbons that have at least on triple bond. It is even stronger than double bond. It is also subject to the same reactions as double bond, although effects can differ.

Alkynes' names are formed the same way as alkenes', but with suffix **-yn**.

E.g. ethine - $\text{H}-\text{C}\equiv\text{C}-\text{H}$ (commonly called acetylene), propyne, but-1-yn, but-2-yn, itd.

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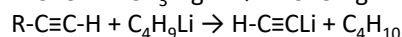
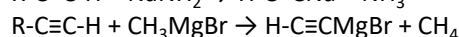
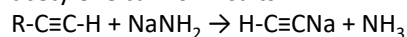
Stereoisomerism

S and R are notation for enantiomers in so-called **absolute configuration** (definition of configuration alternative to (+) and (-) – turning of polarization plane of polarized light). It is determined basing on molecular structure. Substituents of asymmetric carbon are numbered starting with the biggest/heaviest (1-2-3-4) basing on atomic number of atom directly connected to carbon (e.g. $\text{Br} > \text{Cl} > \text{F} > \text{H}$). If there are more than one atom of the same element, than substituents of those identical atoms are considered and so on (e.g. $-\text{CH}_2\text{CH}_2\text{CH}_3 > -\text{CH}_2\text{CH}_3 > -\text{CH}_3$). Then, looking along the asymmetric carbon-4. substituent axis (substituent behind the C^*) one has to determine if 1-2-3 substituents are increasing clockwise (isomer R – *rectus* – right) OR counterclockwise (isomer S – *sinister* – left).

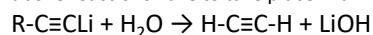
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Alkynes

Hydrogen atoms in alkynes: $\text{R}-\text{C}\equiv\text{C}-\text{H}$ are slightly acidic, that is, in favorable conditions they can dissociate from alkyne. That also means, that acetylene can form salts:



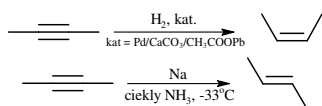
These salts are not stable and easily decomposing (acetylene is so weak acid, that even water is stronger than it, so water is giving up its proton to acetylene; It also means, that all above reactions have to take place in anhydrous conditions):



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Alkynes

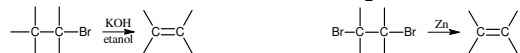
Similarly to alkenes, alkynes can be hydrogenated. Using hydrogen with standard catalyst, like nickel or platinum, causes alkynes to be hydrogenated into alkanes (just like alkenes). In order to selectively obtain *cis* and *trans* alkenes from alkynes, one needs to carry out the following reactions:



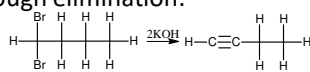
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Alkenes and Alkynes synthesis

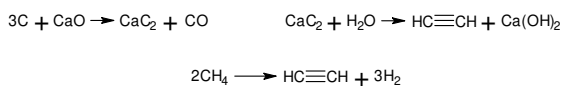
Alkenes' synthesis through elimination (reverse reaction to that of alkenes and Br₂ or HBr):



Alkynes' synthesis through elimination:



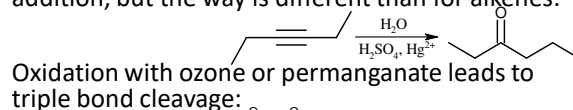
Alkynes' synthesis on the industrial scale (new and old):



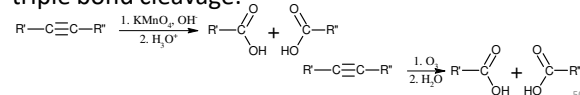
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Alkynes

Reaction with HBr works the same way as in alkenes case (bromine connects to higher order carbon). Also reaction with bromine works the same way. Reaction with HBr in the presence of organic peroxides also substitutes bromine atom to higher order carbon, but results in bromoalkene. Water addition also prefers higher order carbon atom for oxygen addition, but the way is different than for alkenes:



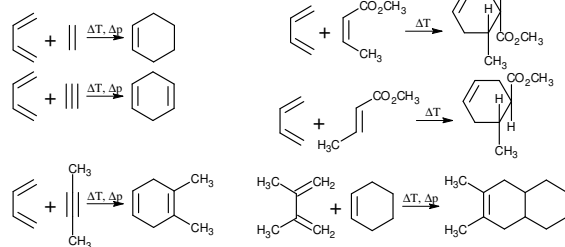
Oxidation with ozone or permanganate leads to triple bond cleavage:



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Diens reactivity and cyclization

Diene (compound with two double bonds) reaction with alkyne in proper conditions can obtain cyclic compounds. Appropriate choice of diene or alkyne enable synthesis of cyclic compounds with required substituents (and required configuration):



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